

**“EXPLORATION OF SOLVATION CONSEQUENCES OF  
SOME IONIC LIQUIDS AND BIOLOGICALLY POTENT  
MOLECULES PREVAILING IN DIFFERENT LIQUID  
ENVIRONMENTS”**



“সমানো মন্ব সমিতি সমানী”

*A Thesis Submitted to the*

**UNIVERSITY OF NORTH BENGAL**

*For the Award of*

***Doctor of Philosophy (Ph. D.)***

*In*

**CHEMISTRY**

*By*

***Sukdev Majumder, (M.Sc. in Chemistry)***

**UNDER THE SUPERVISION OF**

**DR. MAHENDRA NATH ROY**

**PRINCIPAL SUPERVISOR AND PROFESSOR OF CHEMISTRY**

**AND**

**DR. NITISH ROY**

**CO-SUPERVISOR AND ASSISTANT PROFESSOR OF CHEMISTRY**

**DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF NORTH BENGAL,  
DARJEELING, PIN-734013,  
W.B., INDIA  
JANUARY, 2022**

**This Ph.D. Thesis**

**is**

**DEDICATED**

**To**

**MY**

**Respected**

**PARENTS**

**AND**

**MY Ph.D. SUPERVISORS**

**For their continuous inspiration**

**and**

**Valuable guidance**

**MY SPECIAL THANKS**

**TO**

**My beloved family members**

**(Wife, sister, brothers and son)**

**For their whole hearted cooperation and heartfelt inspiration**

Photo: Max-Planck-Institut für Kohlenforschung



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**Benjamin List, Germany    David MacMillan, USA**

**“For the development of asymmetric organocatalysis”  
The Nobel Prize In Chemistry 2021  
The Royal Swedish Academy of Science**

## DECLARATION

I declare that the thesis entitled "EXPLORATION OF SOLVATION CONSEQUENCES OF SOME IONIC LIQUID AND BIOLOGICALLY POTENT MOLECULES PREVAILING IN DIFFERENT LIQUID ENVIRONMENTS" has been prepared by me under the proper guidance of Dr. Mahendra Nath Roy, Professor of Chemistry, University of North Bengal. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

*Sukdev Majumder*

**Sukdev Majumder**

Department of Chemistry,

University of North Bengal,

Darjeeling 734013,

West Bengal

Date: 03.01.2022

# UNIVERSITY OF NORTH BENGAL

**Prof (Dr.) M. N. Roy,**

FRSC (London)

Awardee of

UGC One Time Grant Under Basic Scientific Research

Prof. Suresh C. Ameta award from ICS

Bronze Medal from CRSI

Shiksha Ratna from the Govt. of West Bengal

Panchanan Barma Sadbhavana Sanman

and

Dewang Mehta Best Professor in Chemistry

Department of Chemistry



ENLIGHTENMENT TO PERFECTION

Phone: 0353 2776381

Mobile: 09434496154

Fax: 91 353 2699001

Darjeeling 734 013, INDIA

January , 2022

E-mail: [mahendraroy2002@yahoo.co.in](mailto:mahendraroy2002@yahoo.co.in)

## CERTIFICATE

I certify that Mr. Sukdev Majumder, *M. Sc.* in *Chemistry*, has prepared the thesis entitled "EXPLORATION OF SOLVATION CONSEQUENCES OF SOME IONIC LIQUIDS AND BIOLOGICAL POTENT MOLECULES PREVAILING IN DIFFERENT LIQUID ENVIRONMENTS", for the award of *Ph. D. Degree (Doctor of Philosophy)* of the *University of North Bengal*, under my guidance. He has carried out the work at the *Department of Chemistry, University of North Bengal*.

*Mahendra Nath Roy*

**PROF. (DR.) MAHENDRA NATH ROY,**

Professor of Chemistry,

Department of Chemistry,

University of North Bengal,

Dist: Darjeeling, Pin: 734013,

West Bengal, INDIA

DATE: 03-01-2022

*Prof. (Dr.) M.N. Roy*  
FRSC (London), UK  
Department of Chemistry  
University of North Bengal  
Darjeeling-734013, India

# UNIVERSITY OF NORTH BENGAL

**Dr. Nitish Roy**  
**Assistant Professor**  
Raja Rammohunpur,  
Darjeeling, WB-734013 India



Email: [ntu.litg@gmail.com](mailto:ntu.litg@gmail.com)  
Mob: 91 7872808189  
Website: <https://ntu.litg.wixsite.com/ntishroy>  
January, 2022

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*Nitish Roy*  
**DR. NITISH ROY,**  
**(CO-SUPERVISOR)**

Dr. Nitish Roy  
Assistant Professor  
Department of Chemistry  
University of North Bengal  
Raja Rammohunpur,  
Darjeeling, WB-734013, India

Assistant Professor,  
Department of Chemistry,  
University of North Bengal,  
Dist: Darjeeling, Pin: 734013,  
West Bengal, INDIA

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Sukdev Majumder

Signature of candidate

03.01.2022

Nitish Roy

Signature of Co-Supervisor

03/01/2022

Dr. Nitish Roy  
Assistant Professor  
Department of Chemistry  
University of North Bengal  
Raja Ramohanpur,  
Dargajiling, WB-734013, India

Mahendra Nath Roy

Signature of Supervisor (03-01-2022)

Prof. (Dr.) M.N. Roy  
FRSC (London), UK  
Department of Chemistry  
University of North Bengal  
Darjeeling-734013, India

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I am thankful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (**No. F 540/27/ DRS/2007, SAP-1**) for providing financial aid and instrumental assistance in order to continue my research work. I would also like to record my thankfulness to '**ONE TIME GRANT**' Ref No. **F.4-10/2010(BSR)** awarded to my Supervisor, **Prof. M. N. Roy**, under **Basic Scientific Research (BSR), UGC, New Delhi** for financial and instrumental assistance in connection with research work.

I am constantly aware of what a huge debt I owe to the sources of the information required for my research work: the numerous books, monographs, articles, computer website, etc. I put on record some measure of my gratitude to those whose references I have cited in this thesis.

The above list is neither complete in names, nor in deeds of all the people who have helped me towards achieving this Ph.D. degree. I would like to profusely apologize, and state that the omissions were not a meditated slight. This dissertation would not have been possible without their help.

*Sukdev Majumder*  
**Sukdev Majumder**

Research Scholar

Department of Chemistry

University of North Bengal

Dist- Darjeeling, Pin-734013,

West Bengal, INDIA

## **PREFACE**

The excellent work done in this thesis entitled “**EXPLORATION OF SOLVATION CONSEQUENCE OF SOME IONIC LIQUID AND BIOLOGICALLY POTENT MOLECULES PREVAILING IN DIFFERENT LIQUID ENVIRONMENTS**” was started in **March 2018** under the supervision of *Dr. M. N. Roy, Professor of Physical Chemistry, Department of Chemistry, University of North Bengal, and Darjeeling (NBU)*. This research became conscious within the framework of the Programme in the field of “*Ionic Liquids & Solution Thermodynamics*” and Research Group of Professor Roy.

The work is an attempt to explore the solute –solvent as well as ionic level interactions of IONIC LIQUIDS and AMINO ACIDS in aqueous solution systems by studying their thermophysical, thermodynamic, transport, optical, computational and spectroscopic properties.

I was exceedingly enthused by my listening, interacting and cooperating with renowned researchers, experts, reviewers and scientists during the course of my research work through the communicating via email, web-side in internet, with the participation in several meets and attaining, presenting in seminars/symposiums/ conferences across the country. I am even fortunate enough to publish my original research works as article enclosed in the dissertation in National and International Journals of repute.

In trusting with all-purpose perform of reporting scientific observation, due acknowledgement has been made whenever the work described was based on the finding of other investigators. I must take the responsibility of any unintentional oversights and errors, which might have crept in spite of precautions.

## ABSTRACT

Ionic liquids (ILs) and amino acids are very significant molecules for our Environment system and it can be important in the field of medical application.

ILs are the salt in the liquid state/phase that consist both organic part and inorganic part. ILs have been classified those salts whose melting point generally less than 100 °C (212 °F). The ILs have some special properties like low melting point, vapour pressure, good solvent behaviour for polymeric, organic part and as well as inorganic materials, adjustable polarity. Low viscosity, over an inclusive range of potentials, high conductivity, selective catalytic effect, for this it has wide range of industrial applications, pharmaceuticals, cellulose processing, gas handling, gas treatment, solar thermal energy, nuclear fuel processing, food and by-products, waste recycling, batteries etc. In the earlier few years for sustainable environment, chemical process led to growing attention in the arena of IL for investigation and applied as a green solvent instead of very harmful organic solvents. Biological potent molecules i.e. *amino acids (AAs)* are very essential for human body, which are constructing blocks of proteins, peptides, and polypeptides. AAs are also used in nutrition enrichments, food technology, fertilizers industry, consist of the creation of biodegradable plastics, drugs, and chiral catalysts.

Physio-chemical behaviour of electrolytes take place a very crucial role in determining the solute-solute/ ion –ion, solute –solvent/ ion –solvent interactions in solution phase. For the exploration of the nature and strength of different kind of interaction, different parameter like, thermodynamic , transport properties of electrolytes, optical properties, the traditional boundaries of physical , inorganic, analytical and electrochemistry are used for this purpose.

Solution chemistry is very importance especially in the branch of physical chemistry. This branch deals with the change in properties that arise when one molecule dissolve into another molecule. ‘Solution Chemistry’, deals with broadly three types of approaches, which have been made to estimate the extent of solvation. First approaches that involves the studies of viscosity, apparent molar volume, refractive index, conductance, surface tension etc. of electrolytes and the derivation of various factors associated with ionic solvation. The second is the approach of thermodynamic by

measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated with solvation can be elucidated, and the third is to use spectroscopic measurements like, UV-vis, fluorescence Study, FTIR, NMR ,where the spectral solvent shifts or the chemical shift conclude their qualitative and quantitative nature .

Ion –ion and ion –solvent interaction in solution can be understood from the computational study method, observations of transport properties of electrolytes, along with thermodynamic parameters like limiting apparent molar volume and compressibility studies. From the effect of these ion-solvent interactions is origins to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have very significant applications in such diverse areas as organic and inorganic synthesis, studies of reaction mechanisms, in battery technology and extraction.

Solvation is the method to attraction or association of solvent molecules with solute molecules. The solute molecules surround solvent molecules when it is soluble. A solvent complex is made when a molecule or ion of solute is bounded by solvent. Solvation is the technique of rearranging solvent and also solute molecules into solvation complex and the process is so on until the solute molecules is distributed inside the solvent perfectly. The following factors like hydrogen bonding, Vander Waals forces are dependent on solvation. Insoluble solute molecules like to maintain among the interaction rather than break apart from individually and become solvated by the solvent molecules. Hydration in the way of solvation where solute molecules is surrounded by water molecules.

Mixing of different solvent or solute molecules do not have ideal solution property. This type of deviation from ideally is given in the term of thermodynamic parameter, by apparent molar properties in case of solid- liquid mixture and by excess properties in case of liquid-liquid mixture. Thermodynamic properties that are very useful to investigate the molecular interaction and arrangement of the molecule. In particular, the interaction take place between solute – solute, solvent –solvent, solute – solvent species. The modification of solute molecules has been done by the addition of solute molecules in solvent molecules. The level of interaction among molecules depends on interactions taking place between solute-solute, solute-solvent species. The ion-pairing effect of the system is explain on the basis of ionic mobility hence on the conductivity of ions in solutions. Thus, this phenomenon is the way of path for research work in solution

chemistry to deduce the nature of interaction through different experimental observation involving densitometry, viscometry, refractometry, computational study, surface tension, spectroscopy and other suitable method and explained the data collected from experiment. All-over understanding of the phenomena of solution will only reality when solute-solute, solute-solvent interaction are deduced. Thus, the present research work is intimately related to the studies of solute-solute and solute-solvent interactions in some biologically important potent molecules (amino acids) and some industrially important liquid systems.

One of the very interesting phenomena of Solution Chemistry is that the exact structure of the solvent molecule in a solution is not known with certainty. The introduction of an ion or solute modifies the solvent structure largely whereas the solute molecules are also modified as the same way. The interactions between solute-solute, solute-solvent, and solvent-solvent molecules and the resulting ion-solvation become predominant, though the isolated picture of any of the forces is still not known completely to the solution chemists.

## **A.1 CHOICE AND IMPORTANCE OF IONIC LIQUIDS (ELECTROLYTES) AND SOLUTE MOLECULES (NON-ELECTROLYTES) AND SOLVENTS USED**

### **A.1.1 Ionic Liquids: - The following ionic liquid are used for my research work**

1-Butyl-3-methylimidazolium octylsulphate (BMIM) (C<sub>8</sub>SO<sub>4</sub>), 1-Methyl-3-octylimidazolium chloride(MOIM)Cl, Benzyl tri methyl ammonium chloride, 1-Butyl pyridinium Bromide (BP) Br, Benzyl tri butyl ammonium chloride, Tetra butyl ammonium Methane sulphonate, Benzyl tri ethyl ammonium chloride

**A.1.1.2 Non- Electrolytes (amino acids):** following amino acids (non-electrolytes) are used for my research work.

L-tyrosine, L-phenylalanine, L-Ascorbic acid, L-Aspartic acid, L-Glutamic acid, L-Asparagine, L-Glutamine, L-methionine, L-arginine, L-histidine

**A.1.2 SOLVENT:** The only universal solvent, water has been carried out for my research work throughout the experiment.

The study of ionic liquid (used as an electrolyte), amino acid (non-electrolyte) and solvent is great significant due to their wide-ranging use in many industrial purposes ranging from pharmaceutical to cosmetic by means of solvent, solute and also solubilizing agents. By mixing of above mentioned solvent as a binary, ternary, quaternary etc. mixture with huge range of variation of viscosities and dielectric constants, which gives us a best array for the study.

## **A.2 METHODS OF INVESTIGATION:-**

It is of curiosity to employ different experimental methods to develop a better vision into the behavior of solvation and different interactions prevailing in biologically potent molecules in solution systems. therefore I have tried to incorporate with some important thermophysical methods, namely, *Densitometry*, *Surface chemistry (surface tension)*; transport properties *viz.*, *Viscometric*, *Conductometric*; optical property *Refractometric* and spectroscopic property *FTIR Spectroscopic* method, UV-visible, fluorescence study, NMR technique to examine, probing, exploring of various interactions occurring in the solution systems.

## **A.3 PHYSICO-CHEMICAL PARAMETERS AND THEIR IMPORTANCE:**

Using experimental density values to calculate the  $\phi_v^0$  of the solutions. The magnitude as well as sign of limiting molar volumes provides information about the nature and magnitude of solute/ion-solvent interaction while the experimental slope ( $S_v^*$ ) provides information about ion/solute-ion /solute interactions.

From experimental viscosity data the Viscosity *B*-coefficients obtained which are another tool gives the useful scheme of ion/solute-solvent interaction in solutions.

The optical property such as refractive index, spectroscopic property as FTIR, UV-visible, NMR Spectroscopy, and fluoresces are used for supporting parameters to confirm the interaction occurring in the solution systems.

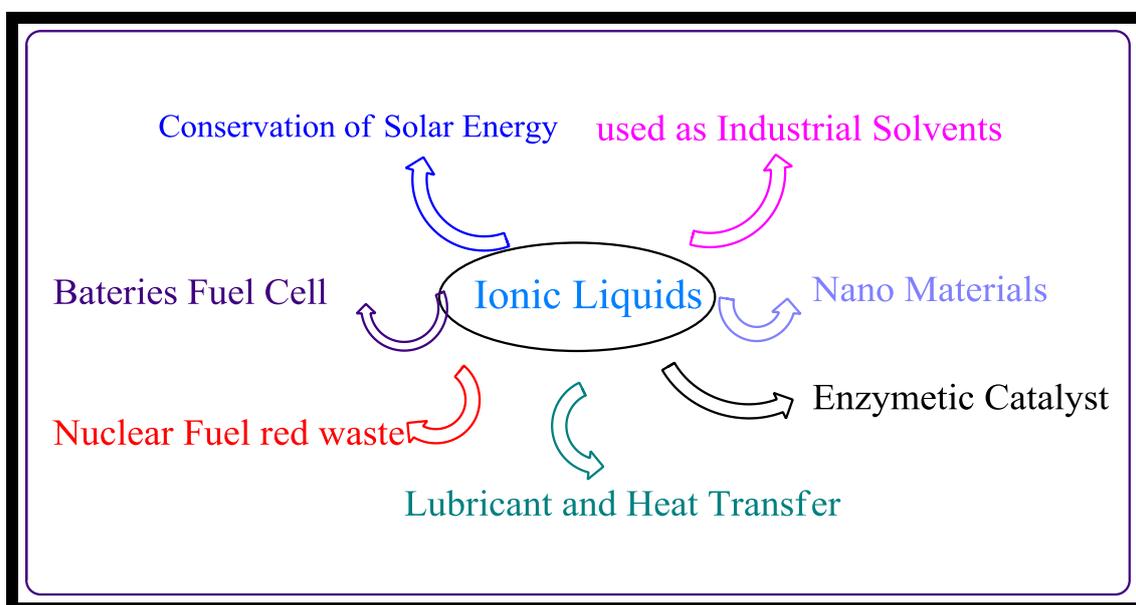
The computational study, surface tension measurement also give the type of interaction associated in molecules in solution system.

Limiting molar conductance ( $\Lambda_0$ ) obtained from using specific conductance values and also molar conductance gives a central idea about the ion-solvent interaction in the solution mixtures. More the magnitude of molar conductance values in solution less is the ion-solvent interaction. Another important parameters that are getting from the conductance study *i.e.*, association constant, Gibbs free energy, gives an idea about the solvation properties of ions in solutions.

#### A.4. SUMMARY OF THE WORKS EMPHASIZE IN THE THESIS:

##### CHAPTER-I

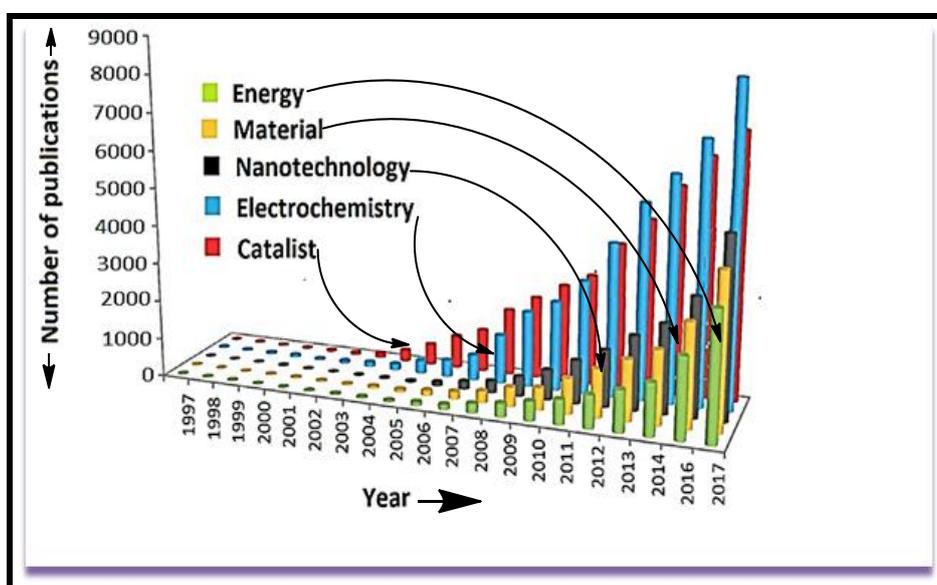
This chapter encloses the *objective, utility and applications of the research work*, the important of electrolytes/solute molecules and solvents used and methods of investigation. This also occupies the summary of the works done connected with the thesis.

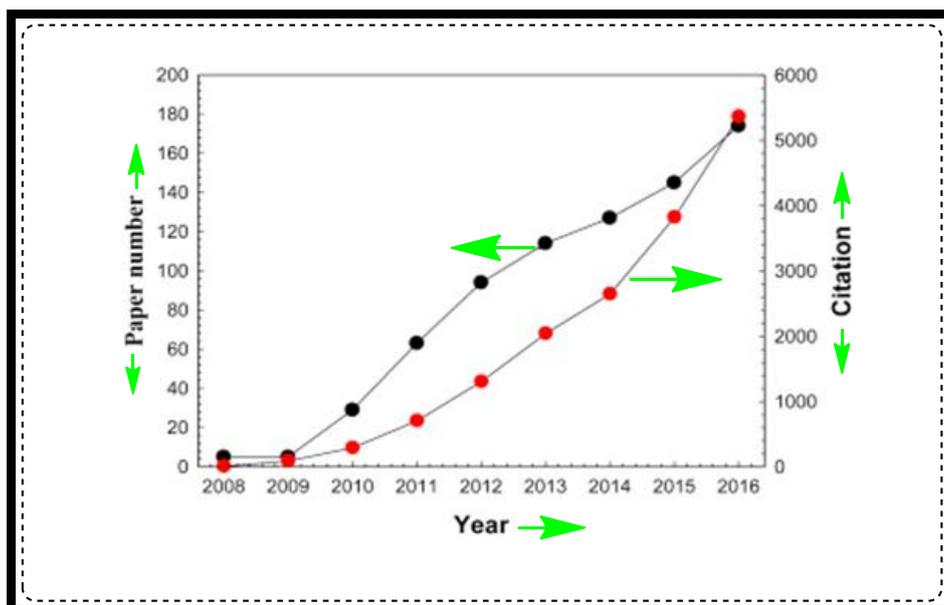


##### CHAPTER-II

The chapter contains *the general introduction* (Review of the Earlier Work) of the thesis and forms and the very strong background of the work embodied in the thesis. A brief criticism of remarkable works in the field of solute-solvent, solute-solute and solvent-solvent interactions has been given. In this chapter, the discussion includes the ion-solvent/solute-solvent, ion-ion/solute-solute and solvent-solvent interactions in binary, ternary mixed solvent systems and of electrolytes in pure and non-aqueous solvent

systems at various temperatures in terms of various derived parameters, estimated from the experimentally detected thermophysical properties *viz.*, *density, refractive index, viscosity and conductance*. Several semi-empirical models to approximation dynamic viscosity of binary liquid mixtures have been deliberated. Using Stokes' law and Walden rule, Ionic association and its necessity on ion-size parameters as well as relation between solution viscosity and limiting conductance of an ion has been deliberated. The molecular interactions are understood based on various derived parameters. Key assessment of different methods on the relative merits and demerits based on various types of assumptions employed from time to time of obtaining the single ion values (viscosity B coefficient and limiting equivalent conductance) and their implications have been understood. Different spectroscopic technique also discussed in this chapter. The molecular interactions are also made based on various type of equations.





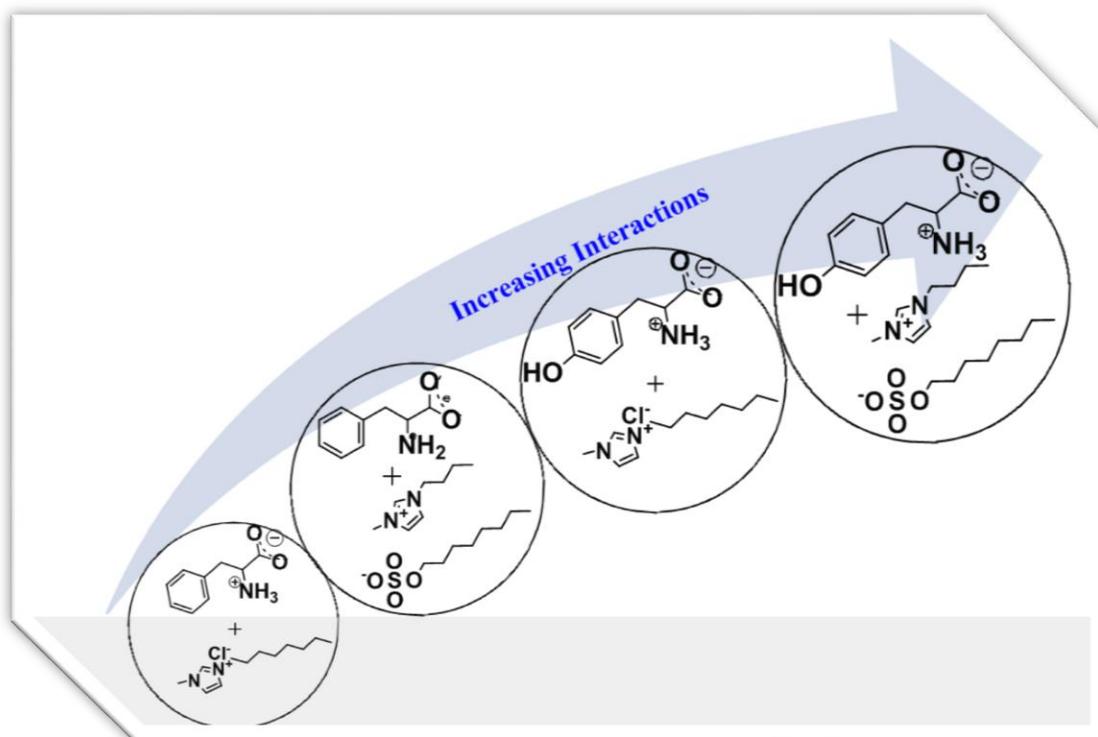
### CHAPTER-III

This chapter includes *the experimental section*, which mostly contains the basic information's, structure, source, purification and uses of the ionic liquids, electrolytes/non-electrolytes or solutes, and solvents have been used throughout the whole research work. It is also confines the details of the procedure, instruments working principle and equations that are employed to know the thermophysical/thermodynamic, transport, optical and spectroscopic assets.



## CHAPTER-IV

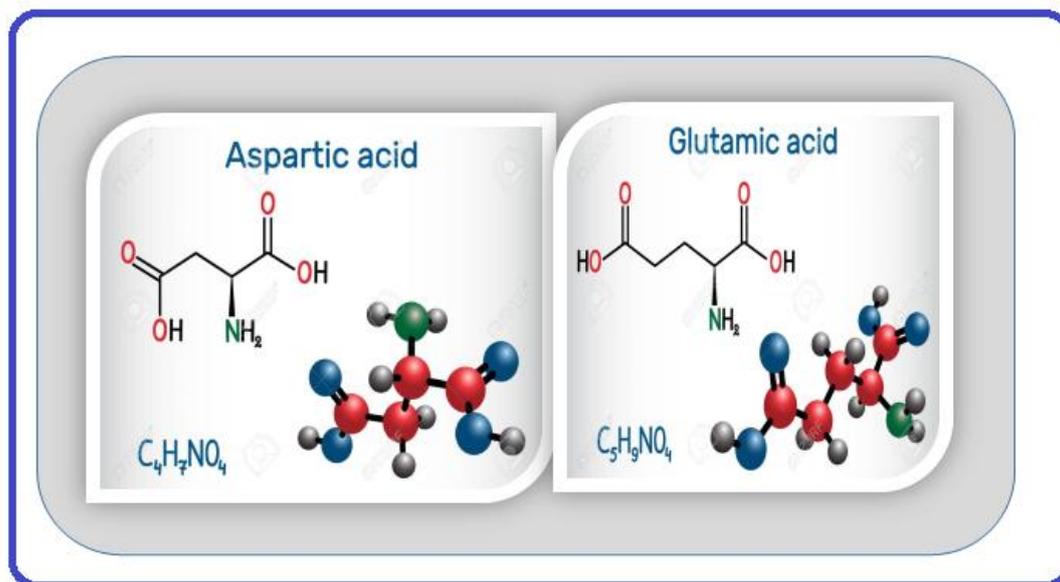
The chapter deals with the precise measurements on electrical conductance ( $\Lambda$ ) steady state fluorescence, UV visible spectroscopy, determination of association constant, Gibbs free energy, study of proton NMR of solutions of an ionic liquid (ILs), L-Tyrosine, L-Phenyl alanine and their binary mixtures have been reported at 298.15K. From the above experiments, data reported which can explain the nature of interaction properties associated with the ionic liquids and the solute molecules. Also from the value of proton NMR, data can help the chemical environment of different protons and different types of interactions (non-covalent bond, weak pi-pi interaction).



## CHAPTER-V

The chapter embraces the analysis of solute-solute and solute-solvent interactions between IL(BTAC) and two solute molecules(L-glutamic acid and L-Aspartic acid at different temperature(298.15k,303.15k,30815k) quantitatively by precise measurement of density, viscosity, refractive index, molar conductance( $\Lambda$ ), in the solution systems. From limiting apparent molar volume, ( $\Phi v^\circ$ ) experimental slopes ( $SV^*$ ), viscosity B-

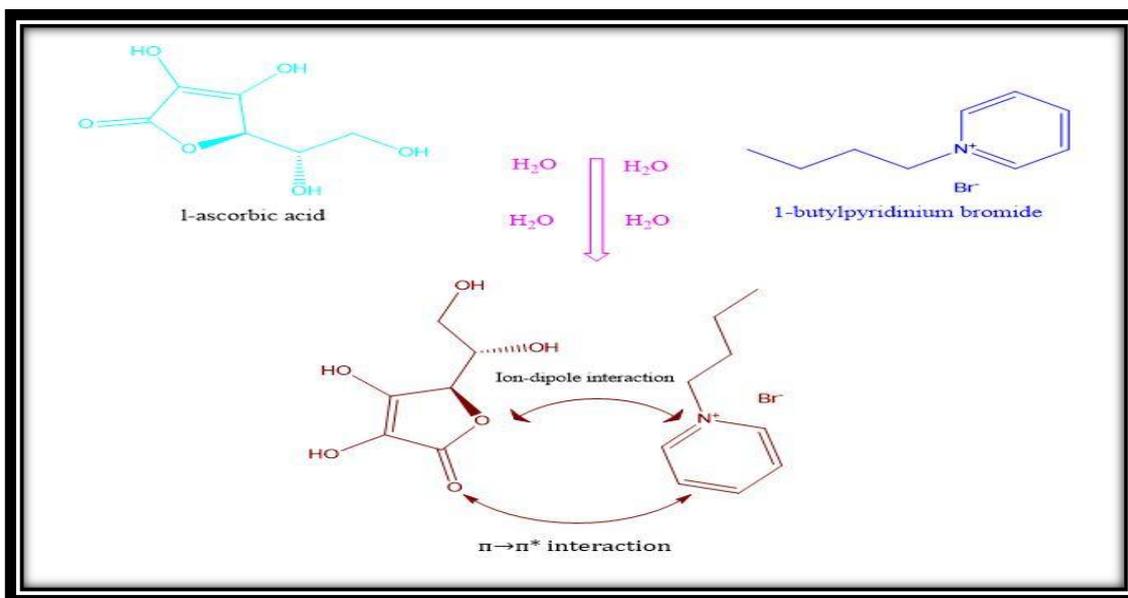
Coefficient data, molar refraction data explained the interaction phenomenon (solute-solvent and solute-solute interactions). Formation of Hydrogen bonding, Dipole-dipole interaction configurational theory, structural aspect, are the powerful forces, for the discussion of the results. The solvation behaviour is manifested by the variation of the difference parameters explained in this chapter in the presence of ionic liquids.



## CHAPTER-VI

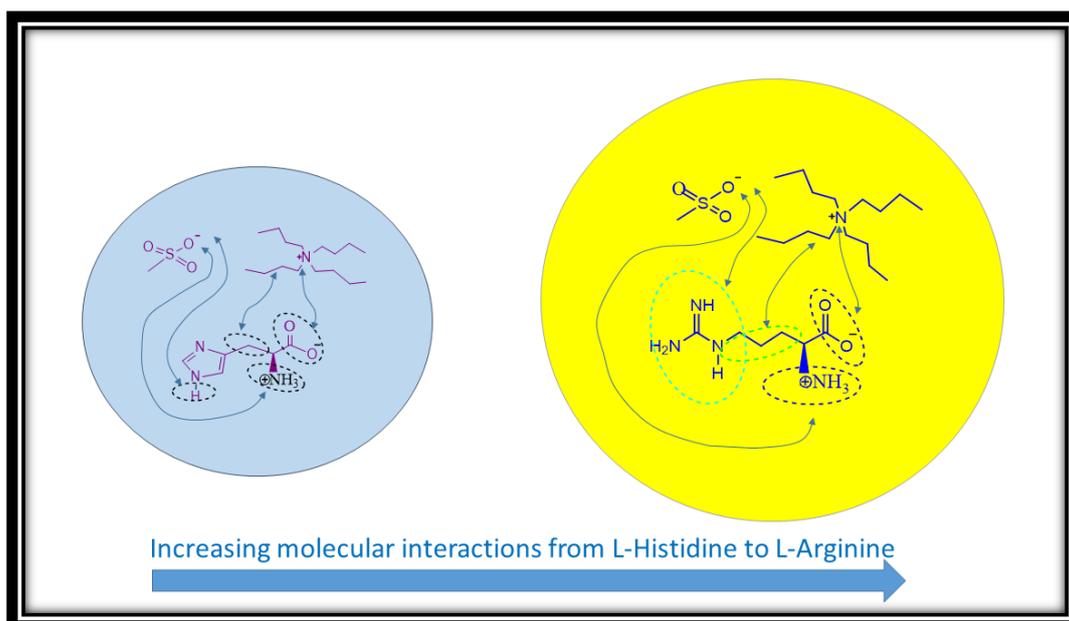
Apparent molar volumes ( $\phi_v$ ), viscosity  $B$ -coefficients, refractive index, specific conductance for L-Ascorbic acid (0.001, 0.003, and 0.005 mol.dm<sup>-3</sup>) in aqueous ionic liquid, 1-Butylpyridiniumbromide ( $C_9H_{14}NBr$ ) solutions were calculated from density of solution. Also viscosity measurements at three different temperature (298.15, 308.15, and 318.15 K) and  $p = 0.1$  MPa as a function of the concentration (Molality) of L-Ascorbic acid have been reported in this chapter. At infinite dilution, extrapolated of the apparent molar volumes upto zero concentration, the limiting apparent molar volumes ( $\phi_v^o$ ), obtained. Solute-solvent interactions can be explain from the different parameters obtained from the Redlich-Meyer equation. Using Jones-Dole equation, the viscosity values were discussed, and solute- solvent interactions have been explained from the resulting parameters  $A$  and  $B$  in the mixed solutions. Ability to structure making or -breaking of the electrolyte (L-Ascorbic acid) has been analyzed with the help of sign of

$dB/dT$ . Conductance values also supported the solute-solvent interactions associated with vitamin C (L-Ascorbic acid) and ionic liquid (1-Butylpyridinium bromide).



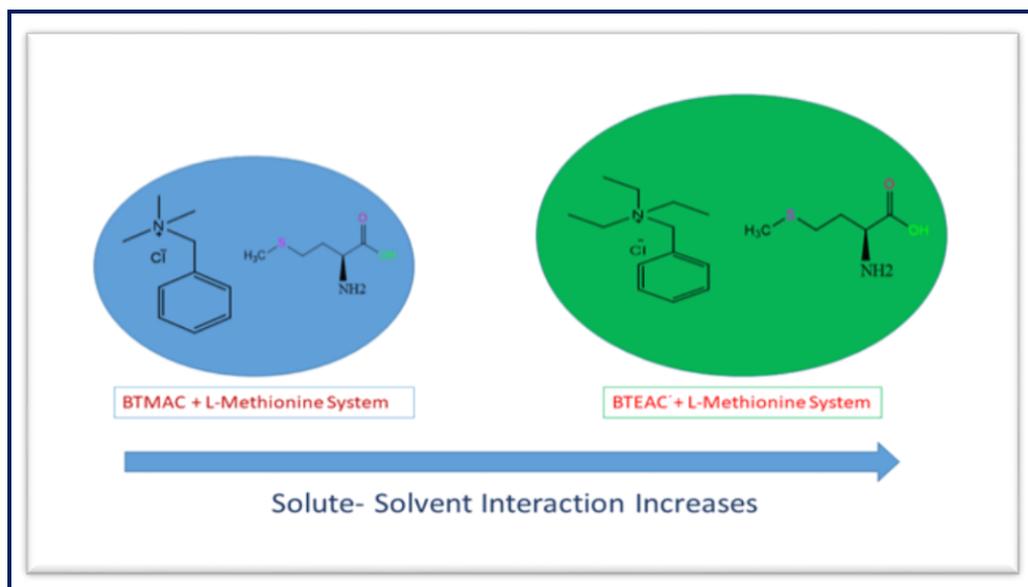
## CHAPTER-VII

Custody in mind the uses of amino acids the apparent molar volume ( $\phi_V$ ), viscosity  $B$ -coefficient, Molar conductance ( $\Lambda$ ) and molar refraction ( $R_M$ ) of L-Arginine and L-Histidine have been determined in IL (Tetra butyl ammonium methane sulfonate) at 298.15 K, 303.15K, 308.15K from density ( $\rho$ ), viscosity ( $\eta$ ), Specific conductance and refractive index ( $n_D$ ) respectively. Using Masson equation, the limiting values at infinite dilution are by extrapolated to zero concentration of apparent molar volumes. Interactions phenomenon of both solute-solute & solute-solvent have been understood from the slopes ( $S_V^*$ ) and ( $\phi_V^0$ ), which obtained from the Masson equation. Viscosity parameter A & B which derived from Jones- Dole equation, using viscosity values have been used to interpretation the molecular interactions in solution. Applying Lorentz-Lorenz equation to evaluated the Molar refraction ( $R_M$ ) values as explain the solvation behaviour of solution mixtures. Molar conductance data also explain the molecular interactions involving in solutions. Interactions properties also explain by computational study. Some thermodynamic parameters also derived by using some equations for explanation of interactions in solution.



## CHAPTER-VIII

This chapter includes the study on interactions between solute-solvent and solute-solute. Here the interactions behaviour between two ionic liquids (solvent) , Benzyl tri methyl ammonium chloride and Benzyl tri ethyl ammonium chloride with one amino acid(solute)L-Methionine have been carried out by volumetric, viscometric, conductometric, refractometric, surface tension, NMR, Computational study measurements. Comparison of solute-solute and solvent-solvent interactions between ILs with amino acid can be explained with the help of some physicochemical parameter such as limiting apparent Molar volumes ( $\Phi_v^\circ$ ), viscosity B-Coefficient, Molar conductance ( $\Lambda$ ) data. In addition, proton NMR, UV-Visible and FTIR spectroscopy help to determine the interaction properties in pure as well as the solution mixtures. Variation of optimization energy calculated theoretically by Gaussian Method of pure ionic liquids and mixture with amino acid gives the same result obtained practically from above mentions of different parameters in this chapter.



## CHAPTER-IX

In this chapter physicochemical properties such as density ( $\rho$ ), viscosity ( $\eta$ ), refractive index ( $n_D$ ), molar conductance ( $\Lambda$ ), surface tension measurements of ionic liquid (Benzyltributylammoniumchloride), solute molecules, Lglutamine ( $C_5H_{10}N_2O_3$ ) & Lasparagine ( $C_4H_8N_2O_3$ ) and their ternary mixtures (IL+AA+H<sub>2</sub>O) have been observed at 298.15 K, 303.15K, 308.15K, respectively. Solute- solute and solute- solvent interaction have been interpreted by some very significant physicochemical parameters namely, Apparent molar volumes ( $\phi_V$ ), and viscosity  $B$ -coefficients accompanied with the data of densities and viscosities respectively. Using the Masson and Jones-Dole equation for elucidating the limiting apparent molar volumes ( $\phi_V^0$ ), slopes ( $S_V^*$ ), viscosity  $A$ ,  $B$  coefficients respectively. Spectroscopic technique such as <sup>1</sup>HNMR, UV-vis. is also applying for determination of molecular interactions. Molar expansibility factor ( $\Phi E^\circ$  and  $\partial\Phi E^\circ/\partial T$ ) obtained by applying polynomial equation which explain the solute- solvent interactions properties. Computational study is also accompanied with the manifestations of interactions prevailing in ionic liquid with two amino acids.

## CHAPTER-X

In this chapter, covers the concluding remarks of the works related or detailed described in the thesis (dissertation).

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## **APPENDIX-A**

### **LIST OF RESEARCH PUBLICATIONS/COMMUNICATIONS**

#### **1. Investigation of Solution Behaviour of an Ionic Liquid in Diverse Cellosolves by Physicochemical Contrivance**



Journal of Advanced Chemical Science-Volume 4 Issue1(2018) 543-548

#### **2. Exploring Diverse Interactions of Some Surface Active Ionic Liquids with Amino Acids Prevalent in Aqueous Environments by Physicochemical Contrivance**



Journal of Advanced Chemical Science- Volume 5 Issue 2 (2019) 637–642.

**(INCLUDED IN THE THESIS)**

#### **3.Exploration of Solvation Consequences of Some Biologically Potent Molecules in Aqueous Ionic Liquid Solutions with the Manifestation of Molecular Interactions**



Journal of chemical, biological and physical sciences, Section A; November 2020 – January 2021, Vol. 11, No. 1; 091-114.

**(INCLUDED IN THE THESIS)**

**4. Physicochemical Investigation of Diverse Interactions of Some Biologically Potent Molecules Prevalent in Aqueous Ionic Liquid Solutions at Different Temperatures**  
(INCLUDED IN THE THESIES)



Indian journal of Advances in Chemical science 2021; 9(2):89-97

(INCLUDED IN THE THESIES)

**5. Subsistence of Assorted Molecular Interactions of Substantial Amino Acids Prevalent in Aqueous Solutions of Ionic Liquid (TBMS) Probed by Experimental and Computational Investigations**

(INCLUDED IN THE THESIS)

**COMMUNICATE**

**6. Exploration of Diverse Interactions of L-Methionine in Aqueous Significant Mixed Ionic Liquid Solutions Optimized by Computational Theory**

(INCLUDED IN THE THESIS)

**COMMUNICATE**

**7. Solvation behaviour of l-asparagine and l-glutamine prevailing in aqueous ionic liquid solution by physicochemical and computational investigations**

(INCLUDED IN THESIS)

**COMMUNICATE**

## APPENDIX-B

### List of Seminar/Symposium/Convention Attended

| Sl. No. | Seminar/Symposium/<br>Convention Attended  | Date   | Organizer and Venue  |
|---------|--|--|--|
| 1.      | National Seminar on”<br>Frontiers in Chemistry-2019  | May,22,2019  | Department of Chemistry of North Bengal&<br>CRSI North Bengal Local Chapter  |
| 2.      | SERB Sponsored National<br>Conference on<br>“Green Chemistry”: An<br>Alternative Of Conventional<br>Chemistry”   | September, 20-21,<br>2019                            | DepartmentofChemistry,CBPBU,WeastBengal,I<br>ndiaInassociationwithIndianChemicalSocietKolk<br>ata  |
| 3.      | International Seminar on”<br>International year of the<br>Periodic Table of Chemical<br>Element-2019   | November 22-23,<br>2019                              | Department of Chemistry, University of North<br>Bengal   |
| 4.      | National Seminar on<br>“Frontiers in Chemistry-<br>2020”   | March,5,2020   | Department of Chemistry, University of North<br>Bengal   |
| 5.      | One Day International<br>Seminar on “ Frontiers in<br>Chemistry 2020(Virtual<br>Mode)  | October,01, 2020                                     | Department of Chemistry, University of North<br>Bengal In Collaboration with Chemical Research<br>Society of India, North Bengal Local Chapter |
| 6.      | One Day International<br>Seminar on” Recent Trends<br>in Chemistry-2020(Virtual<br>Mode)   | October,16,2020                                      | Department of Chemistry, University of North<br>Bengal In Collaboration with Chemical Research<br>Society of India, North Bengal Local Chapter |
| 7.      | Two Days National web-<br>Based Conference On<br>”Environmental<br>Determinism, Diverse<br>Pollutions ,Sources, And<br>Controlling Management<br>Through Sciences And<br>Humanities” | 22 <sup>nd</sup> and 23 <sup>rd</sup> March,<br>2021 | Organized by Alipurduar University   |

## **APPENDIX-C**

### ***LIST OF SYMBOL, ABBREVIATION AND ACRONYMS***

|  |  |
|--|--|
| ILs  | Ionic liquids  |
| RTILs  | Room-temperature ionic liquids   |
| PILs   | protic ionic liquids   |
| AILs   | aprotic ionic liquids  |
| AAs  | Amino acids  |
| [BMIM][C8SO4]                                  | 1-Butyl-3-methylimidazolium octylsulphate  |
| [MOIM]Cl                                       | 1-Methyl-3-octylimidazolium chloride   |
| [BTMA]Cl                                       | Benzyltri methyl ammonium chloride   |
| [BP] Br  | 1-Butyl pyridinium Bromide   |
| [BTBA]Cl                                       | Benzyl tri butyl ammonium chloride   |
| TBMS   | Tetra butyl ammonium Methanesulphonate   |
| [BTEA]Cl                                       | Benzyl tri ethyl ammonium chloride   |
| L-tyr  | L-tyrosine   |
| L-Phe  | L-Phenyl alanine   |
| L-Asc  | L-Ascorbic acid  |
| L-Asp  | L-Aspartic acid  |
| L-Glu  | L-Glutamic acid  |
| L-Asp  | L-Asparagine,  |
| L-Glu  | L-Glutamine  |
| L-Met  | L-methionine   |
| L-Arg  | L-arginine   |
| L-His  | L-histidine  |
| <i>RPM, SMC(0.327), &amp; TK<br/>(0.09373)</i> | Speed, spindle multiplier constant, and viscometer torque constant of DV-III pro viscometer. |
| <i>A</i>                                       | molar Conductance  |
| <i>A<sub>o</sub></i>                           | limiting molar conductance   |
| <i>K<sub>A</sub></i>                           | association constant   |
| <i>R</i>                                       | association diameter   |

|                     |  |
|---------------------|--|
| $\lambda_o^\pm$     | limiting ionic conductance   |
| $c$                 | molar concentration  |
| $\kappa$            | specific conductance   |
| $\epsilon_r$        | relative permittivity  |
| $R_X$               | relaxation field effect  |
| $k^{-1}$            | radius of the ion atmosphere   |
| $e$                 | electron charge  |
| $k_B$               | Boltzmann constant   |
| $K_S$               | association constant of the contact-pairs  |
| $K_R$               | association constant of the solvent-separated pairs  |
| $\gamma$            | fraction of solute present as unpaired ion   |
| $\alpha$            | fraction of contact pairs  |
| $f$                 | activity coefficient   |
| $T$                 | absolute temperature   |
| $\beta$             | twice the Bjerrum distance   |
| $\delta$            | minimum standard deviation   |
| $a = (r_+ + r_-)$   | crystallographic radii of electrolyte. i.e.; sum of the crystallographic radii of the cation ( $r_+$ ) and anion ( $r_-$ ) |
| $d$                 | average distance corresponding to side occupied by solvent molecules   |
| $M$                 | molar mass   |
| $\rho$              | density of the solution  |
| $M_{av}$            | average molar mass by the mole fraction  |
| $w_1$ & $w_2$       | mass fraction of the first & second component of molar mass $M_1$ & $M_2$  |
| $\eta_o$            | solvent viscosity  |
| $\eta$              | Viscosity of solution  |
| $\eta^{-1}$         | fluidity   |
| $\Lambda_o\eta$     | Walden product   |
| $r_{eff}$           | effective solvated radius  |
| $\lambda_o^\pm$     | Limiting ionic conductance   |
| $\lambda_o^\pm\eta$ | limiting ionic Walden product  |
| $r_s$               | Stokes' radii  |

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|                         |  |
|-------------------------|--|
| $r_c$                   | crystallographic radii   |
| $w$                     | mass fraction  |
| $\Delta G^\circ$        | Gibbs energy changes   |
| $R_g$                   | Gas constant   |
| $D_{\pm}$               | diffusion coefficient  |
| $k_B$                   | Boltzmann's constant   |
| $i_{\pm}$               | ionic mobility   |
| $z_{\pm}$               | ionic charge   |
| $F$                     | Faraday constant   |
| $A_{theo}$ -coefficient | Ion-ion interactions from Debye-Hückel theory                      |
| $V_s$                   | Solvated volume of the ion   |
| $V_o$                   | volume of the solvent molecules                                    |
| $n_s$                   | solvation number   |
| $A_0^r$                 | Limiting triple-ionic conductance                                  |
| $K_P$                   | ion-pair formation constant  |
| $K_T$                   | triple-ion formation constant                                      |
| $S$                     | limiting Onsager coefficient                                       |
| $C_P$                   | ion-pair concentrations  |
| $C_T$                   | triple-ion concentrations  |
| $\alpha$                | fraction of ion-pairs present in the solution                      |
| $\alpha_T$              | fraction of triple-ions present in the solution                    |
| $a_{IP}$                | interionic distance parameter for ion-pair                         |
| $Q(b)$ and $b$          | constant of Bjerrum's theory                                       |
| $a_{TI}$                | interionic distance parameter for triple ion                       |
| $I(b_3)$                | a double integral tabulated in Bjerrum's theory                    |
| $b_3$ & $I(b_3)$        | function of $a_{TI}$   |
| $\phi_V$                | Apparent molar volume  |
| $B$ -coefficients       | Viscosity $B$ -coefficient   |
| $\sqrt{c}$              | square root of molar concentration                                 |
| $\phi_V^0$              | partial molar volume at infinite dilution or limiting molar volume |
| $A$ or $A_V$            | Ion-ion or solute-solute interaction from Masson equation          |

|   |   |
|---|---|
| $B$ or $B_V$                              | Ion-solvent or solute-solvent interaction from Masson equation                                      |
| $\eta_r = \eta/\eta_0$                    | Relative viscosity  |
| $\bar{V}_1^0$                             | partial molar volumes of the solvent  |
| $\bar{V}_2^0$                             | partial molar volumes of the solute   |
| $\Delta\mu_1^{0\#}$ or $\Delta G_1^{0\#}$ | free energy of activation per mole of solvent mixture of viscous flow                               |
| $\Delta\mu_2^{0\#}$                       | free energy of activation per mole of the solute of viscous flow                                    |
| $h$                                       | Planck's constant   |
| $N_A$                                     | Avogadro's number   |
| $\Delta S_2^{0\#}$                        | Entropy of the solution   |
| $\Delta H_2^{0\#}$                        | Enthalpy of the solution  |
| $m$                                       | Molality of the solution  |
| $\beta_s$                                 | adiabatic compressibility   |
| $\phi_K$                                  | apparent molar adiabatic compressibility  |
| $\phi_K^0$                                | limiting apparent molar adiabatic compressibilities   |
| $S_K^*$                                   | experimental slopes   |
| $\phi_{\pm}^0$                            | limiting ionic apparent molar volumes   |
| $B_{\pm}$                                 | ionic viscosity $B$ -coefficients   |
| $n_D$                                     | refractive index  |
| $R_M$                                     | molar refraction  |
| $c$                                       | speed of light in the medium  |
| $c_0$                                     | speed of light  |
| $-R$                                      | alkyl chain group of the amino acid   |
| $n_c$                                     | number of carbon atoms in the alkyl chain of the amino acid   |
| $\phi_V^0(\text{NH}_3^+, \text{COO}^-)$   | zwitterionic end group to apparent molar volume   |
| $\phi_V^0(\text{CH}_2)$                   | methylene group contribution to $\phi_V^0$  |
| $\Delta\phi_V^0$                          | standard transfer volume for amino acid from $\text{H}_2\text{O}$ to aqueous ionic liquids solution |
| $\phi_{VW}$                               | van der Waals volume  |

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|   |  |
|---|--|
| $\phi_{VS}$                                   | volume associated with voids or empty space                                |
| $\phi_S$                                      | shrinkage volume due to electrostriction                                   |
| $\Delta\phi_V^0(\text{NH}_3^+, \text{COO}^-)$ | standard partial molar volumes of transfer of the zwitterionic end group   |
| $\Delta\phi_V^0(\text{R})$                    | standard partial molar volumes of transfer of other alkyl chain groups     |
| $n_H$   | hydrated to the amino acids  |
| $\phi_V^0(\text{int})$                        | intrinsic partial molar volumes of the amino acids                         |
| $\phi_V^0(\text{elect})$                      | electrostriction partial molar volume resulting of hydration of amino acid |
| $\phi_V^0(\text{cryst})$                      | molar volume of crystal  |
| $\phi_E^0$                                    | limiting apparent molar expansibilities                                    |
| $B(\text{NH}_3^+, \text{COO}^-)$              | zwitterionic end group to viscosity $B$ -coefficient                       |
| $B(\text{CH}_2)$                              | methylene group to apparent molar volume                                   |
| $B(\text{R})$                                 | side chain contributions to $B$ -coefficients                              |
| $\Delta\mu^{0\#}$                             | total free energy of activation of viscous flow of the solution            |
| $n_1$ & $n_2$                                 | number of moles of mixed solvent and solute, respectively                  |
| $R^2$   | squared correlation coefficient or linear regression coefficient           |
| $\lambda$                                     | Wave length  |
| <i>Eq.</i>                                    | Equation   |
| <i>Fig.</i>                                   | figure   |

**Some Important Dimensional Constants Used**

| Name of the constant            | Symbol   | Value  |
|---------------------------------|----------|--|
| Density of the water at 298.15K | $\rho_0$ | : $0.99713 \times 10^3 \text{ kg m}^{-3}$                                  |
| Viscosity of water              | $\eta_0$ | : 0.890 mP s   |
| Conductivity of water           |          | : $<1 \times 10^{-6} \text{ S cm}^{-1}$                                    |
| Relative permittivity of water  | $\mu_0$  | : 78.30  |
| Boltzmann's Constant            | $k_B$    | : $1.3806488 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$ |
| Faraday                         | $F$      | : 96500 coulomb  |
| $\Pi$                           |          | : 3.143  |
| Avogadro number                 | $N_A$    | : $6.023 \times 10^{23} \text{ mol}^{-1}$                                  |
| Universal Gas constant          | $R_g$    | : $8.314 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1}$                  |
| plank Constant                  | $h$      | : $6.63 \times 10^{-34} \text{ J s}^{-1}$                                  |
| Speed of light                  | $c_0$    | : $3.00 \times 10^8 \text{ m s}^{-1}$                                      |
| Permeability of free space      | $\mu_0$  | : $1.256637 \times 10^{-6} \text{ Henry m}^{-1}$                           |
| Electronic charge Relative:     | $E$      | $1.60 \times 10^{-19} \text{ C}$   |

**Useful Relations**

|                    |                     |
|--------------------|---------------------|
| $\rho = n \cdot m$ | $N_A = n \cdot v_N$ |
| $m = M/N_0$        | $v_N = V/N$         |
| $R_g = R_0/M$      | $N = W/M$           |
| $R_0 = N_0 k_B$    |                     |

| <b><u>Unity</u></b> |                             |                     |
|---------------------|-----------------------------|---------------------|
|                     | mL : milliliter             | g : gram            |
|                     | eq. : equivalents           | h : hour            |
|                     | min. : minute               | mg : milligram      |
|                     | mol : mole                  | °C : degree Celsius |
|                     | mmol : millimole            | K : degree Kelvin   |
|                     | ppm : part per million      | Hz : Hertz          |
|                     | $\mu\text{mol}$ : micromole |                     |

# **CHAPTER -I**

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## **NECESSITY OF THE RESEARCH WORK**

### **I. 1 SCOPE, OBJECTIVE AND APPLICATIONS OF THE RESEARCH WORK**

Physico-chemical Investigation of electrolytes take plays a very significant role in understanding the nature of solute-solute, solute-solvent, solvent-solvent interactions involving in the solutions phase. Exploration of the nature of interactions and as well as the strength of transport properties of electrolytes, and thermodynamic revisions linking with binary and ternary systems of liquid and of one or more solutes in pure and mixed systems of liquid are very valuable.

The significance and uses of the Chemistry of electrolytes in aqueous, non-aqueous (amino acids) and mixed solvents are well planned. The both applications & implications of studies of the reactions in non-aqueous and mixed solvents have been summarized Meck <sup>(1)</sup> by Franks <sup>(2)</sup>, Popovych <sup>(3)</sup>, Parker <sup>(4-5)</sup>, Bates <sup>(6-7)</sup>, Criss and Salomon <sup>(8)</sup>, Mercus <sup>(9)</sup> and others <sup>(10-12)</sup>. Now days the ion-ion or solute-solute and solute-solvent interactions have been subject of inclusive interest as apparent from recent Faraday Trans. of the chemical society <sup>(13)</sup>.

The accurate understanding of the solute-solvent interactions would form the basis of explaining quantitatively the stimulus of the solvent and the extent of interaction of ions in solvents and thus cover the way for real understanding of the different phenomena associated with solution chemistry. Approximation of solute-solvent interactions can be obtained thermodynamically and also from the measurement of partial molar volumes, refractive index viscosity *B*-coefficient, and conductivity studies.

Also, thermophysical revisions or studies are of great importance, provided that a inclusive range of services and huge amount of products by amending the inner properties of raw materials. The bulky nature of solutions are very beneficial to obtain the information on the intermolecular interactions and also geometrical effects. In spite of the great benefits obtained from these observes, all-inclusive understanding of the properties of raw materials is crucial to the triumph or success of process design. Exact

knowledge of thermodynamic properties of solution mixtures has great importance in theoretical side as well as applied areas of research.

ILs are materials of a new class, which has attracted a lot of courtesy in the field of scientific and industrial research recently. The ILs has both chemical and physical properties; they significantly differ from collective molecular liquids. An ionic liquid (IL) is often well-defined salt in the liquid state of melting point below some arbitrary temperature usually lower 373 K <sup>[14]</sup> The simple combinatorial analysis specifies that nearby  $10^{18}$  ILs can be possibly blended. This variety unlocks wide opportunities in the fashion design of ILs suitable for practical applications. The understanding of the behavior of ILs and their properties is vital for any practical application. But the availability of chemical and physical data are inappropriately infrequent in comparison to the amount of already commercially available ILs. Moreover, the prevailing or existing data are often unpredictable. In this research work, we dedicated on the consistent determination of thermodynamic characteristic of ILs using different independent methods.

ILs have gained Worldwide attention because they are used as “designer solvents” and “green” replacements for organic solvents used in reactions involving inorganic and bio catalytic reactions in the last decade. This study discovered the fundamental science and engineering of using ionic liquids as a new peer group of solvents to substitute the traditional organic solvents. They are offered as novel solvents for the standby of organic solvents and the formation of smart liquids. The investigation also suggested Nano- and atom-scale structuring of ionic liquids, a feature that appears to totally fortify their sole behavioral characteristics and facilitate accurate predictions of trends. The study of physico-chemical behavior involves the clarification of the excess properties as a mean of unravelling the nature of intermolecular interactions among the mixed components. The interactions consisting among molecules can be deduced from a investigation of characteristic deviation from ideal behavior of some physical properties such as density, viscosity, and refractive index etc. <sup>(15, 16)</sup>. The rheological and molecular behavior of a formulation can influence aspects such as, patient suitability, since it has been well demonstrated that viscosity and density both influence the absorption rate of such products in the body. <sup>(17,18)</sup>. Rheology, the branch of science<sup>(19)</sup> that investigate deformation of material and flow, and is connected in the mixing and flow of medicinal preparations and cosmetics and is increasingly applied to

the analysis of the viscous behavior of many pharmaceutical products, <sup>(20-24)</sup> and to establish their stability and even bio-availability.

Density of solvent mixtures and related volumetric properties like excess molar volume are essential parameter for not only theoretical but also practical aspects. Depend on both sign and value of excess molar volume imparts guess of strength of unlike interactions in binary(IL+AA) systems. The particular interactions <sup>(25)</sup> among mixing components are obtained from the negative values of excess molar volume ( $V^E$ ). The positive values suggest supremacy of dispersion forces <sup>(25)</sup> between them. The negative ( $V^E$ ) values of excess molar volume<sup>(25)</sup> also give the intermolecular hydrogen bonding interactions and interstitial accommodation of mixing components .

It is very important that Knowledge of the properties of the RTILs is required for selecting an appropriate liquid for each of their envisioned industrial applications. Additionally, complete data sets of RTIL properties are used for validating and civilizing the molecular interaction and properties of prediction methods <sup>(26)</sup> which later will be applied to process interaction and process improvement and strategy.

The idiom '*solution*' is commonly used for particular case of a mixture between different components. A idiom solution is made by a small amount of substance, solute (solid, liquid or gas) dissolves to a definite limit in a liquid or solid substance (pure, or a mixture itself), solvent. A solution may be considered as a prima facie and largely get-together of molecules held composed by non-covalent interactions. The investigation of such type of interactions in physical systems of increasing the complexity should start with dimmers to continue through larger clusters, and end with solutions. In general, solutions are more complex than assemblies of feebly interacting molecules are and in particular, the study of reactivity in the presence of a solvent cannot be reduced to that of non-covalent interactions in the solutions.

Solvation and reaction dynamics are the complex process. The most fundamental properties of an ionic liquid in solution to determine the organization of solvent molecules. It is believed that exclusive ordering in ionic liquids results form a balance between cation-cation, anion-cation and most prominently, ion-pair formation. The final parameter has been found to be acute to the '*iconicity*' or transport properties of the liquids and these atom-atom interactions arbitrate the dissociation of the ions and thus the capability to form solvation shells associated with the '*ionic liquid effect*'. To probe

ionic liquid behavior, the effect of cation changes were examined experimentally and compared to that of model systems drawn for conservative molecular solvents.

The physical and chemical properties of a solution (liquid) is a result of the forte of their intermolecular forces. Differing charges on head-to-head molecules that lead to electrostatic attractions and governed by coulombs law. The intermolecular forces that appeared by the partial charges in molecules are dipole-dipole forces, dipole-induced dipole forces, hydrogen bonding, Van der Waal forces and electrostatic interaction hydrogen bonding, etc. *Intermolecular forces* in a solution switch their thermophysical/thermodynamic properties and the understanding of the solvation thermodynamics is very necessary to the characterization and elucidation of any process performed in the liquid systems. These thermophysical/thermodynamic properties are quantities, which are either trait of an entire system or are functions of position, which is endless and does not vary rapidly over microscopic distances, except in cases where there are sudden changes at boundaries between phases of the system. Therefore, the studies on the thermophysical properties along with the transport properties of solutions would provide a perfect or clear knowledge about the nature of the forces involving, an interacting way existing between the constituents of the solution.

It is thus, specious that the real understanding of the molecular interactions is a very difficult task to us. The aspect hold a wide range of topics but we have boarded on a series of investigations based on the volumetric, refract metric, viscometric, interferometric, conductometric and spectroscopic behavior to study the nature of the chemical structure of electrolytes/nonelectrolytes and solvents and their communal and exact interactions in solution systems.

### **1.1.1 What is the main Objective of this research work?**

Considering these contradictory results, the following questions arise:

- a) What is the reasonable linking between experimental results and theory and the spread of the experimental results?
- b) Are the interpretations in the experimental and theoretical results depends on functional groups, the chain length of alkyl groups in ionic liquids, functional groups, size , structure and shape of the cation and anion, a result of the ionic interactions?

- c) What makes the need and advantage of ionic liquids, different in contrast with?

The molecular liquids?

- d) How can be act amino acids in the molecular interaction with

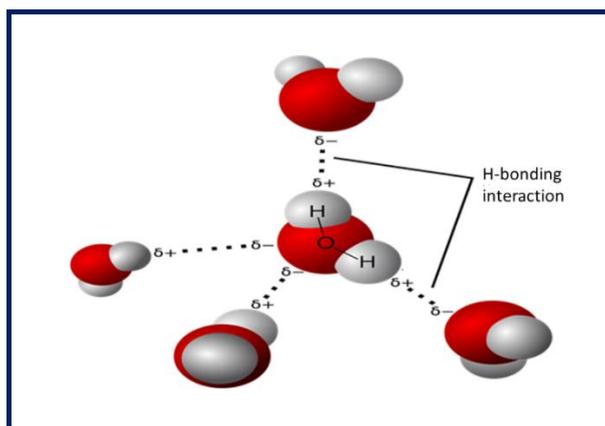
Aqueous solvents?

- e) How they can apply in research area, academic, industry and other supportable Chemistry, biochemistry and engineering?

We tried to answer of these questions using a combination of exact or precise experimental measurements and derivative thermophysical/thermodynamic properties to study the molecular interactions taking place in the solutions system.

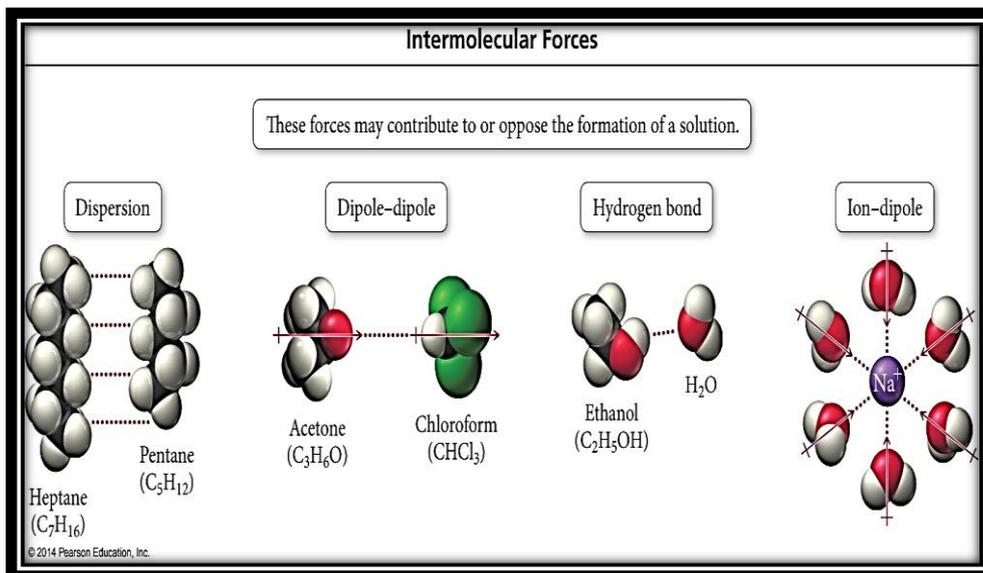
The key objective of the present research work is to explore and to recognize the molecular as well as ionic level of interactions prevailing in solutions by studying their thermophysical properties of ionic liquids and amino acids in some liquid systems. To keep away from needless effort in synthesis of ionic liquids(ILs) taken from the huge pool of possible ion combinations, several approaches were tried for the prediction of physical properties.

The molecular interaction in fluids by thermophysical, thermodynamic methods has attracted attention, as thermophysical parameters are convenient for interpreting intermolecular interaction patterns in non-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents. Due to different sequence of solubility, power of different solvation and possibilities of chemical or electrochemical reactions unacquainted in aqueous chemistry have open vistas for chemists and interest in the organic solvents exceeds the traditional boundaries of physical, inorganic, organic, analytical and electrochemistry<sup>(27)</sup>



### I.1.2 Importance of Thermophysical Parameters

The thermo- physical parameter such as *thermophysical*, *thermodynamic*, *transport*, *optical*, and *spectroscopic* are of great importance in characterizing the properties and structural aspects of solutions. The nature of intermolecular interactions can be showing from the interpretation of the resulting properties through the thermophysical study.



Of the solutions. From the density values of solvent mixtures and related volumetric properties like apparent molar volume are of also massive significance in measured the properties and feature of solutions. The magnitude and sign of partial molar volume ( $\phi_V^0$ ), a thermodynamic quantity, provides a huge information about the nature of ion-solvent interactions. While the experimental slope ( $S_V^*$ ) provides information about (solute- solute interactions).<sup>(28)</sup> Furthermore, the different parameters resulting from the experimental data density, viscosity and subsequent interpretation of the nature and strength of intermolecular interaction help in analysis and development of various theories of solution. Thus, the properties provide significant information both the nature and strength of intermolecular forces operating among mixed components

In order to develop industrial processes, the very significant parameter, and refractive index is also give the optical physical property of liquids and liquid mixtures influence the solution of different problems in chemical engineering. Knowledge obtained from refractive index measurements of multicomponent systems provides pivotal information about the molecular interactions occurring in the solutions,<sup>(29-31)</sup> that

is essential for many thermophysical calculations counting the correlation of with density. <sup>(32-34)</sup>

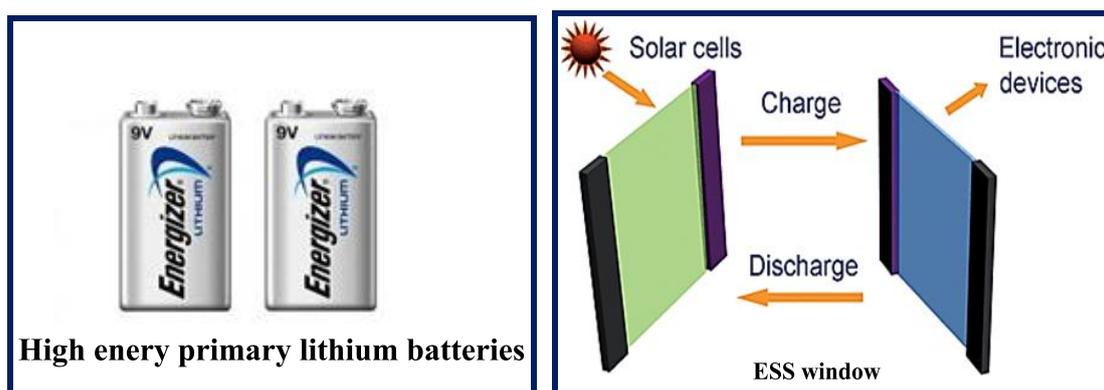
Information of viscosity of fluids is very essential in most engineering calculations where flow of fluid, mass transport and transport of heat are important factors. Valuable information concerning the nature and strength of forces of electrolytes/non-electrolytes operative in solutions mixture can be obtained from the viscosity data. The use of computer simulation of molecular dynamics has led to major development in the direction of an undefeated molecular theory of transport properties in fluids and a proper understanding of molecular motions and pattern of interactions in non-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents has been renowned <sup>(35-36)</sup>

The study of interactions like dissociation or association from ultrasonic speed measurements and from the calculation of isentropic compressibility has achieved a great deal. It can also be used for the test of various solvent theories, statistical models and are responsive for alteration in ionic concentration in addition to useful in illuminating the solute-solvent interactions.

The study of thermophysical behaviors like dissociation or association from acoustic measurements and from the calculation of isentropic compressibility has gained much importance. Measurements of accoustice properties are also applied for the test of various solvent theories and statistical models and are quite sensitive to changes in ionic concentrations as well as useful in elucidating the solute-solvent interactions. Thermophysical properties connecting with excess thermodynamic functions have applied in engineering and industrial separation processes. The importance and use of the chemistry of electrolytes in non-aqueous and mixed solvents are well recognized. However, the experimental observations of aqueous solution of different mixtures have provided enough information on the thermodynamic properties of various electrolytes and non-electrolytes. The above observations also give the effects of variation in ionic structure, ionic mobility and common ions along with a host of other properties. <sup>(37)</sup>

Elementary research on non-aqueous electrolyte solution has catalyzed their wide technical application in many fields. They are really challenging with other ionic conductors, especially at ambient and at low temperatures, due to their high flexibility based on the choice of numerous solvents, additives and electrolytes with widely varying

properties. Primary and secondary batteries with high energy, wet double-layer capacitors and super capacitors, electro-deposition and electroplating are some devices and processes for which the use of non-aqueous electrolytes solutions has brought the biggest success. (38-40) The non-aqueous electrolyte solutions are used largely in other fields of science, include electrochromic displays and smart windows, photo electrochemical cells, electro machining, etching, polishing and electro synthesis. In spite of the wide technical applications, our understanding of these systems at a quantitative level is still not clear. The main reason for this is the absence of detailed information about the nature and strength of molecular interactions and their influence on the structural and dynamic properties of non-aqueous electrolyte solution.



## 1.2. CHOICE AND IMPORTANCE OF SOLUTES AND SOLVENTS USED

A short description of the electrolytes (ionic liquids), non-electrolytes (amino acids), and solvents has been used throughout the research work is given below. The detailed description has been given in *Chapter II*.

### I.2.1 Electrolytes

During the research work, the most remarkable ionic liquids have been used as electrolytes for my experiment, as given in the following.

- 1-Butyl-3-methylimidazolium octyl sulphate(BMIM)(C8SO4)
- 1-Methyl-3-octylimidazolium chloride(MOIM)Cl
- Benzyltri methyl ammonium chloride
- 1-Butyl pyridinium Bromide(BP) Br
- Benzyl tri butyl ammonium chloride
- Tetra butyl ammonium Methanesulphonate

- (g) Benzyl tri ethyl ammonium chloride

### I.2.2 Non-Electrolytes

Selected Amino acids:

- (a) L-tyrosine
- (b) L-phenyl alanine
- (c) L-Ascorbic acid
- (d) L-Aspartic acid
- (e) L-Glutamic acid
- (f) L-Asparagine
- (g) L-Glutamine
- (h) L-methionine
- (I) L-arginine
- (j) L-histidine

### I.2.3 Solvents

The universal solvent water has been used throughout the work and the non-aqueous solutions are not taken for my research work.

The study of electrolytes (ionic liquids), non-electrolytes (amino acids), and solvents is of great importance because of their wide use as solvents, solutes and solubilizing agents in many industries ranging from pharmaceutical to cosmetics.

## 1.3. METHODS OF INVESTIGATION

The interactions and equilibria of ions in aqueous and non-aqueous media in different concentration regions are of immense importance to the technologist and theoretician as most of the chemical processes occur in these systems(9). Existence of free ions, solvated ions, ion-pairs and triple-ions of the electrolytes/non-electrolytes in aqueous and non-aqueous media depends upon the concentrations of the solution, size of ions, and *intermolecular forces*, e.g., electronegativity of the atom, dipole-dipole forces, dipole-induced dipole forces, H-bonding, Van der Waal forces, columbic forces and electrostriction, +I, -I effect, side chain effect etc. Hence, the study of assorted

interactions and equilibrium of ions in diverse concentration regions are of massive importance to the technologist, theoretician, industrialist, researchers as most of the chemical processes take place in these systems.

Stimulatingly the different experimental techniques have been employed to find out a better understanding the occurrence of solvation and different interactions prevailing in solution. Therefore, we have engaged the five significant thermophysical methods, namely, densitometry, conductometry, viscometry, and refractometry spectroscopy to reconnoiter or explore the solvation phenomena.

Using density measurement, apparent molar volumes, excess molar volume and partial molar volume obtained are usually convenient parameters for interpreting the ion-solvent/solute-solvent and ion-ion/solute-solute interactions in solution. Ionic apparent molar volume for the individual ions has been obtained with the help of “*reference electrolyte*” method. The compressibility, a second derivative to Gibbs energy is also a sensitive indicator of molecular interactions. This provide useful information in such cases where partial molar volume data alone cannot provide an clear interpretation of these interactions.

The change in viscosity of pure ionic liquid and solutions (containing ionic liquid with amino acid) of different concentration is used to recognize the inter-ionic and ion-solvent effects. The viscosity *B*-coefficients are also detached into ionic components by the ‘*reference electrolyte*’ method and from the temperature dependence of ionic values, a reasonable or satisfactory interpretation of ion-solvent interactions such as the effects of structure-breaking or structure-making, solvation, polarization, etc. has been given.

The transport properties of the ions involving in the solution, most of cases have been studied using the conductance data, especially the conductance at infinite dilution. Molar Conductance data obtained from specific conductance as a function of concentration can be used to study the ion-association with the help of appropriate equations. The ionic conductance are also play the decisive role to the interpretation of the ionic level of interaction, association or ion-solvent interactions of ions as well as molecules.

The spectroscopic study has been customary by the investigation of UV visible spectroscopy, fluorescence, NMR Technique. The study has been taking into account to

qualitative interpreting the molecular as well as ionic association of the electrolytes (amino acid) in the solutions.

#### I. 4 SUMMARY OF THE RESEARCH WORKS EMPHASIZE IN THE THESIS

##### CHAPTER-I

This chapter encloses the *objective, utility and applications of the research work*, the important of electrolytes/solute molecules and solvents used and methods of investigation. This also occupies the summary of the works done connected with the thesis.

##### CHAPTER-II

The chapter contains *the general introduction* (Review of the Earlier Work) of the thesis and forms and the very strong background of the work embodied in the thesis. A brief criticism of remarkable works in the field of solute-solvent, solute-solute and solvent-solvent interactions has been given. In this chapter, the discussion includes the ion-solvent/solute-solvent, ion-ion/solute-solute and solvent-solvent interactions in binary, ternary mixed solvent systems and of electrolytes in pure and non-aqueous solvent systems at various temperatures in terms of various derived parameters, estimated from the experimentally detected thermophysical properties *viz.*, *density, refractive index, viscosity and conductance*. Several semi-empirical models to approximation dynamic viscosity of binary liquid mixtures have been deliberated. Using Stokes' law and Walden rule, Ionic association and its necessity on ion-size parameters as well as relation between solution viscosity and limiting conductance of an ion has been deliberated. The molecular interactions are understood based on various derived parameters. Key assessment of different methods on the relative merits and demerits based on various types of assumptions employed from time to time of obtaining the single ion values (viscosity B coefficient and limiting equivalent conductance) and their implications have been understood. The molecular interactions are also made based on various type of equations.

##### CHAPTER-III

This chapter includes *the experimental section*, which mostly contains the basic information's, structure, source, purification and uses of the ionic liquids, electrolytes/non-electrolytes or solutes, and solvents have been used throughout the

whole research work. It is also confines the details of the procedure, instruments working principle and equations that are employed to know the thermophysical/thermodynamic, transport, optical and spectroscopic assets.

#### CHAPTER-IV

The chapter deals with the precise measurements on electrical conductance ( $\Lambda$ ) steady state fluorescence, Uv visible spectroscopy, determination of association constant, Gibbs free energy, study of proton NMR of solutions of an ionic liquid (ILs), L-Tyrosine, L-Phenyl alanine and their binary mixtures have been reported at 298.15K. From the above experiments, data reported which can explain the nature of interaction properties associated with the ionic liquids and the solute molecules. Also from the value of proton NMR, data can help the chemical environment of different protons and different types of interactions (non-covalent bond, weak pi-pi interaction).

#### CHAPTER-V

The chapter embraces the analysis of solute-solute and solute-solvent interactions between IL(BTAC) and two solute molecules(L-glutamic acid and L-Aspartic acid at different temperature(298.15k,303.15k,308.15k) quantitatively by precise measurement of density, viscosity, refractive index, molar conductance( $\Lambda$ ), in the solution systems. From limiting apparent molar volume, ( $\Phi_V^\circ$ ) experimental slopes ( $SV^*$ ), viscosity B-Coefficient data, molar refraction data explained the interaction phenomenon (solute-solvent and solute-solute interactions). Hydrogen bonding formation, Dipole-dipole interaction configurational theory, structural aspect, are the driving forces, have been employed for discussion of the results. The solvation phenomenon is manifested by the change of the difference parameters explained in this chapter in the presence of ionic liquids.

#### CHAPTER-VI

Apparent molar volumes ( $\phi_V$ ), viscosity B-coefficients, refractive index, specific conductance for L-Ascorbic acid in (0.001, 0.003, and 0.005) mol.dm<sup>-3</sup> aqueous ionic liquid, 1-Butylpyridiniumbromide, C<sub>9</sub>H<sub>14</sub>NBr) solutions, determined from density of solution and viscosity measurements at  $T = (298.15, 308.15, \text{ and } 318.15) \text{ K}$  and  $p = 0.1 \text{ MPa}$  as a function of the concentration (Molality) of L-Ascorbic acid have been reported in this chapter. To obtain the limiting values ( $\phi_V^\circ$ ), at infinite dilution, the apparent

molar volumes have been extrapolated to zero concentration. Solute-solvent interaction can be explain from the different parameters which obtained by using the Redlich-Meyer equation. The viscosity data were analyzed using the Jones-Dole equation, and the resulting parameters  $A$  and  $B$  have been interpreted in terms of solute-solute and solute-solvent interactions, respectively, in the mixed solutions. Ability to structure making or -breaking of the electrolyte (L-Ascorbic acid) has been discussed in terms of sign of  $dB/dT$ . For the ternary solutions ,the activation parameters of viscous flow studied have also been calculated and elucidated by the application of transition state theory.

## CHAPTER-VII

Custody in mind the uses of amino acids the apparent molar volume ( $\phi_V$ ), viscosity  $B$ -coefficient, Molar conductance ( $\Lambda$ ) and molar refraction ( $R_M$ ) of L-Arginine and L-Histidine have been determined in IL (Tetra butyl ammonium methansulfonate )at 298.15 K, 303.15K, 308.15K from density ( $\rho$ ), viscosity ( $\eta$ ), Specific conductance and refractive index ( $n_D$ ) respectively. Using Masson equation, the limiting values at infinite dilution are by extrapolated to zero concentration of apparent molar volumes. The experimental slopes ( $s_V^*$ ) and as well as limiting apparent molar volume ( $\phi_V^0$ ) obtained from the Masson equation have been understood in terms of solute-solute and solute-solvent interactions, respectively. From Jones- Dole equation, viscosity parameter  $A$  and  $B$  derived using viscosity data have been interpreted in terms of solute-solute and solute-solvent interactions, respectively in the solutions. Applying Lorentz-Lorenz equation to evaluated the Molar refraction ( $R_M$ ) values as explain the solvation properties associated in the solution mixture. Molar conductance data also explain the molecular interactions involving in the solutions. Interactions properties also explain by computational study.

## CHAPTER-VIII

This chapter includes the study on interactions between solute-solvent and solute-solute. Here the - ethyl ammonium chloride with one amino acid(solute) L-Methionine have been carried out by volumetric, viscometric , conductometric, refractometric, surfacetension, NMR, Computationals measurements . Comparism of solute-solute and solvent-solvent interactions between ILS with amino acid can be explained with the help of some physicochemical parameter such as limiting apparent

Molar volumes ( $\Phi_V^\circ$ ), viscosity B-Coefficient, Molar conductance( $\Lambda$ ) data. In addition, proton NMR, UV-Visible and FTIR spectroscopy help to determine the interaction properties in pure as well as the solution mixtures. Variation of optimization energy calculated theoretically by interactions behaviour between two ionic liquids (solvents), Benzyltri -methyl ammonium chloride and Benzyl tri Gaussian Method of pure ionic liquids and mixture with amino acid gives the same result obtained practically from above mentions of different parameters in this chapter.

## CHAPTER-IX

In this chapter physicochemical properties such as density ( $\rho$ ), viscosity ( $\eta$ ), refractive index( $n_D$ ), molar conductance( $\Lambda$ ), surface tension measurements of ionic liquid(Benzyltri butyl ammonium chloride), solute molecules, L-glutamine( $C_5H_{10}N_2O_3$ )&L-asparagine( $C_4H_8N_2O_3$ ) and their binary mixtures have been studied over the entire range of composition at 298.15 K,303.15K,308.15K, respectively. Solute- solute and solute- solvent interaction have been interpreted by some very significant physicochemical parameters namely, Apparent molar volumes ( $\phi_V$ ), and viscosity *B*-coefficients accompanied with the data of densities and viscosities respectively. Using the Masson and Jones-Dole equation for explaining the limiting apparent molar volumes ( $\phi_V^0$ ), experimental slopes ( $S_V^*$ ) and viscosity *A* and *B* coefficients. Spectroscopic technique such as  $^1H$ NMR, UV-vis. is also applying for the determination of molecular interactions. Molar expansibility factor ( $\Phi E^\circ$  and  $\partial\Phi E^\circ/\partial T$ ) obtained by applying polynomial equation which explain the solute- solvent interactions properties. Computational study is also accompanied with the manifestations of interactions prevailing in ionic liquid with two amino acids.

## CHAPTER-X

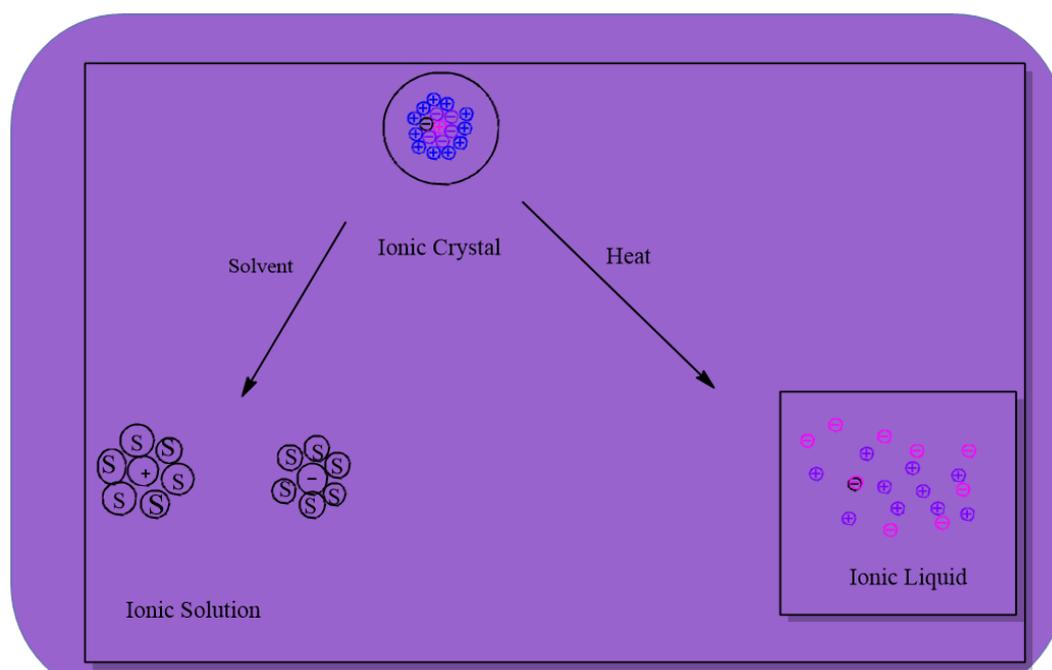
In this chapter, covers the concluding remarks of the works related or detailed described in the thesis (dissertation).

## CHAPTER -II

### *General Introduction (Review of the Earlier Works)*

#### 11.1. IONIC LIQUIDS

Ionic liquids (ILs) are very important salt that exist in liquid state/phase. In some contexts, the term has been categorized to ionic species existing in liquid state. The melting point of ionic liquid is below some arbitrary temperature, 100°C (212°F). In general, Ionic Liquids (ILs) are liquid state salts that involve organic-organic or organic-inorganic cation or anions respectively (Figure II. 1).



**Figure II.1: Difference between an ionic solution and an ionic liquid.**

Decreasing of melting temperature <sup>(II.1)</sup> of ionic liquid by increasing size of the ions and making them asymmetric. This is easily elucidated as follows: owing to electrostatic forces happens in ionic liquid system they tends to attract to each other. If the size of the ions are very small and symmetric, as for example, in sodium chloride, the ions will become very near to each other and interact among strongly. Furthermore, due to their nature of symmetry, the crystals formation is favourable. If the size of the ions

is increased, the distance between them will increase and as consequence, the electrostatic attractive force will decrease. The above-mentioned process is used to control the melting point of ionic liquid. Due to their versatile nature, it is possible to synthesize thousands of ionic liquid by only varying a functional group, and the variation of the functional groups will determine the final macroscopic features of that ionic liquid. In the last years, it has been found that ionic liquids have different applications at different field of science, e.g. as catalysers, electroplating solvents and electrolytes.<sup>(II.2)</sup> For the specific case of electrolytes, the interest in ionic liquid has greatly increased and already some possible applications are found in fuel cells,<sup>(II.3)</sup> in solar cells,<sup>(II.4)</sup> and lithium-ion batteries.<sup>(II.5)</sup> Inspire of it has already mentioned qualities of the ionic liquids, they are relatively new as elect roles, and as such, there are some draw backs of the ionic liquid such as compatibility, toxicity, with the actual materials used, production cost, and all the problems that come with the introduction of a new technology.

In the last periods, many research groups at different place around the world, focused on a new class of compounds of ionic liquids (IL). The last ten years it was observed that the count of publications with the topic “*ionic liquids*” grew gradually. However, it seem to be what are ionic liquids and why are they so interesting? The following section gives a short overview over this broad field. A much more comprehensive overview about the possible properties and applications of ionic liquids can be observed in the recent book “*Ionic Liquids in Syntheses*”, edited by Peter Wasserscheid and Tom Welton.<sup>(II.6)</sup> The generally conventional definition of ionic liquids is that they are “*ionic materials that are liquid below 373 K*”.<sup>(II.7)</sup> However, the ideas about the definition of “*ionic material*” are more spread. Many organic solvents that have been proposed over the last two decades. Water frequently used as the ultimate green solvent can be consider in this respect. Ideally solvent-free conditions or the use of water as the ultimate green solvent can be considered. However, most of the organic compounds do not dissolve in water frequently, and especially a solids cannot be processed without a solvent. Therefore suitable alternatives have been sought and found in the classes of (I) ionic liquids; ionic liquids have gained a lot of attention as emerging environmentally benign solvents.<sup>(II.7)</sup> Ionic liquids used as a replacement solvents instead of conventional organic solvents in several applications due to their unique features. The melting point of Ionic liquids is below 373 K. ILS consist of an

organic cation that combined with an organic or inorganic anion<sup>(II.6)</sup> In generally Ionic liquids display, a very interesting set of properties, used for different applications in chemical industry. Stability of some ionic liquid are up to 500K.<sup>(II.8)</sup> the melting points of these organic salts are commonly found below 150 °C<sup>(II.9)</sup> and rarely as low as -96 °C.<sup>(II.10)</sup> At room temperature due to their ionic nature, they have no measurable vapour pressure.<sup>(II.6)</sup> they typically have high solvency power for polar and non-polar compounds. Billions or more than billions of ionic liquids can be considered and synthesized by selecting different ion pair combinations, which allow them to possess specific properties. Besides, the ability to adjust the solvent properties of the ionic liquids is one of their outstanding properties. It's makes them unique solvents for various reactions and separations.<sup>(II.11)</sup> Moreover ionic liquids are practically highly thermally and non-flammable, and (electro)chemically stable and ILS present a large liquid range.<sup>(II.6)</sup> The key challenges of ionic liquids in the field is that it has the large scale application due to their high costs, their high toxicity (many ionic liquids contain halogens) the unknown long term stability and their relatively high viscosity compared to most common molecular solvents. The latter decreases the rate of mass transfer decrease during the reaction and the separation processes. Though, the viscosity of ionic liquids can drop ominously by addition of co-solvents such as carbon dioxide (CO<sub>2</sub>)<sup>(II.6)</sup> The whole comparison between ionic liquids and organic solvents is represented in Table II.1.<sup>(II.12)</sup>

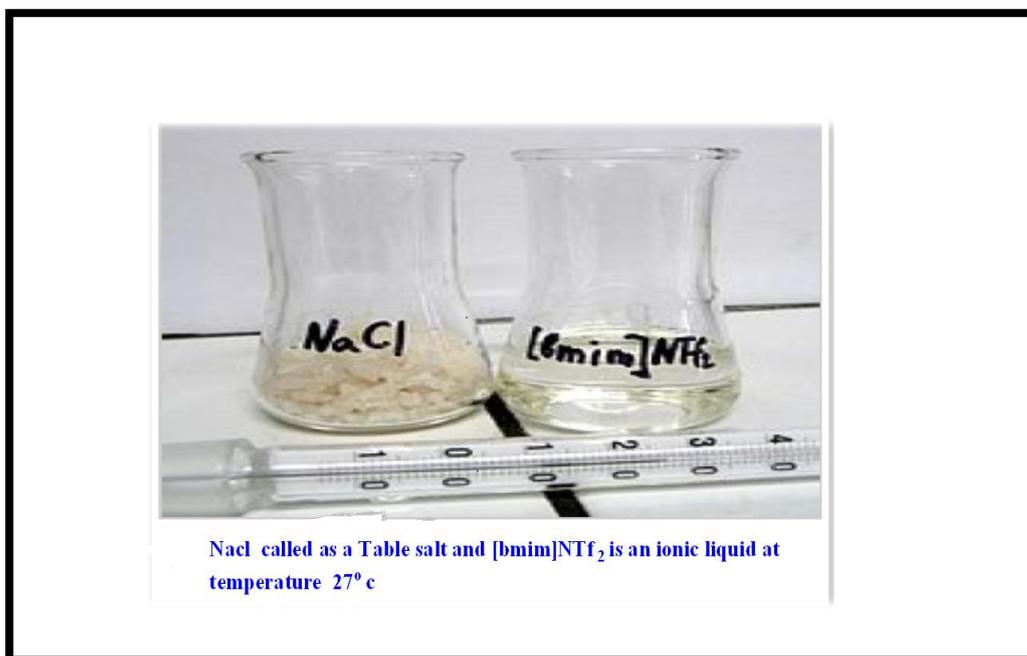
**Table II.1. Comparison between organic solvents and ionic liquids.**<sup>(II.13)</sup>

| characteristic    | Organic solvent                               | Ionic Liquid   |
|-------------------|---|--|
| Number of Solvent | > 1000  | > 10000  |
| Catalytic Ability | rare  | Common and tunable                                       |
| Applicability     | Single function                               | Multifunction  |
| Solvation         | Most of case weakly Solvating                 | Strongly solvated in solution                            |
| Chirality         | rare  | Common and tunable                                       |
| Polarity          | Conventionally polarity concepts apply        | Concept of polarity is Questionable                      |
| Vapour Pressure   | Obeys the rule of Clausius-Clapeyron equation | It has Negligible Vapour pressure under Normal condition |
| Flammability      | Usually flammable                             | Usually nonflammable                                     |

| characteristic              | Organic solvent                | Ionic Liquid   |
|-----------------------------|--------------------------------|--|
| Recyclability               | Green imperative               | Economic imperative  |
| Tunability                  | Available for limited solvents | Huge range of solvents means “Green solvents”                  |
| Cost                        | Generally cheap                | It is Typically two to hundred times more than organic solvent |
| Density(kg/m <sup>3</sup> ) | 600 to 1700                    | 800 to 3300  |
| Viscosity(pa.s)             | 0.0002-0.1                     | 0.022-40   |
| Refractive index            | 1.3 to 1.6                     | 1.5 to 2.2   |

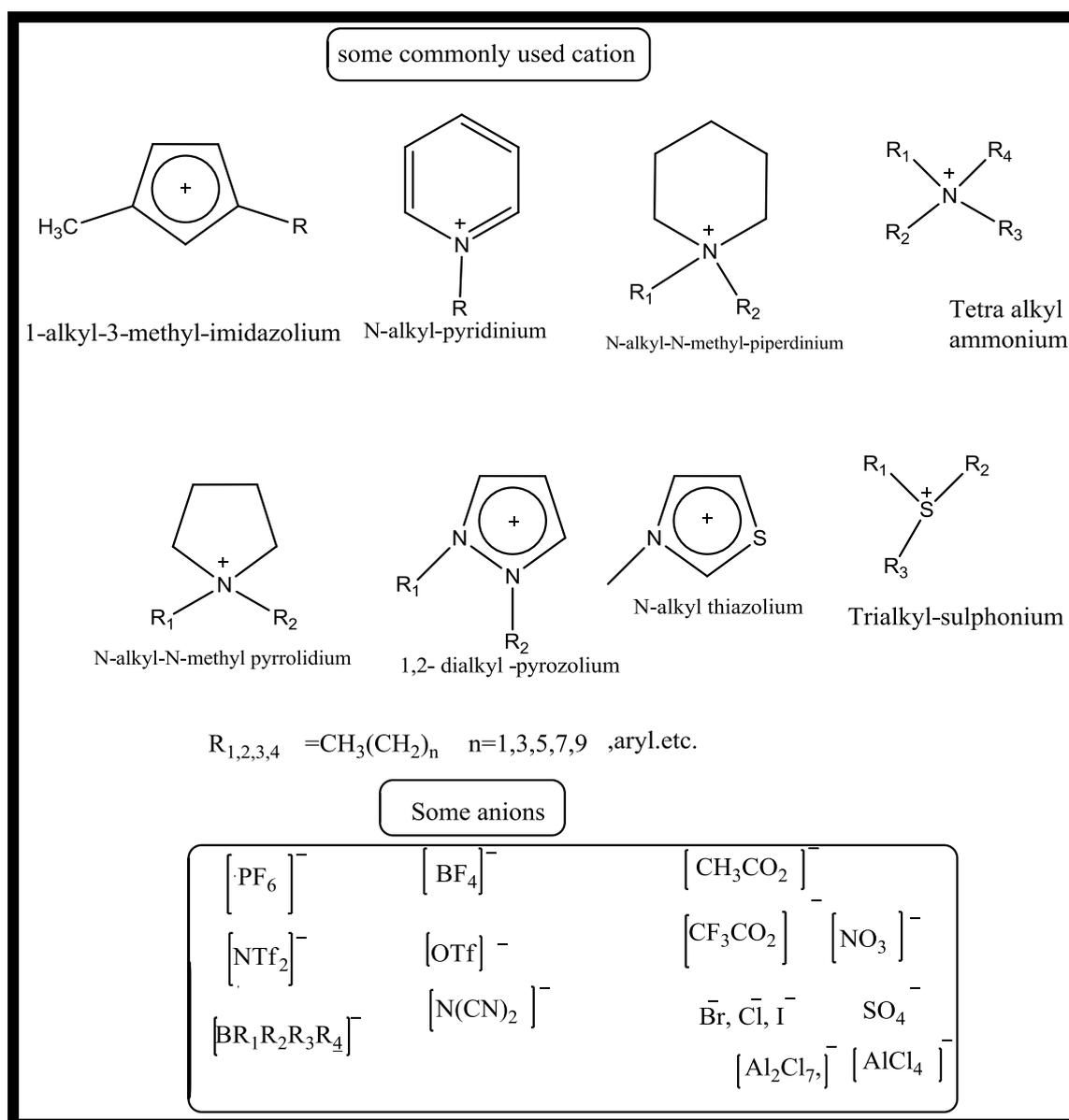
### II.1.2 Room Temperature Ionic Liquids (RTILs)

At room temperature ILs which are liquid is called room temperature ionic liquid (RTIL). From the older and some current literature, ionic liquids are sometimes called liquid organic salts, fused salts, molten salts, ionic melts, NAILs (non-aqueous ionic liquids), OILs (organic ionic liquids) room-temperature molten salts, and ionic fluids. (II.14) sodium chloride (NaCl, *mp* 801°C), normal salts, when heating to high temperature produces also a liquid, that involves entirely of ions, but this is term as a molten salt and do not called them as an ionic liquid.



Commonly, ILs contain of a large bulky and asymmetric organic cations based on 1-alkyl-3-methylimidazolium (abbreviated [C<sub>n</sub>mim]<sup>+</sup>), where *n* is the number of

carbon atoms in a linear alkyl chain) tetraalkylammonium ( $\text{Bu}_4\text{N}^+$ ) or tetraalkylphosphonium ( $\text{Bu}_4\text{P}^+$ ) cations. N-alkylpyridinium (accordingly abbreviated  $[\text{C}_n\text{py}]^+$ ), and many others; and inorganic anions such as tetra fluoroborate  $[\text{BF}_4]^-$ , hexafluorophosphate  $[\text{PF}_6]^-$ , alkylsulfates  $[\text{RSO}_4]^-$ , alkyl sulfonates  $[\text{RSO}_3]^-$ , halides as chloride  $[\text{Cl}]^-$ , bromide  $[\text{Br}]^-$  or iodide  $[\text{I}]^-$ , nitrate  $[\text{NO}_3]^-$ , sulphate  $[\text{SO}_4]^-$ , aluminium chloride  $[\text{AlCl}_4]^-$ , triflate ( $[\text{CF}_3\text{SO}_3]^- = [\text{TfO}]^-$ ), bis(trifluoromethylsulfonyl)imide ( $[(\text{CF}_3\text{SO}_2)_2\text{N}]^- = [\text{Tf}_2\text{N}]^-$ ), etc.<sup>(II.15, II.16)</sup> Lately when the amino acids are act as anionic part of the ionic liquids and then ionic liquids are called amino acid based ionic liquids (AAILs).<sup>(II.17)</sup> Some commonly used ionic liquid systems are presented in Figure II. 2. in the following.



**Figure II. 2:** Some commonly used ionic liquid systems given in the above chart.

Ionic liquids are eco-friendly used as green solvents due to their no volatility compared to conventional solvents, which are often volatile and it has much contribute both to air pollution and the greenhouse effect. Due to suitable for reuse oils consumption of solvent is very less. However, the normally used ILs are toxic in nature and are hard to biodegradable, which are naturally not intrinsically green. In detail, ILs can be designed to be environmentally benign, which is the direction to research and industry should steer towards.

### II.1.3. Properties of Ionic Liquids:

The melting points of ionic liquid is very low due to asymmetry nature of cation is believed to be responsible for the fact., while the nature of the anion part of the ionic liquid is considered to be responsible for many of the physical properties of ionic liquids such as their miscibility with conventional solvents and hygroscopicity. <sup>(II.18)</sup> “*Green Solvents*” are commonly referred to ILS due to their immeasurably low vapour pressure. A crucial feature of ionic liquids is that their various physical properties such as melting point, density, viscosity, and hydrophobicity can be tailored to design different ionic liquids with a specific end use in mind by selection of different cation, anion, and substituents respectively. For this reason, the ionic liquids are also described as “*Designer Solvent*”. <sup>(II.19)</sup> There are number of advantages of ionic liquid as a solvents over molecular Ionic liquids such as high thermal stability negligible vapour pressure, , non-flammability, wide temperature range, hydrophobicity, Lewis acidity gas solubility and hydrogen-bonding capability, therefore, these fluids have been proposed as an attractive alternative to volatile organic compounds (VOCs) for “*green processing*”. To prevent the emission of VOCs, a major source of environmental pollution the ionic liquids used as the replacement of conventional solvents. <sup>(II.20)</sup>

Properties of ionic liquid has listed in the table form:

| property             | value                        |
|----------------------|------------------------------|
| Freezing point       | < 373.15K                    |
| thermal stability    | Very high                    |
| liquid range         | 298.15K-473.15K              |
| dielectric constant  | < 30(F/m)                    |
| viscosity            | < 100cp                      |
| polarity             | 47-49                        |
| specific conductance | <10 (mS/cm)                  |
| molar conductance    | <10( Scm <sup>2</sup> /mol ) |

#### 11.1.4 Generations of ILS

Three categories of Ionic Liquids are first-generation; Second-generation; and Third-generation ionic liquids. <sup>(II.21)</sup>

For the first-generation ionic liquids consist of bulky cations such as one, 3-dialkylimidazolium (or *N*, *N'*-dialkylimidazolium) or 1-alkylpyridinium (or *N*-alkylpyridinium), and anions commonly based on halo aluminate (III); these have been studied widely. Ionic liquid has their merit as a tuneable Lewis acidity. Ionic liquids has their great drawback due to extremely sensitivity towards water, which forms hydroxoaluminate(III) species with the aluminium(III) chloride and therefore it decomposes to ionic liquid easily. The sensitivity of ionic liquids towards water necessitates their handling in a dry-box.

The ionic liquids of the second category gradually absorb water from the atmosphere. <sup>(II.22)</sup>, are usually air-stable and water-stable and can be used on the bench-top. However, it must be carefully noticed that water-stable does not imply that there is no interaction with water at all.

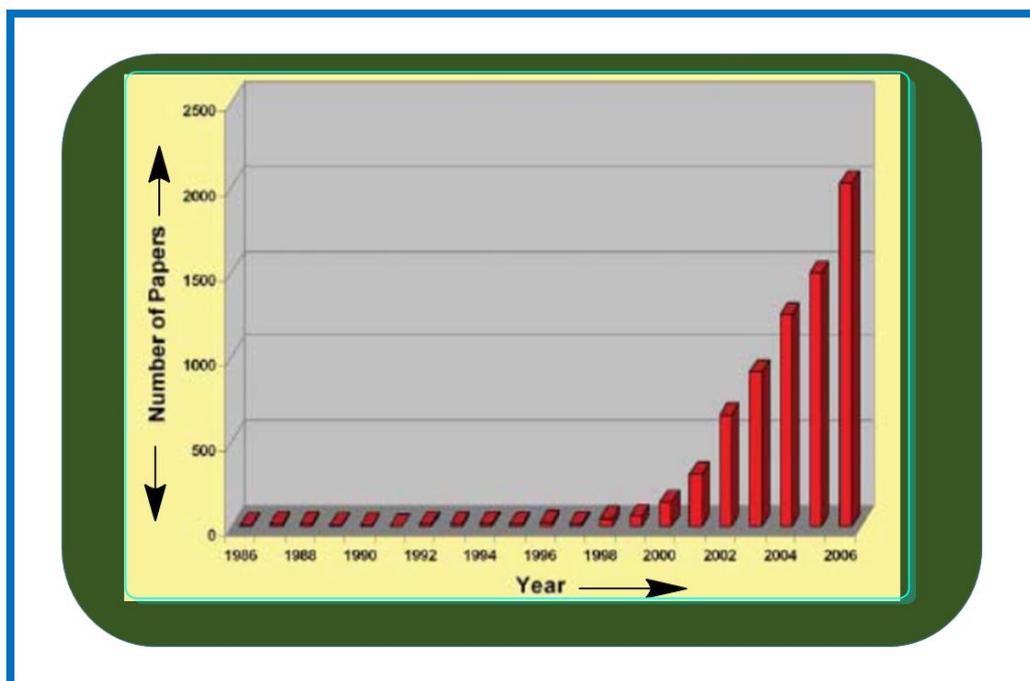
Recently, a third generation of “task-specific” ionic liquids have developed. <sup>(II.23)</sup> These novel ionic liquids have very interesting feature for chemical functionalities which have been designed for particular applications. From the physical properties of ionic liquid very little is known and the future will show if they can bring about an ecological or economic benefit; but that future does look positive.

#### II.1.5. History and New Developments

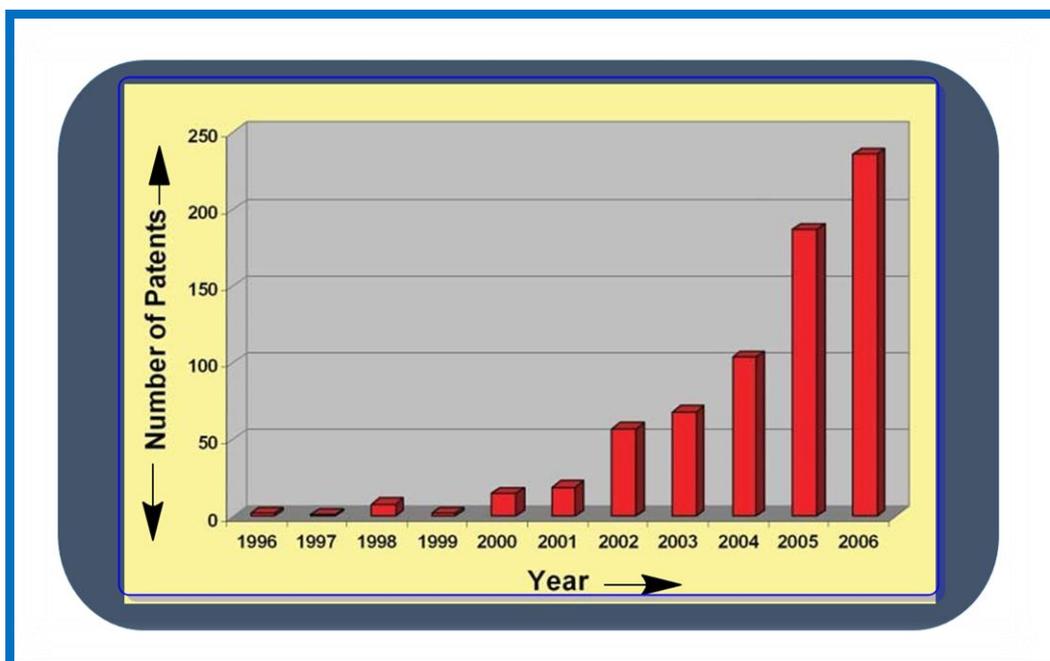
Ionic liquids have their extensive use solvents in chemical processes for synthesis, separation processes and catalysis has recently become noteworthy. By Paul Walden in 1914 <sup>(II.24)</sup> Synthesized the first low melting salt (ionic liquid), ethyl ammonium nitrate ( $[\text{EtNH}_3]^+ [\text{NO}_3]^-$ ), having melting point of 12°C. Aluminium chloride-based molten salts were utilized during 1940s, for electroplating at temperatures of hundreds of degrees Celsius. In 1951, low melting salts with chloroaluminate ions for low-temperature electroplating of aluminium were developed. <sup>(II.25)</sup> During the 1970s and 1980s, these liquids were studied mostly for electrochemical applications in the field of nuclear warheads batteries. <sup>(II.26)</sup> In the early 1970s, Wilkes tried to develop better batteries for nuclear warheads and space probes which is very essential for molten salts to operate. These salts were so hot enough to damage the nearby

materials. For this, reason chemists investigated for salts, which remain liquid at lower temperatures, and finally they identified one, which is liquid at room temperature. For the improvements of ionic liquid, Wilkes and his colleagues use as battery electrolytes and then a small community of researchers began to make ILs and test their properties. (II.27, II.28) In the mid 1980s, low melting point ionic liquids for organic synthesis were suggested. (II.29, II.30) Ionic liquids became one of the most promising chemicals as solvents in the late 1990s. These ILs were very active towards various organic compounds. Due to their instability nature towards air and water new ionic liquids such as organoaluminum, have limited range of applications+. Besides, these ILs were not inert towards various organic compounds. In 1992, synthesis and applications of water and air stable ILs as for example, 1-*n*-butyl-3-methylimidazolium tetra fluoroborate ([bmim] [BF<sub>4</sub>]) and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim] [PF<sub>6</sub>]), the number of air and water stable ILs have started to increase quickly.

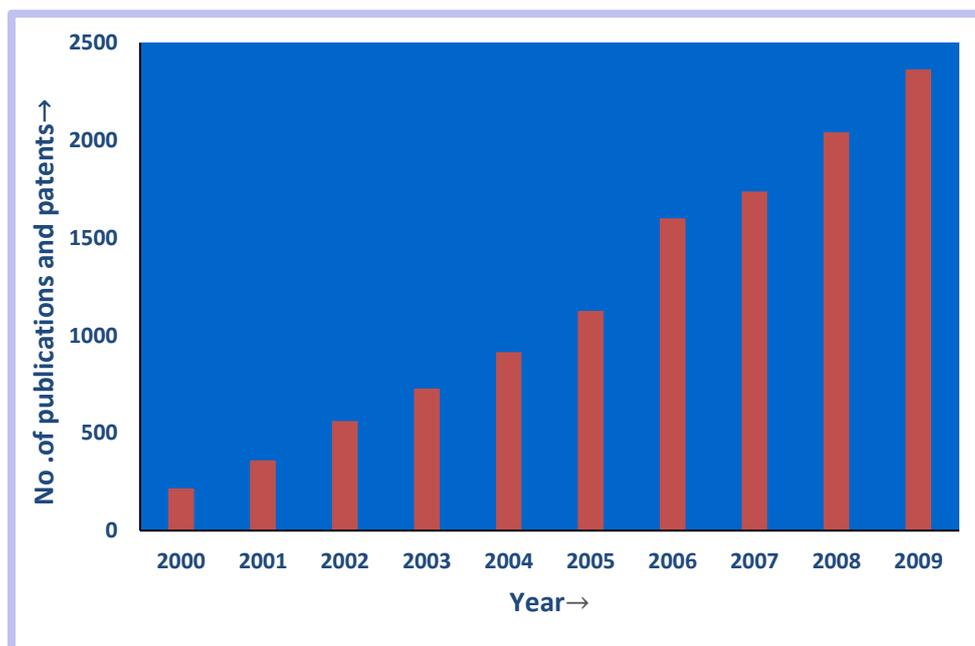
It is very Interest in ionic liquids that it has now been grown dramatically in the scientific community (both in academia as well as industry) in the last decade. (II.15) with over 8000 papers have been published. This growth of publication can be observed in Figure II.3. (II.15) (number of publications per year) and Figure II.4. (II.15) (number of patents per year), it is clear from the given figure that the number of publications and patents are increasing exponentially. In the laboratory, there are about one million ( $10^6$ ) simple ionic liquids that can be easily synthesised by combination of different cations and anions and this total are just for simple primary systems (Figure II.5). There are one billion ( $10^{12}$ ) possible binary combinations of these, and one trillion ( $10^{18}$ ) ternary possible IL systems that can be prepared from the combination of anions, cations, and substituents respectively If there are one million possible simple systems of ionic liquid present. Now days only about 300 ionic liquids are commercialized so one can imagine this in depth, how many chances in this field are still undiscovered and why this field of chemistry is so trying or tempting.



**Figure II. Three:** Growth rate of ionic liquid publications from 1986 to 2006.

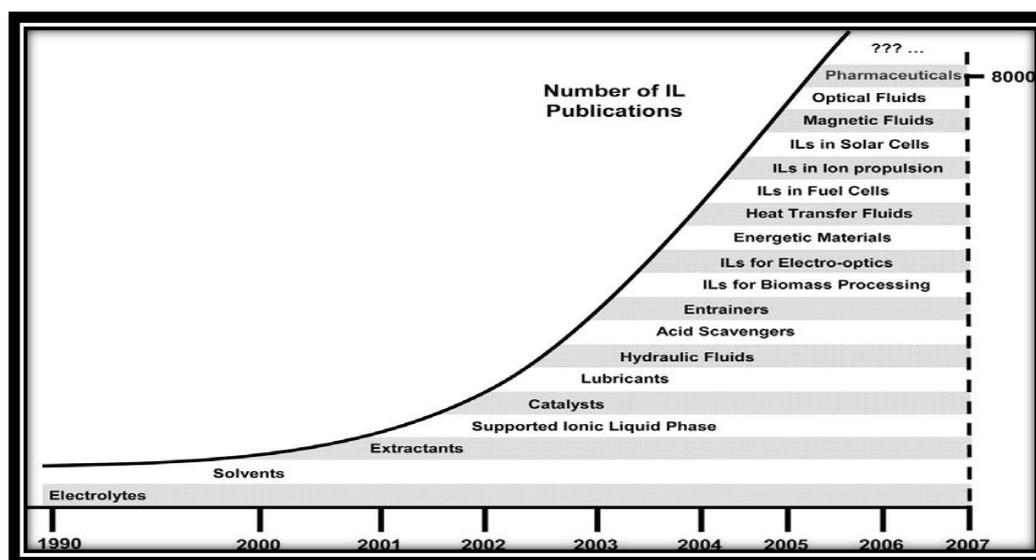


**Figure II. Four:** Annual growth of ionic liquid patents from 1996 to 2006.



**Figure II. Five:** Annual growth of ionic liquid paper and patents, up to 2009

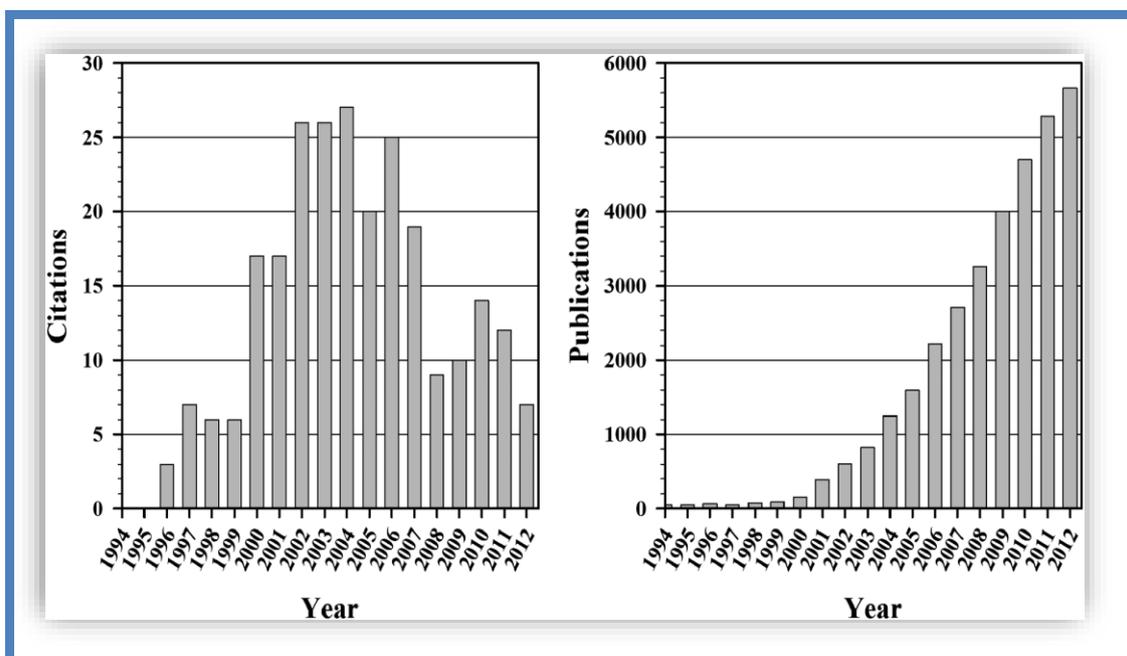
It was observed from the plot Until 1998, the number of entries of publications and papers with the terms “*ionic liquid*” or “*ionic liquids*” in the Chemical Abstracts was below or around twenty per year. After this number is increasing 45 per year to 1255 from 1999 to 2005 and 1717 in 2006 with their different applications in various field of science.<sup>147</sup> The total number of entries is over 8000 (in 2007) which indication in different areas, huge potential of ionic liquids applications as shown in Figure II.6.



**Figure II.6:** Growth in the number of IL publications per year and representative areas of interest. (Data achieved from Sci Finder Scholar using the search terms “*ionic liquid*” OR “*ionic liquids*” and then refined by publication year. The data for entire publications

includes the number of patents, and the area of the particular field does not represent the number of publications in the subfield).

In the 2000s as the IL field grew there are three distinct forces led to ILs becoming the hunting of overgeneralizations that still plague the field today, including a plethora or abundance of new researchers in many different disciplines with little or no background in the IL field (or often not even chemistry). The rise in societal significance of green chemistry and sustainability, and the interesting new science and applications assured by the study of ILs. As shown in [Figure II. 7](#) the inherent concepts of ILs as solvents and green chemistry scolded a dramatic increase in publications in this field (which is not yet slowing down) and primarily an increase in the citations to Fuller et al.<sup>(11.31)</sup>



**Figure II. Seven:** The inherent ideas of ILs as solvents and green chemistry scolded a dramatic increase in publications in this field.

## II. 1. 6. Potential Applications of Ionic Liquids

Ionic liquid is very important as a solvent, in recent years; it has been used for an extensive variety of applications at lab scale, such as desulfurization of diesel oil, the recovery of bio-fuels, and supercritical fluid extractions etc. In addition, Ionic liquids have potential as lubricants, in solar cells, for heat storage, lubricants, in nuclear fuel processing, as sol-gel templates and in the dissolution of cellulose in membrane

technology. The various application in different application of ionic liquids are given in Figure II.8a, II.8b.

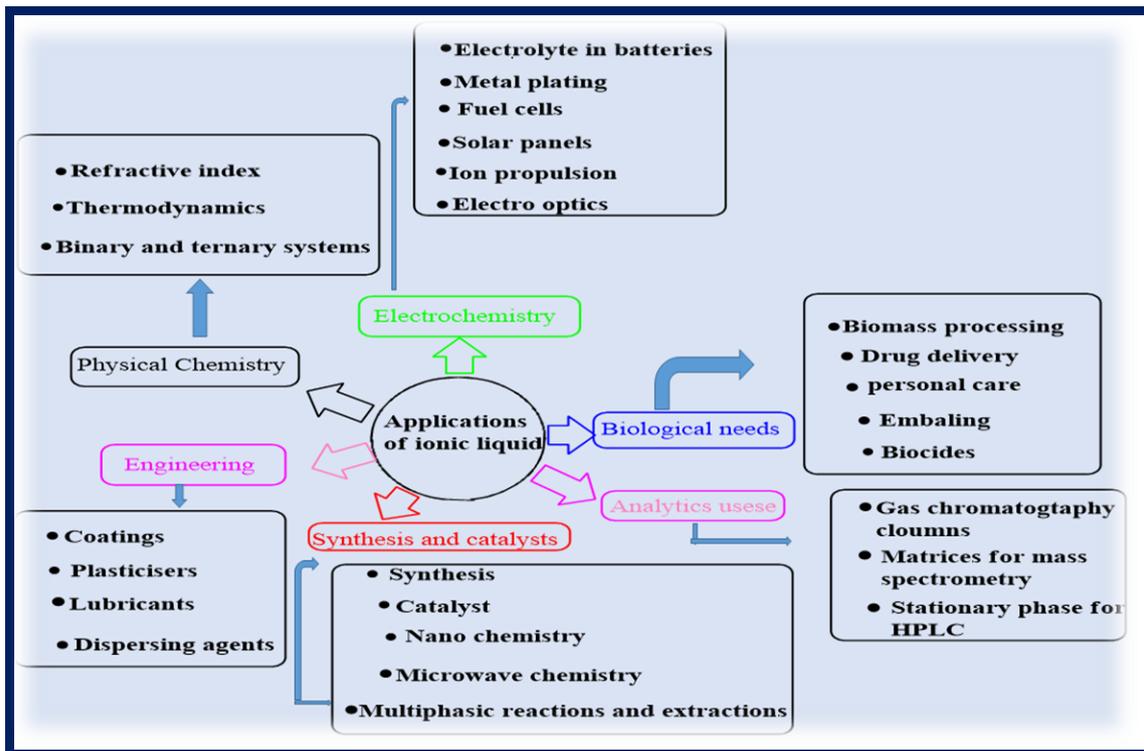


Figure II. 8a: The diverse application of ionic liquids in different field.

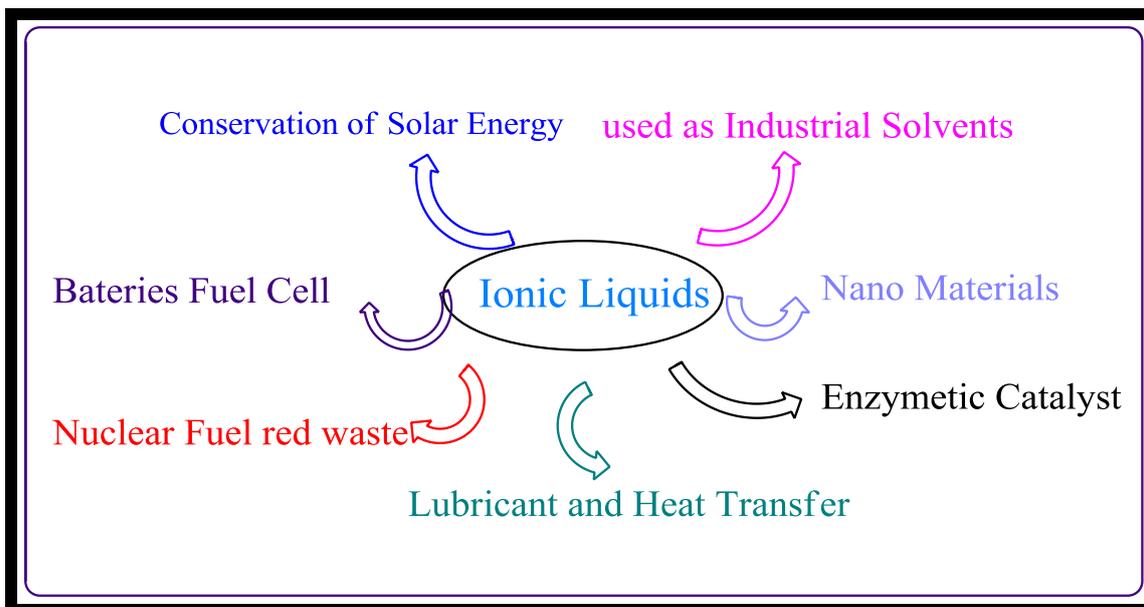


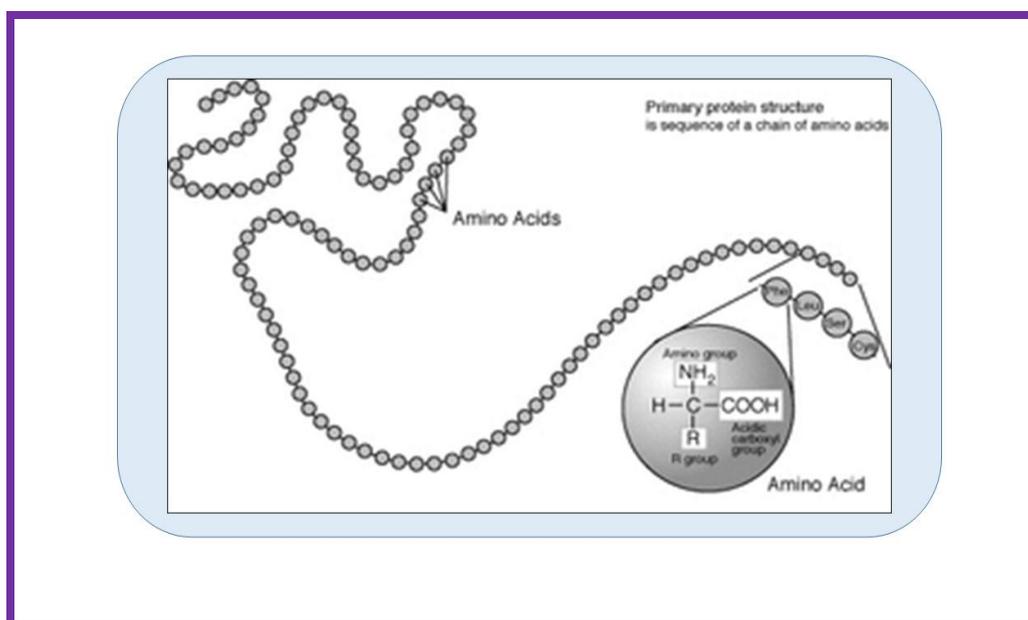
Figure: II.8(b) Selection of applications where ionic liquids have been used

## 11.2. AMINO ACIDS

A very brief description of amino acids are given in **Chapter: I**. Here utility of amino acids are given as below:

### II.2.1 Occurrence and Functions in Biochemistry:

A polypeptide is the unbranched chain of amino acids. Amino acids are very important to make the structural units that make up proteins. Amino acids combine to form short polymer chains which called peptides or longer chains called either polypeptides or proteins. These Polymers are linear within the chain with each amino acid attached to two neighbouring amino acids. The amino acids are added is study through the genetic code from mRNA template, which is a RNA copy of one of the organism's genes.



### II. 2.2. Human Nutrition

When the amino acids taken up into the human body from the diet, proteins and other biomolecules are synthesized by using about twenty-two standard amino acids, which are oxidized to urea and carbon dioxide as a source of energy in human body.

| Essential  | Nonessential |                 |
|------------|--------------|-----------------|
| Histidine  | Alanine      | Proline*        |
| Isoleucine | Arginine*    | Selenocysteine* |
| Leucine    | Asparagine   | Serine*         |

| Essential     | Nonessential  |           |
|---------------|---------------|-----------|
| Lysine        | Aspartic acid | Taurine*  |
| Methionine    | Cysteine*     | Tyrosine* |
| Phenylalanine | Glutamic acid |           |
| Threonine     | Glutamine*    |           |
| Tryptophan    | Glycine       |           |
| Valine        | Ornithine*    |           |

\* Essential only in certain cases. (II.32, II.33)

### II.2.3. Uses in Technology

In industrial purpose, Amino acids are used for a variety of applications. but their key use is as additives to animal feed, such as soybeans, either have low levels or lack some of the essential amino acids: The food industry is also used as a major user of amino acids, in particular, glutamic acid is used as a flavor enhancer and aspartame (aspartyl-phenylalanine-1-methyl ester) as a low-calorie artificial sweetener. The effect of chelating ability of amino acids has been used in fertilizers for agriculture, to assist the delivery of minerals to plants in order to maintain the correct mineral deficiencies, such as iron chlorosis. The remaining part of production of amino acids are utilized in the synthesis of drugs and cosmetics purpose.

### II.2.4. Thermophysical Properties of Amino Acids

Based on different genetic code of amino acids are directly encoded. Based on their properties, amino acid can be divided into several groups. Important factors are hydrophilicity or hydrophobicity, charge, size, and functional groups. the structure of protein and protein-protein interactions are very important properties of amino acids .The water-soluble proteins tend to have their hydrophobic residues (Leu, glu ,asp, Ile, Val, Phe, and Trp) submerged in the middle of the protein, whereas hydrophilic side-chains are manifested to the aqueous solvent. Some modifications of amino acid can readily produce hydrophobic lipoproteins, or hydrophilic glycoproteins. These types of modification permit the reversible targeting of a protein to a membrane. For example, the accumulation and Elimination of the fatty acid palmitic acid to cysteine residues in some signaling proteins result the proteins to attach and then detach from cell membranes.

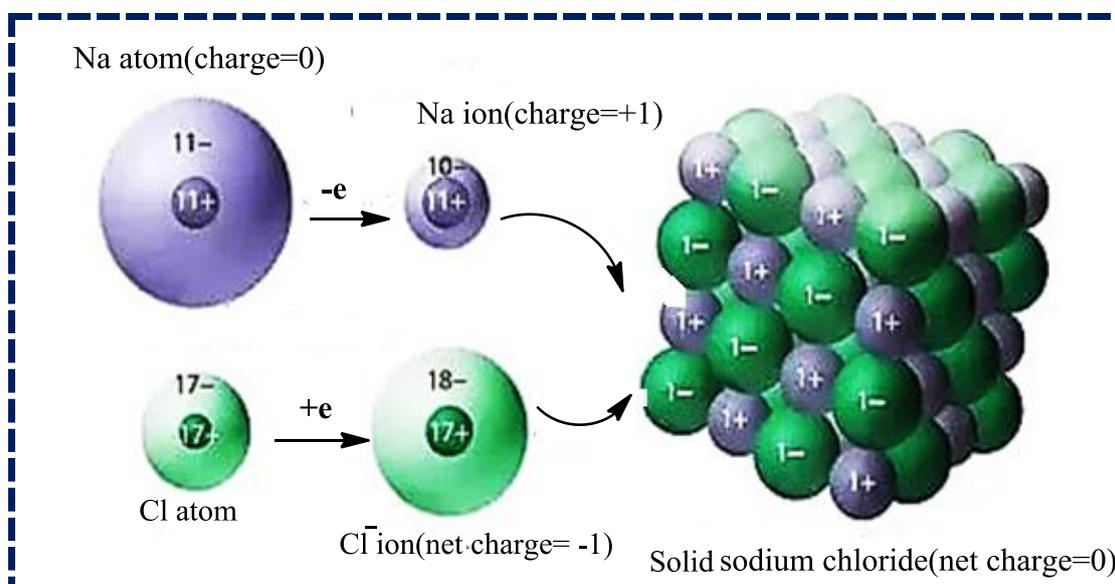
### 11.3. SOLUTION CHEMISTRY

Solution chemistry is the branch of physical chemistry that studies the change in properties that arise when one substance dissolves in another one. In 'Solution Chemistry' the extent of solvation broadly three types of approaches have been made to estimate. In 'Solution Chemistry'. The first is the solvation approach involving the investigation of viscosity, conductance, of electrolytes and the derivation of various factors associated with ionic solvation, (II.34) the second is the thermodynamic approach by measuring the enthalpies, entropies and free energies of solvation of ions from which factors associated with solvation can be elucidated, (II.35) and the third is to measurements of spectroscopic where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature. (II.36)

Ideality of solution mixture do not obey containing different solute or solvent mixed with another solute or solvent. This deviation from ideal behaviour of solution is expressed in terms of thermodynamic parameters, in case of liquid-liquid mixture by excess properties and apparent molar properties in case of solid-liquid mixtures. The above thermodynamic properties of solvent mixtures that corresponds to the difference between the actual property and the property of the system if it behaves an ideally and this is very useful in the study of molecular interactions and arrangements. In reality, they reflect the interaction that take place between solute-solute, solute-solvent and solvent-solvent species respectively. When the solute molecules or ion added with solvent that modified the structure of solvent as well as solute also modified. The extent of interaction taking place between solute-solute, solute-solvent, solvent-solvent species mainly depends on ion-solvation properties of the mixtures. The assessment or measurement of ion-pairing in these systems is very much important because of its effect on the ionic mobility and hence on the ionic conductivity of the ions in solution. The above phenomenon is associated with the path of paves for research in solution chemistry to clarify the nature of interactions through different experimental studies involving densitometry, viscometry, refractometry and other suitable methods involves and to interpret or explanation the experimental data collected. The whole of the phenomena of solution chemistry could understood in reality only when solute-solute, solute-solvent and solvent-solvent interactions are elucidated and thus the present research work is closely related to the studies of solute-solute, solute-solvent and solvent-solvent interactions in some industrially important liquid systems.

## II. 4. VARIOUS DRIVING FORCES OF INTERACTION

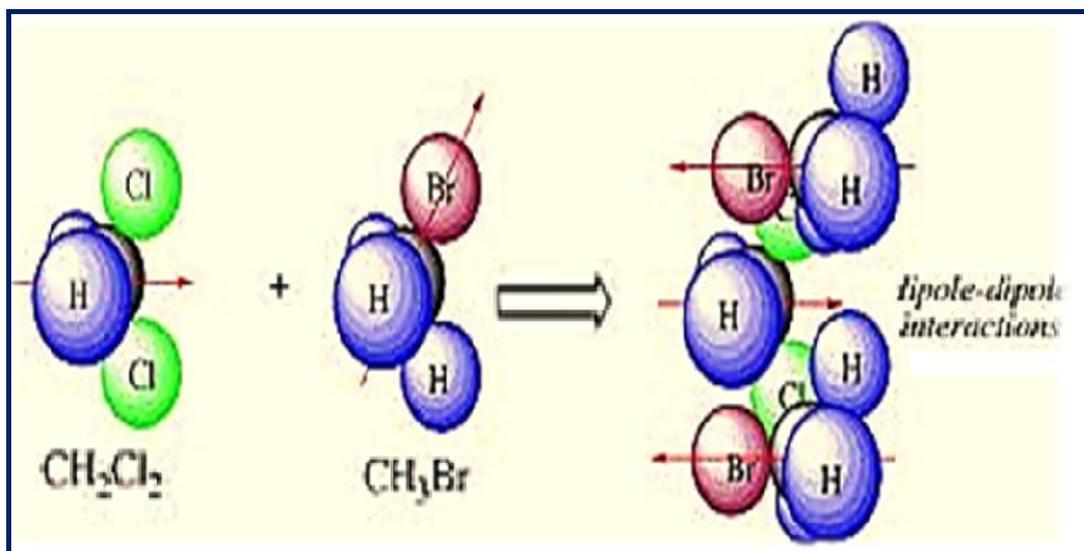
Attraction or repulsion between neighboring particles (atoms, molecules or ions) this term as Intermolecular forces of interactions. In a molecule, the forces of binding nature of atoms are due to chemical bonding. Bond energy is the energy that is required to break the particular bond. For example, it was calculated the average bond-energy for O-H bonds in water is 463kJ/mol. The forces that holding molecules together are generally called intermolecular forces. Typical bond-energy is greater than the energy required to break the apart molecules. Intermolecular forces among the molecules take place very important roles in determining the properties of a substances. [Intermolecular forces](#) are mainly important in terms how molecules can interact with each other and form biological organisms or even life. This connection introduces the interactions consisting between molecules.



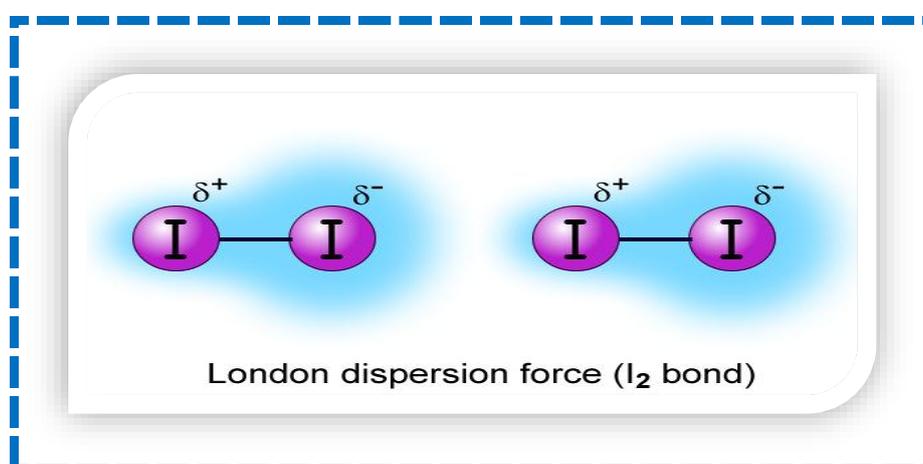
In over-all, there are several types of intermolecular forces can be categorized. The distinguished types are describes in the following.

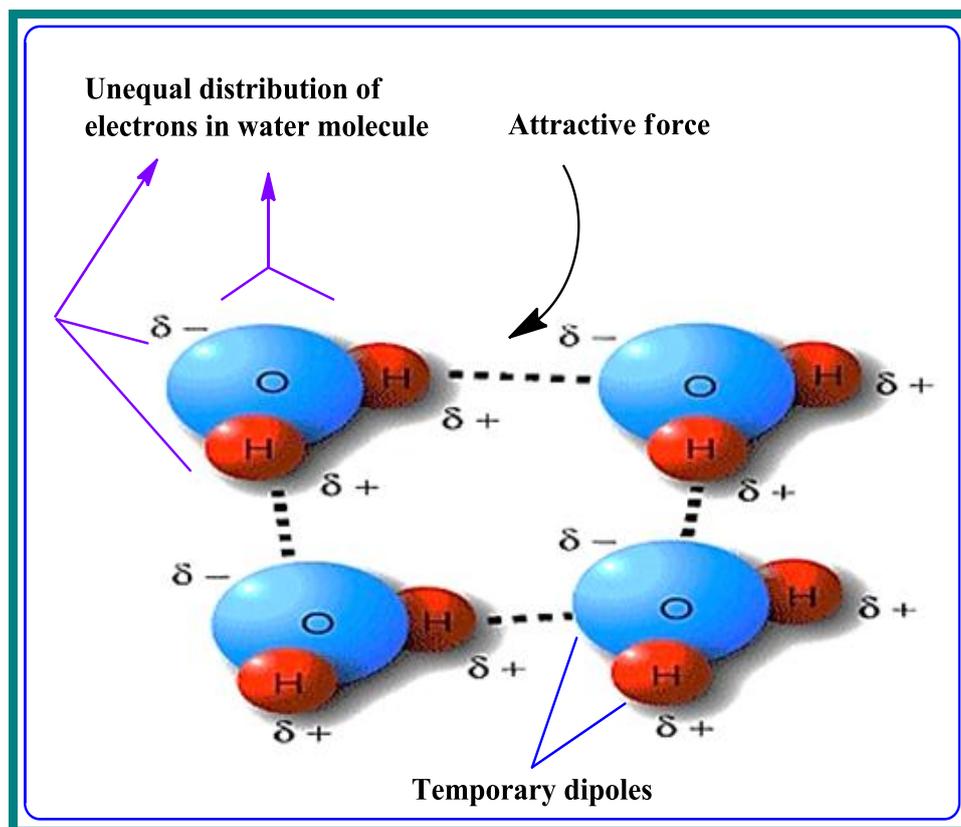
(a) **Strong ionic interaction:** strong ionic interaction is associated with the properties of solids. Higher the lattice energy of solid higher the ionic nature of solid. Here given some ionic solids and their lattice energy respectively, LiF, 1036; LiI, 737; KF, 821; MgF<sub>2</sub>, 2957 kJ/mol. It has been observed from the lattice energy value of ionic solids that the strong ionic interaction is associated with the MgF<sub>2</sub> ionic solid.

(b) **Intermediate dipole-dipole forces:** If the substance of molecules have permanent dipole moment, have higher melting point or boiling point than those of similar molecular mass, having no dipole moment.

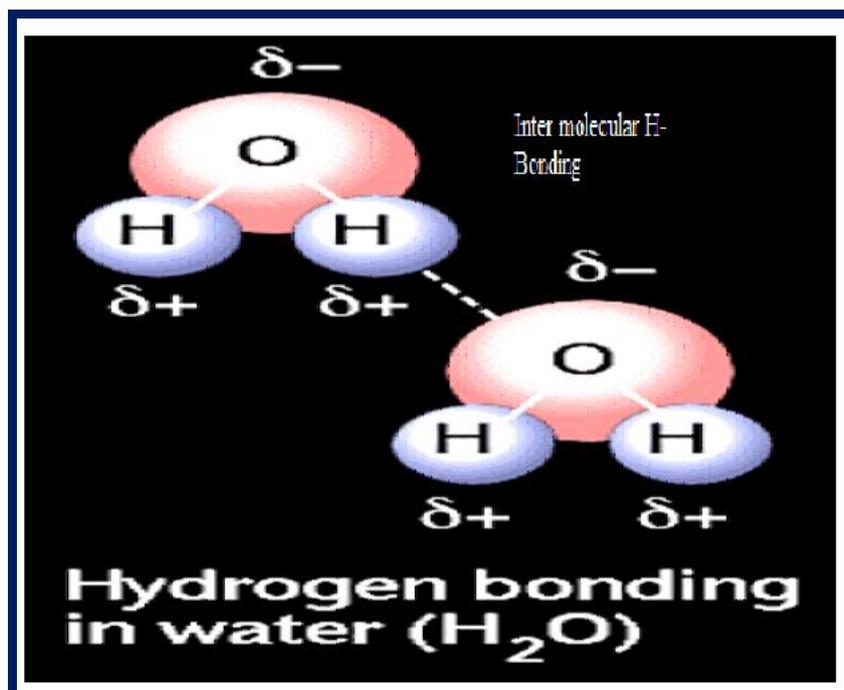


(c) **Weak London dispersion forces or van der Waal's force:** These forces always operate in any substance. The force arisen from induced dipole- dipole interaction and the interaction is obtained due to induce that is weaker than the dipole-dipole interaction. In common, the stronger the van der Waals force of interaction the heavier will be the molecule. As for example, the boiling points of inert gases increase as their atomic masses increases due to stronger Landon dispersion interactions. Weak vander waaal's or Landon dispersion force of interactions is shown by two molecule  $I_2$  and  $H_2O$ .

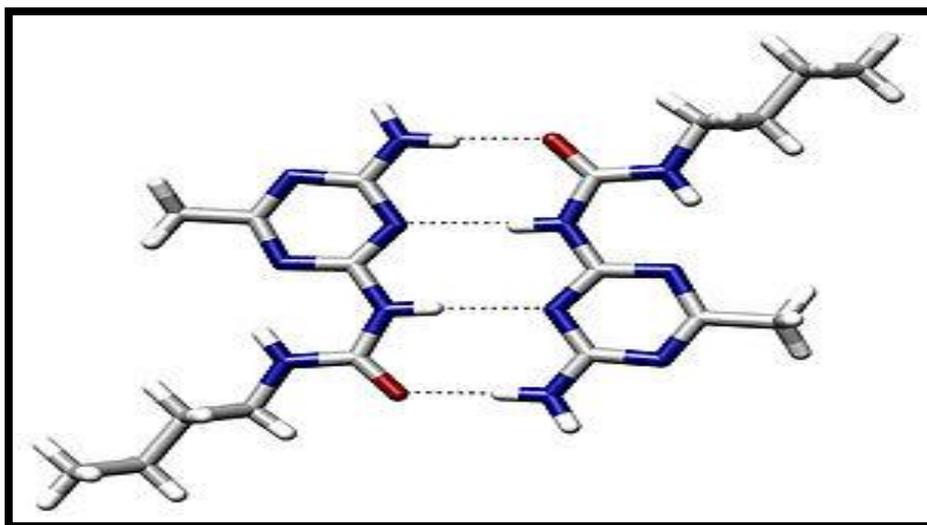




**(d)Hydrogen bonding:** Hydrogen bonding is considered as the attractive interaction of a hydrogen atom with an electronegative atom, such as nitrogen, oxygen or fluorine (thus the name "hydrogen bonding," it is not necessary to form covalent bond with hydrogen). The hydrogen must be covalently bonded to another electronegative atom to form a bond. These bonds may be between different molecules (intermolecular) or within different parts of a same molecule (intramolecular). The hydrogen bond energy 5-30KJ/mole is stronger than of a van der Waals interaction, but this bond is weaker than covalent or ionic bonds. This type of bond generally or often occurs in both inorganic molecules such as water and organic molecules such as DNA. There are certain substances such as  $H_2O$ ,  $HF$ ,  $NH_3$  form hydrogen bonds. The formation of hydrogen bond, which causes some properties (m.p, b.p, solubility) of substance.



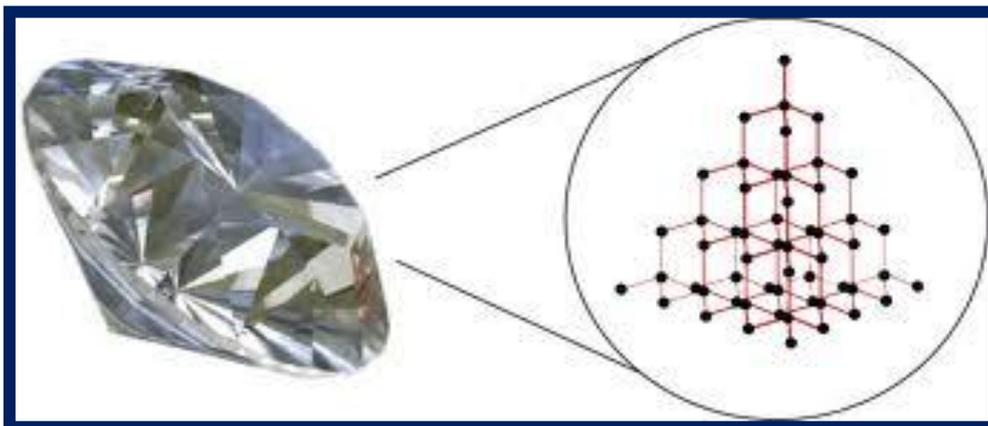
There are another compounds containing OH and  $NH_2$  groups form hydrogen bonds. Molecules of many organic compounds like alcohols, acids, and amino acids amines contain these groups, and thus formation of [hydrogen bonding](#) plays an important role in biological science.



The above cited example is the Intermolecular hydrogen bonding in a [self-assembled dimer complex](#).

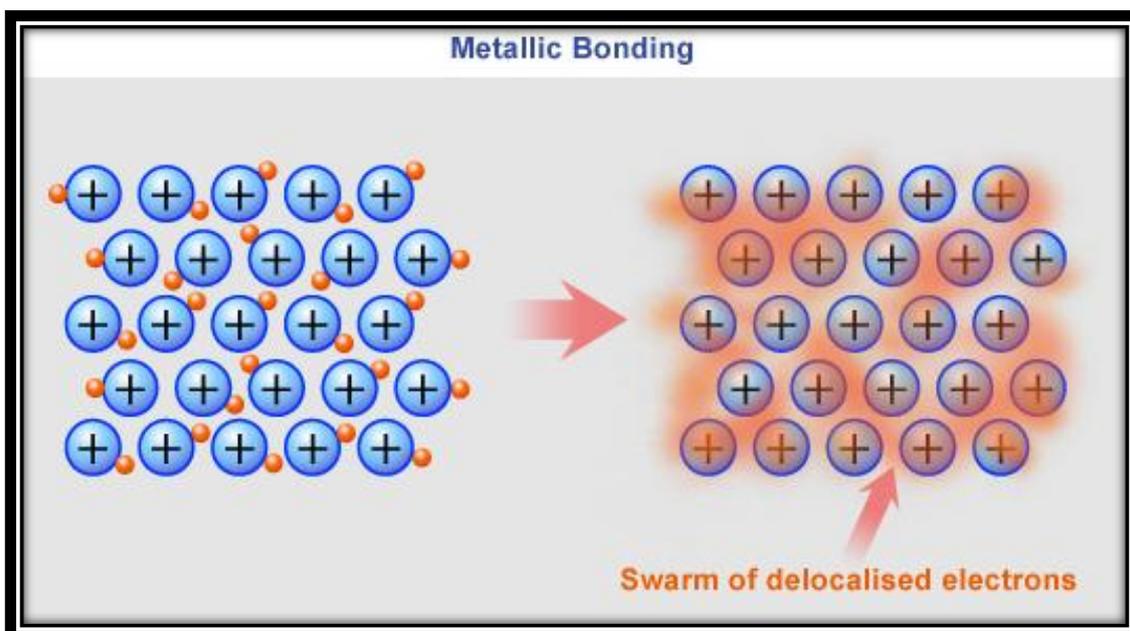
(e)**Covalent bonding:** Covalent is mainly intramolecular force rather than intermolecular force. It is mentioned here, because there are some solids are formed due to formation of covalent bonding. For example, in diamond, silicon, quartz etc., covalent bonding links the whole atoms in the entire crystal structure together. These solids are

very hard, brittle, and have very high melting points. Atoms of molecules in covalent bonding holds atoms tighter than ionic attraction.



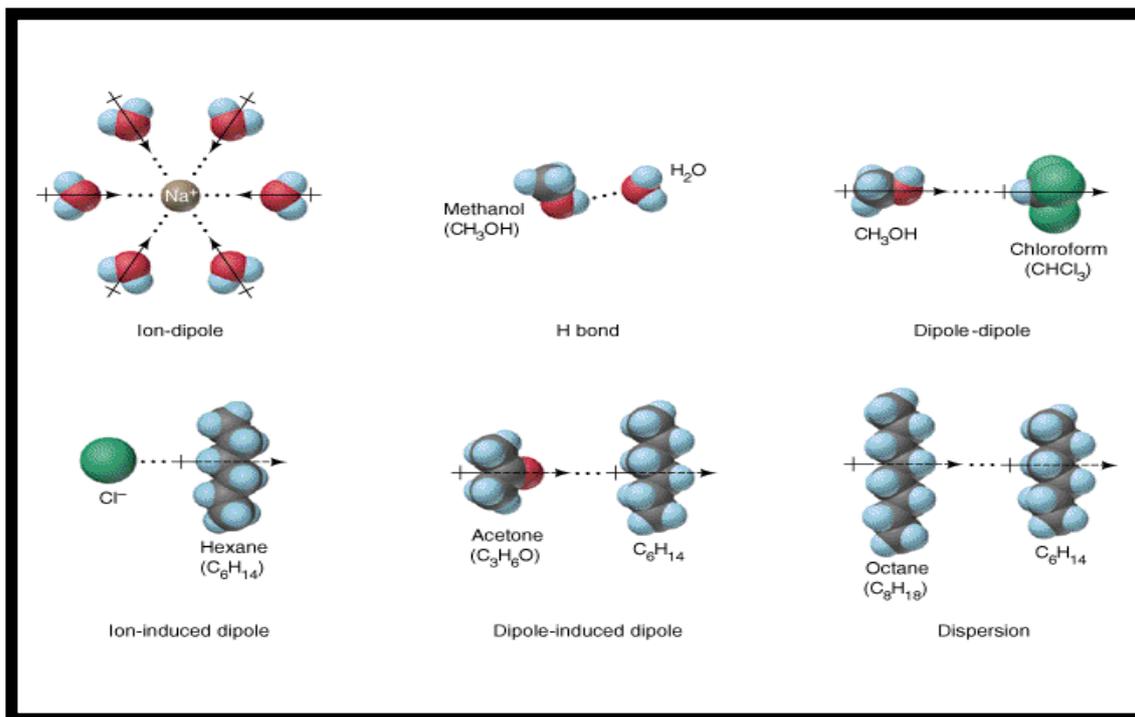
### Covalent Bonding in Diamond

**(f)Metallic bonding:** Forces consist between atoms in metallic solids belong to another category. Valence electrons in metals are widespread. The valence electron are not restricted to certain atoms or bonds. Rather than they run freely in the entire solid crystal that providing good conductivity for heat and as well as electric energy. These behaviors of electrons in the solid crystal give exceptional properties such as ductility and mechanical strength to metals.

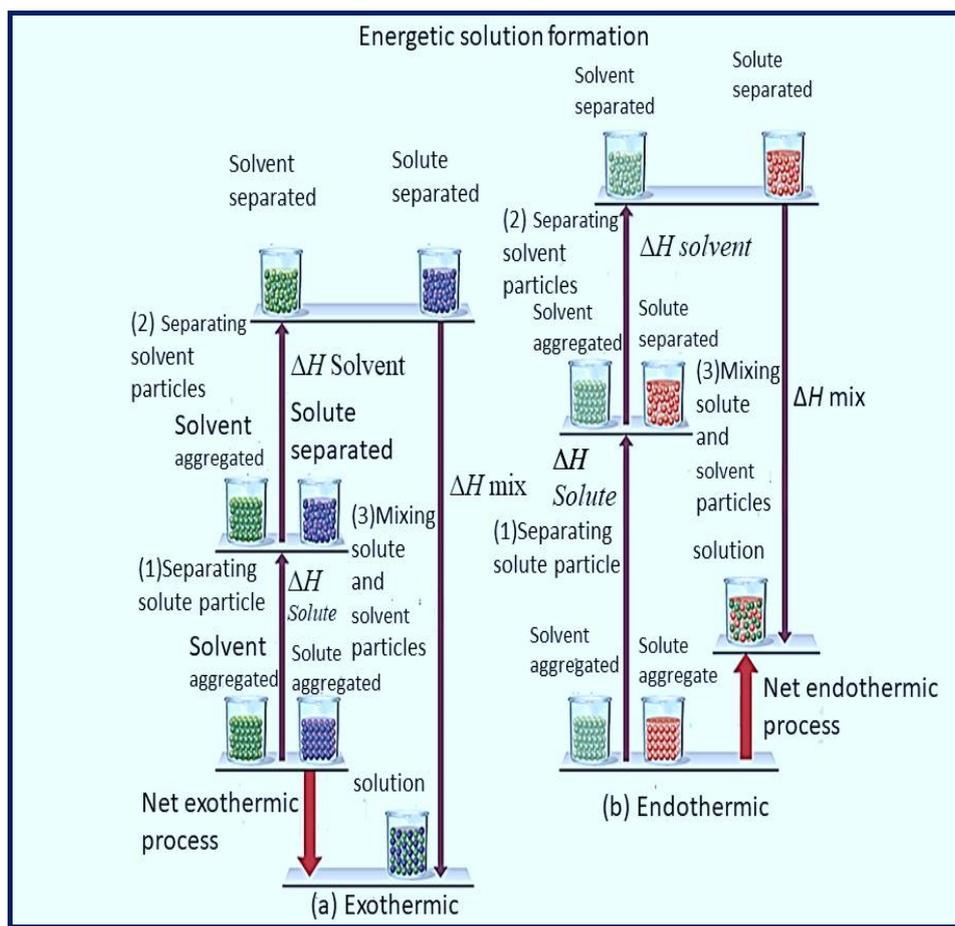


All kinds of of interactions can be present simultaneously for many substances. Usually, intermolecular forces of substance are discussed together with "[The States of](#)

Matter". Intermolecular forces also play vital or important roles in solutions. A brief summary of the interactions is illustrated in the following diagram:



In solution chemistry, the majority of reactions are of chemical or biological in nature. It was supposed earlier that the solvent molecules only provides an inert medium for chemical reactions. The important of ion-solvent interactions was understood after intensive studies in aqueous, non-aqueous and mixed solvents. (II.37, II.38) The solubility of a substance depends on Intermolecular forces. For “*Like*” intermolecular forces for solute molecule and solvent molecule will make the solute soluble in the solvent frequently. In this regard, the value of  $\Delta H_{\text{soln}}$  is sometimes negative and sometimes positive.



Furthermore, solubility is affected by the following factor

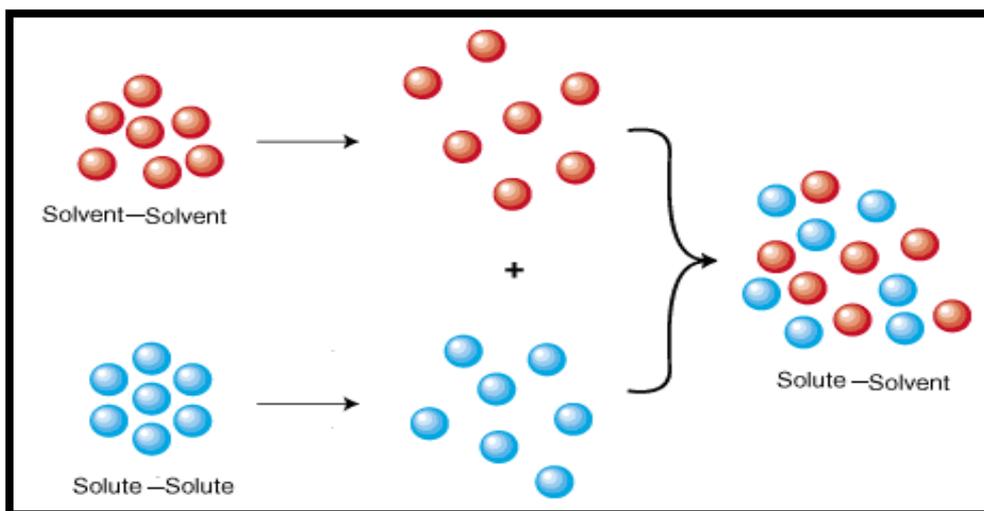
- (i) Due to ion–dipole force the energy of attraction affects the solubility.
- (ii) Lattice energy (the ions holding together in the lattice).
- (iii) Depends on Charge of ions: larger charge means higher lattice energy.
- (iv) Size of the ion: larger the size of ions mean smaller lattice energy.

## II. 5. INTERACTIONS IN SOLUTION SYSTEMS

There are three types of interactions that exist in the solution systems are:

- (a) Solvent–solvent interactions:** In this interaction, less energy is required to break weak bonds between solvent molecules. The solvent molecules isolated from each other .
- (b) Solute–solute interactions:** more energy is required to break intermolecular bonds between the solute molecules. In this process solute molecules separate from each other.

- (c) **Solute–solvent interactions:** Since such type of interaction, value of  $\Delta H$  is negative since bonds are formed easily between them. Solvent and solute molecules mixed together.



The macroscopic properties are usually quite well known for liquid systems, the studied of microscopic structure is often much less used. The characterized of liquid phase by local order and long-range disorder, and to study processes in liquid systems, it is therefore very important or valuable to use methods that prod the local surrounding of the constituent particles. This is also true for solvation processes: a local probe is very important or significant to obtain insight into the physical and chemical processes going on.

### 11.6. INVESTIGATION ON DIFFERENT KIND OF INTERACTIONS

The ions of the salt dissociate from each other and associate with the dipole of the water molecules at the time when salt is dissolved in water, the ions of the salt dissociate from each other. This result in a solution called an ‘electrolyte’.

This means that the forces of interaction (attraction or repulsion) depending on whether like or unlike charges are closer together. Motion of dipoles takes place in a liquid system, themselves to form attractive interactions with their neighbours, but their thermal motion makes some instantaneous configurations unfavourable.

Therefore, if a crystal salt is put in water, the polar water molecules are attracted to ions on the crystal surfaces. The water molecules gradually surround in crystal and isolate the surface ions very effectively. The ions become hydrated. They gradually move

away from the crystal very easily into the solution. 'Dissociation' is the process of separation of ions from each other. The surrounding of solute molecules by solvent molecules is called 'solvation'. When the ions are dissociated, each ionic species in the solution acts as though it were present alone. Thus, a solution of sodium chloride performs as a solution of sodium ions and chloride ions.

The determination of thermodynamic, transport, acoustic and optical properties of different electrolytes in various solvents would thus provide an important step in this direction. Naturally, in the development of theories, dealing with electrolyte solutions, much attention has been devoted to 'ion-solvent interactions' which are the controlling forces in infinitely dilute solutions where ion-ion interactions are absent. It is very much important to separate these functions into ionic contributions to determine the contributions due to cations and anions in the solute-solvent interactions. Thus ion-solvent interactions play a crucial role to understand the thermophysical, thermodynamic and physicochemical properties of solutions.

The ion-solvent interactions can also be studied from the thermophysical, and thermodynamic point of view, where the changes of free energy, enthalpy and entropy, etc. associated with a particular reaction. Qualitatively and as well as quantitatively estimated various thermophysical parameters, from which concluded regarding the factors associated with the ion-solvent interactions occurred in the studied solutions.

Similarly, the ion-solvent interactions can also be studied using solvation approaches involving the studies of different properties such as, density, viscosity, refractive index and conductance of electrolytes and various derived parameters, factors associated with ionic solvation.

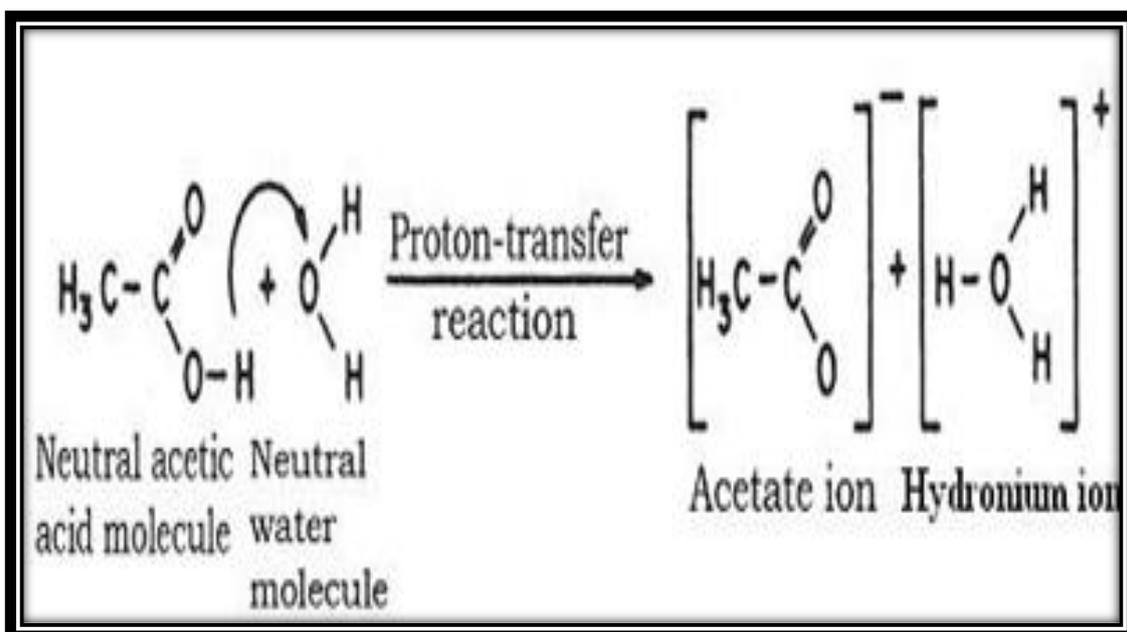
We shall mainly dwell upon the different outlook of these thermophysical, thermodynamic, transports and optical properties as the present research work is warmly allied to the studies of ion-ion, ion-solvent and solvent-solvent interactions.

### **II.6.1. Ion-Solvent Interaction**

Ion-solvation is a fact of primary attention in many framework of chemistry because solvated ions are omnipresent on Earth. Hydrated ions occur in aqueous solution in many chemical and biological systems.<sup>(II.39)</sup> Solvated ions appear in high concentrations in living organisms, where their presence or absence can fundamentally alter the functions of life. Ions solvation in organic solvents, mixtures with water and

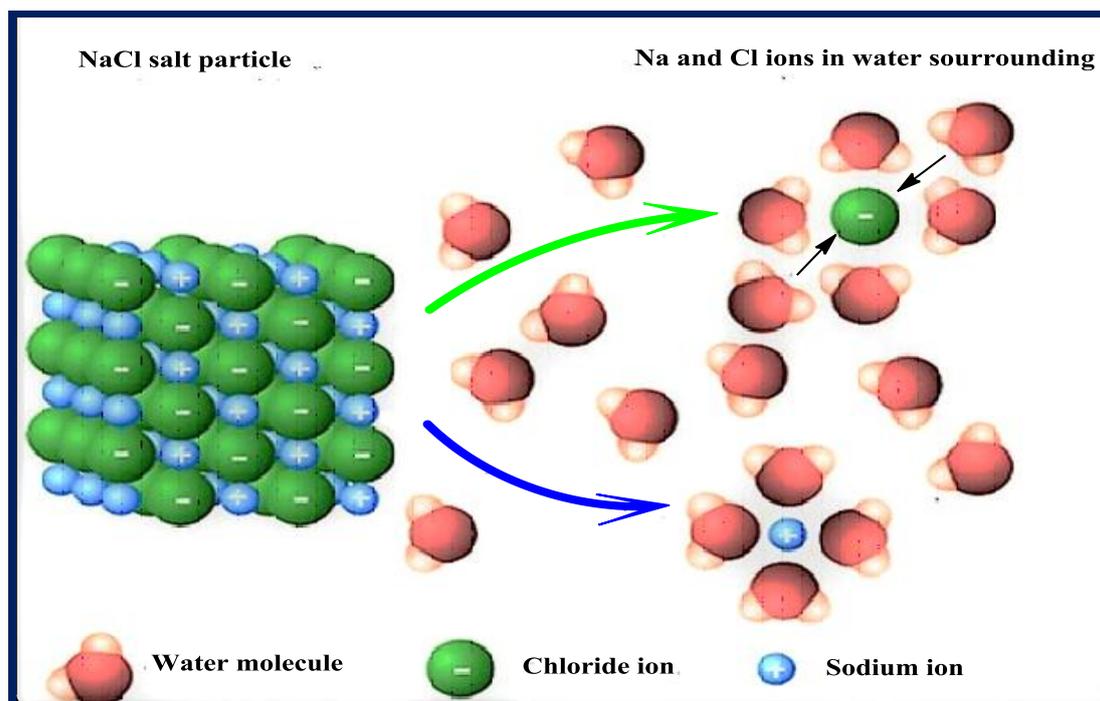
other organic solvents are very common. <sup>(II.40)</sup> The exchange of solvent molecules around ions in solutions is fundamental clue to the understanding of the reactivity of ions in solution. <sup>(II.41)</sup> Solvated ions also play a key role in electrochemical applications, where for instance the conductivity of electrolytes depends on ion-solvent interactions. <sup>(II.42)</sup>

The mobile ions formation in solution is a basic aspect to electrochemistry. There are two distinct ways that mobile ions are formed in solution to create ionically conducting phases. As for example, first one is an illustrated for aqueous acetic acid below.



#### Producing ionic solutions by the chemical method.

The second one involves dissociation of a solid lattice of ions such as the lattice of sodium chloride. In case ion formation, the solvent molecules colliding with the walls of the crystal gives the ions in the crystal lattice is energetically a better deal than they have within the lattice. It attracts them out and into the solution. Thus, there is an appreciable energy of interactions between the ions and the solvent molecules. These types of interactions are collectively termed as ion-solvent interactions.



The spherically symmetrical electric field of the ion may pull apart solvent dipoles out of the solvent lattice and orient them with appropriate charged end toward the central ion. Thus, viewing the ion as a point charge and the solvent molecules as electric dipoles, ion-dipole forces become the principal source of ion-solvent interactions. It was believed earlier that the solvent molecule only provides an inert medium for chemical reactions. The consequences of ion-solvent interactions was understood after extensive studies in aqueous, non-aqueous and mixed solvents. <sup>(II.43-II.52)</sup>

Most of the chemical processes of individual and also biological importance occur in solution. The role of solvent is so great that million fold rate changes take place in some reactions simply by changing the reaction medium. Our bodies contain 65 to 70% water, which acts as a lubricant, as an aid to digestion and more specifically as a stabilizing factor to the double helix conformations of DNA. With the exceptions of heterogeneous catalytic reactions, most reactions in technical importance occur in solutions. In addition, molecules not only have to travel through a solvent to their reaction partner before reacting, but also need to present a sufficiently unsolved rate for collision. The solvent governs the movement and energy of the reacting species to such an extent that a reaction undergoes a several-million fold change in rate when the solvent is changed. As water is the most abundant solvent in nature and its major importance to chemistry, biology, agriculture, geology, etc., water has been extensively used in kinetic

and equilibrium studies. Still our knowledge of molecular interactions in water is extremely limited.

Moreover, the uniqueness of water as a solvent has been questioned<sup>(II.53, II.54)</sup> and it has been realized that the studies of other solvent media like non-aqueous and mixed solvents would be of appreciable help in understanding different molecular interactions and a host of complicated phenomena. The organic solvents have been classified on the basis of dielectric constants, organic group types, acid base properties, or association through hydrogen bonding<sup>(39)</sup> donor-acceptor properties<sup>(II.55, II.56)</sup> hard and soft acid-base principles<sup>(II.57)</sup> etc. As a consequence, the different solvents show a wide change in properties, ultimately influencing their thermophysical, thermodynamic, transport and acoustic properties qualitatively and quantitatively, in presence of electrolytes and non-electrolytes in these solvents. The determination of different thermodynamics parameters like thermophysical, thermodynamic, transport and acoustic properties for various electrolytes or non-electrolytes in a variety of solvents would thus provide important information in this direction. In future, in the improvement of theories of electrolytic solutions, much attention has been devoted to the controlling forces 'ion-solvent interactions' in infinitely dilute solutions where in ion-ion interactions are almost absent. By separating these functions into ionic contributions, it is possible to determine the contributions of cations and anions in the ion-solvent interactions. The introduction of a solute modifies the solvent structure to an uncertain magnitude, the solvent molecule and the interplay of forces like solute-solute, solute-solvent also modify the solute molecule and interactions of solvent-solvent in solution become predominant, though the isolated picture of any of the forces is still not known completely to the solution chemist.

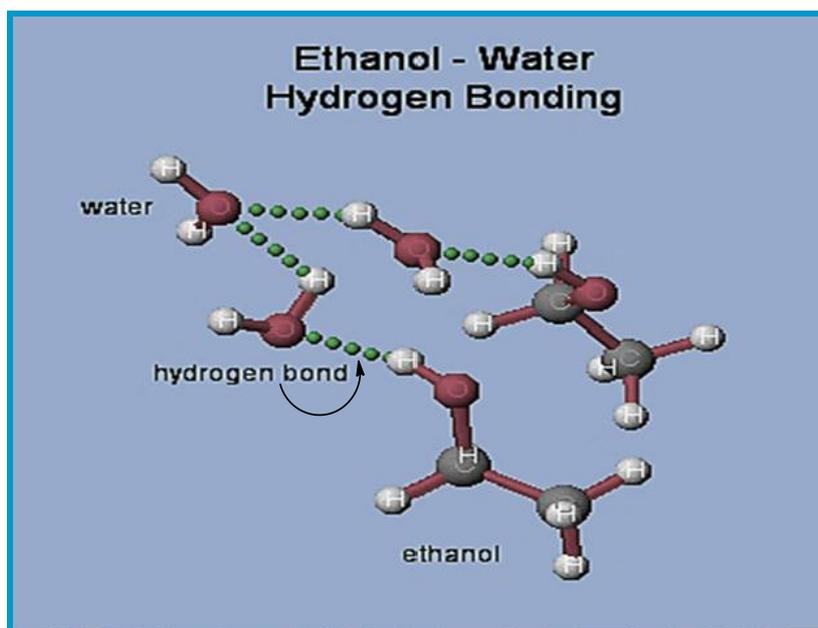
Qualitative analysis of ion-solvent interactions can be studied by FTIR spectrometry.<sup>(II.58, II.59)</sup> The spectral solvent shifts or the chemical shifts can determine the qualitative and quantitative nature of ion-solvent interactions. The real understanding of the ion-solvent interaction is a very difficult task. The outlook embraces a wide range of topics but we concentrated only on the measurement of transport properties like viscosity, conductance etc.; thermophysical, thermodynamic properties as apparent or partial molar volumes, apparent molar adiabatic compressibility, and spectral properties as FTIR spectroscopy ,uv- visible spectroscopy etc .

## II. 6.2. Ion-Ion Interaction

Ion-solvent interactions are only a part of the history of an ion related to its environment. The mutual interactions between these ions represent the essential part 'ion-ion interactions'. The degree of ion-ion interactions that affects the properties of solution and depends on the nature of electrolyte under investigation. Interactions of Ion-ion in general, are stronger than ion-solvent interactions. Theoretically ion-ion interaction occurring in dilute electrolytic solutions is now well understood, but ion-solvent interactions or ion-solvation remains a complex process. While proton transfer reactions are particularly sensitive to the nature of the solvent, it has become cleared that the solvents significantly modify the majority of the solutes. Conversely, the nature of the strongly structured solvents, such as water, is substantially modified by the presence of solutes. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute/ion-ion, solute-solvent/ ion-solvent and solvent-solvent interactions are elucidated. Thus, the present thesis is affectionately related to the studies of solute-solute/ion-ion, solute-solvent/ ion-solvent and solvent-solvent interactions in some liquid systems.

## II. 6. 3. Solvent-Solvent Interactions (Theory of Mixed Solvents)

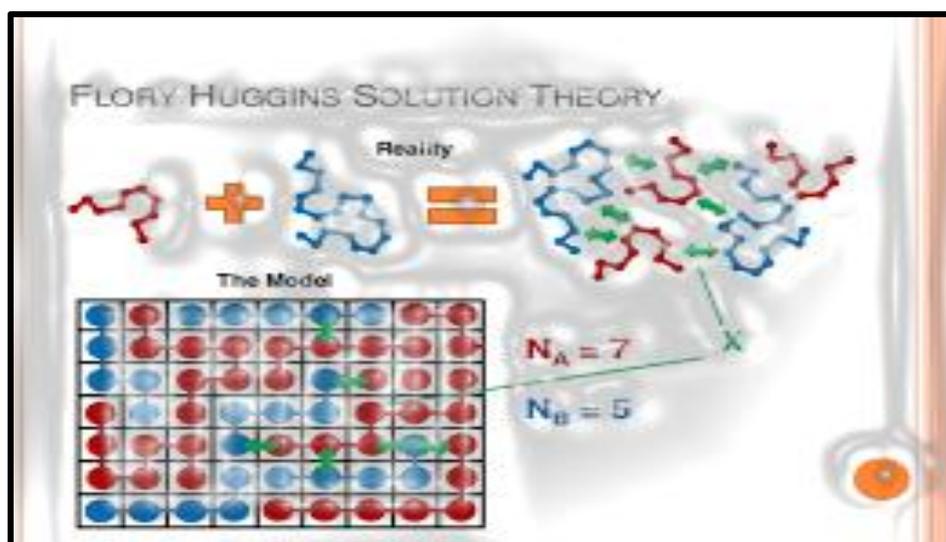
As the mixed and non-aqueous solvents are increasingly used in chromatography, solvent extraction, in the elucidation of reaction mechanism, in preparing high density batteries, etc. a number of molecular theories, based on either the radial distribution function or the choice of suitable physical model, have been developed for mixed solvents. L. Jones and Devonshire<sup>(II.60)</sup> both were first to evaluate the thermodynamic functions for a single fluid in terms of interchange energy parameters. They used "Free volume" or "Cell model". Prigogine and Garikian<sup>(II.61)</sup> extended the above methodology to solvent mixtures. Prigogine and Bellemans<sup>(II.62)</sup> developed a two fluid version of the cell model. They found that while excess molar volume ( $V^E$ ) was negative for mixtures with molecules of almost same size, it was large positive for mixtures with molecules having small difference in their molecular sizes. Treszczanowicz *et. al.*<sup>(II.63)</sup> suggested that  $V^E$  is the result of several contributions from several opposing effects. These may be divided arbitrarily into three types, viz., physical chemical and structural. This is the example of two solvent namely ethanol and water where solvent –solvent interactions can be explain by the hydrogen bonding between two solvent.



Physical contributions contribute a positive term to  $V^E$ . The chemical or specific intermolecular interactions result in a volume decrease and contribute negative values to  $V^E$ . The mostly structural contributions are negative and arise from several effects, especially from interstitial accommodation and changes in the free volume. The actual volume change would therefore depend on the relative strength of these effects. However, it is generally assumed that when  $V^E$  is negative, viscosity deviation ( $\Delta\eta$ ) may be positive and vice-versa. This supposition is not a real one, as evident from some studies. <sup>(II.64, II.65)</sup> Rastogi *et al.* <sup>(II.66)</sup> therefore suggested that the observed excess property is a combination of an interaction and non-interaction part. The non-interaction part of the molecules in the form of size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter. Pitzer <sup>(II.67)</sup>, L. Huggins <sup>(II.68)</sup> introduced a new approach in his theory of conformal solutions. Using a simple perturbation approach, he showed that the properties of mixtures could be obtained from the knowledge of intermolecular forces and thermophysical and thermodynamic properties of the pure components.

Rowlinson *et al.* <sup>(II.69- II.71)</sup> reformulated the average rules for Vander Waal's mixtures and their calculated values were in much better agreement with the experimental values even when one fluid theory was applied. The more recent independent effort is the perturbation theory of Baker and Henderson. <sup>(II.72)</sup> a more successful approach is due to Flory who made the use of certain features of cell theory <sup>(II.73, II.75)</sup> and developed a statistical theory for predicting the excess properties of binary

mixtures by using the equation of state and the properties of pure components along with some adjustable parameters. This theory is applicable to mixtures containing components with molecules of different shapes and sizes. Patterson and Dilamas<sup>(II.76)</sup> united both Prigogine and Flory theories to a unified one for rationalizing various contributions of free volume, internal pressure, etc. to the excess thermodynamic properties. Heintz<sup>(II.77-II.79)</sup> and coworkers recommended a theoretical model which is based on a statistical mechanical derivation and accounts for self-association and cross association in hydrogen bonded solvent mixtures is termed as Extended Real Associated Solution model (ERAS). The combination of the effect of association with non-associative intermolecular interaction occurring in solvent mixtures based on equation of state developed originally by Flory. Subsequently the ERAS model has been successfully applied by many workers<sup>(II.80- II.82)</sup> to describe the excess thermodynamic properties of alkanol-amine mixtures. A new symmetrical reformation on the Extended Real Association (ERAS) model has been described in the literature.<sup>(II.83)</sup> The symmetrical-ERAS (S-ERAS) model that makes it possible to discuss the excess molar enthalpies and excess molar volumes of binary mixtures containing very similar compounds described by extremely small mixing functions.<sup>(II.84)</sup> Gepert *et al.*<sup>(II.85)</sup> applied this model for studying some binary systems containing alcohols.



### 11.7. Volumetric Measurements

The concept of volumetric information includes 'Density' as a function of composition on the bases of weight, volume and mole fraction and excess volumes of mixing. Thermodynamic assets of solutions are not useful for estimating the feasibility

of reactions in solution, but also offer one of the better methods of investigation of theoretical aspects of solution structure. This is particularly true for the heat capacity standard partial molal entropy and volume of the solutes, values of which are sensitive to the rearrangement of solvent molecules around a solute molecule. The above mentioned physical parameters are very need for interpreting the solute-solvent as well as solute – solute interactions.

Various ideas regarding molecular processes in solutions such as, hydrophobic hydration<sup>(II.86)</sup> electrostriction<sup>(II.87)</sup>, micellization<sup>(II.88)</sup> and co-sphere overlap during solute-solute interactions<sup>(II.89)</sup> have to a large extent been resulting and explained from the partial molar volume data of many compounds.

### 11.7.1 APPARENT AND PARTIAL MOLAR VOLUME

The molar volume of a pure substance can be determined by using the data of density. The multi-component systems in a complex such as solutions, it is very easier to define a system in terms of the intrinsic or molal properties rather than the extensive properties. Any extensive property such as partial molal volume of a system can be calculated as the sum of the respective if all the components have a known concentration. Although the preservative definition of partial molal properties is suitable, direct measurement of these solution properties are difficult, due to interactions with other species contribute to partial molal properties. When dealing with solutions it is more common to measure the apparent molal quantities,  $\phi_Y$ , which can be defined as the change in property,  $Y$ , due to a known amount of solute in a known amount of solvent, assuming the contribution by the solvent is the same as that of the pure species. In other words, all changes in the state properties can be attributed to the presence of the solute, even if these changes contribute to a change in partial molal property of the solvent. The apparent molal property of any solute,  $\phi_{2,Y}$  can be defined as

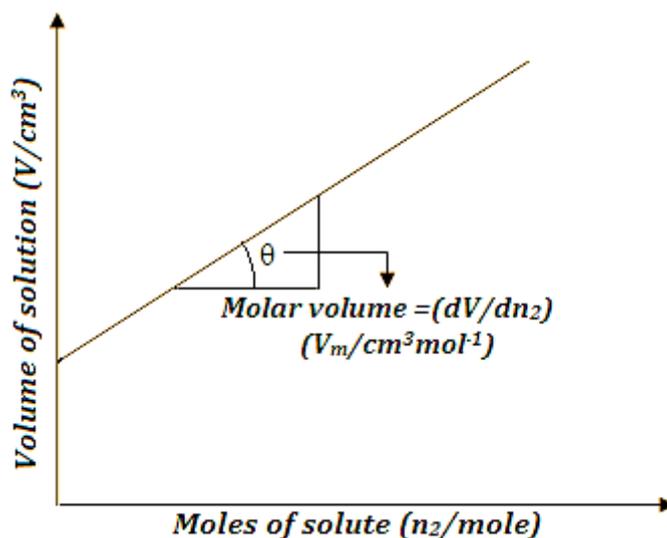
$$\phi_{2,Y} = \frac{Y - n_1 \bar{\phi}_Y^0}{n_2} \quad (\text{II. 1a})$$

Where,  $n_1$  and  $n_2$  characterize the mole of the solvent and solute respectively, in the system.  $\bar{\phi}_Y^0$ , represents the partial molal property of the pure solvent. Then the solvent is expected to contribute a definite, constant quantity for all concentration of solute

molecules at particular temperature and pressure, the partial derivative of the extensive property with respect to the number of moles of solute molecules can be well defined in terms of the apparent molal quantity:

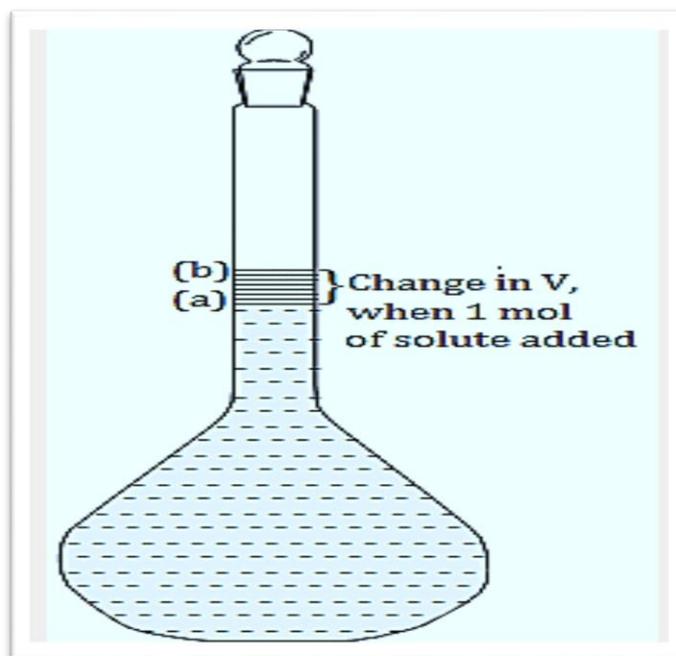
$$\left(\frac{\partial Y}{\partial n_2}\right)_{n_1, T, P} = \left(\frac{\partial \phi_{2,Y}}{\partial n_2}\right)_{n_1} + \phi_{2,Y} \quad (\text{II. 1b})$$

Eqs (II.1a) and (II.1b) displays the partial molal property can be calculated if the apparent molal property and its derivative with respect to moles of solute is known. In other words, if any fitting of the above equations for the apparent molal property with respect to any concentration scale, which is in good, agreement with experimental data is known, the apparent molal property can also be found out at infinite dilution of the experimental solutions. Theoretically, as the concentration approaches to zero, also the apparent molal property approaches to the partial molal property of the solute at infinite dilution, because by definition the solvent is already expected to be in its pure form. If the apparent molal property is supposed to reflect the apparent molal property of the solute molecules only and not for the the solute-solvent complex, then at infinite dilution the apparent molal property,  $\phi_{2,Y}^{\infty}$  would be equal to the standard state molal property of the solute, as defined by Henry's law. Ignoring the earlier equality, equation of state developed for standard state partial molal variables have been used effectively to describe partial molal quantities at infinite dilution.



**Figure II.9a:** molal volume explanation diagram

The easiest process to explain this is in terms of the molal volume,  $V_m$  that is given in the Figure II.9a, with adding the solute molecules, and the volume simultaneously increases. A dissolved solute molecule has its individual property, referred to as partial molal property. Figure II.9b shows an extremely large tank containing one  $\text{mol}\cdot\text{L}^{-1}$  solution of a solute with a certain volume, shown at position (a). If 1 mole of solute is added to the solution in the container, the volume will increase to (b); however, the concentration of the other species of the solution will not change by any noticeable amount.



**Figure II.9b:** A diagram to support in the explanation of a partial molal volume

Therefore, for a two-component system, where one component is the solvent and another component is solute, the total volume of the system can be represented as the sum of the partial molal volumes of the solvent,  $\bar{V}_1$  and the solute,  $\bar{V}_2$ :

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad (\text{II. 1c})$$

Dividing equation (11.1c) by  $n_1 + n_2$ , the molal volume of the solution is obtained as:

$$V_m = x_1 \bar{V}_1 + x_2 \bar{V}_2 \quad (\text{II. 1d})$$

Where,  $x_1$  and  $x_2$  denote the mole fraction of the solvent molecule and the solute molecule, respectively. The property of partial molal of a solute is defined as the change in the total property of the system with respect to the change in the number of moles of solute added, with all other variables ( $T$ ,  $P$ , and the amount of the solvent) are detained constant. An alternative, broadly used property of the solute is the apparent molal property. The apparent molal volume of the solute in solution is the volume that should be attributed to the solute molecules, if it is expected that in pure state of solvent contribute the exact volume.

Under this supposition, Harned and Owen defined the apparent molal volume of the solute,  $\phi_{2,V}$  is the difference between the total volume (and the total molal volume) and the partial molal volume of the pure solvent ( $\bar{V}_1^0$ ) divided by the number of moles (or the mole fraction) of the solute present:

$$\phi_{2,V} = \frac{V - n_1 \bar{V}_1^0}{n_2} \quad (\text{II. 1e})$$

$$\phi_{2,V} = \frac{V_m - x_1 \bar{V}_1^0}{x_2} \quad (\text{II. 1f})$$

In investigation, at constant temperature and pressure,  $\bar{V}_1^0$  is generally considered constant over the range of solute concentration. Hence,  $\phi_{2,V}$  can be easily obtained or calculated by using Eq. (II. 1e) or (II. 1f) when the total volume or molal volume of solution mixture is known. In order to find out the apparent molal volume of a solute Eq. (II. 1e) can be modified by using density of the solution containing the solute and the density of the pure solvent,  $\rho$  and  $\rho_0$ , respectively. Supposing there is 1 kilogram (kg) of solvent:

$$n_1 = \frac{1}{M_1}, \quad \text{therefore,} \quad V = \frac{\bar{V}_1^0}{M_1} + m_2 \cdot \phi_{2,V} \quad (\text{II. 1g})$$

Where,  $M_1$  denotes the molal mass of the solvent.

Since  $\rho_1 = \frac{\bar{V}_1^0}{M_1}$ , Eq. (II. 1g) becomes:

$$V = \frac{1}{\rho_1} + m_2 \cdot \phi_{2,v} \quad (\text{II. 1h})$$

Where,  $m_2$  is the molality of the solute, which is equivalent to  $n_1$  (if 1kg of solvent is present). The total mass of the solution will be collected of the mass of the solvent (1kg) and the mass of the solute ( $m_2 \cdot M_2$ ). Since (v) volume is the ratio of mass to density, the equation becomes:

$$\frac{1 + m_2 \cdot M_2}{\rho_1} = \frac{1}{\rho_1} + m_2 \cdot \phi_{2,v} \quad (\text{II. 1i})$$

An equation for apparent molal volume for 1 kg of the solute is obtained by rearranging this Eq. (II. 1h) and solving for  $\phi_{2,v}$ .

$$\phi_{2,v} = \frac{\rho_2 - \rho_1}{m_2 \rho_1 \rho_2} + \frac{M_2}{\rho_2} \quad (\text{II. 1j})$$

However, the volume contributed to a solvent by the addition of one mole of an ion is difficult to determine. This is so because, upon access into the solvent, the ions change the volume of the solution due to a breakup of the solvent structure near the ions and the compression of the solvent under the effect of the ion's electric field i.e., Electrostriction. The effective volume of an ion in solution and the partial molar volume obtained from a directly attainable quantity apparent molar volume ( $\Phi_v$ ). The following relation is used to calculate the apparent molar volumes of solute molecules: (II.90)

$$V_\phi = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \quad (\text{II.2})$$

Where,  $\rho_0$  and  $\rho$  are the densities of solvent and solution respectively  $M$  is the molecular weight of the solute and  $c$  is the molarity of the solution.

The partial molar volumes,  $B_{K^+} = B_{Cl^-} \bar{V}_2$  can be obtained from the following equation (II.91)

$$\bar{V}_2 = V_\phi + \frac{(1000 - cV_\phi)}{2000 + c^{3/2} \left( \frac{\partial V_\phi}{\partial \sqrt{c}} \right)} c^{1/2} \left( \frac{\partial V_\phi}{\partial \sqrt{c}} \right) \quad (\text{II.3})$$

The expression of the concentration dependence of the apparent molar volume and the extrapolation of the apparent molar volume of electrolyte to infinite dilution have

been made by four main equations over a period of years. Namely the Masson equation, (II.92) the Redlich-Meyer equation, (II.93) the Owen-Brinkley equation, (II.94) and the Pitzer equation. (II.95) The apparent molar volume of electrolyte,  $V_\phi$  vary with the square root of the molar concentration by the following linear equation:

$$V_\phi = V_\phi^0 + S_v^* \sqrt{c} \quad (\text{II.4})$$

Where,  $V_\phi^0$  is the limiting apparent molar volume (equal to the partial molar volume at infinite dilution), and  $S_v^*$  is the experimental slope. The majority of  $V_\phi$  data in

Water (II.96) and nearly all  $V_\phi$  data in non-aqueous (II.97-II.101) solvents have been extrapolated

To infinite dilution with equation (II.4).

The temperature dependence of  $V_\phi^0$  for various investigated electrolytes in various solvents expressed by the general equation as follows:

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \quad (\text{II.5})$$

The limiting apparent molar expansibilities ( $\phi_E^0$ ) of the electrolyte in solutions can be calculated from the

$$\phi_E^0 = \left( \frac{\partial V_\phi^0}{\partial T} \right)_p = a_1 + 2a_2 T \quad (\text{II.6})$$

The limiting apparent molar expansibilities ( $\phi_E^0$ ) of the solute molecule in solutions change in magnitude with the variation of temperature. During the past few years, different workers emphasized that ( $S_v^*$ ) is not the sole criterion for determining the structure-making or structure-breaking nature of any solute. Hepler 73 developed a technique of examining the sign of ( $\partial^2 V_\phi / \partial T^2$ ) for various solutes in terms of long range structure-making and breaking capacity of the solutes in solution using the general thermodynamic expression:

$$\left( \frac{\partial C_p}{\partial P} \right)_T = \left( \frac{\partial^2 V_\phi^0}{\partial T^2} \right)_p \quad (\text{II.7})$$

Depends based on the above expression, it has been assumed that structure-making solutes should have positive value, where as the structure breaking of solute molecules should have negative value.

However, Redlich and Meyer (II.102) have shown that equation (11.7) cannot be more than a limiting law and for a given solvent and temperature the slope, ( $S_v^*$ ) should depend only upon the valence type. They suggested an equation for representing as follows:

$$V_\phi = V_\phi^0 + S_v \sqrt{c} + b_v c \quad (\text{II.8})$$

Where, 
$$S_v = Kw^{1/2} \quad (\text{II.9})$$

$S_v^*$  is the theoretical slope, based on molar concentration, including the valence factor:

$$w = 0.5 \sum_i^j Y_i Z_i^2 \quad (\text{II.10})$$

And, 
$$K = N^2 e^2 \left( \frac{8\pi}{1000 \epsilon^3 RT} \right)^{1/2} \left[ \left( \frac{\partial \ln \epsilon}{\partial p} \right)_T - \frac{\beta}{3} \right]$$
 (II.11)

Where ( $\beta$ ) is the compressibility of the solvent? However, the deviation of dielectric constant with pressure was not known accurately sufficient, even in water, to calculate exact values of the theoretical limiting slope.

Thus for polyvalent electrolytes, the more complete Owen-Brinkley equation (II.103) can be used to help in the extrapolation to infinite dilution and satisfactorily represent the concentration dependency of The Owen-Brinkley equation resulting by including the ion-size parameter is given by:

$$V_\phi = V_\phi^0 + S_v \tau (Ka) \sqrt{c} + 0.5 w_v \theta (Ka) c + 0.5 K_v c \quad (\text{II.12})$$

Where the symbols have their usual significance. However, equation (11.12) has not been widely employed for the treatment of results for non-aqueous solutions

Lately, Pogue and Atkinson <sup>(II.104)</sup> to fit the apparent molal volume data have used the Pitzer formalism. The Pitzer give an equation for the determination of apparent molar volume of a single salt  $M \gamma_X$  is:

$$\phi_V = \phi_V^0 + V |Z_M Z_X| A_V |2b \ln \left( I + bI^{\frac{1}{2}} \right) + 2\gamma_M \gamma_X RT \left[ mB_{MX}^2 + m^2 (\gamma_M \gamma_X)^{\frac{1}{2}} C_{MX}^V \right] \quad (\text{II. 13})$$

Where the symbols have their usual significance.

### 11.7.2. Limiting Ionic Partial Molar Volumes

The individual partial ionic volumes is very significant tools which provide the information appropriate to the general question of the structure near the ion, i.e., its solvation. The calculation of the ionic limiting partial molar volumes is very difficult task in organic solvents. At present, however, in organic solvents most of the existing ionic limiting partial molar volumes were obtained by the application of procedures originally developed for aqueous solutions to non-aqueous electrolyte solutions. In the last few years, Conway *et al* <sup>(II.105)</sup> suggested a method that has been used more frequently. To determination of the limiting partial molar volumes, the authors used the procedure of the anions for a series of homologous tetra-alkyl ammonium chlorides, bromides and iodides respectively in aqueous solution. They plotted the limiting partial molar volume  $\phi_{V, R_4NX}^0$ , with a halide ion as a common function for a series of these salts of the formula weight of the cation,  $M_{R_4N^+}$  and obtained straight-lines for each series. Thus, they suggested the following equation:

$$\phi_{V, R_4NX}^0 = bM_{R_4N^+} + \phi_{V, X^-}^0 \quad (\text{II. 14})$$

The limiting partial molar volumes of the halide ions  $\phi_{V, X^-}^0$  obtained from the extrapolation to zero on the cationic formula weight. Uosaki *et al.* <sup>(II.106)</sup> Krumgalz <sup>(II.107)</sup> used both this technique for the separation of some literature values and of their own  $\phi_{V, R_4NX}^0$  values into ionic contributions in organic electrolyte solutions in a wide range of temperature

### II.7.3. Excess Molar Volumes

$V^E$ , the excess molar volumes are calculated from the molar masses  $M_i$  and the densities of pure liquids and the mixtures according to the following equation; <sup>(II.108, III.109)</sup>

$$V^E = \sum_{i=1}^n x_i M_i \left( \frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (\text{II. 15})$$

where  $\rho_i$  and  $\rho$  are the density of the  $i^{\text{th}}$  component and density of the solution mixture respectively.  $V^E$  is the subsequent of contributions from several contrasting effects. These contributions may be divided randomly into three types, namely, chemical, physical and structural. Contribute a positive term to  $V^E$ . Decrease in volume from the chemical or specific intermolecular interactions, thereby contributing negative  $V^E$  values. These type of phenomena are getting from the results of difference in energies of interaction among molecules being in solutions and in packing effects. The ordered structure of pure component is disruption during the formation of the mixture leads to a positive effect detected on excess volume and in case of order formation in the mixture leads to negative contribution.

Viscosity is the fundamental and significant property of liquids that provide a lot of information on the structures and molecular interactions in liquid systems. Viscosity and volume are not same types of properties of one liquid, and there is a definite relationship between them. So, Viscosity and volume measuring and studying them together, relatively more convincing and comprehensive information expected to be gained. The 'Viscosity' as a function of composition based on weight, volume and mole fraction and comparison of experimental viscosity values with those calculated with several set of equations and excess Gibbs free energy of viscous flow.

One of the most important transport properties is the Viscosity, which is used for the determination of Solute-solvent and solute-solute interactions and studies extensively (II.110-111). Viscosity is not a thermodynamic property but viscosity of an electrolyte solution along with the thermodynamic property, partial molar volume, gives much information and insight concerning the solute-solvent interactions, structures of electrolytic solutions and solvation properties.

### 11.8. Viscosity of Pure Liquids and Liquid Mixtures

Since the movement of molecules in liquids is actually controlled by the influence of the adjacent molecules, at ordinary pressures the transport of momentum in liquids takes place, in sharp contrast with gases, not by the actual movement of molecules but by the strong influence of intermolecular force fields. This is the very importance aspect of the mechanism of momentum transfer, which forms the basis of the techniques for predicting the variations in the viscosity of liquids and liquid mixtures.

### Early Theoretical Considerations on Liquid Viscosity

In early stages Frenkel<sup>(II.113)</sup> and Andrade<sup>(II.112)</sup> has been reviewed for the theoretical development of liquid viscosity, considering the forces of collision to be the only important factor and supposing that at the melting point, the frequency of vibration is equal to that in the solid state and that one-third of the molecules are vibrating along each of the three directions normal to one another. According to Frenkel<sup>(II.113)</sup> considered the shape of molecules of a liquid to be spheres and the molecules are moving with an average velocity with respect to the neighboring medium and using Stokes' law and Einstein's relation for self-diffusion-coefficient, attained at a complicated expression for viscosity of liquid with only limited applicability Andrade<sup>(II.112)</sup> developed equations that is checked well against data on mono atomic metals at their melting point. Furth<sup>(II.114)</sup> and Zmed give the idea of transfer of momentum that take place by the irregular Brownian movement of the holes<sup>(II.115)</sup> that were connected or linked to clusters in a gas and thus, in similarity with the gas theory of viscosity and with guess of the equipartition law of energy, showed that for liquids:

$$\eta = 0.915 \frac{R_g T}{V} \left( \frac{M}{\sigma} \right) e^{\frac{A}{R_g T}} \quad (\text{II. 16})$$

Where  $\eta$ ,  $V$  and  $M$  denotes the viscosity, volume and mass respectively is the temperature in kelvin scale,  $\sigma$  is the surface tension,  $R_g$  is the universal gas constant and  $A$  signify as the work function at the melting point. Andrade<sup>(II.113)</sup> and Ewell & Eyring,<sup>(II.116)</sup> Auluck, De & Kothari<sup>(II.117)</sup> compared his theory with experiment as well as with the theories and they further modified the theory and successfully clarified the variations of the viscosity with pressure. Eisenschitz gives a critical review of these simple theories and their abilities to explain the momentum transport in liquid systems.<sup>(II.118)</sup>

#### 11.8.1. Viscosity of Electrolytic Solutions

The relationships of viscosity of electrolytic solutions are extremely complicated. Because solute-solute (ion-ion) and solute-solvent (ion-solvent) interactions are occurring in the solution and separation of the related forces is a difficult task. However, from very careful analysis, vivid and valid conclusions can be drawn regarding the structure and the nature of the solvation in solution of the particular system. As viscosity is a measure of measurement of viscosity, is depends on the friction between adjacent, relatively moving parallel planes of the liquid, if the interaction among the planes of liquids increase or decrease, which also give the result of viscosity increase or decrease respectively. If placed a large spheres in the liquid system the planes will be keyed together in increasing the viscosity. Likewise, increase in the average degree of hydrogen bonding between the planes that will increase the friction between the planes, as well as viscosity. An ion associate with a large rigid co-sphere for a structure-promoting ion

will perform as a rigid sphere placed in the liquid and increase the inter-planar friction. Similarly, an ion increasing the degree of correlation or the degree of hydrogen bonding among the adjacent solvent molecules will increase the viscosity. Conversely, the viscosity would decrease for the ions destroying correlation. In 1905 Grüneisen <sup>(II.119)</sup> First performed the systematic measurement of viscosities over a extensive range of concentrations of a number of electrolytic solutions. He noted non-linearity and negative curvature in the viscosity concentration curves regardless of low or high concentrations. An empirical equation (II.16), quantitatively correlating the relative viscosities of the electrolytes with molar concentrations ( $c$ ) suggested in 1929 by Jones and Dole <sup>(II.120)</sup>:

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc \quad (\text{II. 17})$$

Rearrange the above equation as follows:

$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} \quad (\text{II. 18})$$

Where  $A$  and  $B$  are constants which denotes the specific to ion-ion and ion-solvent interactions. The equation is not applicable to only aqueous systems but also equally non-aqueous solvent systems where there is absence of ionic association and that has been used extensively. The term of the equation  $AVC$ , originally ascribed to Grüneisen effect, arose from the long-range columbic forces between the ions. The significance of the term had since then been realized due to the development Debye-Hückel theory <sup>(II.121)</sup> of inter-ionic attractions in 1923. The flakenhagen coefficient  $A$ , depends on the ion-ion interactions, can be calculated from the theory of interionic attraction [III.167-III.169], and is given by the Falkenhagen Vernon <sup>(II.122)</sup> equation

$$A_{Theo} = \frac{0.2577 A_o}{\eta_o (\epsilon T)^{0.5} \lambda_+^o \lambda_-^o} \left[ 1 - 0.6863 \left( \frac{\lambda_+^o \lambda_-^o}{A_o} \right)^2 \right] \quad (\text{II.19})$$

where the symbols in the above equation have their usual meaning. The coefficient  $A$  has been obtained by fitting  $\eta_r$  to equation (II. 18) in very careful work on aqueous solutions, <sup>(II.123)</sup> and this was compared with the values calculated from equation (II. 19), the agreement was excellent with the result. However, the correctness attained with partially aqueous solutions was poorer. <sup>(II.124)</sup> it is suggested that  $A$ -coefficient should be calculated from conductivity measurements. Crudden *et al.* <sup>(II.125)</sup> suggested that if association of the ions occurs to an ion pair formation, the viscosity of the solution should be altered and that investigated by the following equation:

$$\frac{\eta_r - 1 - A\sqrt{\alpha c}}{\alpha c} = B_i + B_p \left( \frac{1 - \alpha}{\alpha} \right) \quad (\text{II. 20})$$

Where  $A$ ,  $B_i$  and  $B_p$  are the characteristic constants and  $\alpha$  is the degree of dissociation of ion-pair formation. Therefore, a plot of  $\frac{\eta_r - 1 - A\sqrt{\alpha c}}{\alpha c}$  vs  $\left( \frac{1 - \alpha}{\alpha} \right)$  it give the intercept value  $B_i$  when extrapolated to  $\left( \frac{1 - \alpha}{\alpha} \right) = \text{zero}$  in the equation. However, both aqueous and non-aqueous of electrolytic solutions the [equation \(II. 20\)](#) is valid up to 0.1 (M) [\(II.126, II.127\)](#) within experimental errors. At higher concentration of the solutions the extended Jones-Dole [equation \(II. 21\)](#), involving an additional coefficient  $D$ , originally used by Kaminsky, [\(II.128\)](#) has been used by several workers [\(II.129, II.130\)](#) and is given below:

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc + Dc^2 \quad (\text{II. 21})$$

The coefficient  $D$  in the above equation cannot be calculated properly and the significance of the constant (D) is also not constantly meaningful and consequently, the most of the workers are used to the [equation \(II. 20\)](#).

The value of  $A$ -coefficient should be obtained from the plots of  $\frac{(\eta/\eta_o - 1)}{\sqrt{c}}$  against  $\sqrt{c}$  for the electrolytes. But occasionally, the negative or considerably scatter values come out and also deviation from linearity arise. [\(II.131, II.132, II.133\)](#) Thus, for determining the  $A$ -coefficient, Falkenhagen-Vernon [equation \(II. 19\)](#) is used instead the value obtained least square method.  $A$ -coefficient should be zero for non-electrolytes. According to Jones and Dole, the  $A$ -coefficient possibly represents the stiffening outcome on the solution of the electric forces between the ions that is solute-solute interaction involving with the solutions, which tend to keep or maintain space-lattice structure. [\(II.120\)](#) The value of viscosity  $B$ -coefficient may be either positive or negative and it is really the ion-solvent interaction parameter. Using the least square method the  $B$ -coefficients are obtained as slopes of the straight lines and intercepts equal to the  $A$ -coefficient.

The following factors influencing the Viscosity  $B$ -coefficients are reported as [\(II.134, II.135\)](#)

- a) The result of destruction of the three-dimensional structure of solvent molecules (i.e., structure breaking effect or depolymeriation effect), as a result decreases  $\eta$  values.

- b) The result of ionic solvation in solutions and the action of the arena of the ion in generating long-range order in solvent molecules, increase  $\eta$  or  $B$ -value.
- d) Reduced  $B$ -values are create when the primary solution of ions is sterically hindered in high molal volume solvents or if either ion of a binary electrolyte cannot be specifically solvated.
- e) High  $B$ -values for similar solvents, which yield the very high molal volume and very low dielectric constant.

### 11.8.2. Principle of Corresponding States and Liquid Viscosity

The principle of the corresponding states has been applied to liquids in the similar way as well as gases. <sup>(II.136)</sup> The elementary assumption existence that the intermolecular potential between two molecules is a universal function of the reduced intermolecular separation. This hypothesis is a good approximation for the spherically symmetric mono atomic non-polar molecules. In common, more parameters are introduced in the corresponding state correlations on somewhat empirical grounds in the hope that such modification in some method or way that compensates the shortcomings of the above stated assumption. In this link the studies by Rogers and Brickwedde, <sup>(II.137)</sup> Boon and Thomaes <sup>(II.138-II.139)</sup> Boon, and Hollman and Hijmans <sup>(II.140)</sup> Legros and Thomaes, <sup>(II.141)</sup> are worth mentioning.

### 11.8.3. The Reaction Rate Theory for Viscous Flow

Regarding the viscous flow of a chemical reaction in which a molecule moving in a plane infrequently acquires the activation energy, which is necessary to sleep over the potential barrier to the succeeding equilibrium position in the same plane. The viscosity of the liquid according to Eyring <sup>(II.142)</sup> is given by:

$$\eta = \frac{\lambda_1 h F_n}{\kappa \lambda^2 \lambda_2 \lambda_3 F_a^*} \exp \frac{\Delta E_{act}}{kT} \quad (\text{II. 22})$$

Where  $\lambda$  confines, the average distance between the equilibrium positions in the direction of motion,  $\lambda_1$  is denotes the perpendicular distance between two adjacent layers of molecules in relative motion,  $\lambda_2$  is the distance between nearby molecules in the same direction and  $\lambda_3$  is measure the distance from molecule to molecule in the plane normal to the direction of motion. The term ( $\kappa$ ), transmission coefficient is the measure of the chance that a molecule having once crossed the potential barrier will react and not recross in the opposite direction. For normal molecules  $F_n$  is denotes the partition function,  $F_a^*$  denotes that of the activated molecule with a degree of freedom corresponding to flow, energy of activation for the flow process is denoted by  $\Delta E_{act}$  is the energy of activation,  $h$  is Planck's constant and Boltzmann constant is  $k$ . For a

molecule to passage into a hole, Ewell and Eyring argued it is not necessary that the latter be of the same size as the molecule. So they assume that for viscous flow  $\Delta E_{act}$  is a function of  $\Delta E_{vap}$ , because  $\Delta E_{vap}$  is the energy essential to make a hole in the liquid of the size of a molecule. Applying the idea and criteria, certain relations <sup>(II.116, II.143)</sup> finally gets

$$\eta = \frac{N_A h (2\pi m k T)^{\frac{1}{2}}}{V h} \frac{b R T V^{\frac{1}{3}}}{N_A^{\frac{1}{3}} \Delta E_{vap}} \exp \frac{\Delta E_{vap}}{n R T} \quad (\text{II. 23})$$

Where  $n$  and  $b$  are two constant. It was observed that the theory could reproduce the trend in temperature dependence of  $\eta$  but the observed values are less compare with computed values by a factor of two or three for most liquids. Kincaid, Eyring and Stearn <sup>(II.144)</sup> have shortened all the working relations.

#### II.8.4. the Significant Structural Theory and Liquid Viscosity

The "holes in solid" model theory <sup>(II.144-II.149)</sup> improved by Eyring and coworkers <sup>(II.145-II.148)</sup> to picture the liquid state by identifying three very important structures. In short-term, a molecule has solid like properties for the short time it vibrates about an equilibrium position and then it assumes rapidly the gas like behavior on jumping into the nearby vacancy. The above idea of significant structures leads to the following relation for the viscosity of liquid; <sup>(II.150, II.151)</sup>

$$\eta = \frac{V_s}{V} \eta_s + \frac{V - V_s}{V} \eta_g \quad (\text{II. 24})$$

Where the term  $V_s$  is the molar volume of the solid at the melting point and  $V$  is the molar volume of the liquid at the temperature of interest.  $\eta_s$  and  $\eta_g$  are the viscosity contributions from the solid-like and gas-like degrees of freedom, respectively. Carlson, Eyring and Ree <sup>(II.151)</sup> Eyring and Ree <sup>(II.152)</sup> have discussed for the the expressions of  $\eta_s$  and  $\eta_g$  and in detail the evaluation of  $\eta_s$  from the reaction rate theory of Eyring <sup>(II.152)</sup> assuming that a solid molecule can jump into all adjacent empty sites. The expression for  $\eta_s$  takes the following equation. <sup>(III.152)</sup>

$$\eta = \frac{N_A h}{Z_K} \left( \frac{V}{V_s} \right) \frac{6}{2^{\frac{1}{2}}} \left( \frac{1}{V - V_s} \right) \frac{1}{(1 - e)^{\frac{\theta}{T}}} \exp \left( \frac{a E_s V_s}{(V - V_s) R T} \right) \quad (\text{II. 25})$$

Where Avogadro's number is  $N_A$ ,  $Z$  is the number of nearest neighbors, the term of the equation  $\theta$  is the Einstein characteristic temperature,  $E_s$  is the energy of sublimation and  $a'$  is the proportionality constant. The following relation obtains the term  $\eta_g$  from the kinetic theory of gases <sup>(II.153)</sup>:

$$\eta_g = \frac{2}{3d^2} \left( \frac{MkT}{\pi^3} \right)^{\frac{1}{2}} \quad (\text{II. 26})$$

Where  $d$  and  $M$  represent the molecular diameter and molecular mass respectively.

### 11.8.5. Viscosities at Higher Concentration

The viscosity at high concentration (1M saturation) can be obtained by the empirical formula suggested by Andrade: [\(II.154\)](#)

$$\eta = A \exp^{b/T} \quad (\text{II.27})$$

The several substitute formulations have been suggested for representing the results of viscosity measurements in the high concentration range [\(II.155-II.159\)](#) and the equation proposed by Angell [\(II.160, II.161\)](#) based on an extension of the free volume theory of transport phenomena in liquids and fused salts to ionic solutions is particularly remarkable.

$$\text{The equation is as: } \frac{1}{\eta} = A \exp \left[ \frac{-K_1}{N_0 - N} \right] \quad (\text{II.28})$$

Where,  $N$  denotes the concentration of the salt in eqv.Litre<sup>-1</sup>,  $A$  and  $K_1$  are constants imaginary to be independent of the salt composition and  $N_0$  is the proposed concentration at which the system becomes glass. The equation was changed by Majumder ET al. [\(II.162-II.164\)](#) presenting the limiting condition, that is; which is the viscosity of the pure solvent. Thus, we have:

$$\ln \frac{\eta}{\eta_0} = \ln \eta_{Rel} = \frac{K_1 N}{N_0 (N_0 - N)} \quad (\text{II.29})$$

The above equation predicts a straight line passing through the origin for the plot of  $\ln \eta_{Rel}$  vs.  $N / (N_0 - N)$  if  $N_0$  is made for a suitable choice. Using the literature data as well their own experimental data Majumder et al. tested the equation (11.29). The best choice can get for  $N_0$  and  $K_1$  was selected by trial and error methods. The set of  $K_1$  and  $N_0$  generating minimum deviations between  $\eta_{Rel}^{Exp}$  and  $\eta_{Rel}^{theo}$  was accepted.  $N \ll N_0$  for very dilute solutions and we have:

$$\eta_{Rel} = \exp \left( \frac{K_1 N}{N_0^2} \right) \cong 1 + \frac{K_1 N}{N_0^2} \quad (\text{II.30})$$

Equation (11.29) is nothing but similar to the Jones-Dole equation with the ion-solvent interaction term characterized as  $B = \frac{K_1}{N_0^2}$ . The arrangement between B-values determined in

this technique and using Jones-Dole equation has been set up to be good for several electrolytes.

Further, the equation (11.29) written in the form:

$$\frac{N}{\ln \eta_{Rel}} = \frac{N_0^2}{K_1} - \frac{N_0 N}{K_1} \quad (\text{II.31})$$

It closely resembles the Vand's equation<sup>(II.165)</sup> for fluidity.

$$\frac{2.5c}{2.303 \log \eta_{Rel}} = \frac{1}{V} - Qc \quad (\text{II.32})$$

Where,  $c$  represent the molar concentration of the solute and  $V$  is the effective rigid molar volume of the salt and the interaction constant symbolizes as  $Q$ .

### 11.8.5 Division of $B$ -Coefficients into Ionic Values

The viscosity  $B$ -coefficient undergoes splitting into the contributions of individual ions can not be done in the same mode as the division of limiting equivalent conductance's, as there is no quantity analogous or corresponding to the transport numbers. Therefore, the separation of the experimental  $B$ -coefficient has been an arbitrary process<sup>(II.166-168)</sup>.

In order to classify the separate contributions of both cations as well as anions to the completely solute-solvent interactions, the viscosity  $B$ -coefficients that can be determined by Jones-Dole's equation has to be resolved into ionic components. For this purpose Gurney<sup>(11.167)</sup>, Cox and Wolfenden<sup>(II.168)</sup>, Sacco *ET al*<sup>(II.169)</sup>, Tuan and Fuoss<sup>(II.170)</sup>, and several authors used different approximations and norms or approximations for different kinds of systems. As for example, Sacco *et al*<sup>(II.169)</sup> suggested the widely used 'reference electrolyte' method. Thus, for  $\text{Ph}_4\text{PBPh}_4$  in water, we take,

$$B_{\text{BPh}_4^-} = B_{\text{PPh}_4^+} = B_{\text{BPh}_4\text{PPh}_4} / 2 \quad (\text{II.33})$$

(Since  $\text{Ph}_4\text{PBPh}_4$  is barely soluble in water). These values obtained from the above formula are in good agreement with those obtained by other methods.

$$B_{\text{BPh}_4\text{PPh}_4} = B_{\text{NaBPh}_4} + B_{\text{PPh}_4\text{Br}} - B_{\text{NaBr}} \quad (\text{II.34})$$

However, the process have been strongly criticized by Krumgalz (II.171). According to him, any technique of resolution emerged on the equality of equivalent conductance for certain ions bears from the drawback that it is very difficult to select any two ions for which *cataionpart = anaion part* in all solvents and at suitable temperatures. At infinite dilution, even if the mobility's of some ions are equal but it is not essential to equality of concentrations. Furthermore, equality of *B*-coefficients of these ions are not necessary with the equality of ionic dimensions, as they are likely to be solvent and dependent on Ionic- structure.

Recently, Krumgalz (II.172) has suggested a method for the resolution of *B*-coefficient. The method is depends on the fact that in organic solvents the large tetra alkyl ammonium ions are not solvated properly. For large  $R_4N^+$  cation, the *B*-values of the ionic species in organic solvents are proportional to their ionic dimensions. (Where  $R \geq Bu$ )

$$B_{R_4NX} = a + br^3 R_4N^+ \quad (II.35)$$

Where, *a* equal to  $B_x^+$  and *b* is a constant quantity independent of temperature and nature of solvent. When extrapolation of the plot of  $BR_4NX$  ( $R > Pr$  or  $Bu$ ) against

To zero cations, dimension that give the result of  $B_x^+$  directly from which other ionic *B*-values can be calculated in the proper solvent. The following equations help to calculate the Ionic *B*-values as:

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \quad (II.36)$$

$$\frac{B_{R_4N^+}}{B_{R'_4N^+}} = \frac{r^3_{R_4N^+}}{r^3_{R'_4N^+}} \quad (II.37)$$

Using accurate conductance data (II.173). The radii of the tetraalkylammonium ions have been calculated from the above equation.

Gill and Sharma (II.173) on similar reason used  $Bu_4NBPh_4$  used as a reference electrolyte and proposed the equations

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \left( \frac{5.35}{5.00} \right)^3 \quad (II.38)$$

$$B_{\text{Bu}_4\text{N}^+\text{BPh}_4^-} = B_{\text{Bu}_4\text{N}^+} B_{\text{Ph}_4\text{B}^-} \quad (\text{II.39})$$

Since the ionic radii of both cationic part  $\text{Bu}_4\text{N}^+$  (5.00 Å) and anionic part  $\text{Ph}_4\text{B}^-$  (5.35 Å) have been observed to remain same in different non-aqueous and mixed non-aqueous solvents.

Recently, to modify the reference electrolyte Lawrence and Sacco <sup>(II.174-176)</sup> used  $\text{Bu}_4\text{NBBu}_4$  as reference electrolytes because cations part and anions part of the electrolyte are symmetrically shaped and have practically equal van der Waals volumes. Thus, we have,

$$B(\text{Bu}_4\text{N}^+)/B(\text{Bu}_4\text{B}^-) = V_w(\text{Bu}_4\text{N}^+)/V_w(\text{Bu}_4\text{B}^-) \quad (\text{II.40})$$

Or

$$B(\text{Bu}_4\text{N}^+) = B(\text{Bu}_4\text{NBBu}_4) / 1 + V_w(\text{Bu}_4\text{B}^-) / V_w(\text{Bu}_4\text{N}^+) \quad (\text{II.41})$$

The results and the conclusions obtained from the theory of Thomson *et al* <sup>(II.177)</sup> agreed well with the above reported values.

It is noticeable that most of these procedures are based on certain approximations and exceptional results may arise unless appropriate mathematical theories are developed to calculate  $B$ -values.

### 11.8.6. Thermodynamics of Viscous Flow

According to Eyring's <sup>(II.178)</sup> approaches assuming viscous flow as a rate process the viscosity ( $\eta$ ) can be represented as

$$\eta = A e^{\frac{E_{\text{vis}}}{RT}} = \left( \frac{hN_A}{V} \right) e^{\frac{\Delta G^*}{RT}} = \left( \frac{hN_A}{V} \right) e^{\left( \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \right)} \quad (\text{II. 42})$$

Where  $E_{\text{vis}}$  is the experimental entropy of activation, which can be obtained from a plot of  $\ln \eta$  against  $1/T$ .  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  are signify as free energy, enthalpy and entropy of activation, respectively?

Nightingale and Benck <sup>(II.179)</sup> both of them share out in the problem in a different procedure or way for measuring the thermodynamics feature of viscous flow of salts in aqueous solution by the assistance of the Jones-Dole equation (neglecting both the  $A$ ,  $c$  term). Thus, we have:

$$R \left[ \frac{d \ln \eta}{d \left( \frac{1}{T} \right)} \right] = r \left[ \frac{d \ln \eta_o}{d \left( \frac{1}{T} \right)} \right] + \frac{R}{1+Bc} \frac{d(1+Bc)}{d \left( \frac{1}{T} \right)} \quad (\text{II. 43})$$

$$\Delta E_{\eta(\text{Soln})}^{\neq} = \Delta E_{\eta(\text{Soln})}^{\neq} + \Delta E_V^{\neq} \quad (\text{II. 44})$$

Where  $\Delta E_V^{\neq}$  can be understood as the increase or decrease of the activation energies due to the presence of ions, for viscous flow of the pure solvents i.e., the actual effect of the ions upon the viscous flow of the solvent molecules.

Data of viscosity can also be studied in the light of transition state theory of the relative viscosity of electrolytic solutions proposed by Feakins *et al* (II.180). According to his opinion,  $B$ -coefficient is given as,

$$B = \frac{(\phi_{v,2}^0 - \phi_{v,1}^0)}{1000} + \phi_{v,2}^0 \frac{(\Delta \mu_2^{0\neq} - \Delta \mu_1^{0\neq})}{1000RT} \quad (\text{II.45})$$

$\phi_{v,1}^0$  and  $\phi_{v,2}^0$  denotes the partial molar volumes of the solvent and solute respectively and  $\Delta \mu_2^{0\neq}$  is the contribution per mole of solute to the free energy of activation for viscous flow of solution.  $\Delta \mu_1^{0\neq}$  Signify the free energy of activation for viscous flow per mole of the solvent, which is given by:

$$\Delta \mu_1^{0\neq} = \Delta G_1^{0\neq} = RT \ln(\eta_0 \phi_{v,1}^0 / h N_A) \quad (\text{II. 46})$$

Further, if  $B$  is known at various temperatures, we can calculate the entropy and enthalpy of activation of viscous flow respectively from the following equations as given below:

$$\frac{d(\Delta \mu_2^{0\neq})}{dT} = -\Delta S_2^{0\neq} \quad (\text{II. 47})$$

$$\Delta H_2^{0\neq} = \Delta \mu_2^{0\neq} + T \Delta S_2^{0\neq} \quad (\text{II. 48})$$

### 11.8.7. Effects of Shape and Size

Stokes and Mills have dealt in the characteristic of shape and size comprehensively. The ions remain in solution can be regarded as a rigid spheres suspended in range. Einstein (II.181) leads to the following equation for the treatment of hydrodynamic phenomenon involving in the solution.

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi \quad (\text{II. 49})$$

Where  $\phi$  is symbolize the volume fraction occupied by the particles. (I) Sinha <sup>(II.182)</sup> proposed for the modification of the equation based on departures from spherical shape and (ii) according to Vand based on dependence of the flow patterns around the adjacent particles at higher concentrations. However, regarding the different aspects of the problem, spherical shapes for electrolytes having hydrated ions of large effective size have been assumed. (Especially polyvalent monatomic cations). Thus, we have from [equation \(II. 49\)](#):

$$2.5\phi = A\sqrt{c} + Bc \quad (\text{II. 50})$$

Since the term  $A\sqrt{c}$  can be neglected in comparison with  $Bc$  and  $\phi = c\phi_{v,1}^0$  where  $\phi_{v,1}^0$  denotes the partial molar volume of the ion, we get the following equation

$$2.5\phi_{v,1}^0 = B \quad (\text{II. 51})$$

In case of an ideal situation, the viscosity B -coefficient is a linear function of partial molar volume of the solute molecules  $\phi_{v,1}^0$  with slope to 2.5. Thus,  $B_{\pm}$  can be associated to:

$$B_{\pm} = 2.5\phi_{\pm}^0 = \frac{2.5 \times 4}{3} \frac{(\pi R_{\pm}^3 N)}{1000} \quad (\text{II. 52})$$

Supposing that the ions behave as rigid spheres with effective radii,  $R_{\pm}$  moving in a continuum. Using the above [equation \(II. 52\)](#)  $R_{\pm}$ , can be calculated that should be close to crystallographic radii or corrected Stake's radii if the ions are hardly solvated and perform as spherical entities. However, in common, the radii obtained from the crystallographic, which is less than the radii ( $R_{\pm}$ ), obtained from the above equation that indicating appreciable solvation.

By comparing, the Jones-Dole equation with the Einstein's equation the number  $n_b$  of solvent molecules bound to the ion in the primary solvation shell can be easily calculated:

$$B_{\pm} = \frac{2.5}{1000(\phi_i + n_b\phi_s)} \quad (\text{II. 53})$$

Where  $\phi_i$  and  $\phi_s$  is the molar volume of the base ion, the molar volume of the solvent respectively. To study the nature of solvation and solvation number [equation a number of workers has used \(II. 53\)](#) properly.

### II. 8. 8. Viscosity of Non-Electrolytic Solutions

The three equations of Vand,<sup>(II.183)</sup> Thomas,<sup>(II.184)</sup> and Moulik<sup>(II.185-II.187)</sup> proposed chiefly to account for the determination of viscosity of the concentrated solutions of bigger spherical particles have been also established to correlate with the mixture of viscosities of the normal nonelectrolytes.

$$\text{Vand equation: } \ln \eta_r = \frac{\alpha}{1-Q} = \frac{2.5V_h c}{1-QV_h c} \quad (\text{II. 54})$$

$$\text{Thomas equation: } \eta_r = 1 + 2.5V_h + 10.05cV_h^2 c \quad (\text{II. 55})$$

$$\text{Moulik equation: } \eta^2 = I + Mc^2 \quad (\text{II. 56})$$

where  $\eta_r$  is clarify as the relative viscosity,  $a$  is constant quantity depending on the axial ratios of the particles associated in solution, the interaction constant is  $Q$ ,  $V_h$  is express as the molar volume of the solute including rigidly held solvent molecules due to hydration,  $c$  is the molar concentration of the solute molecules;  $I$  and  $M$  both are constants. The viscosity equation proposed by Eyring and coworkers for pure liquids based on pure noteworthy liquid structures theory, can be extended to predict the viscosity of mixed liquids also. The final expression for the liquid mixtures takes the following form:

$$\eta_m = \frac{6N_A h}{\sqrt{2}r_m(V_m - V_{Sm})} \left[ \sum_i^n \left\{ 1 - \exp\left(\frac{-\theta_i}{T}\right) \right\}^{-x_i} \right] \exp\left[ \frac{a_m E_{Sm} V_{Sm}}{RT(V_m - V_{Sm})} \right] + \frac{V_m - V_{Sm}}{V_m} \left[ \sum_i^n \frac{2}{3d_i^2} \left( \frac{m_i kT}{\pi^3} \right)^{\frac{1}{2}} x_i \right] \quad (\text{II. 57})$$

Where  $n$  is two for binary and three for ternary liquid mixtures.  $r_m$ ,  $E_{Sm}$ ,  $V_m$ ,  $V_{Sm}$  and  $a_m$  the mixture parameters were calculated from the corresponding pure component parameters by using the following relations:

$$r_m = \sum_i^n x_i^2 r_i + \sum_{i \neq j} 2x_i x_j x_{ij} \quad (\text{II. 58})$$

$$E_{Sm} = \sum_i^n x_i^2 E_{Si} + \sum_{i \neq j} 2x_i x_j E_{Sij} \quad (\text{II. 59})$$

$$V_m = \sum_i^n x_i V_i \quad V_{Sm} = \sum_i^n x_i V_{Si} \quad a_m = \sum_i^n x_i a_i \quad (\text{II. 60})$$

$$r_{ij} = (r_i r_j)^{\frac{1}{2}} \quad \text{And } E_{Sij} = (E_{Si} E_{Sj})^{\frac{1}{2}} \quad (\text{II. 61})$$

$$\theta = \frac{h}{\kappa 2\pi} \left( \frac{b}{m} \right)^{\frac{1}{2}} \quad (\text{II.62})$$

$$b = 2Z\varepsilon \left[ 22.106 \left( \frac{N_A \sigma^2}{V_s} \right)^4 - 10.559 \left( \frac{N_A \sigma^3}{V_s} \right)^2 \right] \frac{1}{\sqrt{2}\sigma^2} \left( \frac{N_A \sigma^3}{V_s} \right)^{\frac{2}{3}} \quad (\text{II. 63})$$

Where  $\sigma$ ,  $\varepsilon_r$  are Lennard-Jones potential parameters respectively and the other symbols have their usual significance.

For the purposes, interpolation and limited extrapolation, the viscosities of ternary mixture can be interrelated to a high degree of accuracy in terms of binary contribution by the following equations. [\(II.188-II.194\)](#)

$$\begin{aligned} \eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] \\ & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_3 - x_1) + C_{31}(x_3 - x_1)^2] \end{aligned} \quad (\text{II. 64a})$$

The modification of correlation of ternary system is given in the following form:

$$\begin{aligned} \eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] \\ & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_3 - x_1) + C_{31}(x_3 - x_1)^2] \\ & + A_{123}(x_1 x_2 x_3) \end{aligned} \quad (\text{II. 64b})$$

$$\begin{aligned} \eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] \\ & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_3 - x_1) + C_{31}(x_3 - x_1)^2] \\ & + x_1 x_2 x_3 [A_{123} + B_{123} x_1^2 (x_2 - x_3)^2 + C_{123} x_1^3 (x_2 - x_3)^3] \end{aligned} \quad (\text{II. 64c})$$

Where character of  $A_{12}$ ,  $B_{12}$ ,  $C_{12}$ ,  $A_{23}$ ,  $B_{23}$ ,  $C_{23}$ ,  $A_{31}$ ,  $B_{31}$  and  $C_{31}$ , are the constants for binary mixtures;  $A_{123}$ ,  $B_{123}$  and  $C_{123}$  are constants for the ternaries mixture; and the other symbols have their common importance.

### 11.9. REFRACTIVE INDEX

Optical data (refractive index,  $n_D$ ) provide interesting information related to molecular interactions and structure of the solutions, as well as complementary data on practical procedures, such as concentration measurement or estimation of the extent of salvation of electrolytes/non-electrolytes in liquid systems. (II.195)

The light bending property is a result of variation of the velocity with which light is transmitted. Refractive index ( $n_D$ ) of liquid, changes not only with the wavelength of light used but also with the temperature. Influence of Molar refractions are characterized by the organization of atoms in the molecule or by factors like unsaturation, ring closure etc. linear optical properties of liquids and liquid mixtures have been widely studied to obtain information on their physical, chemical, and molecular properties. Fialkov ET. al. (II.196, II.197) stated that the refractive index is an additive property of pure components when composition is expressed in terms of volume fraction. Several researchers have estimated the refractivity of liquid systems using the well-known mixing rules viz. Arago-Biot, Newton, Heller, Gladstone-Dale, Eyring-John, Eykman, Lorentz-Lorenz, Weiner and Oster relations. (II.198-II.201) these empirical approaches for calculating the excess properties attempt to explain the non-ideality in terms of specific and non-specific intermolecular interactions. Refractive index or refractivity is very important property of intrinsic attention in the fields of pharmaceutical research such as in optoelectronic, formulation of eye preparations and photonic applications.

$$\text{Refractive Index } (n_D) = \frac{\text{Speed of light in vacuum}}{\text{Speed of light in solution systems}}$$

Whenever the speed of light changes when it crosses a boundary from one medium into another, and changes the actual direction of travel of applying light. i.e., it is refracted. The relationship between the speed of light in the selected two mediums ( $V_A$  and  $V_B$ ), the angles of incidence ( $\sin \theta_A$ ) and refraction ( $\sin \theta_B$ ) and the  $n_A$  and  $n_B$  are the refractive indexes of the two mediums is shown below:

$$\frac{V_A}{V_B} = \frac{\sin \theta_A}{\sin \theta_B} = \frac{n_B}{n_A} \quad (\text{II. 65})$$

Thus, it is not very essential to measure the speed of light in a sample in order to determine its refractive index. In its place, by measuring the angle of refraction, and knowing the index of refraction of the layer of the concerned medium that is in contact with the sample, it is also possible to determine the refractive index of the sample quite accurately.

The refractive index of mixing can be correlated by the application of a composition-dependent polynomial equation. Molar refractivity, was obtained from the Lorentz-Lorenz relation (II.202, II.203) by using,  $n_D$  experimental data according to the following expression

$$R_M = \frac{(n_D^2 - 1)}{(n_D^2 + 2)} \left( \frac{M}{\rho} \right) \quad (\text{II. 66})$$

Where  $M$  refers to the mean molecular weight of the mixture and  $\rho$  is the mixture density.  $n_D$  Can be expressed as the following:

$$n_D = \sqrt{\frac{(2A+1)}{(1-A)}} \quad (\text{II. 67})$$

Where  $A$  is given by:

$$A = \left[ \left\{ \frac{(n_1^2 - 1)}{(n_1^2 + 2)} (1/\rho_1) \right\} - \left\{ \frac{(n_1^2 - 1)}{(n_1^2 + 2)} (w_2/\rho_1) \right\} + \left\{ \frac{(n_2^2 - 1)}{(n_2^2 + 2)} (w_2/\rho_2) \right\} \rho \right] \quad (\text{II. 68})$$

Where  $n_1$  and  $n_2$  are the refractive indices of pure component,  $w_j$  refers the weight fraction,  $\rho$  is the mixture of density, and  $\rho_1$  and  $\rho_2$  are the pure component of densities.

The deviation of molar refractivity is calculated by the following expression is as follow:

$$\Delta R = R - \phi_1 R_1 - \phi_2 R_2 \quad (\text{II. 69})$$

Where  $\phi_1$  and  $\phi_2$  are signify the volume fractions and  $R$ ,  $R_1$ , and  $R_2$  denotes as the molar refractivity of the mixture and of the pure components, respectively.

The deviations of refractive index were used for the correlation of the binary solvent mixtures:

$$\Delta n_D = n_D - x_1 n_{D1} - x_2 n_{D2} \quad (\text{II. 70})$$

Where  $\Delta n_D$  is the deviation of the refractive index for this binary system and  $n_D$ ,  $n_{D1}$ , and  $n_{D2}$  are the refractive index of the binary mixture, refractive index of component-1, and refractive index of component-2, respectively, 'x' is the mole fractions.

The computed deviations of refractive indices of the binary mixtures are fitted using the following Redlich-Kister expression. (II.204)

$$\Delta n_{Dew} = w_e w_w \sum_{P=0}^S B_p (w_e w_w)^P \quad (\text{II. 71})$$

Where  $B_p$  are the adjustable parameters obtained by a least squares fitting method,  $w$  is the mass fraction, and  $S$  is the number of terms in the polynomial.

In case of salt-solvent solution, the binary systems were fitted to polynomials of the form:

$$n_{Ds,sol} = n_{Dsol} + \sum_{i=1}^N A_i m^i \quad (\text{II. 72})$$

For the ternary systems of the salt + solvent-1 + solvent-2 solutions a polynomial expansion (II.205) has been employed, similar to that obtained for the salt + solvent solutions was used to represent ternary refractive indices:

$$n_D = n_{Dw} + \sum_{i=1}^P C_i m^i \quad (\text{II. 73})$$

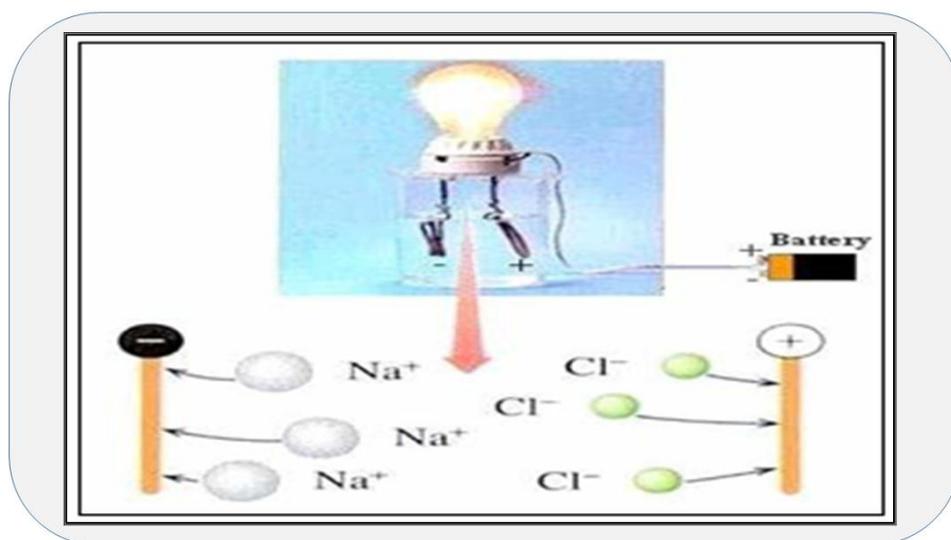
Where  $n_D$  is the refractive index of the ternary solution,  $C_i$  are the parameters, and  $P$  is the number of terms in the polynomial.

There is no common or general rule that states how to calculate the deviation of refractivity function. The ideal behavior may be expressed in terms of mole fraction: in this case, smaller deviations occur but values are more scattered because of the higher compassion of the expression to rounding errors in the mole fraction. For the sake of inclusiveness, deviation function of both calculations of refractivity and also molar

refraction was fitted to a Redlich and Kister-type expression <sup>(II.204)</sup> and the adaptable parameters and the relevant standard deviation  $\delta$  can be calculated for the expression in terms of volume fractions and in terms of mole fractions, correspondingly.

### 11.10. CONDUCTANCE:

Conductance is the most important and also an accurate and direct method available to determine the extent of the dissociation constants of electrolytes in aqueous, mixed and non-aqueous solvents is the “*conducti metric method.*” Conductance data in combination with viscosity measurements, gives much more information pertaining the ion-ion and ion-solvent interaction.



### Dissolved Ions Conduct Electricity

The measurements of conductance studies were followed vigorously throughout the last five decades, both theoretically and as well as experimentally and a number of vital theoretical equations have been evolved. We shall be located in briefly on some of these prospects in relation to the studies in aqueous, non-aqueous, pure and mixed solvents respectively. The successful application of the Debye-Hückel theory of interionic attraction was made by Onsager, <sup>(II.206)</sup> to derive the Kohlrausch's equation representing the molar conductance of an electrolyte.

$$\Lambda = \Lambda_0 - S\sqrt{c} \quad (\text{II. 74})$$

Where,

$$S = \alpha\Lambda_0 + \beta \quad (\text{II. 75})$$

$$\alpha = \frac{(z^2)k}{3(2 + \sqrt{2})\epsilon_r kT \sqrt{c}} = \frac{82.406 \times 10^4 z^3}{(\epsilon_r T)^{\frac{3}{2}}} \quad (\text{II. 76a})$$

$$\beta = \frac{z^2 e F k}{3\pi\eta\sqrt{c}} = \frac{82.487 z^3}{\eta\sqrt{\epsilon_r T}} \quad (\text{II. 76b})$$

The equation took no account for the short-range of interactions and of shape or size of the ions in solution. The ions were considered as rigid charged spheres in an electrostatic and as well as hydrodynamic continuum, i.e., the solvent. (II.207) In the subsequent years, Pitts (1953) (II.208) and Fuoss and Onsager (1957) (II.209) independently calculate the solution of the problem of electrolytic conductance bookkeeping for both interactions long-range and short-range respectively. However, the  $A_o$  values obtained for the conductance at infinite dilution using Fuoss-Onsager theory differed considerably from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation. (II.210, II.211) Fuoss and Hsia (II.212) who again calculated the relaxation field, retaining the terms which had previously been neglected.

The results obtained from the conductance theories can be expressed in a general form:

$$A = \frac{A_o - \alpha A_o \sqrt{c}}{(1 + \kappa\alpha)} \left( \frac{1 + \kappa\alpha}{\sqrt{2}} \right) - \frac{\beta\sqrt{c}}{(1 + \kappa\alpha)} + G(\kappa\alpha) \quad (\text{II. 77})$$

Where  $G(\kappa\alpha)$  is a complicated function of the variable. The simplified form:

$$A = A_o - S\sqrt{c} + Ec \ln c + J_1 c + J_2 \sqrt[3]{c} \quad (\text{II. 78})$$

However, it has been found that these equations have certain limitations, in some cases it fails to fit experimental data. Some of these results have been deliberate elaborately by Fernandez-Prini. (II.213, II.214) Fuoss and Accascini made more correction of the equation (II. 89). For considering the change in viscosity of the concerned solutions, they assumed the backbone of Walden's rule. The new equation becomes in the following form.

$$A = A_o - S\sqrt{c} + Ec \ln c + J_1 c + J_2 \sqrt[3]{c} - FAc \quad (\text{II. 79})$$

$$\text{Where, } Fc = \frac{4\pi R^3 N_A}{3} \quad (\text{II. 80})$$

In most cases, however,  $J_2$  is made zero but this leads to a systematic deviation of the experimental data from the theoretical equations. It has been observed that Pitt's equation gives better fit to the experimental data in aqueous solutions. (II.215)

### 11.10.1. Ionic Association

The behavior of completely dissociated electrolytes successfully can be represents by the equation (II. 89). The nature of dissociation or association of electrolytes can be obtained by the plotting of  $\Lambda$  against  $\sqrt{c}$  (limiting Onsager equation). The association between cations and anions result the large electrostatic interactions. The difference in  $\Lambda_{o\text{ exp}}$  and  $\Lambda_{o\text{ theo}}$  would be more prominent with increasing association among the ions. (II.216)

Conductance measurements is very helpful for the determination of values for the ion-pair association constant,  $K_A$  for the process:



$$K_A = \frac{(1-\alpha)}{\alpha^2 c \gamma_{\pm}^2} \quad (\text{II. 82})$$

$$\alpha = 1 - \alpha^2 K_A c \gamma_{\pm}^2 \quad (\text{II. 83})$$

Where, mean activity coefficient denotes  $\gamma_{\pm}$  of the free ions at concentration  $\alpha C$ . The value of constant  $K_A$  and  $\Lambda_o$  have been determined using Fuoss-Kraus equation (II.217) or Shedlovsky's equation. (II.218)

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda_o} + \frac{K_A}{\Lambda_o^2} \cdot \frac{c \gamma_{\pm}^2 \Lambda}{T(z)} \quad (\text{II. 84})$$

According to (Fuoss-Kraus method  $T(z) = F(z)$  ) and  $1/T(z) = S(z)$  signify the (Shedlovsky's method).

$$F(z) = 1 - z(1 - z(1 - \dots))^{\frac{1}{2}} \quad (\text{II. 85a})$$

$$\text{And} \quad \frac{1}{T(z)} = S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \dots \quad (\text{II. 85b})$$

A plot of  $T(z)/\Lambda$  vs  $c\gamma_{\pm}^2\Lambda/T(z)$  should be a straight line having the value of intercept parameter is  $1/\Lambda_0$  and slope of the plot is  $K_A/\Lambda_0^2$ . Wherever  $K_A$  is large, there will be great uncertainty in the determined values of  $\Lambda_0$  and  $K_A$  from equation (II. 84).

The conductance equation for associated electrolytes is given by Fuoss-Hsia (II.219)

$$\Lambda = \Lambda_0 - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{\frac{3}{2}} - K_A\Lambda\gamma_{\pm}^2(\alpha c) \quad (\text{II. 86})$$

Justice modified the above equation. (II.220) The conductance of symmetrical electrolytes in dilute solutions can be represented by the following equations:

$$\Lambda = \alpha(\Lambda_0 - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1R(\alpha c) - J_2R(\alpha c)^{\frac{3}{2}}) \quad (\text{II. 87})$$

$$\frac{(1-\alpha)}{\alpha^2 c \gamma_{\pm}^2} = K_A \quad (\text{II. 88})$$

$$\ln \gamma_{\pm} = \frac{-k\sqrt{q}}{(1+kR\sqrt{\alpha c})} \quad (\text{II. 89})$$

From least square treatment, the parameter of conductance are obtained least after setting,  $R = q = \frac{e^2}{2\epsilon kT}$  (Bjerrum's critical distance).

According to equity the method of fixing the  $J$ -coefficient by setting,  $R = q$  clearly consents a better value of  $K_A$  to be found. Since the equation (II. 87) is a series expansion truncated at the  $c^{3/2}$  term, it would be better that the resulting errors be immersed as must as possible by  $J_2$  rather than by  $K_A$ , whose theoretical interest is greater as it covers the information concerning short-range cation-anion interaction. From the experimental values of the association constant  $K_A$ , one can use two methods in order to determine the distance of closest approach, 'a', of two free ions to form an ion-pair. Fuoss; (II.221) proposed the following equation to determination of  $K_A$ ,

$$K_A = \frac{4\pi N_A \alpha^3}{3000} \exp\left(\frac{e^2}{\alpha \epsilon kT}\right) \quad (\text{II. 90})$$

In most of the cases, the magnitude of  $K_A$  was too small to allow or permit a calculation of  $a$ . The distance parameter was lastly considered from the more common equation due to Bjerrum. <sup>(II.222)</sup>

$$K_A = \frac{4\pi N_A \alpha}{1000} \int_{r=a}^{r=q} r^2 \exp\left(\frac{z^2 e^2}{r \epsilon k T}\right) dr \quad (\text{II. 91})$$

In the above equation there is absent of specific short-range interactions except for solvation in which the solvated ion can be approximated by a hard sphere model. Douheret has successfully applied the process. <sup>(II.223)</sup>

### 11.11. FTIR SPECTROSCOPY

The spectroscopic study has been established by the investigation of FTIR spectroscopy. The study has been taking into account to qualitative interpreting the molecular as well as ionic association of the electrolytes in the solutions. FTIR spectroscopy is one of the most appropriate optical properties, which qualitatively interpreted the nature, mode, manner of the electrolytes and non-electrolytes in the solution system, eventually it also is able to give information about the configurational structure of the solute or solvents present in the solutions.

Both organic and inorganic chemists is used the Infrared (IR) spectroscopy which is one of the most common spectroscopic techniques in science. It is the measurement of absorption of different IR frequencies by a sample placed in the path of an IR beam. The main aim of IR spectroscopic investigation is to determine the chemical functional groups present in the sample. The characteristic frequencies of IR radiation absorb by various functional groups exist in the sample. Infrared spectrometers can accept a wide range of sample types such as gases liquids, and solids using various sampling accessories. Thus, IR spectroscopy is a significant and exoteric tool for structural elucidation and identification of compound.

Approximately 13,000 to 10  $\text{cm}^{-1}$ , or wavelengths from 0.78 to 1000  $\mu\text{m}$  are the wave number electromagnetic spectrum range of Infrared radiation. This spectrum region is bounded at high frequencies and at low frequencies by the red end of the visible and microwave region respectively.

Either positions of absorption of IR are generally represented as wavelengths ( $\lambda$ ) or wavenumbers ( $\nu$ ). Definition of Wavenumber is the number of waves per unit length.

Thus, wavenumbers are not only directly proportional to frequency and as well as the energy of the IR absorption. The unit of wavenumber is denoted as ( $\text{cm}^{-1}$ , reciprocal centimetre) is more frequently applied in modern IR instruments that are linear in the  $\text{cm}^{-1}$  scale. In the contrast, where the wavelengths are inversely proportional to frequencies and their associated energy. At present, the suggested unit of wavelength is m (micrometres), but  $\mu$  (micron) is often used in some older literature.

Information of IR absorption is generally represented in the form of a spectrum with wavelength or wavenumber as remain in the x-axis and intensity of absorption percentage of transmittance as in the y-axis.

T, Transmittance, is the ratio of radiant power transmitted by the sample ( $I$ ) with respect to the radiant power incident on the sample ( $I_0$ ).

$$A = \log_{10}(1/T) = -\log_{10}(T) = -\log_{10}\left(\frac{I}{I_0}\right) \quad (\text{II.92})$$

The spectra of the transmittance provide better disparity between intensities of strong and weak bands as the ranges of transmittance from zero to 100%  $T$  whereas the absorbance ranges from infinity to zero. It will appear only if some of IR bands have been contracted or expanded.

Near IR, mid IR, and far IR are three IR region is usually divided into three smaller areas:

|            | Near IR                       | Mid IR                     | Far IR                  |
|------------|-------------------------------|----------------------------|-------------------------|
| Wavenumber | 13,000–4,000 $\text{cm}^{-1}$ | 4,000–200 $\text{cm}^{-1}$ | 200–10 $\text{cm}^{-1}$ |
| Wavelength | 0.78–2.5 $\mu\text{m}$        | 2.5–50 $\mu\text{m}$       | 50–1,000 $\mu\text{m}$  |

This chapter emphasizes on the most commonly used mid IR region, between 4000 and 400  $\text{cm}^{-1}$  (2.5 to 25  $\mu\text{m}$ ).

From the analysis of the above, it is apparent that the problem of molecular interactions is intriguing as well as interesting. We have, therefore, utilized five important methods, viz., and volumetric, viscometric, interferometric, conduct metric and refract metric as the quantitative and FT-IR spectroscopy as the qualitative analysis for the studies of the thermophysical, physicochemical, thermodynamics, transport properties

occurring in different studied liquid systems. Utilizing the theoretical and experimental results, we have employed all the studies for application in different fields.

## II.12.UV-Visible-Spectroscopy

Various electronic energy level of molecules can undergoes electronic excitation from lower energy level to higher energy level and as a result a broad peak in UV-Visible spectrum. Bonding and non-bonding electrons in different energy level of molecules absorb different energy in the form of ultraviolet or visible light, which is responsible to excite these electrons from lower energy level to higher or anti bonding orbital. If the energy gap between HOMO and LUMO is not so high then the electron can easily excited to lower energy state to higher energy state. There are four possible types of transitions are  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$ ,  $\sigma \rightarrow \sigma^*$   $n \rightarrow \sigma^*$ . The order of energy gap among the four is given as  $n \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^* < \sigma \rightarrow \sigma^*$ .

The following is the equation of Lambert-Beers law, which shows the relation of absorbance of light of a sample in a UV-Visible spectrum.

$$A = \log(I_0/I) = \epsilon cl \text{ for a particular wavelength of light}$$

A= denotes as Absorbance

$I_0$ = signify the Intensity of incident light

I= Intensity of the light that leaving from sample

$\epsilon$ = Molar absorptivity

c= signify molar concentration of solution of the sample

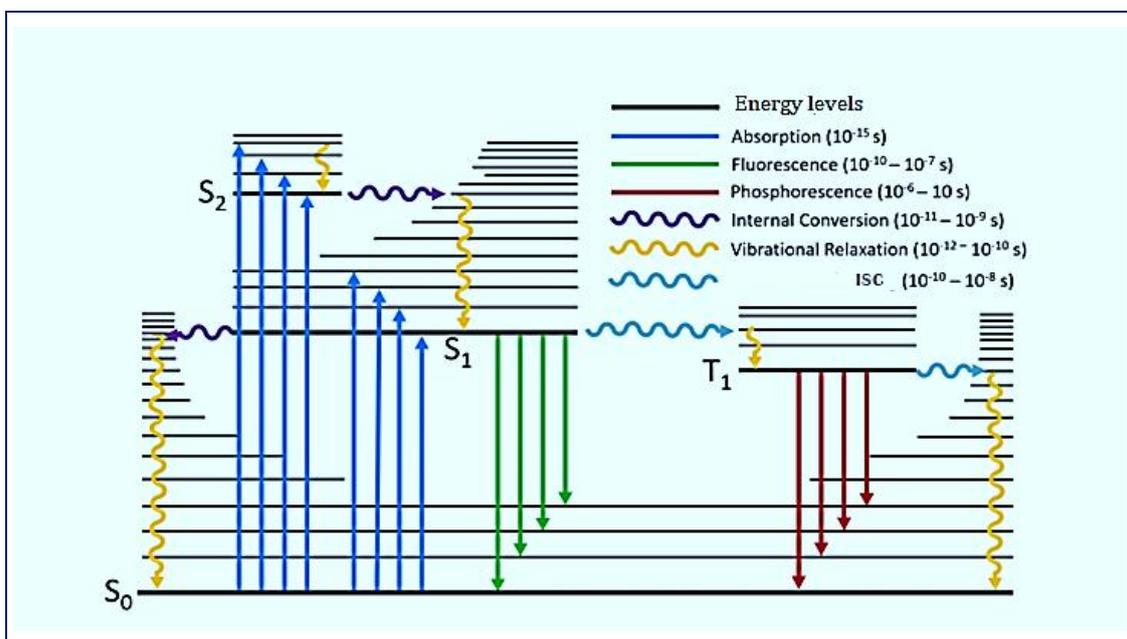
l=denotes as a length of cuvette containing sample

In this thesis of my research work, the data obtained from UV-Visible spectroscopy were fitted with the Benesi –Hildebrand equation for calculation the binding or stability constant to determination the different interactions occurring between the amino acids with ionic liquids.

## II.13 Fluorescence Spectroscopy

It is the opposite spectra from UV-Visible spectra. It is called emission spectra. This spectra of emission is originated by the transitions of electron from higher energy state to lower energy state, shows fluorescence. In molecules, there are different electronic energy level as well as different vibrational energy level. In florescence, a

photon excited at first the species from its ground state to the next higher vibrational level of different states in the excited electronic state. After the excitation of the molecules, the molecules undergoes collisions with other molecules and as a result deactivates of the molecules. The excited species lose their vibrational energy simultaneously and reaches lowest vibrational energy of electronic state according to the opinion of Jablonski diagram. At last the molecules drops to one of the different vibrational energy state as a result again photons get emitted process giving the fluorescence.



**Fig: Jablonski diagram**

## II.14 Surface Tension Measurements

Molecules at the surface of a liquid exerted by the molecules at the bulk and trends to molecules towards the bulk of the liquid. In this situation the shape of the liquid, assume the least surface area.

In my research work, using ionic liquids in Aquous medium and amino acids in ionic liquid solutions. The surface tension of pure ionic liquid in water is less than pure water because hydrophobic part of the ionic liquid encapsulated in water molecules as a result the surface tension decrease. But with addition of some amino acid into the ionic liquid solutions again increase the surface tension. This is beau case the amino acid interact with ionic liquid as a result water molecules come out from the ionic liquid solution. Higher the interaction between amino acid with the ionic liquid higher is the value of surface tension

### II.15.1HNMR Spectroscopy

NMR Spectroscopy is very important and most acceptable technique among all of the spectroscopic techniques to determination of characteristic an organic compound. From these techniques, it gives us the information about the neighboring magnetic environment of atomic nuclei and magnetically different environment of total number of hydrogen atoms.

In a magnetic field, the experimental sample is put and NMR signal is generated by the excitation of the nuclei of the sample into nuclear magnetic resonance with radio waves which is collected with sensitive radio receivers. The resonance frequency of an atom changes with the help of surrounding intramolecular magnetic field. NMR also gives us the nature of electronic structure of a molecule and associate individual functional groups. Since these fields are generally unique for particular compounds therefore in modern organic chemistry, NMR technique is definitive process to detect monomolecular organic molecules. In the same way, biochemists apply this technique also to detect the structure of protein as well as complex molecules. Not only identification, but also NMR spectroscopy procedure gives the detailed information about the structure of molecules, state of reaction, dynamics and chemical environment of the molecules. Proton NMR and <sup>13</sup>-carbon NMR Spectroscopy is the most common types of NMR, but it is only acceptable when the nuclei of atoms of molecule processing spin.

Long timescale of NMR Spectroscopy that does not indicates the fast phenomenon, so it produce an average spectrum. NMR spectrum does not show the spectra of samples having a large extent of impurities of the samples. Therefore, for higher sensitivity of the instrument higher strength of external field may be required to detect the spectrum of the samples.

#### Integrals and integrations

We can analysis the peak intensity as well as the number of protons of different types with the help of software very easily. With the help of intregation we can measure the intensity of the signal obtained from NMR Spectroscopy and also the total number of atoms presents. The number of protons is directly proptional with the intensity of the NMR signal obtained from the simplest NMR technique. The integral of signals obtained

from  $^{13}\text{C}$ -NMR spectra also depends on the dipolar coupling constants and also the relaxations rate of the concentrate nucleus of atoms.

### Chemical shift

Nature of proton in NMR spectroscopy can be determined from the chemical shift value. With the help of chemical shift values of protons the magnetic environment and also the signal in different positions obtained in  $^1\text{H}$ NMR spectrum. The position of signals in spectrum depends on the strength of the external magnetic field. TMS (tetramethylsilane) is usually used as a reference for calculating the chemical shift value determination in NMR Spectrum of corresponding protons of a molecule. A local magnetic field is generated by the electron density around the nucleus which is opposed the external magnetic field. As a result of shielding of proton in  $^1\text{H}$ NMR spectrum take place. If electronegative atom consisting around the nucleus which withdraw itself around its neighboring atoms as a result the electron density of neighboring atom decrease, hence the proton experience downfield shift.

In my research work in this thesis, interacting protons of amino acids with the ionic liquids result in shifting of chemical shift values from the chemical shift value of pure amino acid and pure ionic liquid.

## CHAPTER -III

### Experimental section

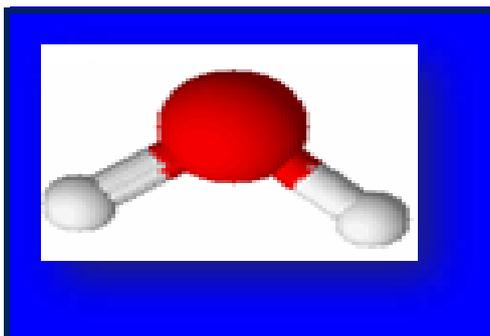
#### III. 1 NAME AND THEIR STRUCTURE, PHYSICAL AND CHEMICAL PROPERTIES, PURIFICATION AND APPLICATIONS OF THE CHEMICALS USED IN THE RESEARCH WORK

##### III.1.1 SOLVENTS

The details of the aqueous solvent used in the research work is described below.

##### Water (H<sub>2</sub>O):

Water is a pervasive chemical substance is composed of two element, hydrogen and oxygen and it is very essential for all kinds of known forms of life. In typical convention, water states only to its liquid form or state, but also the substance exists as solid state, ice, and a gaseous state, water vapour or steam. Water is used as a good solvent and is often referred to as the collective or universal solvent.



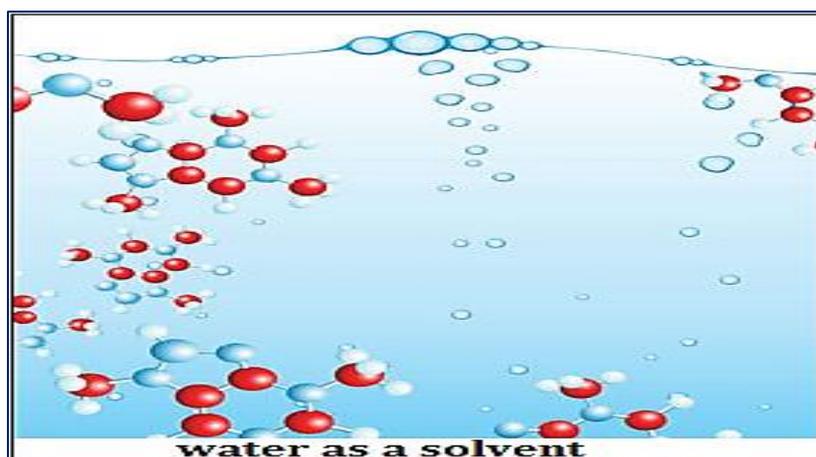
Structure of Water (H<sub>2</sub>O)

| Physical appearance   | Liquid                               |
|-----------------------|--------------------------------------|
| Molecular formula     | H <sub>2</sub> O                     |
| Molecular weight      | 18.01528 g.mol <sup>-1</sup>         |
| Density value         | 0.999700 g.cm <sup>3</sup> (298.15K) |
| Refractive index      | 1.3333                               |
| Viscosity             | 0.890mP.s                            |
| Ultra sonic speeds    | 1500ms <sup>-1</sup>                 |
| Dielectrical constant | 78.35(298.15K)                       |

**Source:** Distilled water used for experimental purpose, distilled from fractional distillation method in the Lab.

**Purification:** At first, water was deionized and then distilled in an all glass distilling set along with alkaline  $\text{KMnO}_4$  solution was used to remove any organic matter in that. Finally, the doubly distilled water was distilled using an all glass distilling set for making perspective solution. Accurate Precautions were taken to prevent contamination from  $\text{CO}_2$  and other contaminations. Specific conductance of the triply distilled water was less than  $1 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ .

**Application:** Water is broadly used as a solvent or reactant in many chemical reactions and less commonly used as a solute or catalyst. Water is a conjoint solvent, dissolving many ionic compounds for solvation. Recently, Supercritical water has been a focus of research field of science. Oxygen saturated supercritical water combusts organic pollutants competently. In various industries also uses water for their many purposive work. It is a fantastic solvent, generally taken as the common solvent, due to tendency to form hydrogen bonds with other molecules and as well as the marked polarity of the water molecule. Water is so precise that our life on earth totally depends on it. Not for only a high percentage of living thing remain water, but also both plants and animals are found in water, all life on earth is believed to have stand up from water and the bodies of all living organisms are tranquil largely of water. Ln organic matter About 70 to 90 percent water is present. The chemical reactions in all types of plants and animals that provision or supportive of our life take place in a water medium. Water not only brings the medium to make these life-sustaining reactions possible, but water itself is often vital reactant or product of these reactions. In short, the chemistry of life is named as water chemistry.



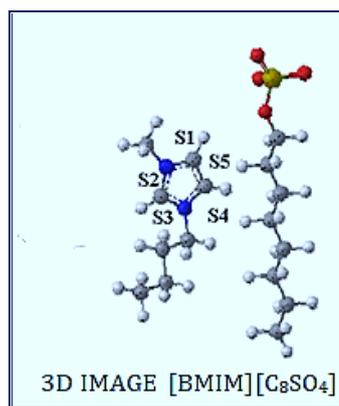
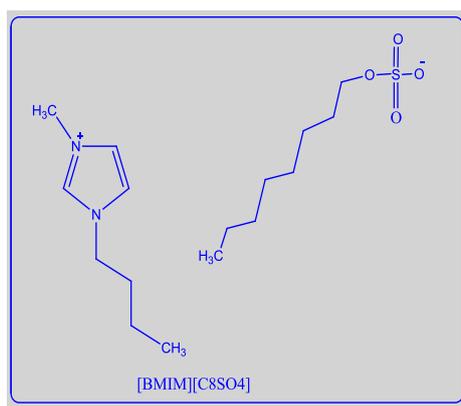
### III.1.2 ELECTROLYTES AND NON-ELECTROLYTES

The ionic liquids, (electrolytes) and amino acids, (non-electrolytes) are two categories that are used in the research work which have been described in the following:

#### III.1.2.1 Ionic Liquids

##### 1-butyl-3-methylimidazolium octyl sulfate [BMIM][C<sub>8</sub>SO<sub>4</sub>] (CASNO-445473-58-5)

1-Butyl-3-methylimidazolium octyl sulfate is an ionic liquid which is free of halogen elements. This ionic liquid is a hydrolysis-stable compound. The critical micelle concentration (CMC) is above 0.031 M, it behaves as a surfactant.



The Physical Property of [BMIM][C<sub>8</sub>SO<sub>4</sub>] is given as follows:

|                          |  |
|--------------------------|--|
| <b>Molecular formula</b> | <b>C<sub>16</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>S</b> |
| <b>Density</b>           | <b>1.07 g/cm<sup>3</sup></b>                                   |
| <b>Melting point</b>     | <b>37<sup>o</sup> C</b>  |
| <b>Boiling point</b>     | <b>N/A</b>   |
| <b>Molecular weight</b>  | <b>348.50</b>  |
| <b>Colour</b>            | <b>Beige</b>   |
| <b>PH-Value</b>          | <b>2-3 (H<sub>2</sub>O, 20°C)</b>                              |
| <b>Solubility</b>        | <b>water</b>   |

**Source:** Sigma Aldrich (Germany)

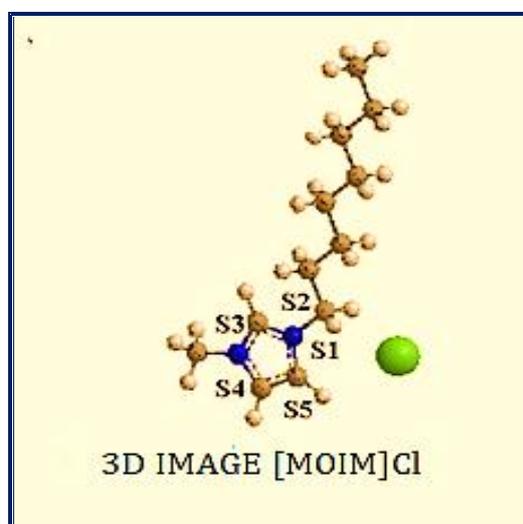
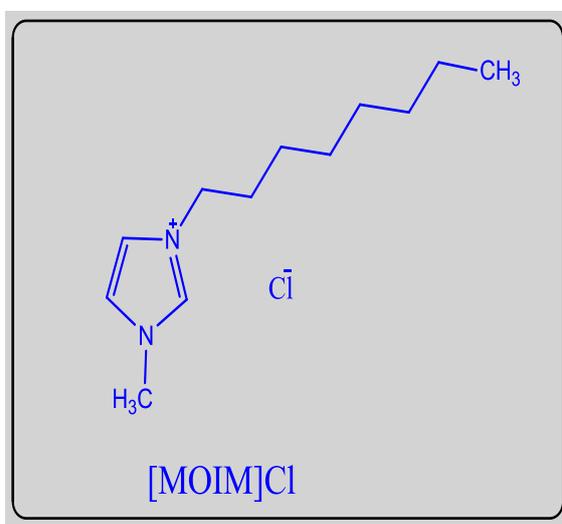
**Purification:** It is used as purchased. The purity of the chemical that was used for the experiment was about  $\geq 95.0\%$

**Application:** In the presence of a rhodium catalyst, 1-butyl-3-methylimidazolium octyl sulfate [BMIM][C<sub>8</sub>SO<sub>4</sub>] can be used as a solvent during the hydroformylation reaction to convert 1-octene to form nonane. The technical accessibility and the well-documented

toxicology of the octylsulfate anion behaves this ionic liquid as a highly interesting candidate for industrial purpose.

### 1-methyl-3-octylimidazolium chloride [MOIM]Cl (CASNO-64697-40-1)

1-Methyl-3-octylimidazolium chloride is a ionic liquid containing imidazolium ring in this structure. The molecular formula of this ionic liquid is  $C_{12}H_{23}ClN_2$ .



The Physical property of [MOIM]Cl is given as follow

|                                |                           |
|--------------------------------|---------------------------|
|                                | $C_{12} H_{23} ClN_2$     |
| <b>Density 20<sup>0</sup>C</b> | <b>1.071g/MI at</b>       |
| <b>Melting point</b>           | <b>&lt; RT</b>            |
| <b>Conductivity</b>            | <b>0.09 mS/cm (30 °C)</b> |
| <b>Molecular weight</b>        | <b>230.78</b>             |
| <b>Refractivity</b>            | <b>1.505-1.515</b>        |
| <b>Viscosity value</b>         | <b>3690cP(35° C)</b>      |
| <b>Solubility</b>              | <b>water</b>              |

**Source:** Sigma Aldrich purchased from Germany.

**Purification:** It is used as purchased. The purity of the using chemical was  $\geq 97.0\%$

**Application:** 1-Methyl-3-octylimidazolium chloride ionic liquid ([MOIM]Cl) can be used as: In the presence of a metal chloride as a catalyst and HCl in the reaction medium for the hydrolysis of sucrose to form hydroxymethylfurfural. It is used as a structure-directing agent during the preparation of organized mesoporous alumina.

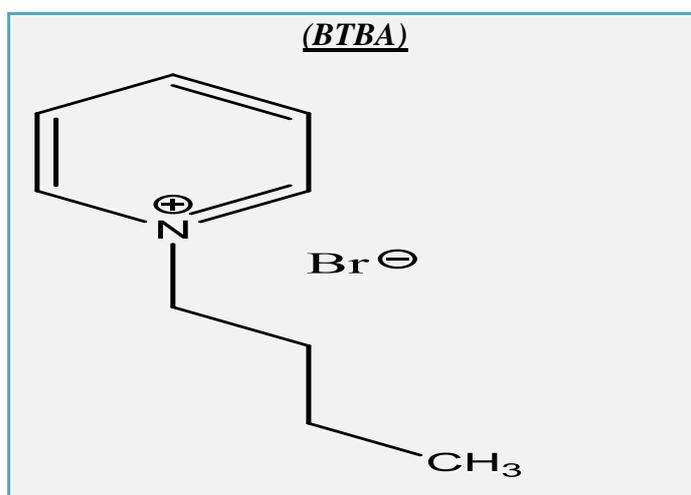
**1-Butylpyridinium Bromide (BTPB) (CAS NO-874-80-6)**

1-Butylpyridinium bromide is the ammonium based ionic liquid, containing bulky alkyl (n-butyl) group of molecular formula ( $C_9H_{14}BrN$ ) exists as a molten solid phase (white crystalline) with the melting point 96-99°C.

**Source:** Germany (Sigma Aldrich)

**Purification:** It is used as purchased. The purity of the using chemical was  $\pm 99.0\%$

**Application:** 1-Butylpyridinium Bromide is widely used as electrolytes in electrochemical frames when control of electrode potentials is required source. The ionic liquid may be used in dye sensitized-cells, organic synthesis and also used as bio-catalysis batteries, electrochemical application and phase transfer catalyst, etc.

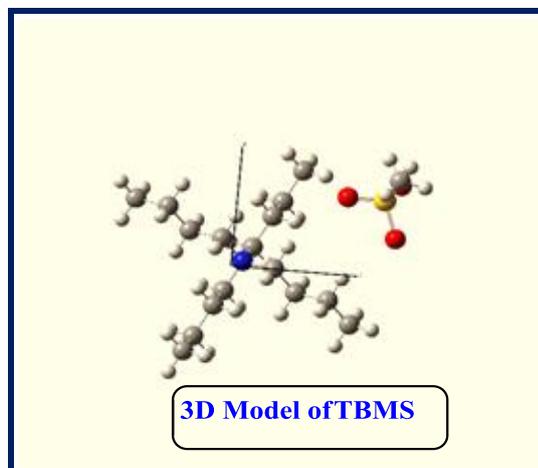
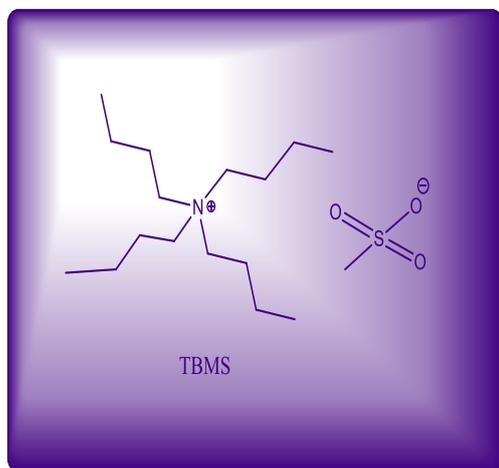


The physical property of PBr is given as follow

|                   |  |
|-------------------|--|
| Appearance        | :White Crystalline                       |
| Molecular Formula | : $C_9H_{14}BrN$                         |
| Molecular Weight  | : $216.12 \text{ g}\cdot\text{mol}^{-1}$ |
| Melting Point     | :369-372 K                               |
| Relative Density  | :No data available                       |

### TETRA BUTYL AMMONIUM METHANE SULFONATE(TBMS):(CASNO-65411-49-6)

Tetra butyl ammonium methane sulfonate is the also ammonium based ionic liquid, containing bulky alkyl (n-butyl) group of molecular formula exists as a molten solid phase (white crystalline) with the melting point 96-99°C.



The Physical property of TBMS is given as follow

|                   |  |
|-------------------|--|
| Appearance        | :White Crystalline   |
| Molecular Formula | :C <sub>17</sub> H <sub>39</sub> NSO <sub>3</sub>  |
| Molecular Weight  | :337.56 g·mol <sup>-1</sup>  |
| Melting Point     | :78-80 C   |
| Relative Density  | :NotData Available   |
| Ionic radii       | :4.42 (Å) of Bu <sub>4</sub> N <sup>+</sup><br>2.83(Å) of CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup> |

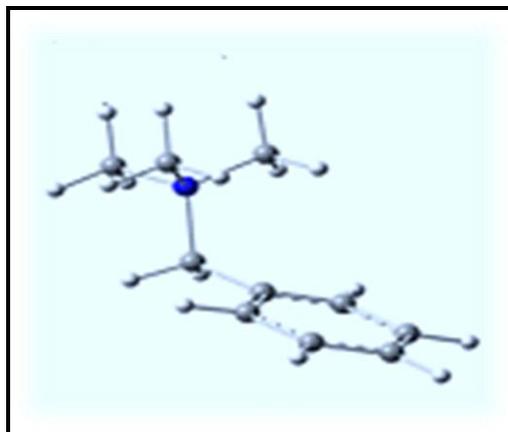
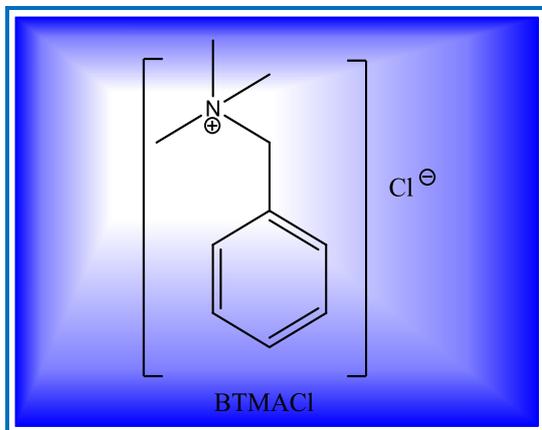
**Source:** Sigma Aldrich, Germany

**Purification:** It is used as purchased. The purity of the chemical was about >99.0%

**Application:-**Tetrabutylammonium methane sulfonate (TBAMS) is perhaps used as same as 1-butyl bromide as electrolytes in electrochemical windows when switch of electrode potentials is required source. The ionic liquid may be used in bio-catalysis organic creation or synthesis an, dye sensitized-cells, batteries, electrochemical application and phase transfer catalyst, etc.

**BENZYL TRI METHYL AMMONIUM CHLORIDE (BTMAC) (CAS NO-56-37-1)**

It is a ammonium based ionic liquid containing three alkyl chain in its structure. It is a white crystalline solid and Faint Almond like odor. The molecular formula of the ionic liquid is  $C_{10}H_{16}ClN$ .



**Stick and ball model of BTMAC (3D Image)**

The physical property of BTMAC is given in the follow:

|  |  |
|--|--|
| <b>Physical state –solid</b>               | <b>density-1.07(gm/cm<sup>3</sup>)</b> |
| <b>Molecular weight-185.70</b>             | <b>PH value-6-8</b>                    |
| <b>Boiling point-105C</b>                  | <b>Evaporation rate-&lt;1</b>          |
| <b>Melting point-239c</b>                  | <b>solubility- water</b>               |
| <b>Vapour pressure-&lt;0.001hPa at 20c</b> |  |

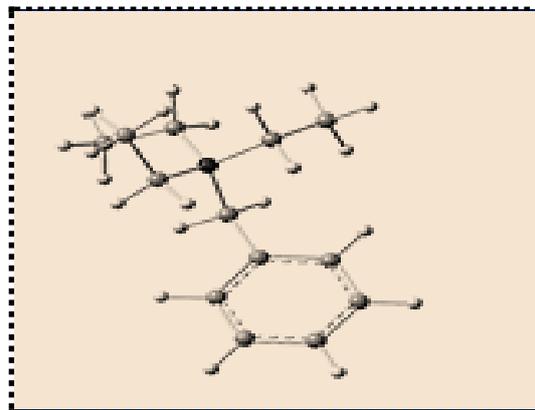
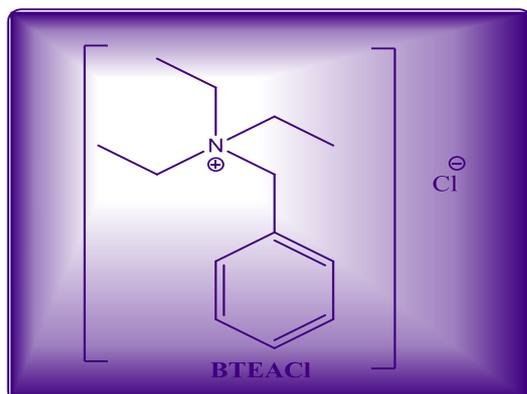
**SOURCE:** It was purchase From Japan, sigma Aldrich

**PURIFICATION:** The purity of salt was taken 0.99. further purification was not taken.

**APPLICATION:** BATC is used for many reactions as a versatile phase transfer catalyst. It is also used as the field of industries purpose such as polymer, agrochemical, pharmaceutical etc. In oilfield it is used as a corrosion inhibitor.

**BENZYL TRIETHYL AMMONIUM CHLORIDE: (BTEAC)(CAS NO-56-93-9)**

It is also an ammonium based ionic liquid. It has three-alkyl chain (ethyl). The molecular formula is C<sub>13</sub>H<sub>22</sub>ClN. It is a white crystalline solid.



Stick and ball model of BTEAC (3D)

The physical properties of this ionic liquid is describes as the follows.

|  |                                       |
|--|---------------------------------------|
| <b>Physical state- solid</b>                 | <b>density- 700kg/m<sup>3</sup></b>   |
| <b>Flash point -&gt;275C</b>                 | <b>melting point-185<sup>0</sup>c</b> |
| <b>Ignition Temperature-300<sup>o</sup>c</b> | <b>solubility- 630g/L</b>             |

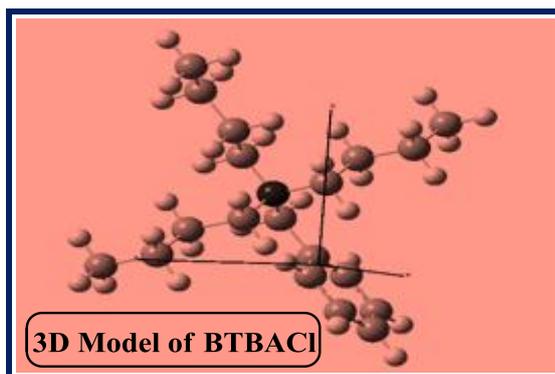
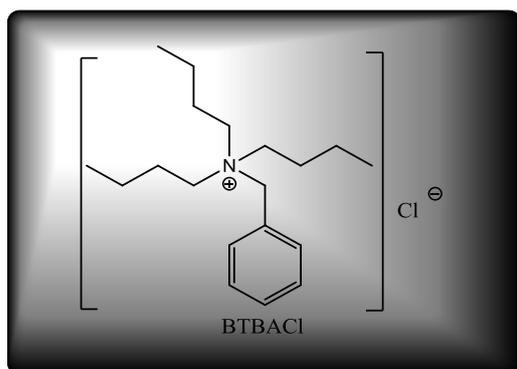
**SOURCE:** Sigma Aldrich, purchased from japan.

**PURIFICATION:** The purity of mass of the taken salt was 0.98. Further purification was not needed.

**APPLICATION:** Benzyl tri ethyl ammonium chloride is applied for the making of consumer products. It is used for plastic products, industry for plastic, plastic additives, manufacturing of plastics. It is also can be used as an Accelerators, activators, oxidation agents, reducing age.

### BENZYL TETRA BUTYL AMMONIUM CHLORIDE (BTBAC)(CASNO-23616-79-7)

Tri butyl ammonium chloride is an ammonium based long alkyl chains ionic liquid organic chloride salt containing of a [tri butyl ammonium](#) cation and [chloride anion](#). It is a tri butyl ammonium salt and also name as a an organic chloride salt. It is used as a purifying or cleansing agents, normally the salts of long-chain aliphatic bases or acids, that exert cleansing (oil-dissolving) and antimicrobial effects through a surface action that depends on holding both hydrophilic and hydrophobic properties of the ionic liquid.



|                          |  |
|--------------------------|--|
| <b>Physical state</b>    | <b>Solid</b>                             |
| <b>Molecular formula</b> | <b>C<sub>19</sub> H<sub>34</sub> ClN</b> |
| <b>Melting point</b>     | <b>(155-165)°C</b>                       |
| <b>Solubility</b>        | <b>water(easily)</b>                     |
| <b>Molecular weight</b>  | <b>311.94 gm/mole</b>                    |

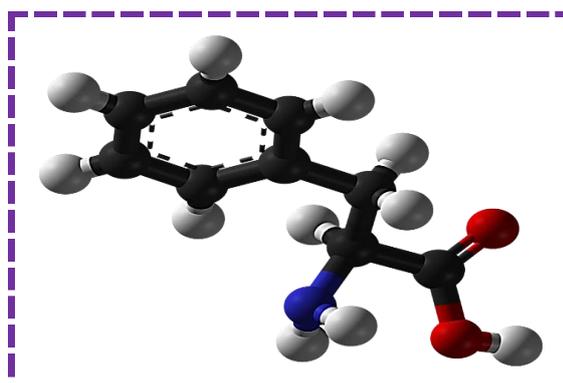
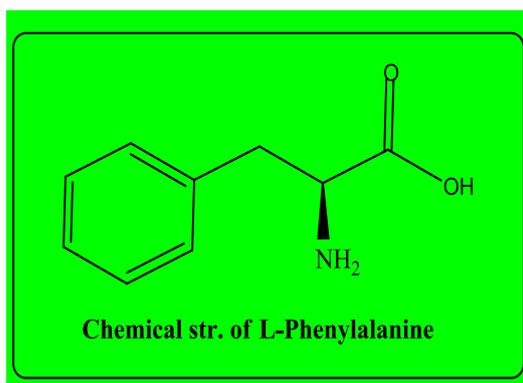
**SOURCE:** It was Purchased from Sigma ALDRICH (CHINA)

**PURIFICATION:** The purity of taken salt was 0.98.

**APPLICATION:** Benzyl tri butyl ammonium chloride is used for the manufacturing of many industrial goods. It is used in laboratory for chemical purpose. It is successfully applicable of the above ionic liquid for the purpose of Accelerators, activators, oxidation agents, reducing agents, etc

**AMINO ACIDS:****L-PHENYLALANINE: (CAS NO-63-91-2)**

Phenylalanine is an essential amino acid (containing aromatic ring) in humans (provided by food). It is an Amino acid of erythrose4-phosphate/phosphoenolpyruvate family. It is also designated as a proteinogenic amino acid, a phenylalanine and a L-alpha-amino acid, Phenylalanine takes a very vital role in the biosynthesis of other amino acids. It is very important in the structure and function of many proteins and enzymes. [L-phenylalaninium](#) and [L-phenylalaninate](#) are the conjugate base and conjugate acid respectively of L-phenylalanine. L-Phenylalanine is the enantiomer of a [D-phenylalanine](#). It also exists as a tautomer of a L-phenylalanine zwitterion.



3D IMAGE OF L-PHENYL ALANINE

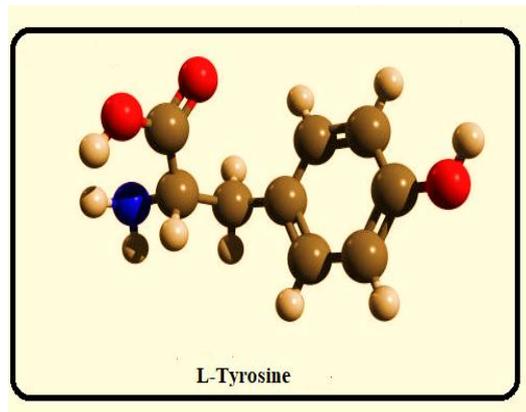
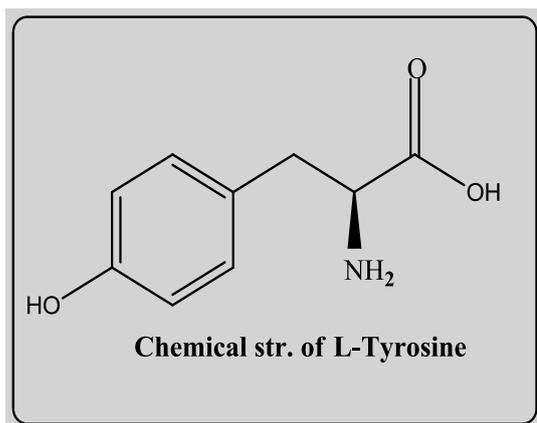
The Physical property of L-phenylalanine is listed in the table form

|                          |   |
|--------------------------|---|
| <b>Molecular formula</b> | <b>C<sub>9</sub>H<sub>11</sub>O<sub>2</sub></b> |
| <b>Molecular weight</b>  | <b>165.19 gm/mole</b>                           |
| <b>Physical state</b>    | <b>Solid(White) better in taste</b>             |
| <b>PH Value</b>          | <b>5.4-6(1% aqueous solution)</b>               |
| <b>Solubility</b>        | <b>26.9 gm/L</b>                                |
| <b>Melting point</b>     | <b>541°F(760mm Hg)</b>                          |
| <b>Boiling point</b>     | <b>563° F(760mm Hg)</b>                         |

**SOURCE:** Sigma Aldrich, from German.(purchased)

**PURIFICATION:** The mass purification of this salt was  $\geq 0.97\%$

**APPLICATION:** The phenylalanine is used to make food and also for drinking products. It is a source of nutritional supplement. It is used as antidepressant and analgesic agent. It is also a source of dietary supplement. Phenylalanine also used as a blood-brain barrier.

**L-TYROSINE: (CAS NO-60-18-4)**

Physical properties of L-Tyrosine is listed as bellow

|                  |  |
|------------------|--|
| Chemical formula | C <sub>9</sub> H <sub>11</sub> NO <sub>3</sub> |
| Molar mass       | 181.191 gram/mole                              |
| Solubility       | 0.453 gm/100MI(water)                          |

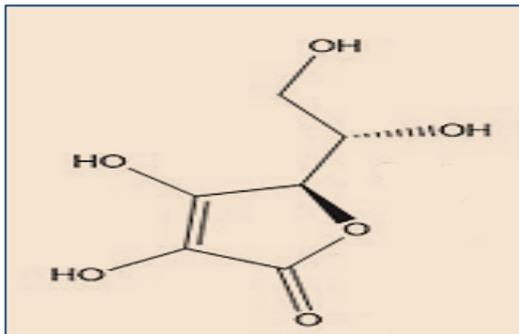
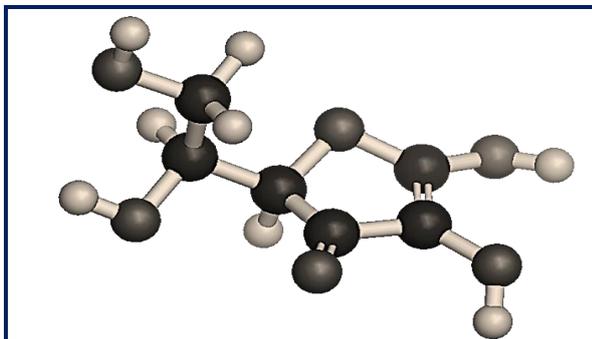
**SOURCE:** This salt was purchased from Sigma Aldrich (Germany)

**PURIFICATION:** The purification of mass of this salt was  $\geq 0.98\%$

**APPLICATION:** Since tyrosine has contain -OH functional group at the virtue of phenol and therefore it has very especially role. It is a receiver of phosphate group and it has great role in the signal transduction process. The activity of a particular protein changes when phosphorylation of hydroxyl group take place. In case of photosynthesis the tyrosine residue has took place very important role and in the process of reduction Of oxidized chlorophyll, tyrosine residue act as a electron donor. It is also used as a ancestor to hormones and neurotransmitters.

**L-ASCORBIC ACID :(CAS NO-50-81-7)**

Vitamin C (Ascorbic acid) is water soluble molecules continuing many –OH functional group in their structure.

**Chemical str. of L-Ascorbic acid****3D IMAGE OF L-ASCORIC ACID**

The physical property of L-Ascorbic acid is listed as below

|   |  |
|---|--|
| <b>Physical state- White or light yellow solid</b>                  | <b>density- 1.65gm/cm<sup>3</sup></b>                  |
| <b>Chemical formula-&gt;C<sub>6</sub>H<sub>8</sub>O<sub>6</sub></b> | <b>melting point-190<sup>0</sup>C-192<sup>0</sup>C</b> |
| <b>Molecular weight-176.16 g.mole<sup>-1</sup></b>                  | <b>solubility- 330g/L( In water)</b>                   |

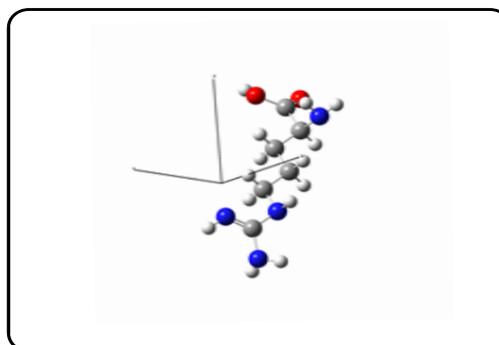
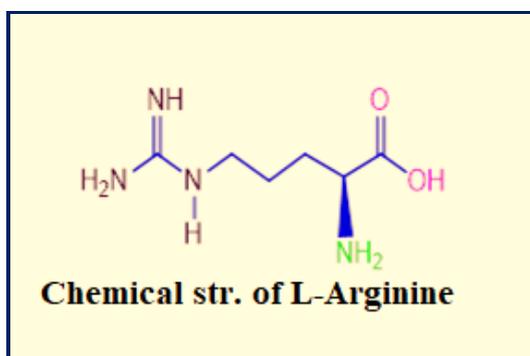
**SOURCE:** This salt was taken from sigma Aldrich.

**PURIFICATION:**  $\geq 99.7\%$  was the purity of mass. The solute molecule was placed in the dessicators over phosphorous pentoxide for keeping the molecule in dry atmosphere. No further purification was carried out for experiments.

**APPLICATION:** L-Ascorbic acid helps to save and treat from the very dangerous disease scurvy and common cold. This is very need for the making of collagen, neutron transmitters and creatinine(5) due to very essential of vitamin C for mankind ,this can be used in several field of analytical chemistry such as food and also pharmaceutical applications. It is also used for the transport properties since the body fluid is always circulating. Since this is very simple molecule and it is very essay to mix with other solute molecules so it has dissolution effect.

**L-ARGININE (CASNO-74-79-3)**

Arginine or L-Arginine is a alpha- amino acid. In this structure there contain alpha-amino group , alpha-COOH group, three carbon aliphatic chain and also contain at the ending of straight chain a guanidine group.



**Stick and ball model of L-Arginine (3D)**

**The physical property of L-Arginine is listed as bellow**

|                      |                               |
|----------------------|-------------------------------|
| <b>Appearance</b>    | <b>Crystalline(white)</b>     |
| <b>Odour</b>         | <b>odourless</b>              |
| <b>Melting point</b> | <b>high(260<sup>0</sup>c)</b> |
| <b>Boiling point</b> | <b>high(368<sup>0</sup>c)</b> |

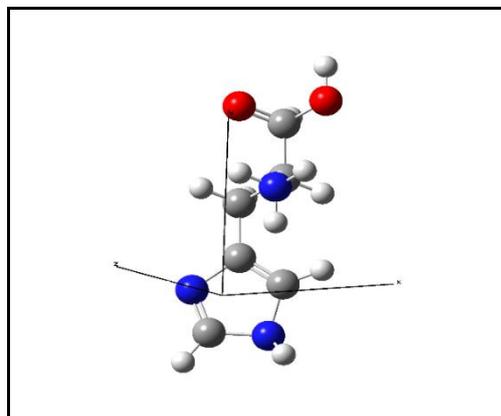
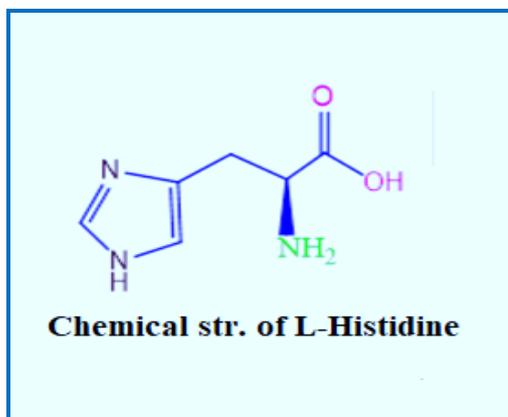
**SOURCE:**The salt was obtained from SRL, India.

**PURIFICATION:** The mass purification of salt was  $\geq 0.99\%$ . The amino acid was dried in vacuum over blue silica gel for 72hr at room temperature.

**APPLICATION :** L-Arginine is used as biosynthesis of proteins. It is used as a precursor for the biosynthesis of nitric oxide and making it very important in the directive of blood pressure. It takes very important role for cell division and wound healing. Its function is as removing ammonia from the body and it helps to remove the hormone. Arginine is also used as a precursor for ornithine, agmatine and urea. It is also used for making polyamines. It is also used as a dietary source. Since arginine removes the blood vessels, so it has cardiovascular benefits. It is also used to improve the symptoms of kidney inflammation and assist the function of kidney after a replacement.

**L-HISTIDINE: (CAS NO-71-00-1)**

In 1984 the German physician Albrecht Kossel and Sven Gustaf Hedin was first isolated this amino acid (L-Histidine). L-His is a alpha amino acid. In this molecule, contain an alpha amino group and carboxylic group. Under biological condition the –NH<sub>2</sub> group protonated to form NH<sub>3</sub><sup>+</sup> and same condition –COOH group deprotonated to form –COO<sup>-</sup>. In this molecule their contain a imidazole ring residue.



Stick and ball model of L-Histidine (3D)

The physical property of L-Histidine is listed below

|                         |   |
|-------------------------|---|
| <b>Chemical formula</b> | <b>C<sub>6</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub></b> |
| <b>Molar mass</b>       | <b>155.16 gm/mole</b>                                       |
| <b>Solubility</b>       | <b>Water(easily)</b>  |

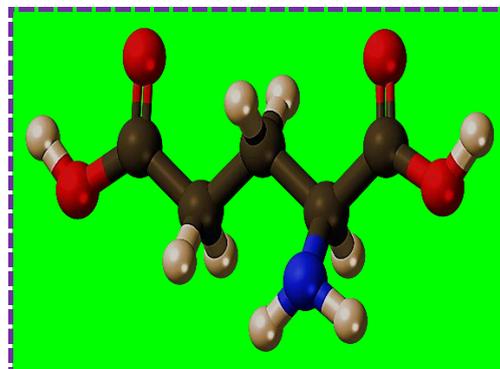
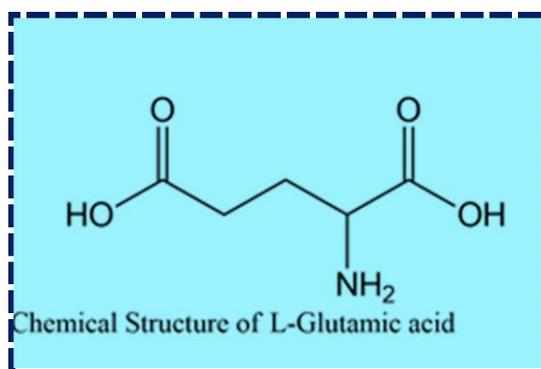
**SOURCE:** This Salt was purchased from TLC, Japan.

**PURIFICATION:** Purification of mass of this salt was  $\geq 0.99\%$ . The amino acid was dried in vacuum over blue silica gel for 72hr at room temperature

**APPLICATION:** L-Histidine undergoes to complex formation with some metal ions. The side chain ring residue (imidazole) of l-Histidine behaves as a ligand in metalloproteins. The microorganisms, plants, animals take l-Histidine for their proper growth. It act as a precursor for histaminie that is used in the body for inflammation. It protect the muscle from damage. The l-histidine take important role to regulation in the biosynthesis process. We use Histidine as a medicine. It is used for some very serious diseases in our body such as allergic ulcers, rheumatoid arthritis and anemia that caused by failure of kidney i.e. dialysis of kidney.

**L-GLUTAMICACID (CAS NO-56-86-0)**

L-Glutamic acid are both water soluble polar aliphatic amino acids having very weak dipole-ion interaction. In this molecule, contain an alpha amino group and carboxylic group. Under biological condition the  $\text{-NH}_2$  group protonated to form  $\text{NH}_3^+$  and same condition  $\text{-COOH}$  group deprotonated to form  $\text{-COO}^-$

**3D MODEL OF L-GLUTAMIC ACID**

The physical property of L-Glutamic acid listed in the table form

|               |                           |
|---------------|---------------------------|
| Appearance    | White crystalline         |
| Density       | 1.4601 gm/cm <sup>3</sup> |
| Melting point | 199°C                     |
| Solubility    | 7.5gm/L(20°C)             |

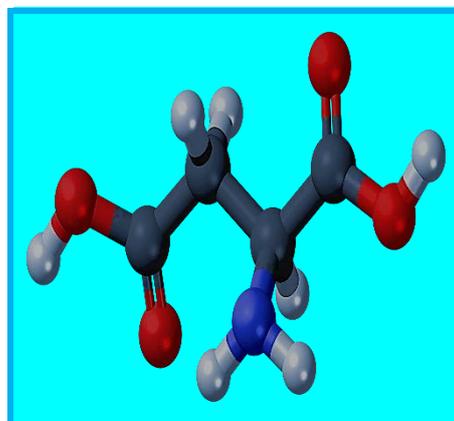
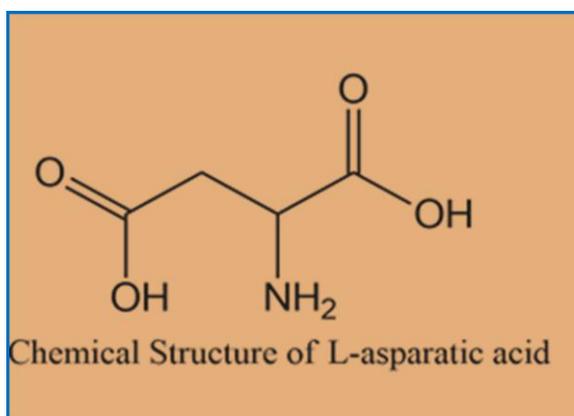
**SOURCE:** It was purchased from TLC, Japan

**PURIFICATION:** No required for further purification of this salt. Purity of mass was 0.99

**APPLICATION:** L-Glutamic acid is an  $\alpha$ -amino acid. It is used for all living beings in the biosynthesis of proteins. It is also used an excitatory neurotransmitter in the vertebrate nervous system.

**L-ASPARATIC ACID(CAS NO-56-84-8)**

L-Asparatic acid are both water soluble polar aliphatic amino acids having very weak dipole-ion interaction. In this molecule, contain an alpha amino group and carboxylic group. Under biological condition the  $\text{-NH}_2$  group protonated to form  $\text{NH}_3^+$  and same condition  $\text{-COOH}$  group deprotonated to form  $\text{-COO}^-$

**3D MODEL OF L-ASPARATIC ACID**

The physical property of L-aspartic acid is listed bellow

|                      |                              |
|----------------------|------------------------------|
| <b>Appearance</b>    | <b>Colourless</b>            |
| <b>Density</b>       | <b>1.79gm/cm<sup>3</sup></b> |
| <b>Melting point</b> | <b>270°C</b>                 |
| <b>Boiling point</b> | <b>324° C</b>                |

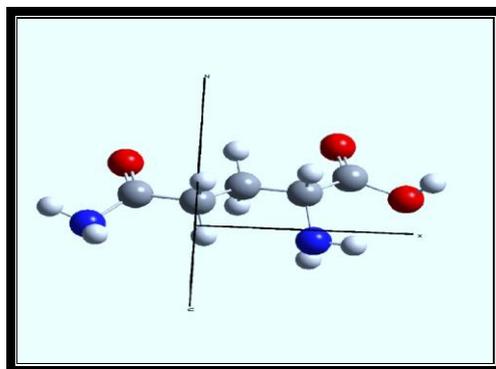
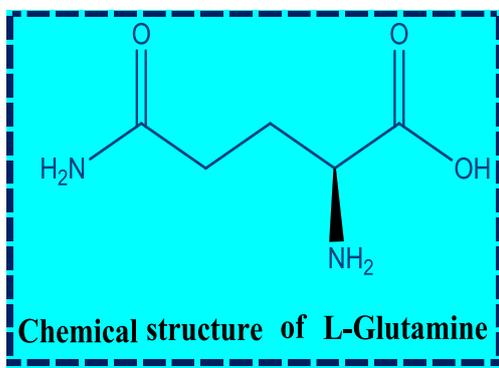
**SOURCE:** purchased from SRL, India

**PURIFICATION:** Purity of mass was 0.99. this salt was used for experiment.

**APPLICATION:** L-Aspartic acid is an  $\alpha$ -amino acid that is used in the biosynthesis of proteins. Aspartic acid is commonly used to reduce feelings of tiredness in our body, improve athletic performance, and increase the size and strength of muscles.

**L-GLUTAMINE: (CASNO-56-85-9)**

L-Glutamine is an alpha amino acid. The chemical formula of this amino acid is  $C_5H_{10}N_2O_3$ . This amino acid is a nutrient that help to synthesize the protein moiety in the human body for nutrition. they can be found in protein-rich foods, including those from both plants and animals.



Stick and ball model of L-glutamine

The physical properties of L-Glutamine is listed below in the table form

|                                   |                            |
|-----------------------------------|----------------------------|
| <b>Chemical formula</b>           | $C_5H_{10}N_2O_3$          |
| <b>Molar mass</b>                 | $146.146g.mol^{-1}$        |
| <b>Solubility</b>                 | soluble in water           |
| <b>Melting point</b>              | approximate $185^{\circ}C$ |
| <b>Appearances</b>                | colourless solid           |
| <b>Acidity(<math>pK_a</math>)</b> | 2.2(carboxyl), 9.1(amino)  |
| <b>Density</b>                    | $0.99700 g/cm^3$           |
| <b>Dielectric constant</b>        | 38.35 at 298.15K           |
| <b>Refractive index</b>           | 1.3333                     |

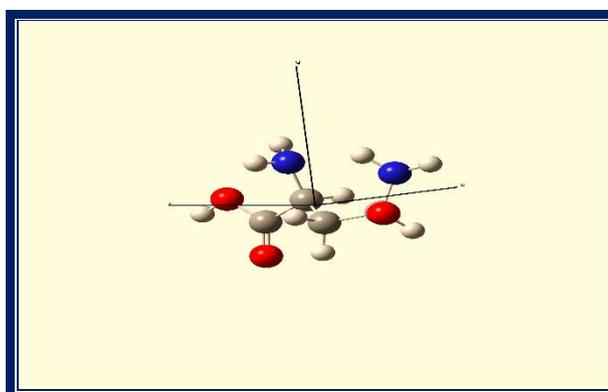
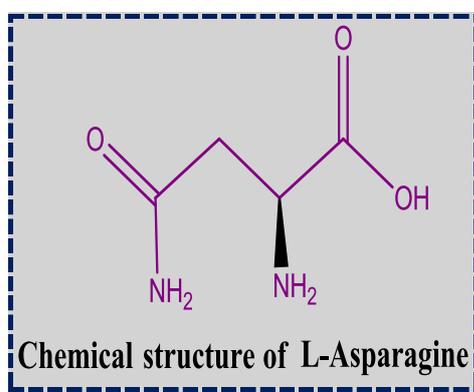
**SOURCE:** Sigma Aldrich, TLC (Product from Brazil)

**PURIFICATION :** The mass purity of this compound was 0.99 . Further purification of this compound is not required for experiment.

**APPLICATION :** Glutamine provides the most suitable example of the versatility of amino acid metabolism and immune function among the 20 amino acids detailed in the genetic code. Glutamine is such a amino acid in our body that it is most abundant and versatile amino acid and is of fundamental significance to intermediary metabolism, change the nitrogen among the organ via ammonia ( $NH_3$ ) transport between tissues, and pH homeostasis. ([Nutrients](#). 2018 Nov; 10(11): 1564).

**L-ASPARAGINE (CASNO-70-47-3)**

L-Asparagine is an alpha amino acid. L-Asn is written as symbolic form of L-Asparagine. In the structure of L-Asn contain alpha amino group. Under biological condition, amino group is protonated and carboxylic acid is deprotonated. It has carboxamide group as a side chain. It is a non-essentials amino acid so it is synthesis in the human body.



3DStructure of l-Asparagine (stick and ball model)

The physical properties of L-Asparagine is listed below in the Table

|                                |   |
|--------------------------------|---|
| <b>Chemical formula</b>        | <b>C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub></b> |
| <b>Appearance</b>              | <b>White crystals</b>                                       |
| <b>Molar mass</b>              | <b>132.119 gm.mol<sup>-1</sup></b>                          |
| <b>Density</b>                 | <b>1.543 gm/cm<sup>3</sup></b>                              |
| <b>Solubility</b>              | <b>soluble in water(2.94 g/100mL)</b>                       |
| <b>Log P</b>                   | <b>-3.82</b>  |
| <b>Magnetic susceptibility</b> | <b>-69.5·10<sup>-6</sup> cm<sup>3</sup>/mol</b>             |
| <b>Melting point</b>           | <b>234°C (453 °F; 507 K)</b>                                |
| <b>Boiling point</b>           | <b>438 °C (820 °F; 711 K)</b>                               |

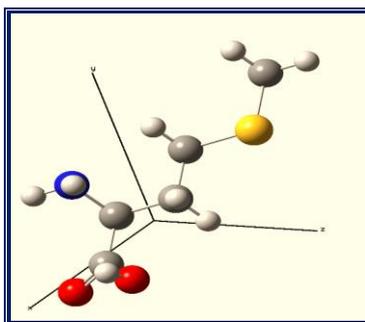
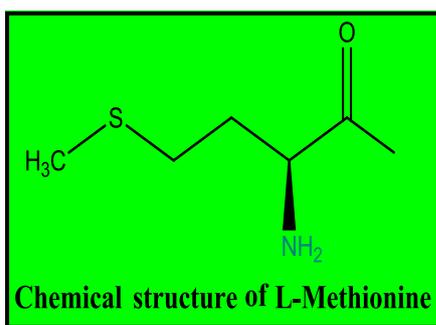
**SOURCE** : Sigma Aldrich TC L (USA)

**PURIFICATION:** 98 was the purity of mass, without further purification was not required.

**APPLICATION:** L- Asparagine is used for biosynthesis of protiens. The oxaloacetate is the precursor of l-asparagine in the biosynthesis process of protein. It takes very key role to development of brain.

**L-METHIONINE: (CASNO-63-68-3)**

Methionine (L-Methionine) is an essential amino acid which is found in our body. It is the supplement of nutrition. It is very need for normal growth and make or repair the tissue of our body. This amino acid can not made by the body , but it must get from the diet; i.e. why it is consider as a essential amino acid in human body. Two types of methionine are found one is naturally occurring(L) another is D-methionine. The chemical make up is same for both types of amino acid. But only one is mirror image to another.(NCBI. PUB CHEM DATABASE)



**3D Structure of l-methionine (stick and ball model)**

The physical property of L-Methionine is listed bellow

|                      |                               |
|----------------------|-------------------------------|
| <b>Appearance</b>    | <b>White crystalline</b>      |
| <b>Density</b>       | <b>1.340gm/cm<sup>3</sup></b> |
| <b>Melting point</b> | <b>281°C</b>                  |
| <b>Solubility</b>    | <b>water(easily)</b>          |

**SOURCE:** It was purchased from TLC, Japan.

**PURIFICATION:** The mass purity of the salt was 98. Further purification was nor required for experiment.

**APPLICATION:** The Sulphur containing amino acid is methionine; it has very importance application in different field of science. It is used as improve the tone and elasticity of skin, it strong the strength of healthy hair, nail. Although it is very effective in the treatment of Tylenol (acetaminophen) poisoning. It is also used for protecting the cell from pollutants, Facilitating the detoxify process, aging proceed, helping and adding

the adsorption of nutrients , excoriation of heavy metal( lead ,mercury) respectively. ( author ,Park Bk, Dear JW, Antoine).

BY acting it as a lipotropic agent that prevent to increase the excess fat in the liver, lowering the cholesterol level by increasing production of lecithin production in the liver. It protect liver from damage, it also prevent the colon cancer(a 2013 meta analyst report) according to Study report 2016 among ten essential amino acid it is best for Brest cancer cell treatment.(CavuotoP,Fench MF Areview).

Although the amino acid is, help to improvement the memory function of brain. According to study (Molecular Neuro degeration) essesive use of this, which causes some types of diseases as heart disease, type 2 diabetes, certain type of cancer.

## 111. 2. EXPERIMENTAL METHODS

### III.2.1 PREPARATION OF SOLUTIONS

Mass measurements for stock solutions were done on a Mettler Toledo AG-285electronic balance with a precision of  $\pm 0.0003$ gm. The experimental density values was used to conversion of molarity into molality. The uncertainty in molality of solution is estimated to be  $\pm 0.0001$ mole/kg.

### III.2.2. PREPARATION OF MULTICOMPONENT LIQUID MIXTURES

**The preparation of binary or multicomponent liquid mixture can be done by the any one methods which is discussed below::**

**(a)Mole fraction (b) Weight fraction(c)volume fraction**

**(a) Mole fraction: for the preparation of multicomponent liquid mixture the relation of mole fraction is used:** the relation is given in the following

$$x_i = \frac{(w_i / M_i)}{\sum_{i=1}^n (w_i / M_i)}$$

where  $w_i$ ,  $M_i$  are signify the weight and molecular weight of  $i^{\text{th}}$  component, respectively. The number of component is apply for the formation of the solution mixture is depends on the value of  $i$  .

(a) **Weight fraction:** The following given relation (mole fraction  $w_i$ ) is utilize for the formation of multicomponent liquid mixtures:

$$w_i = \frac{(x_i / M_i)}{\sum_{i=1}^n (x_i M_i)}$$

**Volume fraction:** The different three methods are used for evaluation or determination of the volume fraction ( $\phi_i$ ) of the multicomponent liquid mixtures.

i. **Using volume:** The volume fraction ( $\phi_i$ ) of the multicomponent liquid mixtures using the volume of pure liquid can be prepared by following relation

$$\phi_i = \frac{V_i}{\sum_{i=1}^n V_i}, \text{ } V_i \text{ is volume of pure liquid}$$

ii. **Using molar volume:** For the preparation of multicomponent liquid mixtures the volume fraction ( $\phi_i^l$ ) of the multicomponent liquid mixtures can be expressed by the following relation

$$\phi_i^l = \frac{x_i V_{mi}}{\sum_{i=1}^n (x_i V_{mi})}$$

where  $V_{mi}$  denotes the molar volume of pure liquid i.

iii. **Using excess volume:** The volume fraction ( $\phi_i^{ex}$ ) of the multicomponent liquid mixtures can also be obtained by following relation

$$\phi_i^{ex} = \frac{x_i V_i}{\sum_{i=1}^n (x_i V_i) + V^E}$$

where  $V^E$  is symbolizes the excess volume of the liquid mixture.

**III.2.4 MEASUREMENTS OF EXPERIMENTAL PROPERTIES:****III.2.4.1 MASS MEASUREMENT:**

A digital electronic analytical balance (Mettler Toledo, AG 285, from Switzerland) were made for the mass measurement of the sample.

This instrument can measure of mass with very high precision and accuracy. The considering cooking pail of a high precision (0.0001g) is inside a translucent enclosure with doors so that dust does not accumulate and so any air currents in the room do not affect the balance's operation.



**Mettler Toledo, AG 285**

**Specification of Instruments:**

|                                  |                                    |
|----------------------------------|------------------------------------|
| Extreme capacity                 | : 210 g/81g/41g                    |
| Readability                      | : 0.1 mg/ 0.01mg                   |
| Taring range                     | : 0 . . . 210 g                    |
| Repeatability                    | : 0.1 mg/ 0.05 mg                  |
| Linearity                        | : $\pm 0.2$ mg/ $\pm 0.1$ mg       |
| Stabilization time               | : 3 s to 15 s                      |
| Adjustment with external weights | : 200 g                            |
| Sensitivity                      | : $\pm 0.003\%$                    |
| Display                          | : LCD                              |
| Interface                        | : Local CAN universal interface    |
| Weighing                         | : $\Phi$ 85 mm, stainless steel    |
| Effective height above pan       | : 240 mm                           |
| Dimensions(w/d/h)                | : 205 $\times$ 330 $\times$ 310 mm |
| Net wt/with packaging            | : 4.9 kg/7.25 kg                   |

### III.2.4.2 CONDUCTIVITY MEASUREMENT:

Systronics Conductivity TDS meter-308 was used to measurements of Conductivity of taken samples. It can provide both automatic and manual temperature compensation. Also another instrument was used to conductivity measurements(METTTLER TOLEDO).

Systronics Conductivity-TDS meter 308 is a microprocessor based instrument used for measuring specific conductivity of solutions. It can provide both automatic and manual temperature compensation. The instrument shows the conductivity of the solution under test at the existing temperature or with temperature compensation. Provision for storing the cell constant and the calibrating solution type, is provided with the help of battery back-up. This data can be further used for measuring the conductivity of an unknown solution, without recalibrating the instrument even after switching it off.

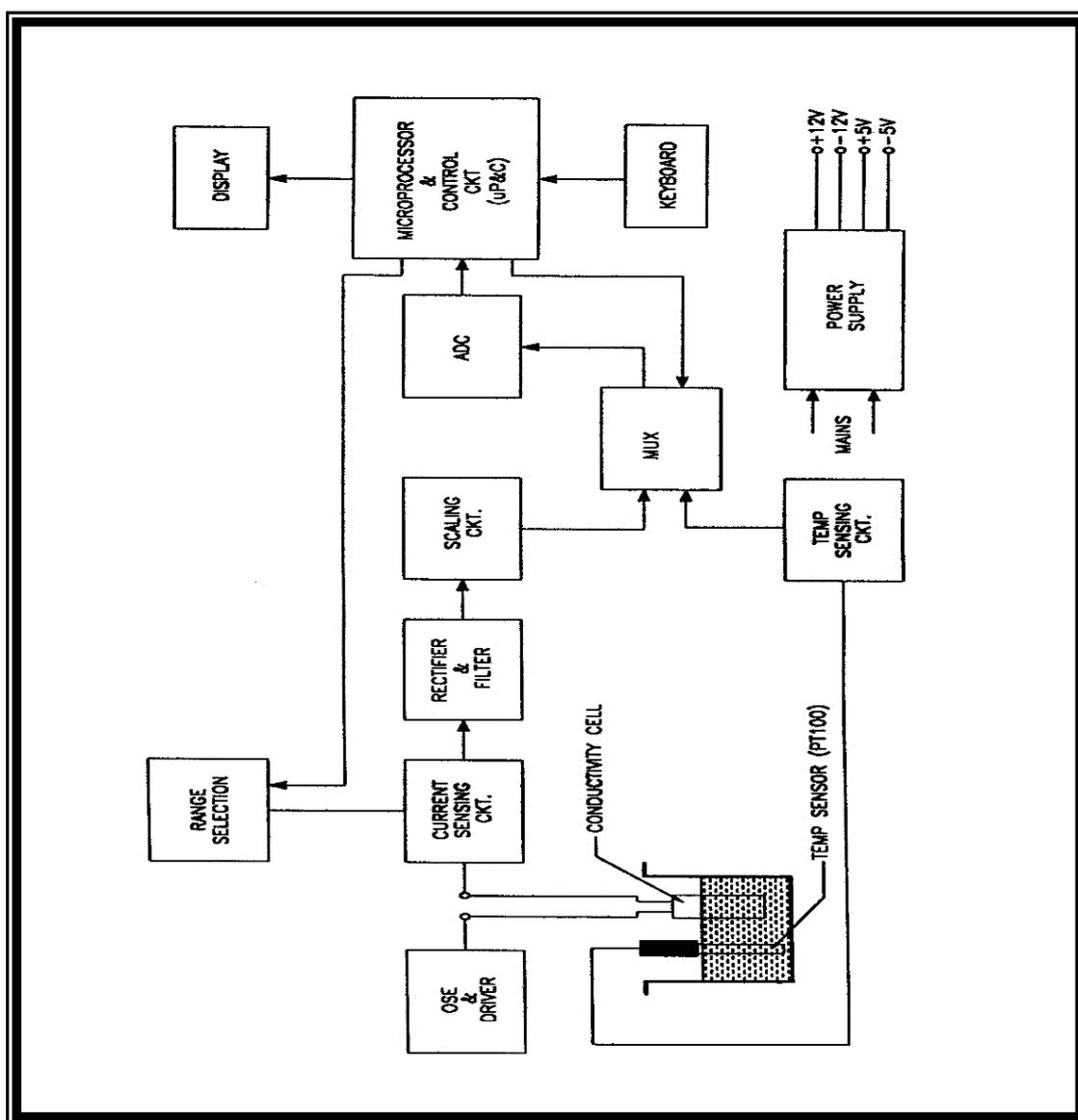


#### Systronic-308 Conductivity Bridge:

Measurements of conductivity of experimental solutions were determined on this conductivity bridge of accuracy  $\pm 0.01\%$ , using a dip-type immersion conductivity cell, CD-10 having a cell constant of nearly  $(0.1 \pm 0.001) \text{ cm}^{-1}$ . Measurements were made in a thermostat water bath kept at  $T = (298.15 \pm 0.01) \text{ K}$ . The cell was calibrated by the technique proposed by Lind et al.<sup>[III.1]</sup> 0.01 M aqueous KCl solution was used to measure the cell constant.<sup>[III.2]</sup> Throughout the conductance measurements, cell constant was kept within the range  $1.10\text{--}1.12 \text{ cm}^{-1}$ . The conductance data of the experimental solutions were measured at a frequency of 1 kHz and the accuracy was  $\pm 0.3\%$ . The conductivity cell was sealed to the side of a 500 ml conical flask closed by a ground glass fitted with a side arm through which dry and pure nitrogen gas was passed to stop admission of air into the cell when solvent or solution was added to the cell. The measurements of the

solutions were made in a thermostatic water bath continued at the required temperature with an accuracy of  $\pm 0.01$  K by means of mercury in glass thermoregulator.<sup>[III.3]</sup>

Experimental Solutions were prepared by weight precise to  $\pm 0.02$  %. All the weights were taken on a Mettler electronic analytical balance (AG 285, Switzerland). The molarity being transformed to molality as required. Several independent solutions were prepared and runs were made to ensure the reproducibility of the results. Due correction was completed for the specific conductance of the solvents at desired temperatures. The figure in the following displays the Block diagram of the Systronics Conductivity-TDS meter 308.



**Block Diagram of the Instrument**

### III.2.4.3 DENSITY MEASUREMENT

The density measurement was accomplished with the help of Anton Paar DMA 4500M digital density-meter. The precision of the instrument was  $\pm 0.0005 \text{ g}\cdot\text{cm}^{-3}$ .

In the digital density meter, the mechanic oscillation of the U-tube is e.g. electromagnetically transformed into an alternating voltage of the same frequency. The period  $\tau$  can be measured with high resolution and stands in simple relation to the density  $\rho$  of the sample in the oscillator



**Anton Paar DMA 4500M digital density-meter**

In the digital (Anton Paar DMA4500M) density meter, the mechanic [oscillation](#) of the U-tube is e.g. electromagnetically oscillation is converted into an alternating [voltage](#) of the same [frequency](#). To calculate the period  $\tau$  with high resolution and standpoints in simple relation to the [density](#)  $\rho$  of the sample in the oscillator is represented in the following:

$$\rho = A \cdot \tau^2 - B \quad (\text{III.1})$$

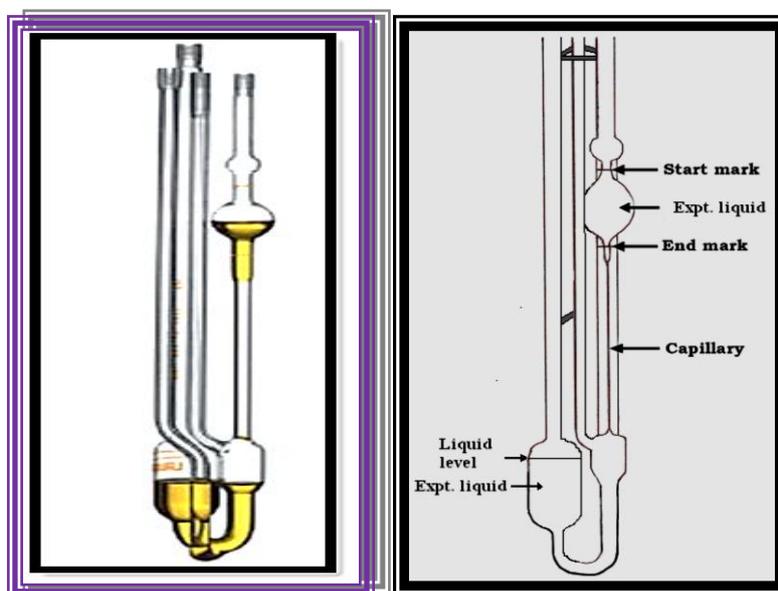
where A and B are denoted the individual instrument constants of each oscillator. With the help of two known density values  $\rho_1$  and  $\rho_2$  of two substances calibrating was done precisely. This Modern instruments was carried out to calculate and store the constants A and B after the two calibration measurements, which are mostly performed with [air](#) and [water](#). They associated appropriate measures to compensate the various effects on the measuring result, e.g. the influences of the sample's viscosity and the non-linearity created by the measuring instrument's finite mass. Triply distilled water and dry air were used to calibration of the instrument.

**Instrument Specification:**

|                                  |                                     |
|----------------------------------|-------------------------------------|
| Density                          | : 0 to 1.5 g.cm <sup>-3</sup>       |
| Pressure                         | : 0 to 6 bar                        |
| Temperature                      | : 15°C to 25°C                      |
| Repeatability Standard Deviation |                                     |
| Density                          | : 0.00001 g.cm <sup>-3</sup>        |
| Temperature                      | : 0.01 °C                           |
| Additional information           |                                     |
| Minimum sample volume            | : approx. 2 ml                      |
| Dimensions (L×W×H)               | : 400×225×231 mm                    |
| Weight                           | : approx. 15 kg                     |
| Automatic bubble detection       | : yes                               |
| Interfaces                       | : 2×CAN                             |
| Power                            | : Supplied by the master instrument |

**III.2.4.4 VISCOSITY MEASUREMENT**

A Suspended level Ubbelohde Viscometer was used to measure the kinematic Viscosity. A stop watch was used to measure the flow of time. In their water bath, the viscometer was always kept in vertical position. The correction of kinetic energy was not needed for the viscometer.



**Suspended-level Ubbelohde Viscometer**

**By Ubbelohde-type viscometer:** Firstly Solution viscosity ( $\eta$ ) was measured by means of suspended Ubbelohde type viscometer, calibrated with the help of triply distilled water, purified it with methanol and dry air with dryer. A cleaned and perfectly dried viscometer (Bose Panda Instruments Pvt. Ltd.) which was filled with experimental solution was placed vertically in a glass-walled thermostat kept to  $\pm 0.01\text{K}$  of the desired temperature. After achieving thermal equilibrium, efflux times of flow were recorded with a stop watch. The flow of times were exact to  $\pm 0.1\text{s}$ . At minimum three repetitions of each data reproducible to  $\pm 0.1\text{s}$  were taken to average the flow of times. Suitable precautions were taken to minimize the evaporation loses during the actual measurements.

| <b>Instrument specification:</b> |                                 |
|----------------------------------|---------------------------------|
| <b>Universal size number</b>     | <b>: 1</b>                      |
| <b>Product Type</b>              | <b>:Glass Capillary</b>         |
| <b>Accuracy</b>                  | <b>: <math>\pm 0.2\%</math></b> |
| <b>Approximate constant</b>      | <b>: 0.01 cSt/sec</b>           |
| <b>Sample volume needed</b>      | <b>: 11 mL</b>                  |
| <b>Range</b>                     | <b>: 2 to 10 cSt</b>            |
| <b>Model</b>                     | <b>: 9721-R59</b>               |
| <b>Brand</b>                     | <b>: Cannon</b>                 |

The relation between absolute viscosity ( $\gamma$ ) and the kinematic viscosity ( $\eta$ ) are given by the following equations.

$$\gamma = \left( K \cdot t - \frac{L}{t} \right) \quad (\text{III.2})$$

$$\eta = \gamma \cdot \rho \quad (\text{III.3})$$

Where,  $t$  denotes the time of flow,  $\rho$  is the density of experimental solution  $K$  and  $L$  are the characteristic constants of the particular viscometer. The accuracy of the viscosity measurement was  $\pm 0.003\%$ . In all cases, the experiments were carried out in at least three replicates and the results were taken as the average of the triplicates.

The relative viscosities ( $\eta_r$ ) were calculated by using the following equation:

$$\eta_r = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0} \quad (\text{III.4})$$

where  $\eta_0$ ,  $\eta$ ,  $\rho$ ,  $\rho_0$  and  $t$ ,  $t_0$  are the absolute viscosities, densities and flow times for the experimental solution and solvent respectively.

**By Brookfield DV-III Ultra Programmable Rheometer** A Brookfield DV-III Ultra Programmable Rheometer was used to measure the viscosity( $\eta$ ) with fitted spindle size-42. The viscosities were obtained by using the following equation

$$\eta = [100 / \text{RPM} \times \text{TK} \times \text{torque} \times \text{SMC}] \quad (\text{III.5})$$

In the above mentions equation(III.5) where RPM,TK (0.09373) and SMC (0.327) are the speed, viscometer torque constant and spindle multiplier constant of the instrument respectively. The calibrated of instrument was against the standard viscosity samples provided with the instrument, water and aqueous  $\text{CaCl}_2$  solutions.<sup>[11.4]</sup> The temperature was kept constant throughout the experiments within  $\pm 0.01^\circ\text{C}$  using Brookfield Digital TC-500 thermostat bath. The viscosities of the solutions were done with an accuracy of  $\pm 1\%$ . Each measurement of data of solutions reported herein is an average of triplicate reading with a precision of 0.3 %.

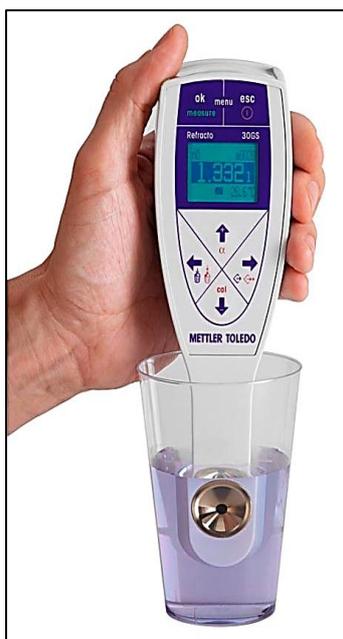


|   |  |
|---|--|
| <b>Speed Range of the instrument</b>        | <b>: 0-250 RPM, 0.1 RPM increments</b>   |
| <b>Viscosity Accuracy of the instrument</b> | <b>: Full scale range (<math>\pm 1.0\%</math>) for a specific spindle running at a specific speed.</b>   |
| <b>Temperature sensing range</b>            | <b>: <math>-100^{\circ}\text{C}</math> to <math>300^{\circ}\text{C}</math> (<math>-148^{\circ}\text{F}</math> to <math>572^{\circ}\text{F}</math>)</b>   |
| <b>Temperature accuracy</b>                 | <b>: <math>\pm 1.0^{\circ}\text{C}</math> from <math>-100^{\circ}\text{C}</math> to <math>150^{\circ}\text{C}</math><br/><math>\pm 2.0^{\circ}\text{C}</math> from <math>+150^{\circ}\text{C}</math> to <math>300^{\circ}\text{C}</math></b> |
| <b>Analog Torque Output</b>                 | <b>: 0 - 1 Volt DC (0 - 100% torque)</b>   |

### III.2.4.6 REFRACTIVE INDEX MEASUREMENT

Measurements of refractive index data was carried out with the help of Digital Refractometer (Mettler Toledo 30GS).

Calibration of refractometer instrument was done by measuring the refractive indices of double-distilled water, cyclohexane, toluene, and carbon tetrachloride at defined temperature. The accuracy of the instrument is  $\pm 0.0005$ . 3-4 drops of the sample was place onto the measurement cell and the reading was taken. The refractive index of a sample are temperature depended. During measurement of the experimental solutions, refractometer determines the temperature and then corrects the refractive index to a temperature as wanted by the user.



REFRACTOMETER 30GS

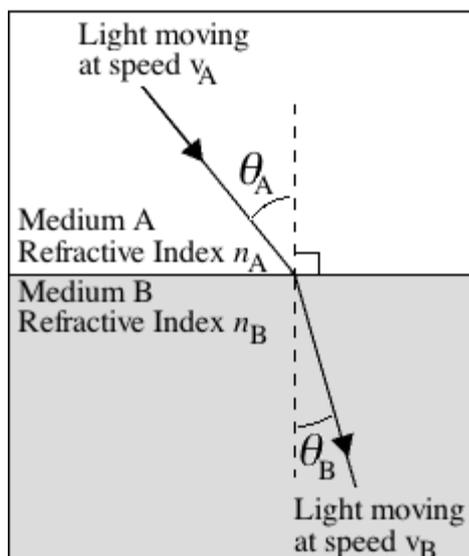
**Specifications-Refracto 30GS- extended RI measuring range**

|   |                        |
|---|------------------------|
| <b>Model</b>                                | <b>: Refracto 30GS</b> |
| Measurement range                           | : 1.32 -1.65           |
| Accuracy                                    | : +/- 0.0005           |
| Resolution                                  | : 0.0001               |
| Measurement range BRIX of the refractometer | : 0 - 85 Brix%         |
| Resolution                                  | : 0.1 Brix%            |
| Accuracy                                    | : +/- 0.2 Brix%        |
| Temperature range                           | : 10 - 40°             |
| Resolution of temperature                   | : 0.1°                 |
| display                                     | : °C or °F             |
| Trade Name                                  | : 51324660             |

The index of refraction is defined as the ratio of the speed of light in a vacuum to the speed of light in another substance is given as

$$\text{Refractive index of the substance } (n_D) = \frac{\text{Speed of light in vacuum}}{\text{Speed of light in substance}} \quad (\text{III.6})$$

When light passes from one medium to another medium not only change its speed but also change the direction of the path i.e., it is refracted that shown in the (Figure 1). (In the special case when the light traveling perpendicular to the boundary there is no change in direction upon entering the new medium.) The relationship between the speed of light in the two mediums ( $V_A$  and  $v_{ibc}$ ), the angles of incidence ( $\theta_A$ ) and refraction ( $\theta_B$ ) and the refractive indexes of the two mediums ( $n_{an}$  and  $n_{ab}$ ) is shown below:



**Figure 1.** Light passage from any transparent medium into another in which it has a different speed, is refracted, i.e., bent from its original path (except when the direction of travel is perpendicular to the boundary). In the above case shown, the speed of light in medium A is greater than the speed of light in medium B.

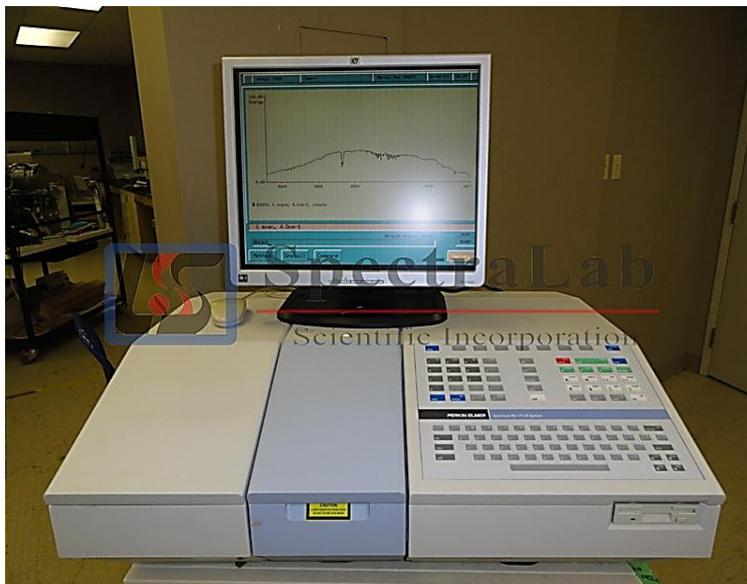
$$\frac{V_A}{V_B} = \frac{\sin \theta_A}{\sin \theta_B} = \frac{n_B}{n_A} \quad (\text{III.7})$$

Indeed, it is not very necessary to measure the speed of light in a sample in order to determine its index of refraction. Instead, measurement of angle of refraction and knowing the index of refraction of the sample that is contact the layer of the sample and determination of refractive index of the sample very precisely. The principle of all the refractometer is same but only difference is their optical defines. (III.5)

Source of a light is projected through the illuminating prism, the bottom surface of the prism which is designated as ground (i.e., roughened like a ground-glass joint), it is thought that each point on this surface can generating the light rays which traveling in all directions. Examination of Figure 2 displays that light when traveling from point A to point B will have the largest angle of incidence ( $q_i$ ) and hence angle of refraction of the sample (QR) would be largest possiblily. All other rays of light that entering the refracting prism will have smaller  $q_{ir}$  value and hence this is lie to the left of point C. Thus, a detector sited on the backside of the refracting prism would display a light region to the left and a dark region to the right.

### III.2.4.7 FTIR MEASUREMENT

FTIR (PerkinElmer, spectrumRXI) was used to determination or recorded the Infrared spectra.



#### Specification of FTIR spectrometer

|                                  |                  |
|----------------------------------|------------------|
| <b>21 CFR Part 11 Compatible</b> | <b>Yes</b>       |
| Wave Length                      | 8                |
| Wave Length Range                | 8,300 – 350 cm-1 |
| Weight                           | 13.0 kg          |
| <b>Width</b>                     | 45.0 cm          |

The intensity of incident light ( $I_0$ ) passing through a blank is measured. The intensity is defined as the number of photons per second. The blank means is a solution that is identical to the sample solution except that the blank does not contain the solution that absorbs light. The measurement of the intensity of light ( $I$ ) were done of the sample solution very carefully. (Indeed, instrument not only measures the power but also the intensity of the light. The power is defined as the the energy per second, which is the product of the intensity (photons per second) and the energy per photon. The transmittance ( $T$ ) and the absorbance ( $A$ ) can be calculated from the experimental data.

$$T = \frac{I}{I_0}; \quad A = -\log_{10} T \quad (\text{III.8})$$

The transmittance is define simply the fraction of light in the original beam that passes through the sample and reaches the detector.

#### III.2.4.8 UV Measurement:

When compounds absorb the Ultra violet and or visible light that gives the characteristic absorbance curves as a function of wavelength. Variation of absorbance occurred due to the molecules get excited to higher energy state. UV visible spectra were recorded with a wavelength accuracy of  $\pm 0.5\text{nm}$  by Utilizing JASCO V-530 and Agilent 8453UV- visible spectrometer. With the help of a digital thermostat, the temperature of cell during the experiment was maintained from 298.15K to308.15K.



#### Agilent 8453 UV-Visible Spectrophotometer

A deuterium lamp for ultra violet light and a tungsten lamp for visible light uses two light source for both the using spectrophotometer. Agilent 8453 spectro photometer is a single beam spectrophotometer whereas JASCO V-530 is a double beam spectro photometric instrument containing a reference cuvette for solvent and another cuvette for measurement of experimental solution.



### JASCO V-530 Spectrophotometer

#### III.2.4.9 Surface Tension Measurement:-

K9 digital TENSIO METER(Kruss GmbH,Hamburg,Germany) instrument was used to determination the Siurface Tension of given experimental solutions.The accuracy of the instrument was  $\pm 0.1$ . For determination of surface Tension the platinum ring detachment technique was used.



This tensiometer is very good precision instrument in which contain a solid and vibration-free base. This instrument put on such a place those same demands on its neighbor as a laboratory balance with a resolution of 0.1mg. In addition a clean and dust-free atmosphere is needed for measurements of surface Tension.

#### III.2.4.10. $^1\text{H}$ NMR Spectroscopic Measurement

$^1\text{H}$  NMR spectra were recorded at 400MHz in Bruker Avance instrument in  $\text{D}_2\text{O}$  solvent at 298.15K. Values of chemical shift ( $\delta$ ) are presented in ppm (parts per million), (HDO,  $\delta$  4.79ppm) the residual protonated signal was used as an internal standard.

NMR spectroscopic technique gives the idea about the local magnetic field around the atomic nuclei. When the sample is placed in magnetic field, nuclei of the sample get excited with radio waves into nuclear magnetic resonance that can be recorded by NMR signal. The nature of electronic structure and as well as the functional groups in a molecule are known from the resonance frequency that obtained by intramolecular magnetic field. This field are exclusive for characterize the different compounds. In modern organic chemistry, NMR is very good technique to determine the monomolecular organic compounds. Also to identify the different complex molecules and proteins by the NMR technique according to biochemist. Over all NMR spectroscopy gives total information about the nature of dynamic, structure, state of reaction, and chemical environment around of molecules.



### III.2.4.11. Fluorescence Spectra Measurement

Fluorescence Spectra were recorded by the bench top spectro fluorimeter (Quanta master -40, USA) at room temperature. In this spectrofluorimeter, a Hellma quartz cuvette was used whose optical path length was 1.0cm. Fluorescent molecules absorb the electromagnetic wave length from visible light spectrum and subsequent it can emit of light from the higher energy to lower energy state. Fluorescence of a molecule occurs when an orbital electron undergoes to its ground state by proton emitting from an excited singlet state. Different path take place for the relaxation of molecules. It can also relaxed by release heat through non-radiative process. This also undergo relaxation by the conversion to triplet to singlet state.

By the fluorescence quenching effect an excited molecule can get relax by another molecule. Avery good example of fluorescence quenching is the triplet state of molecular oxygen.



#### Other Instruments Used:

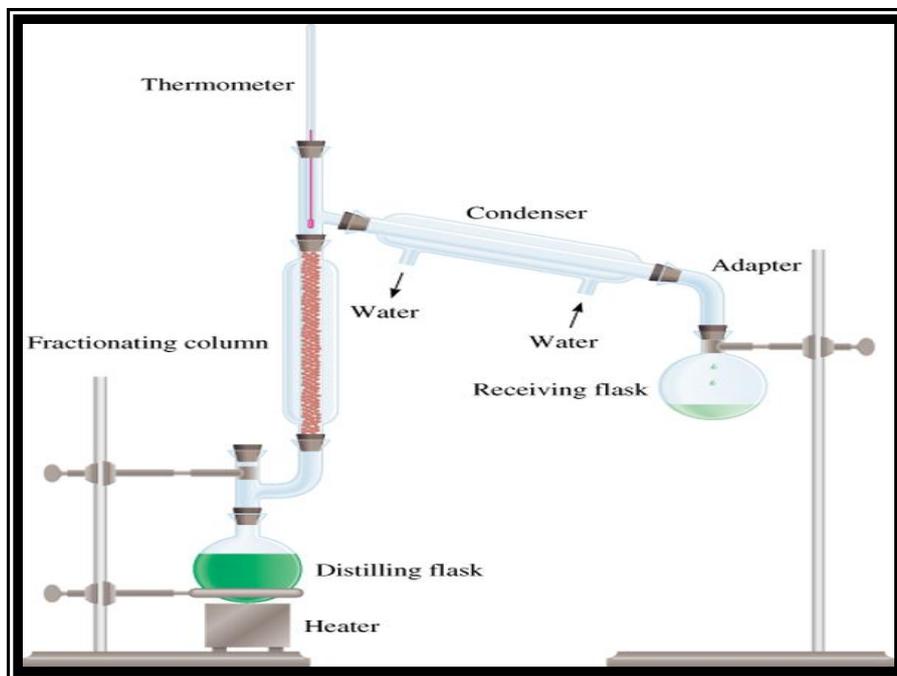
### III.2.4.12. WATER DISTILLER

Water was distilled by using glass distillation unit, bionics Scientific technology private limited.

In the process of water distillation the water purify very quickly, cheaply as well as effectively. For the purpose of water distillation, basically we need a condenser and source of heat. Since boiling point of water is low therefore minerals like salt, contaminants, heavy metal, bacteria, calcium and phosphorous containing in untreated water is carried out to boiled , water easily turns to vaporize and everything leaves behind it. The undesirable elements which can not undergo by the vaporization process along

with water. Through the condensing coil vapor or water is routed such a process that the vapor reverts to the liquid form and the elements that undesirable stay in the boiling tank.

### Fractional Distillation Apparatus



#### III.2.4.13. THERMOSTAT WATER BATH (Science India, Kolkata):

The measurements of experimental solution were carried out in thermostatic water bath and controlled with an accuracy of  $\pm 0.01$  K of the desired temperature. Brook field TC-550 also another thermostatic water bath, this also used for the same purpose.



Laboratory working water bath is a system in which the material is placed into the vessel containing water to be heated quickly. Both digital as well as analogue controls are available to this laboratory equipment's for the purpose of the heating of the experimental solutions. It has greater temperature uniformity, heat retention, durability and recovery. Manufacturing of chambers of water bath lab products was leak proof and highly resistant stainless steel and other lab supplies.



**TC-550**

## CHAPTER-IV

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### **EXPLORING DIVERSE INTERACTIONS OF SOME SURFACE ACTIVE IONIC LIQUIDS WITH AMINO ACIDS PREVALENT IN AQUEOUS ENVIRONMENTS BY PHYSICOCHEMICAL CONTRIVANCE**

**Abstract:** Molecular interactions of two (ILs) [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl with amino acids (AA) (AA= L-tyr, L-phe) in aqueous medium have been investigated by molar conductivities ( $\Lambda$ ) at three different temperatures. Spectroscopic studies have been performed to investigate the association behavior between the ILs and the selected amino acids and the spontaneity of this process. The <sup>1</sup>H NMR spectroscopy has also been carried out to expose the change in electronic conditions of various protons of ILs in the presence of different amino acids. All the results have been interpreted on the light of possible molecular interactions operating in the ternary system and varies in the order of ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-tyr) > ([MOIM]Cl + L-tyr) > ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-phe) > ([MOIM]Cl + L-phe) in water. The obtained experimental parameters will be extremely supportive to understand the mixing effect and other complicated biological process between amino acids and the chosen ionic liquids.

**Key words:** Conductance; UV-vis spectroscopy; fluorescence; association constant; <sup>1</sup>H-NMR.

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#### **1. Introduction**

Ionic liquids (ILs) belong to the family of those organic compounds which are nano-structured molten salts at room temperature and having cationic organic part and anionic inorganic/organic part<sup>1</sup>. ILs has a spacious diversity of unique physical and chemical character such as non-flammability, negligible vapor pressure, ability of dissolving large variety of compounds, high electrical conductivity etc.<sup>2-6</sup> which makes them a source of interest in different fields of science, industries and process such as biology, separation of amino acids electrochemistry, synthesis etc<sup>7-9</sup>. Additionally they can also be considered as green and designer solvent/electrolytes because of their uniqueness<sup>3, 10-14</sup>. In recent years, ILs are also used to frame the thermophysical properties of aqueous solution containing amino acid(s) (AA) and ILs which provides important information about the intermolecular interactions in solution phase<sup>15-20</sup>. Amino acids are used as model compounds as they are building block of proteins. Such interactions and thermodynamic properties studies helps to overcome the difficulties that

arise in case of some biomolecules such as proteins due to their complexed structures and provides the information about the solute-solvent and solute-solute interactions that can be help to understand the effects of electrolytes on proteins.<sup>21-23</sup>

It is already known that 1, 3-disubstituted imidazolium ring based ILs are important enough and widely used in solution chemistry.<sup>24-28</sup> The main significance about the imidazole ring is its existence in various amino acids, proteins and nucleic acids that have many biological activities. Additionally, all protons of 1, 3-disubstituted imidazolium ring are shown acidic character due to delocalization of positive charge over the ring.<sup>29</sup>

This work is related to study the molar conductivities ( $\Lambda$ ) at different temperatures<sup>30</sup> (298.15 K, 305.15 K and 312.15 K) and spectroscopic methods (UV-Vis, FTIR) of two amino acids L-tyrosine (L-tyr) and L-phenylalanine (L-Phe) with 1-butyl-3-methylimidazolium octylsulphate [BMIM][C<sub>8</sub>SO<sub>4</sub>] and 1-methyl-3-octylimidazolium chloride [MOIM]Cl respectively in aqueous solution. All these data have been used to interpret the interactions (non-covalent) involved in ternary (L-tyr/L-Phe + [BMIM][C<sub>8</sub>SO<sub>4</sub>]/ [BMIM][C<sub>8</sub>SO<sub>4</sub>] + water) systems. The structure of both AAs and ILs has been shown in **scheme 1**. Moreover, such interactions of analogue imidazolium ILs with L-tyr and L-Phe systems are reported in theoretical background but no such works have been done to propose a model for the studied ILs and amino acids.<sup>31</sup>

## 2.1. Chemicals

The details of chemicals used in this work are listed in **Table 1**; no further purification has been performed. Triply distilled and degassed water (specific conductivity < 1  $\mu\text{S}\cdot\text{cm}^{-1}$ ) is used for preparation all solutions.

## 2.2 Apparatus

The mass of chemicals is measured by analytical balance METTLER TOLEDO-Model: AG-285 with an uncertainty  $\pm 0.003$  g. All the binary stock solutions are prepared carefully by mass dilution at 298.15 K ( $\pm 0.01$  K).

The conductance has been carried out in systronic-308 conductivity meter (accuracy  $\pm 0.01$ ) using a dip-type immersion conductivity cell, CD-10, having a cell-constant of  $\sim 0.1 \pm 0.001$   $\text{cm}^{-1}$ . Experiments are made in thermostatic jacket to maintain temperatures. The specific conductance ( $\kappa$ ) of IL+ aq. amino acid solutions under investigation in three different temperatures (298.15 K, 305.15 K, 312.15 K) are measured to see the effect of temperatures on conductance for these systems. The molar

conductance ( $\Lambda$ ) for the studied solutions has been calculated using following **equation 1** and given in **Fig. 1 and Fig. 2**.

$$\Lambda = 1000 \kappa / c \quad (1)$$

Where,  $c$  is the molar concentration of amino acids in the studied solution.

UV-visible spectra were recorded by JASCO V-530 UV/VIS Spectrophotometer. All the absorption spectra were recorded at  $25^\circ\text{C} \pm 0.1^\circ\text{C}$ .

A photon Technology International (PTI), USA fluorescence spectrophotometer (Quantmaster-40) was used to record fluorescence spectra.

NMR spectra were recorded at 600 MHz Bruker AVANCE at 298.15K in  $\text{D}_2\text{O}$ . Signals are quoted as  $\delta$  values in ppm using residual protonated solvent signals as internal standard ( $\text{D}_2\text{O}$ :  $\delta$  4.700 ppm). Data are reported as chemical shift.

### **3. Results and discussion**

#### **3.1 Conductance study**

The conductance study of the interaction (solute-solvent) between the ILs ([BMIM][ $\text{C}_8\text{SO}_4$ ]/[MOIM]Cl) with aqueous solution of L-tyr and L-phe amino acids has been performed at three different temperatures. The advantage of this study is that this measurement provides information about the interaction and transport phenomena of the (AA + ILs + water) ternary systems.

The molar conductivities ( $\Lambda$ ) of aqueous [BMIM][ $\text{C}_8\text{SO}_4$ ] and [MOIM]Cl has been monitored with increasing the concentration of L-tyr and L-phe respectively at three different temperatures and have been listed in **Table S1 and S2**. The **Fig. 1-2** show the resulting plots of ([BMIM][ $\text{C}_8\text{SO}_4$ ] + L-tyr + water) (system 1), ([MOIM]Cl + L-tyr + water) (system 2), (([BMIM][ $\text{C}_8\text{SO}_4$ ] + L-phe + water) (system 3) and ([MOIM]Cl + L-phe + water) (system 4) respectively. For each system it has been observed that  $\Lambda$  values increase with increase in temperature and gradual addition of AA to ILs solution causes a continuous decrease in molar conductance.<sup>32-35</sup>

The decrease in molar conductance may be due to two factors- (i) involvement in non-covalent interactions of ILs with AA(s)<sup>20,33,35</sup> and (ii) [BMIM][ $\text{C}_8\text{SO}_4$ ] and [MOIM]Cl is an anionic and cationic surface active ionic liquid (SAILs) respectively.<sup>36</sup> So, they have a positive tendency to form micelles after a certain concentration. Initially as there are no micelles, the free mobile ions of SAILs are accountable for the speedy decrease in  $\Lambda$  values with increasing

amino acids content in solutions because of increasing system viscosity as well as the attractions between ILs and AAs with increasing AAs concentration. The strong intermolecular hydrophobic-hydrophobic attraction, and other non-covalent (hydrophilic,  $\pi\cdots\pi$  interactions, columbic attraction etc.) interactions must have been developed with amino acids<sup>37</sup> but after a certain point the ions contribution are less in transport change and leading to level off. As the [BMIM][C<sub>8</sub>SO<sub>4</sub>] SAIL has to some extent more acidic protons and less hindered imidazolium ring protons<sup>31</sup> and long hydrophobic alkyl chain in counter ion part than the [MOIM]Cl, so the former IL must be involved in good interactions than [MOIM]Cl with the amino acids. Apart from these interactions, L-tyr has an extra hydroxyl (-OH) group at para position which helps to bind the ILs more firmly by H-bond than L-phe and involved in strong interactions with the ILs than L-phe. Thus considering all of these the stability order of interactions follows the order of- (system 1)> (system 2)> (system 3)> (system 4).

### 3.2 UV-vis spectroscopy:

The UV-vis spectroscopy is a suitable method that not only helps to get the important information about interaction behavior in systems but also provide the binding nature of binding partners.<sup>38</sup> The absorption peak of [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl in aqueous solution by varying concentration of amino acids (i.e. L-tyr and L-phe) are shown in **figure 3 and figure 4**. The strong absorption peaks for both two imidazolium based ILs appeared at ~210 nm ( $\lambda_{\max}$ ).<sup>39</sup> From **Fig. 3-4**, it is seen that continuous increase in absorption intensity has been occurred due to regular addition of different concentrated amino acids to both the ILs. Such spectral shifts due to the occurrence of  $\pi\cdots\pi$  and C-H $\cdots\pi$  interactions that may involved in the ILs and L-tyr and L-phe.

### 3.3 Steady state fluorescence Study

The interactions phenomena of the imidazolium ILs with the amino acids have further been further investigated by fluorescence technique.<sup>40</sup> The imidazolium ring of the ILs is responsible for giving significant emission spectra in fluorescence. The emission peaks of both ILs are close enough to each other and appeared at  $\sim\lambda^{\text{flu}}_{\max}$  420 nm<sup>41</sup>. This also implies the less contribution of alkyl chain of [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl imidazolium based ILs in emission spectra. By keeping constant concentration of ILs in aqueous solution and gradually addition of increase in concentration of amino acids causing the continuous enhancement of the fluorescence intensities of both ILs which indicate that molecular interactions/associations are obviously arising there (**Fig. S1-S2**).

### 3.4. Determination of association constant-spontaneity and features of interactions

The association constant in this phenomena i.e. [BMIM][C<sub>8</sub>SO<sub>4</sub>] / [MOIM]Cl ILs interactions with L-tyr and L-phe have been calculated by Benesi-Hildebrand **equation 2**<sup>38,39,42</sup> using the absorption and emission spectral (fluorescence) data (**Table S3-S6**). This is very helpful method for quantitative estimation of extent of binding of two binding events.

$$\frac{1}{I - I_o} = \frac{1}{K_a(I_1 - I_o)} \cdot \frac{1}{[AA]} + \frac{1}{(I_1 - I_o)} \quad (2)$$

Where,  $I_o$  and  $I$  are the intensity values of absorption/ fluorescence of both IL in absence and presence of AAs respectively.  $I_1$  is the intensity of absorption/ fluorescence of ILs due to association with amino acids and  $K_a$  is the association constant.

The double reciprocal plots of  $1/I - I_o$  versus  $1/[AA]$  for all the systems have been shown in **Fig. (5 – 6)** and all system are within good linear correlation ( $R^2 > 0.900$ ) and suggest the 1:1 interaction is present for each systems. The  $K_a$  values have been calculated from the ratio of intercept and slop of each plot. It can be observed from the  $K_a$  value that the association for [BMIM][CSO<sub>4</sub>] is greater with L-tyr than L-phe and least for ([MOIM]Cl +L-phe) system.

Further by using the value of  $K_a$  the free energy changes ( $\Delta G$ ) for the adduct formation of ILs and AAs have been calculated using the following the equation 3

$$\Delta G = -RT \ln K \quad (3)$$

The values of  $\Delta G$  for all adducts have been listed in **Table S3-S6** and the negative values be a sign of the feasibility of the adducts formation by interactions.

The values of  $K_a$  and  $\Delta G$  make known that (system 1) have greater attraction possibility than the others. In theoretically background, the possibility of such an interaction on for an analogue system is reported earlier.<sup>31</sup> Thus, we can endorsed that a stronger H-bond and  $\pi \cdots \pi$  stacking interactions are developed in case of L-tyr than L-phe from S2 side (**scheme 1**) that can enhance the stability and can also be attributed for such order of interactions. Further the weak columbic force of attraction between the

positively charged ring cation and the negatively charged AA plays a role in bringing them close to each other.

### 3.4 NMR Study

Nuclear magnetic resonance (NMR) is a very effectual technique for studying the changes the electronic environment around the different protons of ILs in presence of various kinds of amino acids.<sup>41</sup> In <sup>1</sup>HNMR the binary mixture of [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl with individual L-tyr and L-phe have been recorded in D<sub>2</sub>O a 298.15 K respectively (Table 2).

The chemical shifts of [BMIM][C<sub>8</sub>SO<sub>4</sub>] / [MOIM]Cl depends on the electronic space environment present in their surrounding area. It is found that significant upfield shifts for alkyl protons of the imidazolium ring have been occurred after mixing of amino acids. This indicates the presence of intermolecular hydrophobic- hydrophobic interactions that leading to increase the electron density around the imidazolium ring. It can be seen from chemical shifts that in both ILs the alkyl chain protons attached to imidazolium ring are in good intermolecular interactions with amino acids but comparing the protons of imidazolium ring, downfield shift for C<sub>2</sub> proton and upfield shifts for other imidazolium ring protons (C<sub>3</sub>, C<sub>4</sub>) has been observed (Fig. 7 - 8). It most probably suggests the orientation for imidazolium ring that allows strong H-bond formation with C<sub>2</sub> proton and weak  $\pi\cdots\pi$  interactions involving C<sub>3</sub>, C<sub>4</sub> and benzene ring of AA(s). Thus two opposing influences i.e. H-bond and  $\pi\cdots\pi$  interactions are possibly responsible for distinct shifts for ring protons.<sup>42</sup> The downfield shift for C<sub>2</sub> proton of [BMIM] cation is larger than the [MOIM] cation C<sub>2</sub> protons, thus it has been concluded that ([BMIM] cation $\cdots$ AA) H-bonding are somewhat stronger than ([MOIM] cation $\cdots$ AA) interactions. Thus all the variations in chemical shifts are perhaps due to contribution of various factors: such as- (i) H-bond interactions between the acidic proton of ring with oxygen atom of amino acids [(C-H)<sub>Imidazolium ring</sub> $\cdots$ O<sub>AA</sub>], (ii) aromatic ring current effect: the  $\pi\cdots\pi$  interactions of imidazolium ring with the phenyl ring of amino acid, (iii) weak C-H $\cdots$   $\pi$  between the cation and AA, (iv) hydrophobic interactions, (v) columbic force of attraction are being there<sup>44, 45</sup> (Scheme 2) which are in good agreement with that obtained by our other experiments.

### 4. Conclusion

The solute-solvent interaction behavior of studied ionic liquid and amino acids in aqueous solution have been determined by conductance measurements at three different temperatures and spectroscopic studies. The ILs and amino acids systems in aqueous solution indicate the non-covalent interactions among them and causing an increase of hydrodynamic

radii of ions and a decrease of their ionic mobility, hence we have got the result a decrease in molar conductance. It has been concluded from the association constant values of the selected ILs with AAs obtained by using Uv-vis and fluorescence measurements that among the two ILs, 1-butyl-3-methylimidazolium octylsulphate [BMIM][C<sub>8</sub>SO<sub>4</sub>] interact more firmly with L-tyrosine than L-phenylalanine and in each system both IL and AA have been promoted to each due to non-covalent such as strong hydrophobic- hydrophobic, weak  $\pi \cdots \pi$ , columbic force of attraction, H-bond interactions etc. amongst themselves. The significant chemical shifts of ILs protons in presence of amino acids in <sup>1</sup>HNMR studies also support the results obtained from other spectroscopic and conductance measurements.

Abbreviations: [BMIM][C<sub>8</sub>SO<sub>4</sub>] → 1-butyl-3-methylimidazolium octylsulphate

[MOIM]Cl → 1-methyl-3-octylimidazolium chloride

(ILS) → Ionic liquids

### **Acknowledgement**

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**Table 1: Brief description of the chemicals**

| SL. No. | Name of Chemicals                         | CAS NO.     | Abbreviation                            | supplier      | Purity (mass fraction) |
|---------|---|-------------|---|---------------|------------------------|
| 1       | 1-butyl-3-methylimidazolium octylsulphate | 445473-58-5 | [BMIM][C <sub>8</sub> SO <sub>4</sub> ] | Sigma-Aldrich | ≥ 0.95                 |
| 2       | 1-methyl-3-octylimidazolium chloride      | 64697-40-1  | [MOIM]Cl                                | Sigma-Aldrich | ≥ 0.97                 |
| 3       | L-tyrosine                                | 60-18-4     | L-tyr                                   | Sigma-Aldrich | ≥ 0.98                 |
| 4       | L-phenyl alanine                          | 63-91-2     | L-phe                                   | sigma-Aldrich | ≥ 0.97                 |

**Table 2. Conductivity values for the [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl IL with L-tyr in aqueous at three different temperatures(K<sup>a</sup>)**

| Total vol. (mL) | Conc. of L-tyr (mM) | Molar conductance (S cm <sup>2</sup> mol <sup>-1</sup> ) of [BMIM][C <sub>8</sub> SO <sub>4</sub> ] |        |        | Molar conductance (S cm <sup>2</sup> mol <sup>-1</sup> ) of [MOIM]Cl |        |        |
|-----------------|---------------------|---|--------|--------|--|--------|--------|
|                 |                     | 298.15 K  | 305.15 | 312.15 | 298.15 K   | 305.15 | 312.15 |
| 10              | 0.0                 | 53.14   | 70.72  | 82.92  | 86.93  | 93.40  | 119.51 |
| 11              | 0.1818              | 44.28   | 59.85  | 70.66  | 71.64  | 81.53  | 90.36  |
| 12              | 0.3333              | 37.74   | 52.76  | 62.54  | 62.47  | 72.55  | 80.24  |
| 13              | 0.4615              | 33.83   | 46.77  | 56.47  | 55.25  | 66.23  | 73.45  |
| 14              | 0.5714              | 31.91   | 42.32  | 52.72  | 50.48  | 61.41  | 68.93  |
| 15              | 0.6667              | 30.78   | 40.67  | 49.58  | 48.20  | 58.56  | 65.84  |
| 16              | 0.75                | 29.93   | 39.53  | 47.25  | 46.41  | 56.22  | 63.11  |
| 17              | 0.8235              | 29.26   | 38.17  | 46.51  | 45.23  | 54.37  | 62.38  |
| 18              | 0.8889              | 29.18   | 37.22  | 45.11  | 44.66  | 52.64  | 61.46  |
| 19              | 0.9474              | 28.89   | 36.31  | 44.4   | 43.94  | 51.45  | 60.79  |
| 20              | 1.0                 | 27.59   | 35.62  | 43.26  | 43.17  | 50.62  | 59.74  |
| 21              | 1.0476              | 27.19   | 34.03  | 42.54  | 42.65  | 49.51  | 58.01  |
| 22              | 1.0909              | 26.84   | 33.21  | 41.97  | 41.90  | 48.84  | 57.53  |
| 23              | 1.13                | 25.98   | 32.24  | 41.14  | 41.40  | 48.16  | 57.08  |
| 24              | 1.1667              | 25.32   | 31.67  | 40.25  | 40.93  | 47.61  | 56.53  |

<sup>a</sup> Standard uncertainties in temperature (T)=0.01K**Table 3. Conductivity values for the [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl IL with L-phe in aqueous at three different temperatures(K<sup>a</sup>)**

| Total vol. (mL) | Conc. of L-tyr (mM) | Molar conductance (S cm <sup>2</sup> mol <sup>-1</sup> ) of [BMIM][C <sub>8</sub> SO <sub>4</sub> ] |          |          | Molar conductance (S cm <sup>2</sup> mol <sup>-1</sup> ) of [MOIM]Cl |          |          |
|-----------------|---------------------|---|----------|----------|--|----------|----------|
|                 |                     | 298.15 K  | 305.15 K | 312.15 K | 298.15 K   | 305.15 K | 312.15 K |
| 10              | 0.0                 | 60.35   | 72.27    | 83.62    | 86.92  | 93.55    | 119.34   |
| 11              | 0.1818              | 50.26   | 58.68    | 67.26    | 75.43  | 80.89    | 99.86    |
| 12              | 0.3333              | 42.84   | 50.95    | 59.37    | 67.15  | 72.35    | 87.72    |
| 13              | 0.4615              | 38.19   | 46.15    | 53.82    | 60.27  | 65.51    | 79.59    |
| 14              | 0.5714              | 34.45   | 43.25    | 50.55    | 54.59  | 60.68    | 75.74    |
| 15              | 0.6667              | 32.85   | 40.74    | 47.65    | 50.36  | 57.34    | 71.45    |

| Total vol. (mL) | Conc. of L-tyr (mM) | Molar conductance (S cm <sup>2</sup> mol <sup>-1</sup> ) of [BMIM][C <sub>8</sub> SO <sub>4</sub> ] |       |       | Molar conductance (S cm <sup>2</sup> mol <sup>-1</sup> ) of [MOIM]Cl |       |       |
|-----------------|---------------------|---|-------|-------|--|-------|-------|
|                 |                     |   |       |       |  |       |       |
| 16              | 0.75                | 31.65   | 38.77 | 45.16 | 46.92  | 55.32 | 68.96 |
| 17              | 0.8235              | 29.45   | 37.41 | 44.46 | 45.45  | 53.56 | 66.75 |
| 18              | 0.8889              | 28.91   | 36.53 | 42.86 | 43.78  | 51.88 | 64.34 |
| 19              | 0.9474              | 28.53   | 35.22 | 41.57 | 42.53  | 50.02 | 62.23 |
| 20              | 1.0                 | 27.42   | 33.49 | 40.53 | 41.47  | 49.19 | 60.15 |
| 21              | 1.0476              | 26.09   | 32.31 | 39.25 | 40.39  | 48.45 | 59.04 |
| 22              | 1.0909              | 25.94   | 31.72 | 38.17 | 39.04  | 47.06 | 58.19 |
| 23              | 1.13                | 25.01   | 30.45 | 37.32 | 38.71  | 46.53 | 57.41 |
| 24              | 1.1667              | 24.62   | 29.91 | 36.05 | 37.47  | 45.25 | 56.95 |

<sup>a</sup> Standard uncertainties in temperature (T)=0.01K

**Table 4. Data for the Benesi-Hildebrand double reciprocal plot obtained from UV-Vis spectroscopy for aqueous [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl ILs with L-tyr system at 298.15K<sup>a</sup>**

| [BMIM][C <sub>8</sub> SO <sub>4</sub> ] (M) | Conc. of L-tyr (M) | I <sub>0</sub> | Intensity (I) | K <sub>a</sub> (M <sup>-1</sup> ) | ΔG KJ mol <sup>-1</sup> |
|---|--------------------|----------------|---------------|-----------------------------------|-------------------------|
|   | 0.0004             |                | 2.43106       |                                   |                         |
|   | 0.0008             |                | 2.53914       |                                   | -22.64                  |
| 4 x 10 <sup>-4</sup>                        | 0.0012             |                | 2.56891       | 9260                              |                         |
|   | 0.0016             | 1.61436        | 2.60076       |                                   |                         |
|   | 0.002              |                | 2.65974       |                                   |                         |

| [MOIM]Cl (M)         | Conc. of L-tyr (M) | I <sub>0</sub> | Intensity (I) | K <sub>a</sub> (M <sup>-1</sup> ) | ΔG KJ mol <sup>-1</sup> |
|----------------------|--------------------|----------------|---------------|-----------------------------------|-------------------------|
|                      | 0.0004             |                | 2.31916       |                                   |                         |
|                      | 0.0008             |                | 2.44828       |                                   |                         |
| 4 x 10 <sup>-4</sup> | 0.0012             | 1.67759        | 2.50968       | 4994                              | -21.11                  |
|                      | 0.0016             |                | 2.54860       |                                   |                         |
|                      | 0.002              |                | 2.59924       |                                   |                         |

<sup>a</sup> Standard uncertainties in temperature (T)=0.01K

**Table 5. Data for the Benesi-Hildebrand double reciprocal plot obtained from UV-Vis spectroscopy for aqueous [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl ILs with L-phe system at 298.15K<sup>a</sup>.**

| [BMIM][C <sub>8</sub> SO <sub>4</sub> ]<br>(M) | Conc. of L-<br>phe (M) | I <sub>0</sub> | Intensity (I) | Ka(M <sup>-1</sup> ) | ΔG KJ<br>mol <sup>-1</sup> |
|--|------------------------|----------------|---------------|----------------------|----------------------------|
|  | 0.0004                 |                | 3.45837       |                      |                            |
|  | 0.0008                 |                | 2.60077       |                      |                            |
| 4 x 10 <sup>-4</sup>                           | 0.0012                 | 1.61436        | 2.30684       | 2373.86              | -19.27                     |
|  | 0.0016                 |                | 2.14971       |                      |                            |
|  | 0.002                  |                | 1.94121       |                      |                            |
| [MOIM]Cl (M)                                   | Conc. of L-<br>phe (M) | I <sub>0</sub> | Intensity (I) | Ka(M <sup>-1</sup> ) | ΔG KJ<br>mol <sup>-1</sup> |
|  | 0.0004                 |                | 4.14765       | 2111.78              |                            |
|  | 0.0008                 |                | 3.11910       |                      |                            |
| 4 x 10 <sup>-4</sup>                           | 0.0012                 | 1.67759        | 2.69882       |                      |                            |
|  | 0.0016                 |                | 2.49336       |                      | -18.98                     |
|  | 0.002                  |                | 2.25789       |                      |                            |

<sup>a</sup> Standard uncertainties in temperature (T)=0.01K.

**Table 6. Data for the Benesi-Hildebrand double reciprocal plot obtained from fluorescence spectroscopy for aqueous [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl ILs with L-tyr system at 298.15K<sup>a</sup>**

| [BMIM][C <sub>8</sub> SO <sub>4</sub> ]<br>(M) | Conc. of<br>L- tyr<br>(M) | I <sub>0</sub> |            | Intensity (I) | Ka(M <sup>-1</sup> ) | ΔG KJ<br>mol <sup>-1</sup> |
|--|---------------------------|----------------|------------|---------------|----------------------|----------------------------|
|  | 0.0003                    |                | 202353.032 | 270750.420    |                      |                            |
|  | 0.0006                    |                |            | 299469.176    |                      |                            |
| 10 x 10 <sup>-4</sup>                          | 0.0009                    | 202353         |            | 325637.411    | 1595                 | -18.28                     |
|  | 0.0012                    |                |            | 339150.187    |                      |                            |
|  | 0.0015                    |                |            | 353260.785    |                      |                            |
|  | 0.0018                    |                |            | 360658.554    |                      |                            |
| [MOIM]Cl (M)                                   | Conc. of<br>L- tyr<br>(M) | I <sub>0</sub> |            | Intensity (I) | Ka(M <sup>-1</sup> ) | ΔG KJ<br>mol <sup>-1</sup> |
|  | 0.0003                    |                | 158736.743 | 233021.208    |                      |                            |
|  | 0.0006                    |                |            | 277888.743    |                      |                            |
| 10 x 10 <sup>-4</sup>                          | 0.0009                    | <b>158736</b>  |            | 302731.526    | <b>1164</b>          | <b>-17.50</b>              |
|  | 0.0012                    |                |            | 321062.647    |                      |                            |
|  | 0.0015                    |                |            | 341268.303    |                      |                            |
|  | 0.0018                    |                |            | 360191.789    |                      |                            |

<sup>a</sup> Standard uncertainties in temperature (T)=0.01K

**Table 7. Data for the Benesi-Hildebrand double reciprocal plot obtained from fluorescence spectroscopy for aqueous [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl ILs with L-phe system at 298.15K<sup>a</sup>.**

| [BMIM][C <sub>8</sub> SO <sub>4</sub> ]<br>(M) | Conc. of<br>L-phe<br>(M) | I <sub>0</sub> |            | Intensity<br>(I) | K <sub>a</sub> (M <sup>-1</sup> ) | ΔG KJ mol <sup>-1</sup> |
|--|--------------------------|----------------|------------|------------------|-----------------------------------|-------------------------|
|  | 0.0003                   |                | 202353.032 | 257998.969       |                                   |                         |
|  | 0.0006                   |                |            | 279539.343       |                                   |                         |
| 10 x 10 <sup>-4</sup>                          | 0.0009                   | 202353         |            | 309878.657       | 1080                              | -17.32                  |
|  | 0.0012                   |                |            | 338953.274       |                                   |                         |
|  | 0.0015                   |                |            | 351113.756       |                                   |                         |
|  | 0.0018                   |                |            | 373406.046       |                                   |                         |

| [MOIM]Cl (M)          | Conc. of<br>L- phe<br>(M) | I <sub>0</sub> |            | Intensity<br>(I) | K <sub>a</sub> (M <sup>-1</sup> ) | ΔG KJ mol <sup>-1</sup> |
|-----------------------|---------------------------|----------------|------------|------------------|-----------------------------------|-------------------------|
|                       | 0.0003                    |                | 158736.743 | 190069.494       |                                   |                         |
|                       | 0.0006                    |                |            | 213359.573       |                                   |                         |
| 10 x 10 <sup>-4</sup> | 0.0009                    | <b>158736</b>  |            | 224236.230       | <b>933</b>                        | <b>-16.95</b>           |
|                       | 0.0012                    |                |            | 236632.444       |                                   |                         |
|                       | 0.0015                    |                |            | 237774.593       |                                   |                         |
|                       | 0.0018                    |                |            | 249594.135       |                                   |                         |

<sup>a</sup> Standard uncertainties in temperature (T)=0.01.

**Table 8. <sup>1</sup>H NMR chemical shift displacements of [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl in interaction with L-tyr and L-phe in D<sub>2</sub>O at 298.15 K<sup>a</sup>**

| IL protons                              | Free IL δ (ppm) | IL with L-tyr δ (ppm) | IL with L-phe δ (ppm) |
|---|-----------------|-----------------------|-----------------------|
| [BMIM][C <sub>8</sub> SO <sub>4</sub> ] |                 |                       |                       |
| <b>C1</b>                               | 3.892           | 3.881                 | 3.884                 |
| <b>C2</b>                               | 8.589           | 8.646                 | 8.598                 |
| <b>C3, C4</b>                           | 7.358-7.399     | 7.328-7.374           | 7.348-7.392           |
| <b>C5</b>                               | 4.091-4.103     | 4.070-4.082           | 4.083-4.095           |
| <b>C6</b>                               | 1.726-1.751     | 1.711-1.736           | 1.719-1.744           |
| <b>C7</b>                               | 1.486-1.499     | 1.481-1.495           | 1.483-1.489           |
| <b>C8</b>                               | 0.710-0.716     | 0.707-0.711           | 0.709-0.714           |
| <b>A1</b>                               | 3.794-3.802     | 3.774-3.798           | 3.786-3.800           |
| <b>A2</b>                               | 1.376-1.387     | 1.372-1.381           | 1.374-1.383           |
| <b>A3</b>                               | 1.123-1.252     | 1.115-1.243           | 1.117-1.248           |
| <b>A4</b>                               | 0.818-830       | 0.790-0.815           | 0.787-0.812           |

| [MOIM]Cl |             |             |             |
|----------|-------------|-------------|-------------|
| C1       | 3.771       | 3.756       | 3.757       |
| C2       | 8.552       | 8.602       | 8.590       |
| C3, C4   | 7.310-7.356 | 7.290-7.348 | 7.297-7.353 |
| C5       | 4.057-4.068 | 4.043-4.055 | 4.040-4.056 |
| C6       | 1.738-1.749 | 1.723-1.746 | 1.720-1.748 |
| C7       | 1.129-1.161 | 1.127-1.152 | 1.127-1.153 |
| C8       | 0.717-0.741 | 0.712-0.737 | 0.714-0.740 |

## Figures

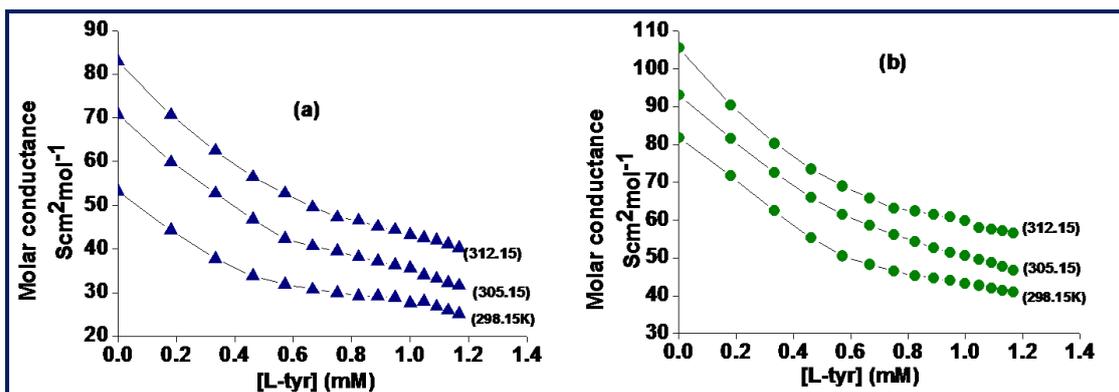


Figure 1. Molar conductance of (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>] in aqueous solution with L-tyr and (b) [MOIM]Cl in aqueous solution with L-tyr at three different temperatures

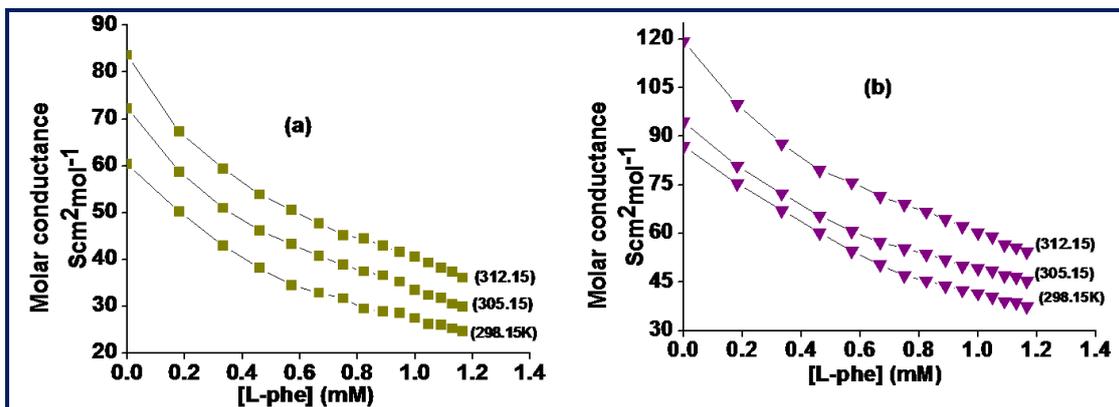
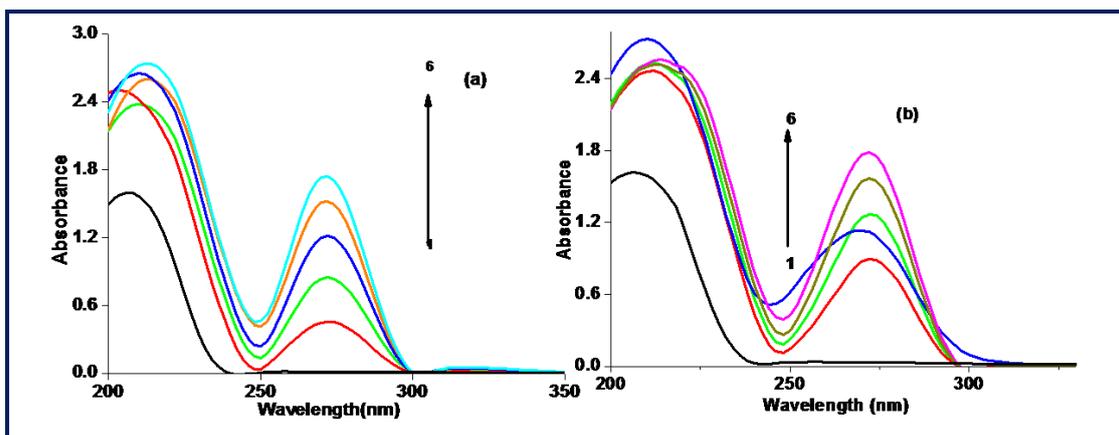
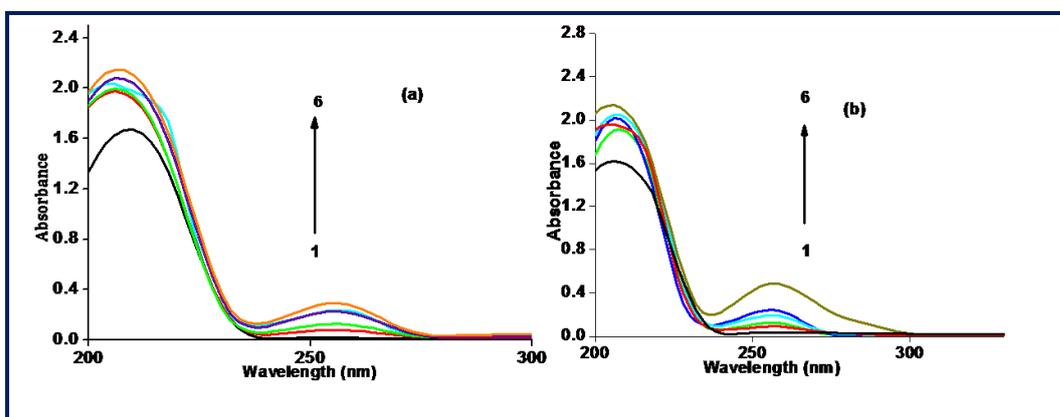


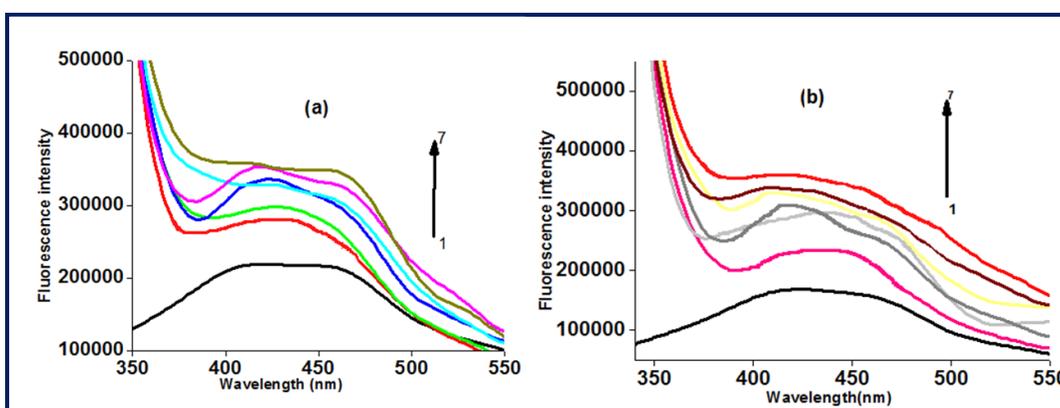
Figure 2. Molar conductance of (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>] in aqueous solution with L-phe and (b) [MOIM]Cl in aqueous solution with L-phe at three different temperatures



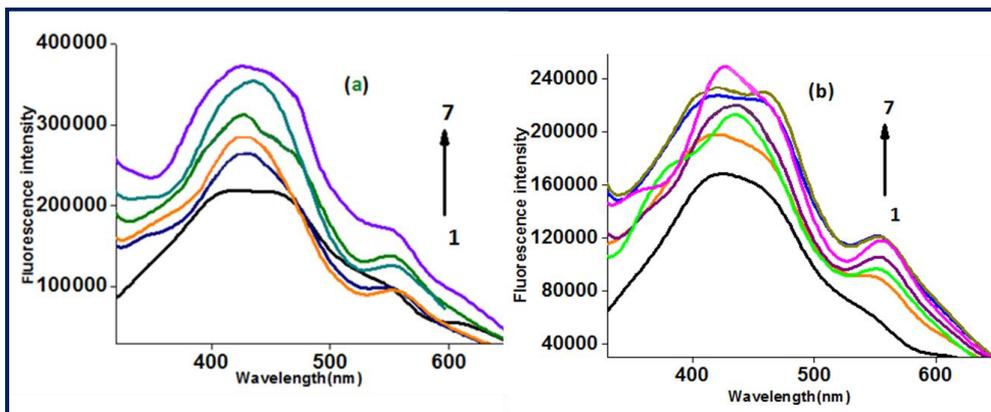
**Figure3.** Increase in absorption spectra of (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>] and (b) [MOIM]Cl at different concentration of L-tyrosine (1) absence of L-tyrosine, (2) 0.0004 M, (3) 0.0008 M, (4) 0.0012 M, (5) 0.0016 M, (6) 0.0018 M, (7)0.002 M respectively



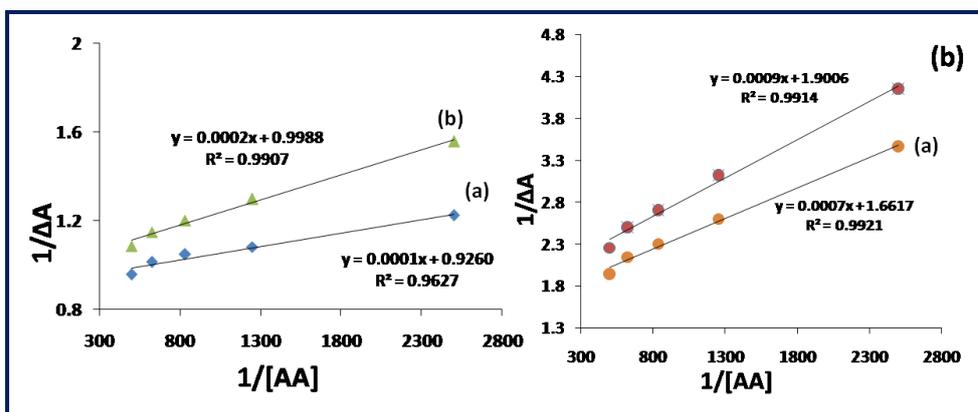
**Figure4.** Increase in absorption spectra of (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>] and (b)[MOIM]Cl at different concentration of L-phenylalanine (1) absence of L-phenylalanine, (2) 0.0004 M, (3) 0.0008 M, (4) 0.0012 M, (5) 0.0016 M, (6) 0.0018 M, (7)0.002 M respectively



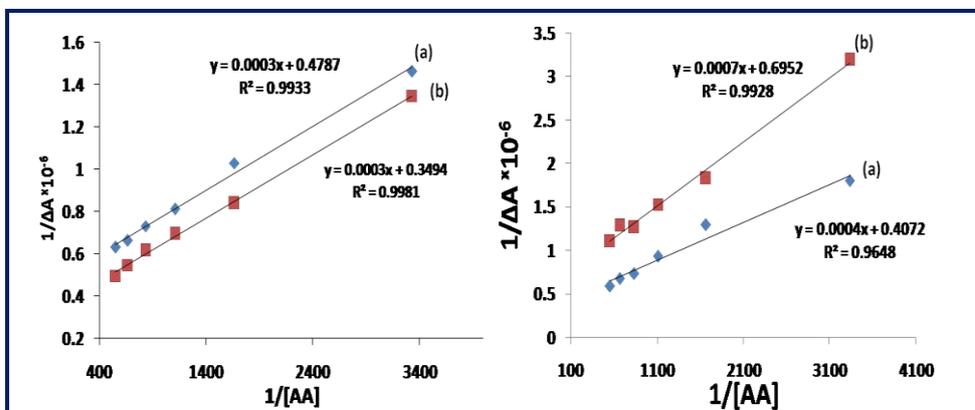
**Figure 5.** Fluorescence spectra of (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>] and (b) [MOIM]Cl at different concentration of L-tyrosine (1) absence of L-tyrosine, (2) 0.0003 M, (3) 0.0006 M, (4) 0.0009 M, (5) 0.0012 M, (6) 0.0015 M, (7)0.0018 M respectively



**Figure 6.** Fluorescence spectra of (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>] and (b) [MOIM]Cl at different concentration of L-phenylalanine (1) absence of L-phenylalanine, (2) 0.0003 M, (3) 0.0006 M, (4) 0.0009 M, (5) 0.0012 M, (6) 0.0015 M, (7)0.0018 M respectively



**Figure7.** Benesi-Hildebrand plot of  $1/\Delta A$  vs.  $1/[AA]$  in UV-vis spectroscopy for (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>] and (b) [MOIM]Cl in L-tyr and for (c)[BMIM][C<sub>8</sub>SO<sub>4</sub>] and (d) [MOIM]Cl in L-phe at 298.15K<sup>a</sup>



**Figure 8.** Benesi-Hildebrand plot of  $1/\Delta A$  vs.  $1/[AA]$  in fluorescence spectroscopy for (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>] and (b) [MOIM]Cl in L-tyr and for (c)[BMIM][C<sub>8</sub>SO<sub>4</sub>] and (d) [MOIM]Cl in L-phe at 298.15K<sup>a</sup>

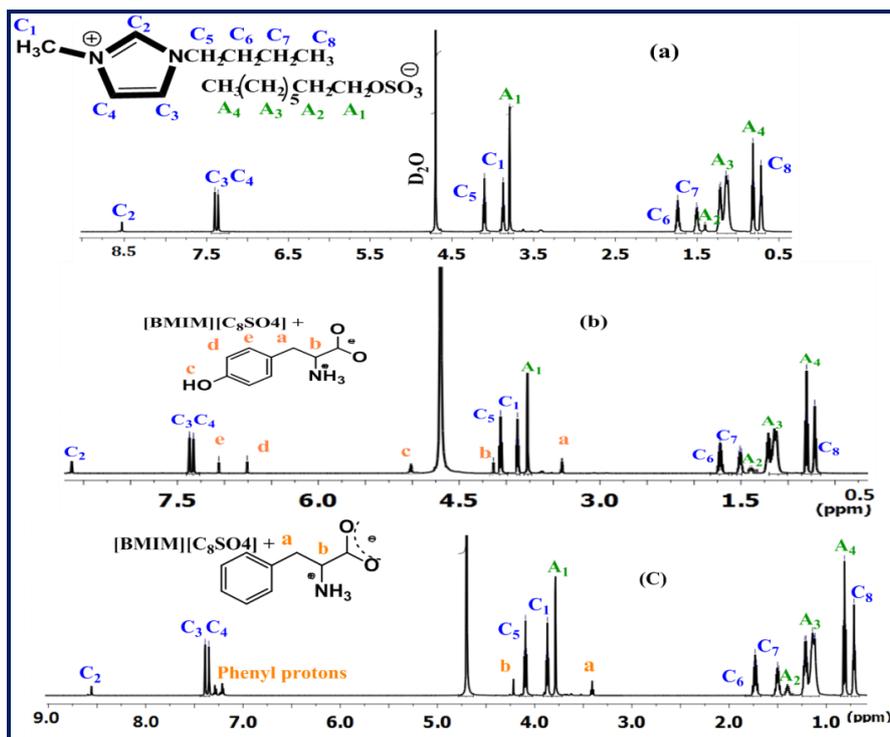


Figure 9. <sup>1</sup>H NMR spectra of (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>], (b) ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-tyr) system and (c) ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-phe) system in D<sub>2</sub>O at 298.15K

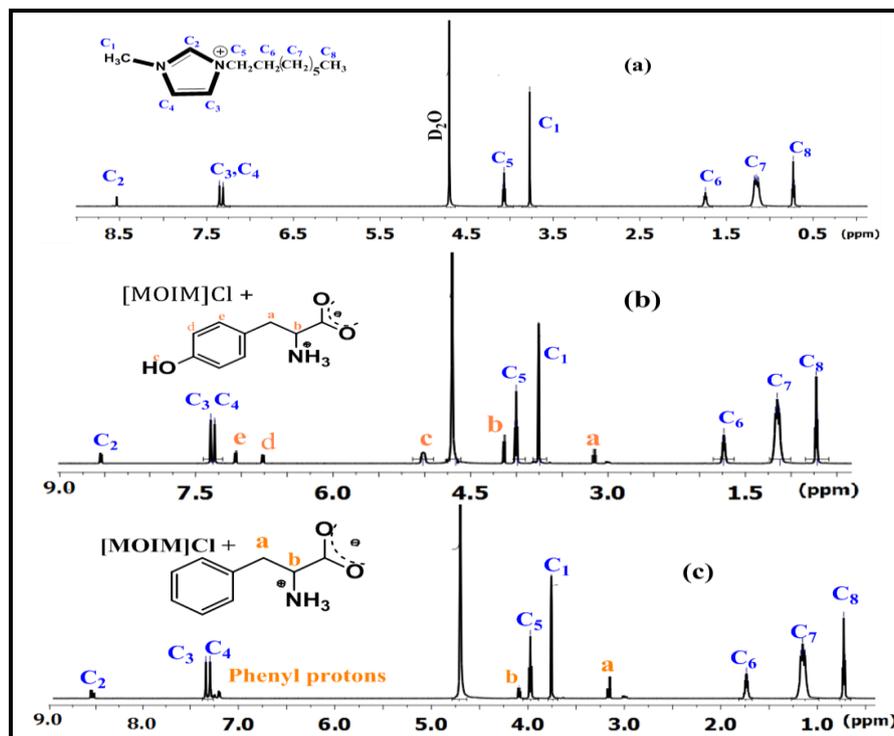
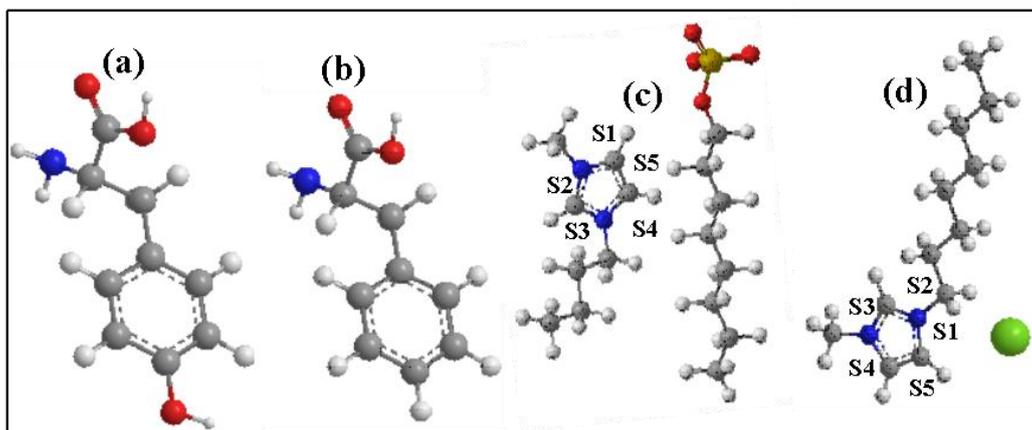
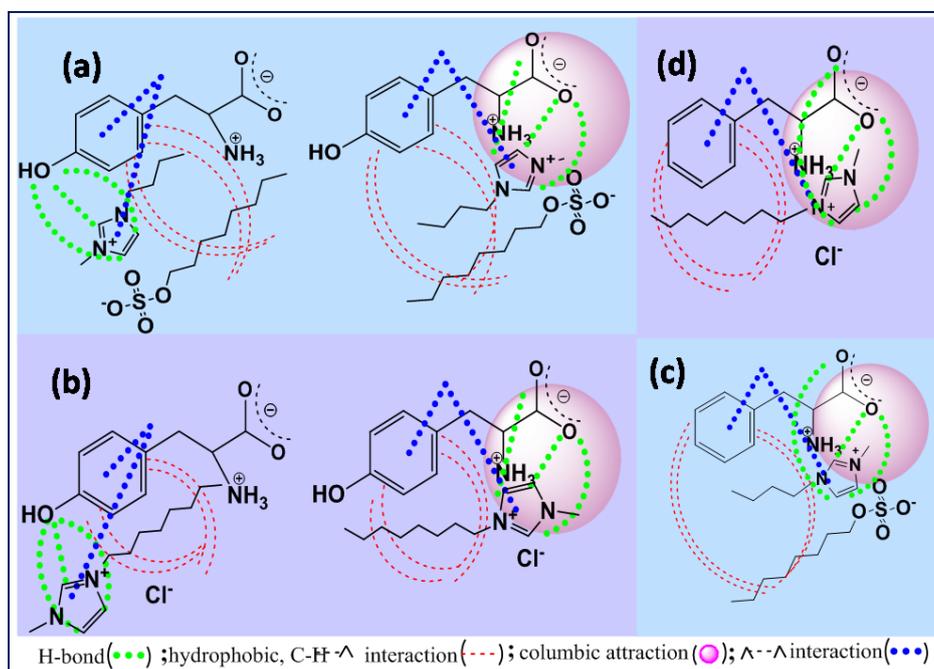


Figure 10. <sup>1</sup>H NMR spectra of (a) [MOIM]Cl, (b) ([MOIM]Cl + L-tyr) system and (c) ([MOIM]Cl + L-phe) system in D<sub>2</sub>O at 298.15K



**Scheme 1.** Ball & stick representation of (a) L-tyrosine, (b) L-phenylalanine, (c) 1-butyl-3-methylimidazoliumoctylsulphate [BMIM][C<sub>8</sub>SO<sub>4</sub>] and (d) 1-methyl-3-octylimidazolium chloride [MOIM]Cl respectively



**Scheme 2.** Schematic representation of interactions between (a) ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-tyr) (b) ([MOIM]Cl + L-tyr) (c) ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-phe) and (d) ([MOIM]Cl + L-phe) systems in aqueous solution respectively

## **CHAPTER –V**

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# **EXPLORATION OF SOLVATION CONSEQUENCES OF SOME BIOLOGICALLY POTENT MOLECULES IN AQUEOUS IONIC LIQUID SOLUTIONS WITH THE MANIFESTATION OF MOLECULAR INTERACTIONS**

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**Absrtact:** L-Aspartic and L-Glutamic acid (two solute molecules) interact with an ionic liquid (Benzyl tri-methyl ammonium chloride) in aqueous medium. The interactions have been explained on the basis of some parameters (apparent molar volume, viscosity B-coefficient, molar refraction, specific conductance) at different temperatures and different concentrations from density, viscosity, refractive index, conductance measurements, respectively. Using Masson equation, the experimental slopes and the limiting apparent molar volumes are obtained which explain the solute-solute and solute-solvent interactions. Viscosity parameters, A and B obtained from Jones-Doles equation explained the solute-solute and solute-solvent interactions in the solution. Molar refraction has been calculated from the Lorentz-Lorenz equation. The specific conductance also explained the interaction properties.

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**Keywords:** L-Aspartic acid; L-Glutamic acid; Benzyl tri-methyl ammonium chloride; solute-solvent interaction; solute-solute interaction; Amino acids; Ionic

### **V.1 INTRODUCTION**

Thermodynamic properties of amino acids in aqueous electrolyte solutions can provide valuable information regarding the conformation stability of proteins in these solutions, their solubility, denaturation, dissociation into subunits, the activity of enzymes, separation and purification, solute-solvent and solute-solute interactions <sup>[1-4]</sup>. In fact, to optimize and control the extraction of biomolecules by ionic liquids (ILs) from aqueous media, knowledge of their thermophysical and thermodynamic properties is required. There are extensive volumetric and viscometric studies of amino acids in aqueous electrolyte solutions <sup>[5-7]</sup>. Consequently, the study of the volumetric properties of amino acids in aqueous ionic liquid solutions will be very useful for obtaining information about various types of interactions occurring in these solutions, which are mostly hydrophobic and electrostatic. Studying these interactions can provide important insight into the conformational stability and unfolding behavior of globular proteins. Thermodynamic properties of amino acids in aqueous solutions containing salts can provide valuable information about solute-solute and solute-solvent interactions. The aqueous solution

containing salts affect conformational properties of amino acids and cause denaturation of proteins which is an important biological phenomenon. Therefore, keeping the importance and applicability in view, the systematic thermodynamic investigation of mixtures containing IL and amino acids is undertaken to understand the solvation behaviour of these biomolecules [8]. Study of transport properties of electrolytes in aqueous media is extremely important to obtain information regarding the solvation and association behaviour of ions in solutions. The electrical conductivity of electrolytes in solvents mainly depends on the concentration of the electrolyte and the viscosity of the solvent. The application of the salt is well understood from the study of ionic solvation. Volumetric, viscometric, refractometric and conductometric techniques render an insight into the molecular interactions that are prevailing in solution and helps in the better understanding of the behaviour of the salt in water.

An ionic liquid (IL) is a salt in the liquid state of melting point below some arbitrary temperature such as 373 K. They have specific intrinsic properties, such as negligible vapour pressure, high thermal stability, large liquid range, ability of dissolving a variety of chemicals, large electrochemical window. They are used as “designer solvents” and “green” replacements for volatile organic solvents used in reactions involving inorganic and biocatalytic reactions, etc. They are also utilized as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells). They are used in analytical equipment. They make up electrolytes in lithium-ion batteries, super capacitors and metal plating baths [9-14]. The chemicals used in this study find wide industrial usage. Benzyl tri-methyl ammonium chloride or BTAC is soluble in water and has lyophilic and hydrophilic group. It can be used as phase transfer catalyst in many biphasic organic transitions used in the agrochemicals, polymer and pharmaceutical industries. BTAC can also be used as a corrosion inhibitor in oilfield. L-Aspartic acid and L-Glutamic acid are both water soluble polar aliphatic amino acids having very weak dipole-ion interaction. L-Aspartic acid is an  $\alpha$ -amino acid that is used in the biosynthesis of proteins. Aspartic acid is commonly used to reduce feelings of tiredness, improve athletic performance, and increase the size and strength of muscles. Glutamic acid is an  $\alpha$ -amino acid that is used by almost all living beings in the biosynthesis of proteins. It is also an excitatory neurotransmitter in the vertebrate nervous system.

In the modern technology, the application of the salt is well understood from the study of ionic solvation or ion association. Ionic association of electrolytes in solution depends on the mode of solvation of its ions that in turn depends on the nature of the solvent/solvent mixtures [15-18]. The association and solvation behaviour of ions in solution is obtained from the conductance measurement. Moreover, solvent properties as viscosity and the relative permittivity help in determining the extent of ion association

and the solvent-solvent interactions. The volumetric, viscometric, refractometric and conductometric behaviour of solutes has been found to be very useful in elucidating the various interactions occurring in solutions.

In continuation of our investigation, the present work deals with the transport and thermodynamic properties of L-Aspartic acid and L-Glutamic acid in aqueous Benzyl tri-methyl ammonium chloride at 293K, 303K and 313K.

## **V.2. EXPERIMENTAL SECTION**

### **2.1. Source and purity of samples**

The studied IL, Benzyl tri-methyl ammonium chloride,  $C_{10}H_{16}ClN$  (M.W. 185.69 g/mole) and amino acids, L-Aspartic acid,  $C_4H_7NO_4$  (M.W. 133.11 g/mole) and L-Glutamic acid,  $C_5H_9NO_4$  (M.W. 147.13 g/mole) of puriss grade were purchased from Sigma Aldrich Germany, SRL India and TLC Japan, respectively and was used as purchased. The purity of mass of taken salts were  $\geq 0.99$ . The amino acids were dried in vacuum over blue silica gel for at least 72 h at room temperature. The other chemicals were used without further purification. Doubly distilled deionized water with a conductivity of approximately  $0.7 \mu S \cdot cm^{-1}$  was used for preparation of the solutions.

### **2.2. Apparatus and procedure**

The vibrating-tube Anton Paar Density-Meter (DMA 4500M) was used to measure the density ( $\rho$ ) with a precision of  $0.00001 \times 10^{-3} (kg \cdot m^{-3})$ . The double-distilled water and dry air was used to calibrate the density meter <sup>[19]</sup>. The temperature was kept constant automatically within range  $\pm 0.01$  K.

The viscosity was measured with the help of suspended Ubbelohde viscometer which was calibrated at room temperature (298K) using doubly distilled water. It was purified with methanol and using viscosity, density data from literature <sup>[20-21]</sup>. The viscometer was dried and cleaned perfectly through hot thermostat and then filled with experimental solution, vertically placed in a glass-walled thermostat (Bose-Panda instruments Pvt. Ltd.) This instrument was maintained to 0.01K. At thermal equilibrium the flow-time were recorded with the help of a stop watch with an accuracy of  $\pm 0.01$ s. The uncertainty for the measurement of viscosity was  $\pm 0.2 \times 10^{-3} mPa \cdot s$ .

Measurement of refractive index has been done with the help of a Digital Refractometer Mettler Toledo instrument. The accuracy for the refractive index measurement was  $\pm 0.0002$  units approximately. The refractometer was calibrated twice using distilled water for measurement of the refractive indices of experimental solutions. The calibration of instrument was made after

few seconds of each measurement <sup>[19]</sup>. The light source was light-emitting diode,  $\lambda=589.3$  nm. The temperature of the solution was maintained during the experiment in a Brookfield Digital TC-500 Thermostatic water bath.

The conductivity measurement was done by Mettler Toledo Instrument (In Lab730 probe cell). The specification of the cell has measurement of conductivity range (0.01-1000 mS/cm). The cell type 4 graphite having a cell constant  $0.56\text{ cm}^{-1}$ . The calibration of the cell has been done with 0.01 N (NaCl solution). The accuracy of the conductance measurement was  $\pm 0.5\%$ . The specific conductance of the experimental solution having concentration (0.0010, 0.0025, 0.0040, 0.0055, 0.0070, 0.0085) m was reported at 293K, 303K, 313K and was converted into molar conductance by the following equation,  $\Lambda = 1000 \kappa / c$  (where c is the molar concentration of the studied amino acid solutions in the ionic liquid.  $\kappa$  is the specific conductance of the specified solutions <sup>[22-23]</sup>).

The mixtures were prepared by mixing known volume of solutions in airtight-stoppered bottles. At first, we prepared 0.01m IL, 0.03m IL, 0.05m IL in 250ml water. Then there was preparation of 0.1m L-Aspartic acid and 0.1m L-Glutamic acid in the aqueous ionic liquid solutions. We prepared and used: 20ml, 0.01m IL + 0.01m amino acid in six sets (0.0010m, 0.0025m, 0.0040m, 0.0055m, 0.0070m, 0.0085m by dilution), 0.03m IL + 0.01m amino acid in six sets (0.0010m, 0.0025m, 0.0040m, 0.0055m, 0.0070m, 0.0085m by dilution), 0.05m IL + 0.01m amino acid in six sets (0.0010m, 0.0025m, 0.0040m, 0.0055m, 0.0070m, 0.0085m by dilution) at 293K, 303K, 313K for experimental purpose. Adequate precautions were taken to minimize evaporation losses during the actual measurements. Mass measurements for stock solutions were done on a Mettler AG-285 electronic balance with a precision of  $\pm 0.0003 \times 10^{-3}$  kg. The conversion of molarity into molality was accomplished using experimental density values. The uncertainty in molality of solution is estimated to be  $\pm 0.0001$  mol.  $\text{kg}^{-1}$ .

### **V.3. RESULTS AND DISCUSSION**

Experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of different molality (m) of aqueous ionic liquid (BTAC) solution at 293K, 303K and 313K are shown in **Table 1**. **Table 2** gives the experimental values of refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of different molality (m) of aqueous ionic liquid (BTAC) solution at 293K, 303K and 313K.

#### **V.3.1. Density**

In **Table 3** and **Table 4**, the density ( $\rho$ ) values at 0.01m, 0.03m and 0.05m concentrations of aqueous (BTAC) ionic liquid solutions have been reported at 293K, 303K and 313K for different concentrations of L-Aspartic acid and L-Glutamic amino acid solutions, respectively which have been obtained by dilution method.

**Table 5** and **Table 6** give the apparent molar volume ( $\Phi_v$ ) of L-Aspartic acid and L-Glutamic acid solution, respectively in 0.01m, 0.03m and 0.05m aqueous ionic liquid (BTAC) solution at different temperatures (293K, 303K, 313K). The apparent molar volumes ( $\Phi_v$ ) were determined from the solution densities using the following equation:

$$\Phi_v = M / \rho_0 - 1000 (\rho - \rho_0) / c \rho_0 \quad (1)$$

where,  $M$  is the molar mass of the solute,  $c$  is the molarity of the solution,  $\rho$  and  $\rho_0$  are the densities of the solution and solvent, respectively. It was observed that  $\Phi_v$  values are positive and decreases with increase in concentration of L-Aspartic acid and L-Glutamic acid solutions. However, it increases with increase in temperature at lower concentration of the amino acids but the trend changes as concentration of amino acid increases in solution. The  $\Phi_v$  values also increase with increase in concentration of the aqueous IL solutions at lower concentration of the amino acids but again the trend changes at higher concentration of the amino acid solutions. It was further observed that L-Glutamic acid have  $\Phi_v$  values higher than that of L-Aspartic acid.

For the analysis of the interactions occurring here, the knowledge of the limiting apparent molar volumes are important. The limiting apparent molar volumes ( $\Phi_v^0$ ) were calculated using a least-squares treatment to the plots of ( $\Phi_v$ ) versus  $\sqrt{c}$  using the following Masson equation [24]:

$$\Phi_v = \Phi_v^0 + S_v^* \sqrt{c} \quad (2)$$

where,  $\Phi_v^0$  is the limiting apparent molar volume at infinite dilution and  $S_v^*$  is the experimental slope. **Table 8(a)** and **Table 8(b)** gives the limiting apparent molar volumes ( $\Phi_v^0$ ) and the experimental slopes ( $S_v^*$ ) of L-Aspartic acid and L-Glutamic acid solutions, respectively in BTAC at different temperatures. In **Fig. 1(a)** and **Fig. 1(b)** we see the variation of  $\Phi_v^0$  values of L-Aspartic acid and L-Glutamic acid solutions, respectively at 0.01m, 0.03m and 0.05m of the IL at (293, 303 and 313) K. The  $\Phi_v^0$  values are positive and seem to increase with the increase in concentration of BTAC and also with the increase in temperature for both the amino acids. But  $S_v^*$  values are negative and decreases with the increase in concentration of the IL and with rise in temperature. Also it is observed that L-Glutamic acid have higher  $\Phi_v^0$  and  $S_v^*$  values than L-Aspartic acid at all conditions.

$\Phi_v^0$  values indicate the extent of solute-solvent interaction. A perusal of **Table 8(a)** and **Table 8(b)** reveals that the  $\Phi_v^0$  values are positive and is maximum for L-Glutamic acid in 0.05m aqueous ionic liquid solution at 313K indicating highest solute-solvent interaction here and minimum for L-Aspartic acid in 0.01m aqueous ionic liquid solution at 293K, indicating that the

solute-solvent interaction is the least here. This is probably due to the release of a number of the solvent molecules from loose solvation layers during the solute-solvent interactions [25]. Also the higher  $\Phi_v^0$  values of L-Glutamic acid indicates that it interacts more with BTAC than L-Aspartic acid under any conditions. On the contrary, the  $S_v^*$  indicates the extent of solute-solute interaction. The values of  $S_v^*$  show that the extent of solute-solute interaction is highest in L-Glutamic acid 0.01m IL solution at 293K and minimum in 0.05m IL solution at 313K. Here again the higher values of  $S_v^*$  in L-Glutamic acid indicates that it exhibits better interaction among itself than L-Aspartic acid molecules under any conditions. Possible reasons for this behavior could be the structural orientation of the larger alkyl group of L-Glutamic acid than L-Aspartic acid as depicted by their molecular structures in **Scheme 1**. A quantitative comparison of the magnitude of  $\Phi_v^0$  values shows that it is much greater in magnitude than  $S_v^*$  values for the solutions. This suggests that strong solute-solvent interactions dominate over the weak solute-solute interactions in all the solutions [26-27]. There is hydrophobic hydration, or the caging effect of water molecules [28] which reflects hydrophobic interactions in the amino acids that cause volume contractions. Similar linear correlations have been observed earlier for homologous series of amino acids in aqueous electrolytes [29].

Temperature dependency of the limiting apparent molar volume ( $\Phi_v^0$ ) were studied between the temperature range 293K to 313K and the results obtained were found to follow the following polynomial equation [30]:

$$\Phi_v^0 = a_0 + a_1T + a_2T^2 \quad (3)$$

where,  $a_0$ ,  $a_1$  and  $a_2$  are the empirical coefficients depending on the nature of solute and mass fraction (W) of co-solvent whereas T is the temperature in Kelvin scale. **Table 9** shows the empirical coefficient values ( $a_0$ ,  $a_1$  and  $a_2$ ) of L-Aspartic acid solution & L-Glutamic acid in different concentration of the IL (0.01m, 0.03m, 0.05m) at 293K, 303K, 313K.

First derivative of Equation (3) gives the values of limiting apparent molar expansibilities ( $\Phi_E^0$ ) which have been calculated for various temperatures and listed in **Table 10(a)** and **Table 10(b)** for L-Aspartic acid and L-Glutamic acid solutions, respectively.

$$\Phi_E^0 = (\delta\Phi_v^0 / \delta T)_P = a_1 + 2a_2T \quad (4)$$

Limiting apparent molar expansibilities ( $\Phi_E^0$ ) for all the systems are found positive except for 0.05m IL at 313K in both the amino acids signifying the absence of caging or packing effect in the other solutions except this one. The solute-solvent interaction studied so far is now at a state that, it may be structure-breaker or synergistic structure-maker interaction. In this connection, Hepler developed a way to examine the nature of the solute-solvent interaction

taking place in the solution phase<sup>[31]</sup>. According to Hepler, values of  $(\delta\Phi_E^0/\delta T)_P$  in the expression given below, determines whether, it is structure-breaker or structure-maker interaction<sup>[32]</sup>:

$$(\delta\Phi_E^0/\delta T)_P = (\delta^2\Phi_V^0/\delta T^2)_P = 2a_2 \quad (5)$$

Generally, positive or small negative values of  $(\delta\Phi_E^0/\delta T)_P$  strongly suggests structure-making rather than structure-breaking interaction. Here, the small negative values listed in **Table 10(a)** and **Table 10(b)** respectively for L-Aspartic acid and L-Glutamic acid solutions in IL (BTAC) at different temperatures confirms the mode of solute–solvent interaction is structure-making and as supported earlier the structure-making effect is strongest in 0.05m aqueous IL solution at 313K for both the amino acids and the effect being greater in L-Glutamic acid solutions with highest packing or caging effect.

### V.3.2. Viscosity

In aqueous electrolytic solutions the extent of ionic hydration and structural interactions<sup>[33-35]</sup> within the ionic hydration cospheres<sup>[36]</sup> can be explored easily by studying viscosity coefficient with varying concentration and temperature of the aqueous solution. Experimental values of viscosity ( $\eta$ ) of different molality of aqueous ionic liquid (BTAC) solution at 293K, 303K and 313K have been given in **Table 1**. Viscosity ( $\eta$ ) values of L-Aspartic acid and L-Glutamic acid in aqueous (BTAC) ionic liquid, IL solution at 293K, 303K and 313K are given in **Table 3** and **Table 4**, respectively. The results show that the viscosity of the solutions increases with increasing molality of IL. This is due to the fact that upon increasing the molality of the ionic liquid, the number of collisions among the molecules also increases, resulting in a loss of kinetic energy. Therefore, the molecules tend to stick together with increasing viscosity.

Viscosity data so obtained were analysed with the help of Jones-Dole equation<sup>[37]</sup>.

$$\eta_r = \eta/\eta^0 = 1 + A\sqrt{c} + Bc \quad (6)$$

where,  $\eta$  and  $\eta^0$  are viscosities of solution and solvent respectively,  $c$  is the concentration of solution in molality. In **Table 5** and **Table 6**, respectively  $(\eta/\eta^0 - 1) / \sqrt{m}$  values of L-Aspartic acid and L-Glutamic acid solutions have been shown in 0.01m, 0.03m and 0.05m in aqueous IL (BTAC) solution at different temperatures (293K, 303K, 313K).

The  $(\eta/\eta^0 - 1) / \sqrt{m}$  values are positive and seem to increase with increase in concentration of the amino acid in solutions and with increase in temperature from 293K to 313K. However, the  $(\eta/\eta^0 - 1) / \sqrt{m}$  values are found to decrease and then increase as we increase the concentration of aqueous IL solution from 0.01m to 0.03m to 0.05m for 293K and 313K but trend changes for 303K. Same trend is noted for both L-Aspartic acid and L-Glutamic acid but the  $(\eta$

$(\eta^0 - 1) / \sqrt{m}$  values are greater in L-Glutamic acid under all conditions. This is possibly due to stronger hydrophobic–hydrophobic interactions for longer alkyl chains of L-Glutamic acid.

Rearrangement of the above Equation (6) gives following:

$$(\eta_r - 1) / \sqrt{c} = A + B\sqrt{c} \quad (7)$$

Here, viscosity A-coefficient is a constant, also known as Falkenhagen coefficient<sup>[25]</sup>, stands for long-range coulombic forces, so represents the solute-solute interaction in solution, while B-coefficient is an adjustable parameter, which is the measure of the effective hydrodynamic volume, reflects the solute-solvent interaction. Magnitude of viscosity B-coefficient depends on the shape, size and partial molar entropies of the ions. According to the Jones-Dole equation from the plots of  $(\eta_r - 1) / \sqrt{c}$  vs  $\sqrt{c}$ , the viscosity A, B-coefficients obtained by linear least-square analysis, are reported in **Table 8(a)** and **Table 8(b)** for L-Aspartic acid and L-Glutamic acid solutions at (293, 303 and 313)K, respectively. **Fig. 2(a)** and **Fig. 2(b)** shows the variation of B values of L-Aspartic acid and L-Glutamic acid, respectively against 0.01m IL, 0.03m IL and 0.05m IL solutions at different temperatures.

The viscosity B-coefficient is an empirical constant which depends on size and shape effects as well as structural effects induced by solute+solvent interactions<sup>[7]</sup>. In all cases the viscosity B-coefficients are larger in the aqueous ionic liquid solutions which indicates promotion of the liquid structure in the presence of an ionic liquid, thus supporting the conclusions obtained from volumetric properties. From **Table 8(a)** and **Table 8(b)** it is evident that the values of the B-coefficient are positive, thereby suggesting the presence of strong solute-solvent interactions, that strengthened with an increase in the solvent viscosity value, in accordance with the results obtained from  $\Phi_v^0$  values explained earlier. The values of the A-coefficient are found to very small as compared to B-coefficients. These results indicate the presence of very weak solute–solute interactions. These results are in outstanding agreement with those obtained from  $S_v^*$  values. The extent of solute–solvent interaction obtained from the B-coefficient occurs into the local vicinity of the solute molecules in the solutions. The higher B-coefficient values for higher viscosity values is due to the solvated solute molecules associated by the solvent molecules all around because of the formation of associated molecule by solute-solvent interactions<sup>[38]</sup>. Further, these types of interactions are strengthened with rise in temperatures. It shows that the solute-solvent interaction increases with increase in temperature and the concentration of the IL solutions with more interaction between L-Glutamic acid and aqueous BTAC solutions. The replacement of water molecules by more co-solvent molecules from the solvation sphere brings solute and co-solvent closer thereby increasing viscosity B-coefficients and accounts for the higher solute-solvent interaction. The overall viscometric studies show that, viscosity B-

coefficients are positive and greater than viscosity A-coefficient, suggesting solute–solvent interaction predominant over the solute-solute interaction.

Extensive study of the viscosity B-coefficient such that, its first derivative over temperature is an upgradation of viscosity B-coefficient in predicting the nature of solute–solvent interaction as structure-maker or structure-breaker. The value of  $dB/dT$  is a measure of activation energy required for the viscous flow in solution. This is the reason, why the measure of  $dB/dT$  is indicative towards the structure making or structure breaking ability than sign or magnitude of the B-coefficient [39-41]. Viscosity B-coefficients of L-Aspartic acid and L-Glutamic acid solutions along with  $dB/dT$  values in different concentrations of IL at (293, 303 and 313) K are given in **Table 11(a)** and **Table 11(b)**, respectively. The small positive value of  $dB/dT$  signifies structure-making (kosmotropic) whereas the larger positive value identifies it as structure-breaking (chaotropic). Here the small positive  $dB/dT$  values indicate the amino acids to behave as structure-maker in the aqueous ionic liquid solution.

### V.3.3. Refractive Index

Optical data of refractive index of the studied systems has provided interesting information allied to molecular interactions, structure of solutions in these assay. The refractive index of mixing can be interconnected by the application of a composition dependent polynomial equation and molar refraction,  $R_M$  in solution.

The molar refraction  $R_M$  can be evaluated from the Lorentz–Lorenz relation [42]:

$$R_M = \{(n_D^2 - 1) / (n_D^2 + 2)\}(M/\rho) \quad (8)$$

where  $R_M$ ,  $n_D$ ,  $M$  and  $\rho$  are the molar refraction, the refractive index, the molar mass and the density of the solution, respectively. The refractive index of a substance is defined as the ratio  $c/c_0$ , where  $c$  is the speed of light in the medium and  $c_0$  is the speed of light in vacuum. Stated more simply, the refractive index of a compound describes its ability to refract light as it moves from one medium to another and thus, the higher the refractive index of a compound, the more the light is refracted [43]. As stated by Deetlefs et al. the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser [44]. Generally, refractive index of a system is the ability to refract light and hence it can simultaneously measure the compactness of that system.

**Table 1** and **Table 2** gives the experimental values of molar refraction ( $R_M$ ) and refractive index ( $n_D$ ) of different molality of aqueous IL (BTAC) solution at 293K, 303K and

313K, respectively. **Table 3** and **Table 4** show the molar refraction ( $R_M$ ) variation of L-Aspartic acid and L-Glutamic acid, respectively in aqueous (BTAC) ionic liquid, IL solution at 293K, 303K and 313K. **Table 7(a)** and **Table 7(b)** displays the refractive index ( $n_D$ ) of L-Aspartic acid and L-Glutamic acid solutions in aqueous IL (BTAC) solution at 293K, 303K and 313K, respectively.

Hence, it is observed that the refractive index ( $n_D$ ) decrease but the molar refraction ( $R_M$ ) increases with increase in temperature. However, both the parameters show an increase with increase in concentration of the amino acids and IL solutions. Again L-Glutamic acid have higher values than L-Aspartic acid. This is in good agreement with the volumetric and viscometric results attained here. The higher refractive index shows that the molecules are more tightly packed in the solution.

The limiting molar refraction, ( $R_M^0$ ) listed in **Table 8(a)** and **Table 8(b)** can be calculated using the following equation-

$$R_M = R_M^0 + R_S \sqrt{m} \quad (9)$$

where, 'm' is the molality of solution and  $R_M^0$  is the limiting molar refraction that signifies solute–solvent interaction. So, this measurement operates as an expensive tool for studying the molecular interaction in solution. Gradual increase in the values of  $R_M^0$  as shown in **Fig. 3(a)** and **Fig. 3(b)** with rise in mass fraction of co-solvent and temperature also signifies that solute–solvent interaction predominant over solute-solute interactions.

#### **V.3.4. Electrical Conductance**

Experimental values of specific conductance ( $\kappa$ ) of different molality of aqueous IL (BTAC) solution at 293K, 303K and 313K are given in **Table 2**. **Table 7(a)** and **Table 7(b)** show the specific conductance ( $\kappa$ ) of L-Aspartic acid and L-Glutamic acid in aqueous IL (BTAC) solution at 293K, 303K and 313K, respectively. **Table 12** shows the molar conductance ( $\Lambda$ ) of L-Aspartic acid and L-Glutamic acid solution in (0.01m, 0.03m, 0.05m) IL at 293K, 303K and 313K. **Fig. 4(a)** and **Fig. 4(b)** gives the variation of molar conductance ( $\Lambda$ ) with different concentrations of L-Aspartic acid in aqueous (0.01m, 0.03m, 0.05m) BTAC (IL) solution at 293K, 303K, 313K. The specific conductance ( $\kappa$ ) values increase with increase in temperature and increase in concentration of aqueous IL solution and the amino acid solutions but the molar conductance ( $\Lambda$ ) values decrease with the increase in concentration of amino acid solutions. However, the values are lesser in L-Glutamic acid solutions under all conditions.

The molar conductance ( $\Lambda$ ) has been obtained from the specific conductance ( $\kappa$ ) value using the following equation [38]:

$$\Lambda = (1000 \kappa) / C \quad (10)$$

Linear conductivity curves ( $\Lambda$  vs.  $C$ ) were obtained for the amino acids in IL solutions and extrapolation of  $\sqrt{C} = 0$  was used to evaluate the limiting molar conductance for the IL. The amino acids have terminal carboxylic (-COOH) group on both ends. IL has benzyl trimethyl ammonium cation and chloride anion. The terminal  $-\text{COO}^-$  functional group of the amino acids interact with the  $\text{N}^+$  centre of benzyl trimethyl ammonium ring through ion-dipole interaction. The molecular structure of the amino acids, L-Aspartic acid and L-Glutamic acid, and the ionic liquid, Benzyl tri-methyl ammonium chloride shown in **Scheme 1** gives an overview.

Another contributing factor in the amino acids is the carboxylic (-O-) atom. The lone pair donating tendency of carboxylic oxygen increases with the increase in +I effect of alkyl group of the studied amino acids. Thus +I effect in L-Glutamic acid is greater than in L-Aspartic acid. Hence, the interaction is more prominent in L-Glutamic acid due to the presence of more lone pair availability of oxygen atom, making the interaction strong with IL. So the free ions are more available for L-Aspartic acid giving higher conductance values than L-Glutamic acid.

#### **V.4. CONCLUSIONS**

Density, viscosity, refractive index and conductance measurements provide the information about ion-dipole interaction and show that the solute-solvent interaction between BTAC ionic liquid and L-Aspartic acid and L-Glutamic amino acid systems is higher than the solute-solute interaction. This is resulted by hydrophobic interactions which lead to volume contraction. The physico-chemical methodologies, describes the mode of interaction in solution. Calculation of limiting apparent molar volume, limiting molar refraction, viscosity B-coefficient and molar conductance makes it possible to identify the interaction as predominant solute-solvent interaction and indicate the predominance of solute-solvent interaction than the solute-solute interaction. The values of  $(\delta\Phi_E^0/\delta T)_P$  and  $(dB/dT)$  have been calculated to provide the information that the solute-solvent interaction is structure-making. The extent of solvation is highest in L-Glutamic acid at 0.05m 313K and lowest in L-Aspartic acid at 0.01m 293K. The derived parameters obtained by analyzing various equations supplemented with experimental data sustain the same finale as discussed and explained above.

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## TABLES

**Table 1.** Experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of different molality (m) of aqueous IL (BTAC) solution at 293K, 303K and 313K

| Conc. of Aq. IL (BTAC) soln. in molality, m (mol.kg <sup>-1</sup> ) | $\rho \times 10^{-3}(\text{kg.m}^{-3})$ |             |             | $\eta(\text{mPa.s})$ |             |             | $R_M$       |             |             |
|---|---|-------------|-------------|----------------------|-------------|-------------|-------------|-------------|-------------|
|   | <u>293K</u>                             | <u>303K</u> | <u>313K</u> | <u>293K</u>          | <u>303K</u> | <u>313K</u> | <u>293K</u> | <u>303K</u> | <u>313K</u> |
| 0.01  | .99840                                  | .99584      | .99239      | 1.064                | 0.818       | 0.696       | 27.3547     | 27.3800     | 27.4676     |
| 0.03  | .99872                                  | .99614      | .99270      | 1.231                | 1.010       | 0.892       | 27.3683     | 27.4317     | 27.5117     |
| 0.05  | .99912                                  | .99652      | .99306      | 1.266                | 1.085       | 0.970       | 27.4246     | 27.4737     | 27.5544     |

**Table 2.** Experimental values of refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of different molality (m) of aqueous IL (BTAC) solution at 293K, 303K and 313K

| Conc. of Aq. IL (BTAC) soln. in molality, m (mol.kg <sup>-1</sup> ) | $n_D$       |             |             | $\kappa$ (mS/cm) |             |             |
|---|-------------|-------------|-------------|------------------|-------------|-------------|
|   | <u>293K</u> | <u>303K</u> | <u>313K</u> | <u>293K</u>      | <u>303K</u> | <u>313K</u> |
| 0.01  | 1.3321      | 1.3315      | 1.3313      | 0.940            | 1.047       | 1.073       |
| 0.03  | 1.3324      | 1.3322      | 1.3320      | 2.710            | 2.860       | 2.970       |
| 0.05  | 1.3332      | 1.3330      | 1.3327      | 4.140            | 5.200       | 5.390       |

**Table 3.** Density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of L-Aspartic acid in aqueous (BTAC) ionic liquid solutions at 293K, 303K and 313K

| Conc. of L-Aspartic acid soln. in molality, m (mol.kg <sup>-1</sup> ) | $\rho \times 10^{-3}$ (kg.m <sup>-3</sup> ) |         |         | $\eta$ (mPa.s) |       |       | $R_M$   |         |         |
|---|---|---------|---------|----------------|-------|-------|---------|---------|---------|
|   | 293K  | 303K    | 313K    | 293K           | 303K  | 313K  | 293K    | 303K    | 313K    |
| 0.01m IL  |   |         |         |                |       |       |         |         |         |
| 0.0010  | 0.99843                                     | 0.99587 | 0.99242 | 1.071          | 0.825 | 0.704 | 27.3688 | 27.4146 | 27.4819 |
| 0.0025  | 0.99851                                     | 0.99597 | 0.99250 | 1.081          | 0.836 | 0.715 | 27.3890 | 27.4219 | 27.4947 |
| 0.0040  | 0.99857                                     | 0.99603 | 0.99260 | 1.090          | 0.846 | 0.727 | 27.4030 | 27.4272 | 27.5070 |
| 0.0055  | 0.99866                                     | 0.99613 | 0.99272 | 1.100          | 0.857 | 0.740 | 27.4148 | 27.4320 | 27.5112 |
| 0.0070  | 0.99876                                     | 0.99624 | 0.99285 | 1.109          | 0.867 | 0.751 | 27.4195 | 27.4362 | 27.5226 |
| 0.0085  | 0.99887                                     | 0.99638 | 0.99298 | 1.117          | 0.877 | 0.763 | 27.4315 | 27.4398 | 27.5265 |
| 0.03m IL  |   |         |         |                |       |       |         |         |         |
| 0.0010  | 0.99875                                     | 0.99617 | 0.99273 | 1.239          | 1.019 | 0.900 | 27.3899 | 27.4459 | 27.5184 |
| 0.0025  | 0.99885                                     | 0.99624 | 0.99281 | 1.249          | 1.032 | 0.915 | 27.4021 | 27.4535 | 27.5312 |
| 0.0040  | 0.99891                                     | 0.99633 | 0.99291 | 1.260          | 1.046 | 0.930 | 27.4079 | 27.4612 | 27.5435 |
| 0.0055  | 0.99901                                     | 0.99644 | 0.99303 | 1.272          | 1.060 | 0.945 | 27.4127 | 27.4668 | 27.5552 |
| 0.0070  | 0.99911                                     | 0.99656 | 0.99317 | 1.282          | 1.074 | 0.960 | 27.4174 | 27.4723 | 27.5588 |
| 0.0085  | 0.99924                                     | 0.99669 | 0.99332 | 1.292          | 1.088 | 0.975 | 27.4216 | 27.4765 | 27.5697 |
| 0.05m IL  |   |         |         |                |       |       |         |         |         |
| 0.0010  | 0.99915                                     | 0.99655 | 0.99309 | 1.273          | 1.093 | 0.979 | 27.4312 | 27.4878 | 27.5686 |
| 0.0025  | 0.99923                                     | 0.99662 | 0.99316 | 1.285          | 1.108 | 0.997 | 27.4365 | 27.4934 | 27.5741 |
| 0.0040  | 0.99931                                     | 0.99672 | 0.99326 | 1.297          | 1.123 | 1.015 | 27.4418 | 27.4981 | 27.5789 |
| 0.0055  | 0.99942                                     | 0.99684 | 0.99338 | 1.310          | 1.138 | 1.033 | 27.4462 | 27.5023 | 27.5831 |
| 0.0070  | 0.99954                                     | 0.99698 | 0.99351 | 1.322          | 1.153 | 1.051 | 27.4504 | 27.5059 | 27.5870 |
| 0.0085  | 0.99968                                     | 0.99709 | 0.99367 | 1.334          | 1.169 | 1.068 | 27.4540 | 27.5103 | 27.5900 |

**Table 4.** Density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of L-Glutamic acid in aqueous (BTAC) ionic liquid solutions at 293K, 303K and 313K

| Conc. of L-Glutamic acid soln. in molality (mol.kg <sup>-1</sup> ) | $\rho \times 10^{-3}$ (kg.m <sup>-3</sup> ) |             |             | $\eta$ (mPa.s) |             |             | $R_M$       |             |             |
|--|---|-------------|-------------|----------------|-------------|-------------|-------------|-------------|-------------|
|  | <u>293K</u>                                 | <u>303K</u> | <u>313K</u> | <u>293K</u>    | <u>303K</u> | <u>313K</u> | <u>293K</u> | <u>303K</u> | <u>313K</u> |
| 0.01m IL   |   |             |             |                |             |             |             |             |             |
| 0.0010   | 0.99844                                     | 0.99588     | 0.99243     | 1.073          | 0.827       | 0.706       | 30.2369     | 30.2897     | 30.3201     |
| 0.0025   | 0.99852                                     | 0.99596     | 0.99255     | 1.086          | 0.840       | 0.721       | 30.2593     | 30.3122     | 30.3498     |
| 0.0040   | 0.99861                                     | 0.99606     | 0.99262     | 1.099          | 0.853       | 0.735       | 30.2731     | 30.3340     | 30.3643     |
| 0.0055   | 0.99871                                     | 0.99617     | 0.99274     | 1.111          | 0.866       | 0.750       | 30.2865     | 30.3472     | 30.3855     |
| 0.0070   | 0.99881                                     | 0.99629     | 0.99287     | 1.124          | 0.880       | 0.765       | 30.3000     | 30.3601     | 30.3982     |
| 0.0085   | 0.99892                                     | 0.99642     | 0.99301     | 1.136          | 0.892       | 0.781       | 30.3132     | 30.3727     | 30.4105     |
| 0.03m IL   |   |             |             |                |             |             |             |             |             |
| 0.0010   | 0.99876                                     | 0.99618     | 0.99274     | 1.241          | 1.023       | 0.903       | 30.2437     | 30.2972     | 30.3356     |
| 0.0025   | 0.99889                                     | 0.99627     | 0.99286     | 1.256          | 1.041       | 0.923       | 30.2646     | 30.3276     | 30.3566     |
| 0.0040   | 0.99896                                     | 0.99637     | 0.99295     | 1.270          | 1.059       | 0.942       | 30.2790     | 30.3405     | 30.3791     |
| 0.0055   | 0.99908                                     | 0.99649     | 0.99310     | 1.285          | 1.078       | 0.960       | 30.3001     | 30.3540     | 30.3918     |
| 0.0070   | 0.99920                                     | 0.99662     | 0.99325     | 1.300          | 1.097       | 0.979       | 30.3130     | 30.3660     | 30.4038     |
| 0.0085   | 0.99930                                     | 0.99677     | 0.99334     | 1.313          | 1.117       | 0.998       | 30.3182     | 30.3783     | 30.4155     |
| 0.05m IL   |   |             |             |                |             |             |             |             |             |
| 0.0010   | 0.99916                                     | 0.99656     | 0.99310     | 1.278          | 1.096       | 0.983       | 30.2564     | 30.3048     | 30.3433     |
| 0.0025   | 0.99924                                     | 0.99665     | 0.99323     | 1.294          | 1.118       | 1.007       | 30.2787     | 30.3360     | 30.3726     |
| 0.0040   | 0.99933                                     | 0.99676     | 0.99331     | 1.311          | 1.141       | 1.032       | 30.2925     | 30.3479     | 30.3868     |
| 0.0055   | 0.99944                                     | 0.99689     | 0.99345     | 1.329          | 1.162       | 1.055       | 30.3057     | 30.3605     | 30.4074     |
| 0.0070   | 0.99957                                     | 0.99703     | 0.99360     | 1.347          | 1.185       | 1.080       | 30.3186     | 30.3727     | 30.4195     |
| 0.0085   | 0.99971                                     | 0.99717     | 0.99377     | 1.364          | 1.209       | 1.109       | 30.3311     | 30.3850     | 30.4309     |

**Table 5.** Apparent molar volume, ( $\Phi_V$ ) and  $(\eta/\eta^0 - 1)/\sqrt{m}$  of L-Aspartic acid solution in 0.01m, 0.03m and 0.05m aqueous BTAC solution at different temperatures (293K, 303K, 313K)

| Conc. of L-Aspartic acid soln. in molality, m (mol.kg <sup>-1</sup> ) | $\Phi_V \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_V \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_V \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) |
|---|---|--|---|--|---|--|
|   |   |  |   |  |   |  |
| 0.01m IL  | <b>293K</b>   |  | <b>303K</b>   |  | <b>313K</b>   |  |
| 0.0010  | 103.2104  | 0.206  | 103.4017  | 0.270  | 103.6557  | 0.357  |
| 0.0025  | 93.5224   | 0.319  | 89.9481   | 0.437  | 89.4333   | 0.542  |
| 0.0040  | 90.6615   | 0.386  | 85.9802   | 0.540  | 81.4533   | 0.702  |
| 0.0055  | 86.0340   | 0.456  | 80.6564   | 0.642  | 75.4453   | 0.851  |
| 0.0070  | 81.6876   | 0.505  | 76.1683   | 0.715  | 69.2768   | 0.943  |
| 0.0085  | 77.9260   | 0.540  | 69.7073   | 0.781  | 64.5830   | 1.043  |
| 0.03m IL  | <b>293K</b>   |  | <b>303K</b>   |  | <b>313K</b>   |  |
| 0.0010  | 103.4883  | 0.202  | 103.9725  | 0.278  | 104.2297  | 0.280  |
| 0.0025  | 89.8144   | 0.290  | 93.2958   | 0.432  | 89.4194   | 0.512  |
| 0.0040  | 85.6325   | 0.372  | 85.9687   | 0.562  | 81.0517   | 0.671  |
| 0.0055  | 80.5762   | 0.447  | 78.8222   | 0.667  | 73.7893   | 0.799  |
| 0.0070  | 77.3832   | 0.494  | 73.2053   | 0.756  | 66.2024   | 0.909  |
| 0.0085  | 73.2205   | 0.537  | 68.5227   | 0.836  | 60.3699   | 1.008  |
| 0.05m IL  | <b>293K</b>   |  | <b>303K</b>   |  | <b>313K</b>   |  |
| 0.0010  | 103.7505  | 0.172  | 104.0310  | 0.231  | 104.4923  | 0.291  |
| 0.0025  | 90.1393   | 0.298  | 93.2756   | 0.420  | 93.4597   | 0.555  |
| 0.0040  | 85.9127   | 0.387  | 83.4487   | 0.551  | 83.9379   | 0.732  |
| 0.0055  | 78.6512   | 0.468  | 75.1641   | 0.657  | 75.4340   | 0.874  |
| 0.0070  | 73.1665   | 0.528  | 67.6419   | 0.748  | 69.2737   | 0.997  |
| 0.0085  | 67.8722   | 0.582  | 66.0784   | 0.838  | 62.2337   | 1.094  |

**Table 6.** Apparent molar volume, ( $\Phi_v$ ) and  $(\eta/\eta^0 - 1)/\sqrt{m}$  of L-Glutamic acid solution in 0.01m, 0.03m and 0.05m in aqueous (BTAC) solution at different temperatures (293K, 303K, 313K)

| Conc. of L-Glutamic acid soln. in molality, m (mol.kg <sup>-1</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) |
|---|---|--|---|--|---|--|
| 0.01m IL  | <b>293K</b>   |  | <b>303K</b>   |  | <b>313K</b>   |  |
| 0.0010  | 107.2332  | 0.265  | 107.4054  | 0.346  | 107.6381  | 0.451  |
| 0.0025  | 99.2768   | 0.413  | 99.4066   | 0.536  | 90.0886   | 0.717  |
| 0.0040  | 94.6775   | 0.520  | 92.2638   | 0.674  | 89.8522   | 0.833  |
| 0.0055  | 90.9240   | 0.595  | 87.3579   | 0.789  | 83.3127   | 1.045  |
| 0.0070  | 88.7094   | 0.672  | 85.9177   | 0.905  | 78.6931   | 1.184  |
| 0.0085  | 86.1094   | 0.733  | 79.0880   | 0.980  | 74.2348   | 1.324  |
| 0.03m IL  | <b>293K</b>   |  | <b>303K</b>   |  | <b>313K</b>   |  |
| 0.0010  | 107.2117  | 0.254  | 107.7843  | 0.402  | 107.6172  | 0.385  |
| 0.0025  | 93.8334   | 0.405  | 95.3694   | 0.612  | 90.6933   | 0.694  |
| 0.0040  | 92.1572   | 0.500  | 89.7329   | 0.766  | 87.3052   | 0.833  |
| 0.0055  | 87.3538   | 0.591  | 83.6384   | 0.907  | 81.7615   | 1.027  |
| 0.0070  | 84.2631   | 0.699  | 78.6561   | 1.029  | 72.7915   | 1.164  |
| 0.0085  | 80.1998   | 0.722  | 73.0749   | 1.148  | 67.0805   | 1.287  |
| 0.05m IL  | <b>293K</b>   |  | <b>303K</b>   |  | <b>313K</b>   |  |
| 0.0010  | 107.5815  | 0.296  | 107.7584  | 0.318  | 107.9944  | 0.418  |
| 0.0025  | 99.2207   | 0.441  | 95.9558   | 0.607  | 90.6812   | 0.762  |
| 0.0040  | 94.7233   | 0.560  | 87.4871   | 0.812  | 84.7603   | 1.007  |
| 0.0055  | 89.0525   | 0.670  | 80.1161   | 0.956  | 76.2246   | 1.180  |
| 0.0070  | 82.9417   | 0.762  | 74.3435   | 1.099  | 69.8954   | 1.355  |
| 0.0085  | 80.1718   | 0.838  | 69.6760   | 1.238  | 63.5114   | 1.550  |

**Table-7(a).** Refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of L-Aspartic acid in aqueous IL (BTAC) solution at 293K, 303K and 313K.

| Conc. of L-Aspartic acid<br>soln. in molality, m<br>(mol.kg <sup>-1</sup> ) | $n_D$       |             |             | $\kappa$ (mS/cm) |             |             |
|---|-------------|-------------|-------------|------------------|-------------|-------------|
|   | <u>293K</u> | <u>303K</u> | <u>313K</u> | <u>293K</u>      | <u>303K</u> | <u>313K</u> |
| 0.01m IL  |             |             |             |                  |             |             |
| 0.0010  | 1.3323      | 1.3320      | 1.3316      | 1.05             | 1.15        | 1.19        |
| 0.0025  | 1.3326      | 1.3321      | 1.3318      | 1.09             | 1.20        | 1.24        |
| 0.0040  | 1.3328      | 1.3322      | 1.3320      | 1.16             | 1.25        | 1.28        |
| 0.0055  | 1.3330      | 1.3323      | 1.3321      | 1.19             | 1.29        | 1.32        |
| 0.0070  | 1.3331      | 1.3324      | 1.3323      | 1.25             | 1.34        | 1.37        |
| 0.0085  | 1.3333      | 1.3326      | 1.3324      | 1.29             | 1.39        | 1.42        |
| 0.03m IL  |             |             |             |                  |             |             |
| 0.0010  | 1.3327      | 1.3325      | 1.3322      | 2.91             | 3.13        | 3.21        |
| 0.0025  | 1.3329      | 1.3327      | 1.3324      | 2.99             | 3.18        | 3.26        |
| 0.0040  | 1.3330      | 1.3329      | 1.3326      | 3.08             | 3.23        | 3.31        |
| 0.0055  | 1.3331      | 1.3330      | 1.3328      | 3.15             | 3.31        | 3.38        |
| 0.0070  | 1.3332      | 1.3331      | 1.3329      | 3.24             | 3.35        | 3.45        |
| 0.0085  | 1.3333      | 1.3332      | 1.3331      | 3.33             | 3.42        | 3.56        |
| 0.05m IL  |             |             |             |                  |             |             |
| 0.0010  | 1.3334      | 1.3332      | 1.3330      | 4.29             | 5.28        | 5.46        |
| 0.0025  | 1.3336      | 1.3333      | 1.3331      | 4.38             | 5.36        | 5.59        |
| 0.0040  | 1.3337      | 1.3335      | 1.3333      | 4.45             | 5.42        | 5.84        |
| 0.0055  | 1.3338      | 1.3336      | 1.3334      | 4.49             | 5.48        | 6.10        |
| 0.0070  | 1.3340      | 1.3338      | 1.3336      | 4.53             | 5.55        | 6.46        |
| 0.0085  | 1.3341      | 1.3339      | 1.3337      | 4.63             | 5.61        | 6.65        |

**Table-7(b).**viscosity ( $\eta$ ) and  $(\eta/\eta^0-1)/\sqrt{m}$  of L-Histidine in aqueous IL (BTBACl) solution at 298.15K, 303.15K and 308.15K.

| Conc. of L-Histidine soln. in molality, m (mol.kg <sup>-1</sup> ) | $\eta$ (mPa.s) |         |         | $(\eta/\eta^0-1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) |         |         |
|---|----------------|---------|---------|--|---------|---------|
|   | 298.15K        | 303.15K | 308.15K | 298.15K  | 303.15K | 308.15K |
| 0.001m IL   |                |         |         |  |         |         |
| 0.010040  | 0.993          | 0.911   | 0.866   | 0.122  | 0.133   | 0.140   |
| 0.025138  | 1.011          | 0.929   | 0.884   | 0.193  | 0.210   | 0.221   |
| 0.042820  | 1.030          | 0.948   | 0.903   | 0.241  | 0.271   | 0.284   |
| 0.0555472   | 1.045          | 0.965   | 0.923   | 0.277  | 0.311   | 0.343   |
| 0.070071  | 1.063          | 0.983   | 0.942   | 0.316  | 0.351   | 0.387   |
| 0.085988  | 1.083          | 1.002   | 0.961   | 0.355  | 0.390   | 0.427   |
| 0.003m IL   |                |         |         |  |         |         |
| 0.010039  | 1.026          | 0.943   | 0.874   | 0.128  | 0.139   | 0.139   |
| 0.025137  | 1.043          | 0.965   | 0.893   | 0.187  | 0.237   | 0.227   |
| 0.040281  | 1.062          | 0.986   | 0.912   | 0.241  | 0.300   | 0.289   |
| 0.0555470   | 1.080          | 1.004   | 0.932   | 0.281  | 0.338   | 0.345   |
| 0.070706  | 1.100          | 1.025   | 0.955   | 0.323  | 0.384   | 0.406   |
| 0.085986  | 1.120          | 1.048   | 0.978   | 0.360  | 0.432   | 0.459   |
| 0.005m IL   |                |         |         |  |         |         |
| 0.010040  | 1.042          | 0.951   | 0.898   | 0.136  | 0.161   | 0.146   |
| 0.025124  | 1.060          | 0.970   | 0.921   | 0.196  | 0.229   | 0.256   |
| 0.040279  | 1.080          | 0.994   | 0.945   | 0.252  | 0.309   | 0.337   |
| 0.055469  | 1.100          | 1.015   | 0.968   | 0.297  | 0.358   | 0.398   |
| 0.070704  | 1.121          | 1.040   | 0.992   | 0.340  | 0.418   | 0.454   |
| 0.085985  | 1.143          | 1.063   | 1.015   | 0.381  | 0.463   | 0.500   |

**Table 8(a).** Viscosity A, B-coefficients of L-Glutamine and L-Asparagine solution in different concentration of IL at 298.15K,303.15K, 308.15K

| Temperature(K) | B (kg <sup>1/2</sup> . mol <sup>-1/2</sup> ) | A (kg.mol <sup>-1</sup> ) | Temperature(K) | B (kg <sup>1/2</sup> . mol <sup>-1/2</sup> ) | A (kg. mol <sup>-1</sup> ) |
|----------------|--|---------------------------|----------------|--|----------------------------|
| 0.01m IL       |  |                           |                |  |                            |
| 298.15         | 2.2104                                       | 0.0003                    | 298.15         | 1.1866                                       | 0.0016                     |
| 303.15         | 2.3155                                       | -0.0008                   | 303.15         | 1.3232                                       | 0.0012                     |
| 308.15         | 2.54004                                      | -0.0150                   | 308.15         | 1.4985                                       | -0.0139                    |
| 0.03m IL       |  |                           |                |  |                            |
| 298.15         | 2.4001                                       | -0.0026                   | 298.15         | 1.2077                                       | 0.0009                     |
| 303.15         | 2.7347                                       | -0.012                    | 303.15         | 1.4727                                       | -0.003                     |
| 308.15         | 3.0271                                       | -0.0481                   | 308.15         | 1.6438                                       | -0.0329                    |
| 0.05m IL       |  |                           |                |  |                            |
| 298.15         | 2.6441                                       | -0.0092                   | 298.15         | 1.2755                                       | 0.0007                     |
| 303.15         | 3.253  | -0.0212                   | 303.15         | 1.5895                                       | -0.0092                    |
| 308.15         | 3.4996                                       | -0.0532                   | 308.15         | 1.8347                                       | -0.0360                    |

**Table 8(b).** Limiting apparent molar volumes ( $\Phi_V^0$ ), Limiting molar refraction ( $R_M^0$ ), experimental slopes ( $S_V^*$ ), viscosity A, B-coefficients of L-Glutamic acid solution in IL at different temperatures

| Temperature(K) | $\Phi_V^0 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> ) | $R_M^0$ | $S_V^* \times 10^6$ (m <sup>3</sup> . mol <sup>-3/2</sup> .kg <sup>1/2</sup> ) | B (kg <sup>1/2</sup> . mol <sup>-1/2</sup> ) | A (kg. mol <sup>-1</sup> ) |
|----------------|--|---------|--|--|----------------------------|
| 0.01m IL       |  |         |  |  |                            |
| 293            | 117.17   | 30.197  | -344.26  | 7.7232                                       | 0.0237                     |
| 303            | 121.57   | 30.245  | -450.23  | 7.8217                                       | 0.0073                     |
| 313            | 124.71   | 30.273  | -551.01  | 9.1001                                       | -0.0062                    |
| 0.03m IL       |  |         |  |  |                            |
| 293            | 119.47   | 30.201  | -429.65  | 10.602                                       | 0.0055                     |
| 303            | 124.65   | 30.258  | -555.52  | 12.331                                       | -0.0030                    |
| 313            | 128.15   | 30.292  | -654.62  | 15.045                                       | -0.1542                    |
| 0.05m IL       |  |         |  |  |                            |
| 293            | 122.55   | 30.217  | -459.38  | 14.278                                       | -0.0079                    |
| 303            | 128.09   | 30.268  | -640.65  | 14.745                                       | -0.0665                    |
| 313            | 131.15   | 30.298  | -734.15  | 18.372                                       | -0.1669                    |

**Table 9.** The empirical coefficient values ( $a_0$ ,  $a_1$  and  $a_2$ ) of L-Aspartic acid solution & L-Glutamic acid in different concentration of the IL (0.01, 0.03m, 0.05m) at 293K, 303K and 313K

| Conc. of aq. IL soln. in molality, m (mol.kg <sup>-1</sup> ) | $a_0 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $a_1 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-1</sup> ) | $a_2 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-2</sup> ) | $a_0 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> ) | $a_1 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-1</sup> ) | $a_2 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-2</sup> ) |
|--|--|---|---|---|---|---|
|  | L-Aspartic acid  |   |   | L-Glutamic acid   |   |   |
|  | 293K   | 303K  | 313K  | 293K  | 303K  | 313K  |
| 0.01   | -1890.7  | 12.636  | -0.0198   | -2420.5   | 16.025  | -0.0252   |
| 0.03   | -2982.8  | 19.643  | -0.0310   | -3223.1   | 21.230  | -0.0336   |
| 0.05   | -4071.0  | 27.062  | -0.0436   | -4686.2   | 30.918  | -0.0496   |

**Table 10(a).** Values of limiting molar expansibilities ( $\Phi_E^0$ ) for L-Aspartic acid solution in IL(BTAC) at different temperatures.

| Conc. of aq. IL soln. in molality, m (mol.kg <sup>-1</sup> ) | $\Phi_E^0 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-1</sup> ) |        |         | $(\delta\Phi_E^0/\delta T)_P \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-2</sup> ) |
|--|--|--------|---------|---|
|  | 293K   | 303K   | 313K    |   |
| 0.01   | 1.0332   | 0.6372 | 0.2412  | -0.0396   |
| 0.03   | 1.4770   | 0.8570 | 0.2370  | -0.0620   |
| 0.05   | 1.5124   | 0.6404 | -0.2316 | -0.0872   |

**Table 10(b).** Values of limiting molar expansibilities ( $\Phi_E^0$ ) for L-Glutamic acid solution in IL(BTAC) at different temperatures

| Conc. of aq. IL soln. in molality, m (mol.kg <sup>-1</sup> ) | $\Phi_E^0 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-1</sup> ) |        |         | $(\delta\Phi_E^0/\delta T)_P \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-2</sup> ) |
|--|--|--------|---------|---|
|  | 293K   | 303K   | 313K    |   |
| 0.01   | 0.2578   | 0.7538 | 0.2498  | -0.0504   |
| 0.03   | 1.5404   | 0.8684 | 0.1964  | -0.0672   |
| 0.05   | 1.8524   | 0.8604 | -0.1316 | -0.0992   |

**Table 11(a).** Viscosity B-coefficients of L-Arginine along with dB/dT values in different concentrations of IL at (298.15, 303.15 and 308.15) K

| Temperature (K) | 0.01m IL |  | 0.03m IL |  | 0.05m IL |  | dB/dT  |
|-----------------|----------|--|----------|--|----------|--|--------|
|                 | B        |  | B        |  | B        |  |        |
| 293             | 2.2104   |  | 2.4001   |  | 2.6441   |  | 0.029  |
| 303             | 2.3155   |  | 2.7347   |  | 3.253    |  | 0.0627 |
| 313             | 2.5004   |  | 3.0271   |  | 3.4996   |  | 0.0856 |

**Table 11(b).** Viscosity B-coefficients of L-Histidine along with dB/dT values in different concentrations of IL at (298.15, 303.15 and 308.15) K

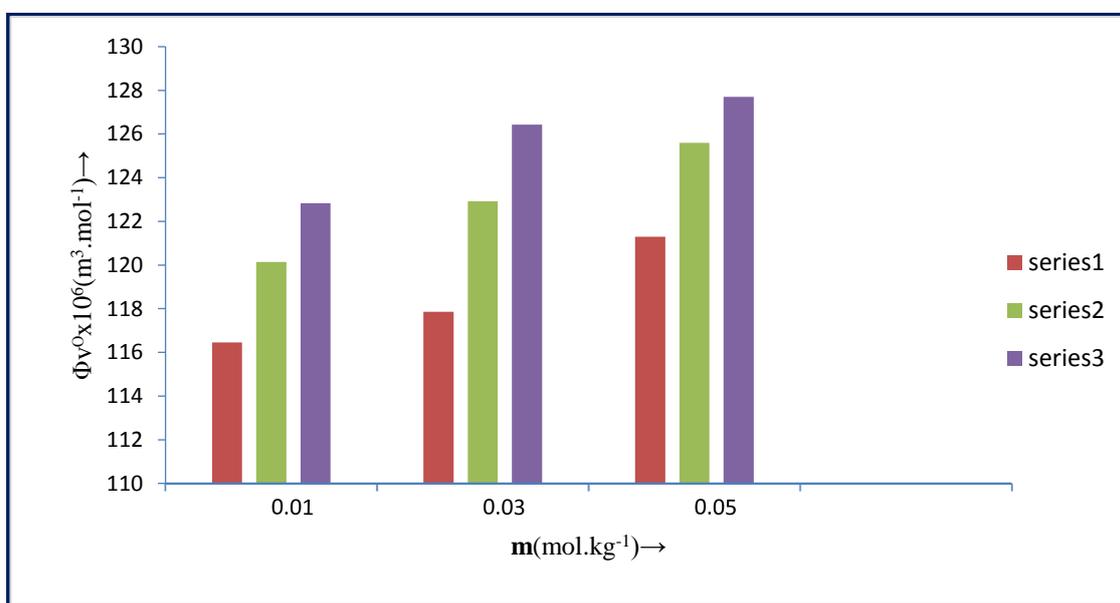
| Temperature (K) | 0.01m IL |  | 0.03m IL |  | 0.05m IL |  | dB/dT  |
|-----------------|----------|--|----------|--|----------|--|--------|
|                 | B        |  | B        |  | B        |  |        |
| 293             | 1.1866   |  | 1.2077   |  | 1.2755   |  | 0.0312 |
| 303             | 1.3233   |  | 1.4724   |  | 1.5895   |  | 0.0436 |
| 313             | 1.4985   |  | 1.6438   |  | 1.8347   |  | 0.0559 |

**Table-12.** Molar conductance ( $\Lambda$ ) of L-Aspartic acid and L-Glutamic acid solution in (0.01m, 0.03m, 0.05m) IL at 293K, 303K and 313K

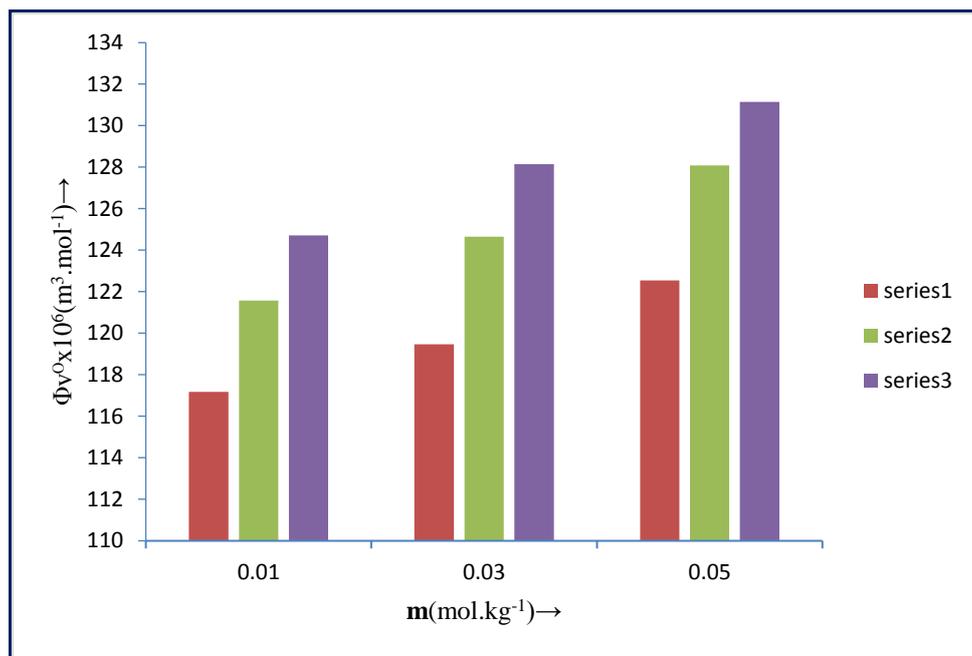
| Concentration of amino acid solutions in molality, m (mol.kg <sup>-1</sup> ) | Molar Conductance of L-Aspartic acid solution $\Lambda$ (S.cm <sup>2</sup> .mol <sup>-1</sup> ) |         |         | Molar conductance of L-Glutamic acid solution $\Lambda$ (S.cm <sup>2</sup> .mol <sup>-1</sup> ) |         |         |
|--|---|---------|---------|---|---------|---------|
|  | 293K  | 303K    | 313K    | 293K  | 303K    | 313K    |
|  | <b>0.01m IL</b>   |         |         |   |         |         |
| 0.0010   | 1053.00   | 1152.00 | 1195.00 | 1010.00   | 1090.00 | 1160.00 |
| 0.0025   | 437.60  | 480.40  | 495.20  | 416.00  | 448.00  | 488.00  |
| 0.0040   | 291.00  | 312.75  | 318.75  | 267.50  | 285.00  | 312.50  |
| 0.0055   | 218.00  | 227.45  | 240.00  | 198.18  | 210.90  | 230.90  |
| 0.0070   | 177.85  | 191.57  | 195.28  | 160.00  | 168.57  | 190.00  |
| 0.0085   | 151.64  | 163.17  | 167.06  | 134.117   | 142.35  | 161.18  |
| <b>0.03m IL</b>  |   |         |         |   |         |         |
| 0.0010   | 2910.00   | 3130.00 | 3210.00 | 2890.00   | 3060.00 | 3110.00 |

|                 |         |         |         |         |         |         |
|-----------------|---------|---------|---------|---------|---------|---------|
| 0.0025          | 1198.80 | 1272.00 | 1304.00 | 1180.0  | 1236.00 | 1260.00 |
| 0.0040          | 770.50  | 810.00  | 827.50  | 752.50  | 780.00  | 807.50  |
| 0.0055          | 573.09  | 610.81  | 614.54  | 558.18  | 572.72  | 601.82  |
| 0.0070          | 462.88  | 478.57  | 492.85  | 447.14  | 454.29  | 485.65  |
| 0.0085          | 391.76  | 402.35  | 411.76  | 375.29  | 378.82  | 409.41  |
| <b>0.05m IL</b> |         |         |         |         |         |         |
| 0.0010          | 4290.00 | 5280.00 | 5460.00 | 4270.00 | 5170.00 | 5350.00 |
| 0.0025          | 1752.00 | 2144.00 | 2236.00 | 1760.00 | 2080.00 | 2204.00 |
| 0.0040          | 1112.50 | 1352.00 | 1460.00 | 1092.50 | 1307.50 | 1435.00 |
| 0.0055          | 816.36  | 996.36  | 1109.09 | 800.00  | 954.54  | 1087.27 |
| 0.0070          | 651.42  | 792.88  | 922.88  | 637.14  | 752.85  | 902.85  |
| 0.0085          | 544.70  | 660.00  | 782.35  | 528.23  | 623.53  | 757.64  |

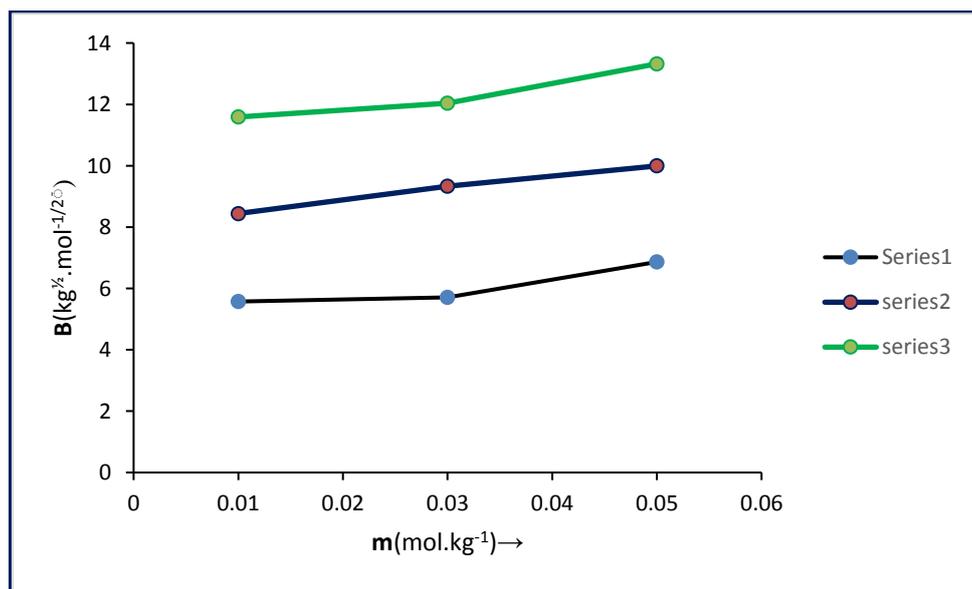
## FIGURES



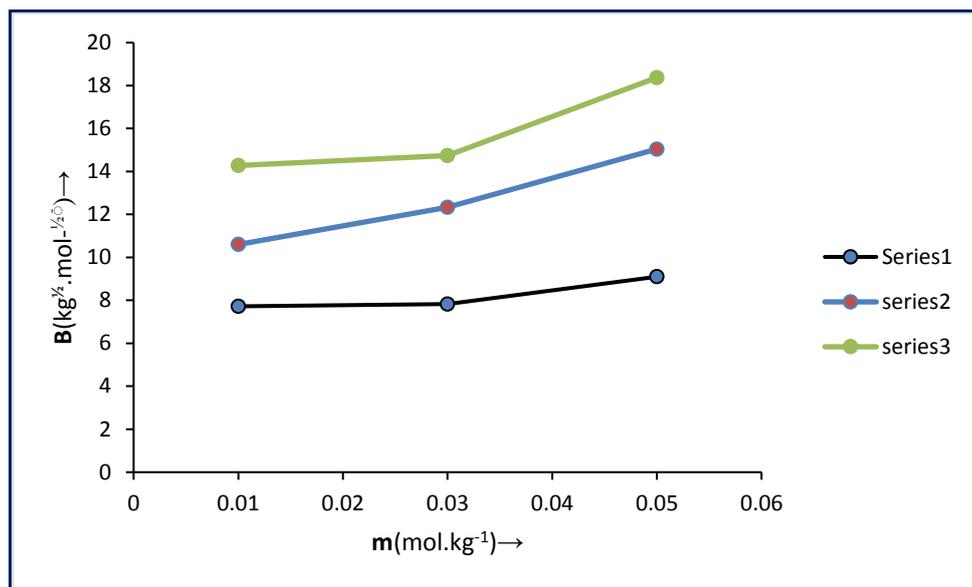
**Figure 1(a)** Variation of limiting apparent molar volume ( $\Phi_v^0$ ) of L-Aspartic acid solution at 0.01m, 0.03m and 0.05m of the aqueous IL solutions at 293K(Series1), 303K(Series2) and 313K(Series3)



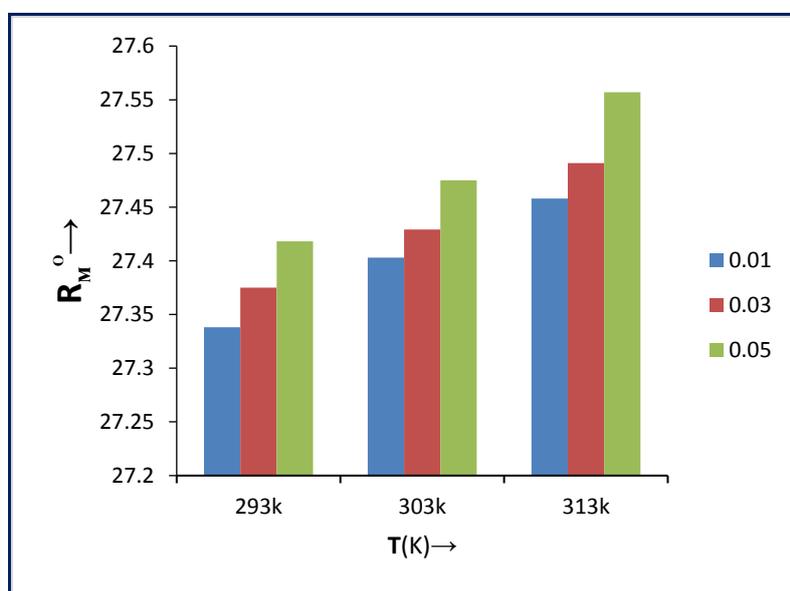
**Figure 1(b)** Variation of limiting apparent molar volume ( $\Phi_v^0$ ) of L-Glutamic acid solution at 0.01m, 0.03m and 0.05m of the aqueous IL solutions at 293K(Series1), 303K(Series2) and 313K(Series3)



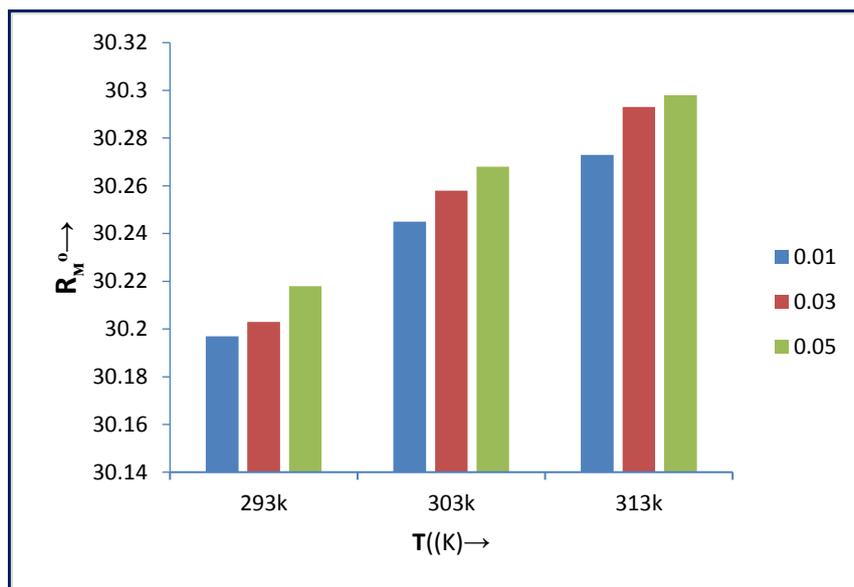
**Figure 2(a)** Variation of B values of L-Aspartic acid against 0.01m IL, 0.03m IL and 0.05m IL solutions at 293K(Series1), 303K(Series2) and 313K(Series3)



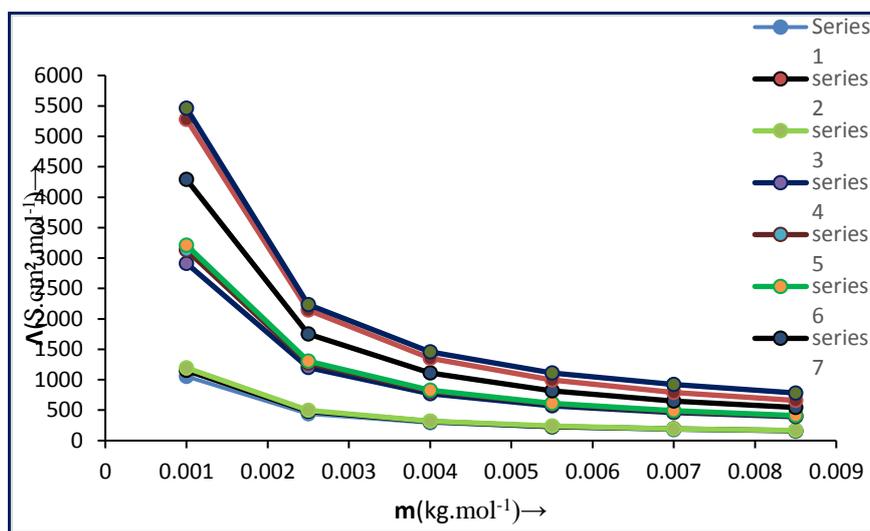
**Figure 2(b).** Variation of B values of L-Glutamic acid against 0.01m IL, 0.03m IL and 0.05m IL solutions at 293K(Series1), 303K(Series2) and 313K(Series3)



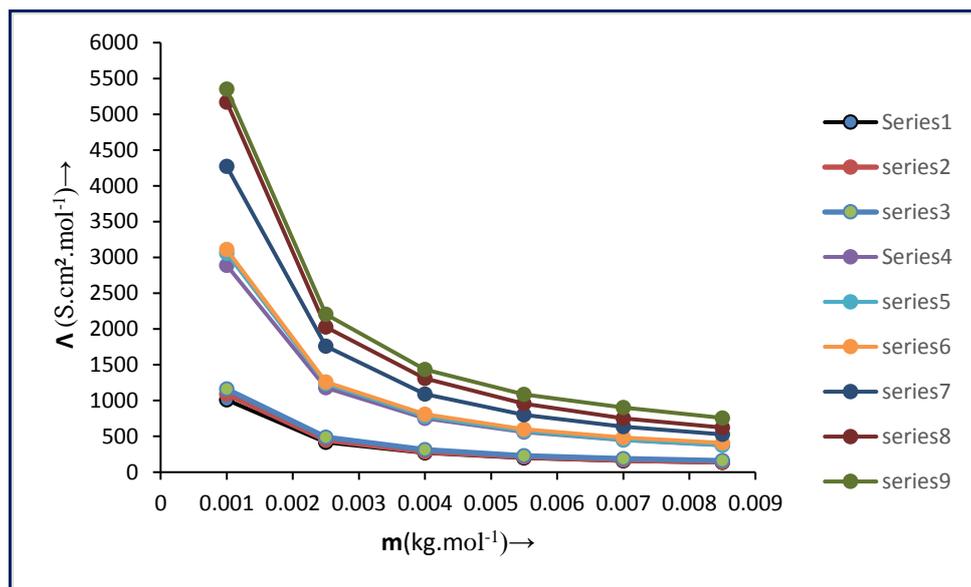
**Figure 3(a).** Variation of  $R_M^0$  values of L-Aspartic acid solution against 293K, 303K and 313K in aqueous solution of IL at 0.01m(Series1), 0.03m(Series2) and 0.05m(Series3)



**Figure 3(b).** Variation of  $R_M^0$  values of L-Glutamic acid solution against 293K, 303K and 313K in aqueous solution of IL at 0.01m (Series1), 0.03m(Series2) and 0.05m(Series3).

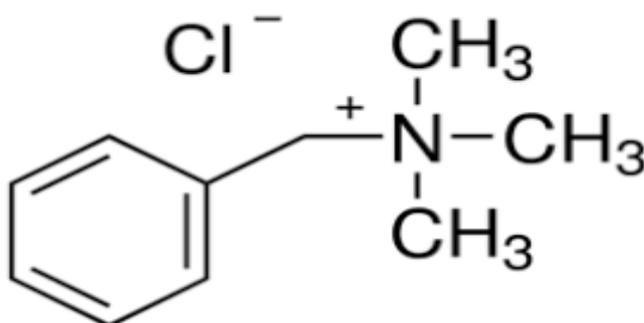


**Figure 4(a).** Variation of molar conductance ( $\Lambda$ ) with different concentrations of L-Aspartic acid in aqueous (0.01m,0.03m,0.05m) BTAC (IL) solution at 293K, 303K, 313K 0.01m at 293K (Series1), 0.01m at 303K (Series2), 0.01m at 313K (Series3)0.03m at 293K (Series4), 0.03m at 303K (Series5), 0.03m at 313K (Series6)0.05m at 293K (Series7), 0.05m at 303K(Series8), 0.05m at 313K(Series9)

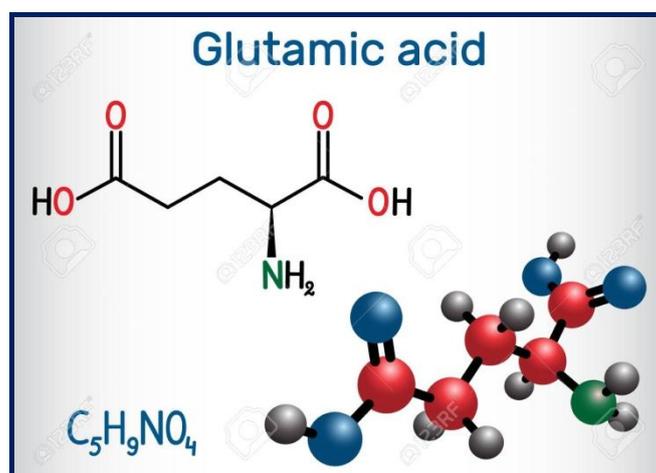
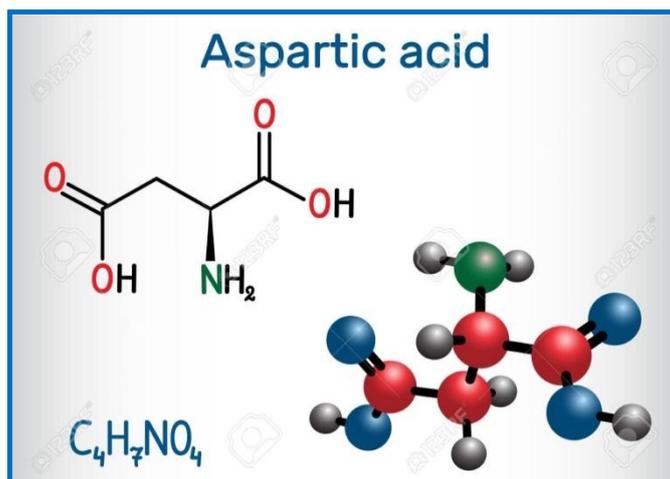


**Figure 4(b).** Variation of molar conductance ( $\Lambda$ ) with different concentrations of L-Glutamic acid in aqueous (0.01m,0.03m,0.05m) BTAC (IL) solution at 293K, 303K, 313K 0.01m at 293K(Series1), 0.01m at 303K(Series2), 0.01m at 313K(Series3)0.03m at 293K(Series4), 0.03m at 303K(Series5), 0.03m at 313K(Series6)0.05m at 293K(Series7), 0.05m at 303K(Series8), 0.05m at 313K(Series9)

**SCHEMES:**



Benzyl tri methyl ammonium chloride



Scheme 1. Molecular structure of ionic liquid and amino acid

# CHAPTER- VI

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## PHYSICOCHEMICAL INVESTIGATION OF DIVERSE INTERACTIONS OF SOME BIOLOGICALLY POTENT MOLECULES PREVALENT IN AQUEOUS IONIC LIQUID SOLUTIONS AT DIFFERENT TEMPERATURES

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**Abstract:** Densities, viscosities, conductivity and refractive indices of L-ascorbic acid in aqueous solutions of an ionic liquid, 1-butylpyridinium bromide, have been measured at five different temperatures ranging from 293.15K to 313.15K. Some important parameters have been derived from the above physicochemical experiments, namely, limiting apparent molar volume ( $\phi_V^\theta$ ) and viscosity  $B$ -coefficients using extended Masson equation and Jones-Dole equation respectively. Lorentz-Lorenz equation has used to evaluate molar refractive index ( $R_M$ ) and limiting molar index ( $R_M^\theta$ ). Specific Conductivity measurement applied to ascertain ionic nature of the system.

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**Keywords:** Solute-co-solute interactions, apparent molar volume, viscosity  $B$ -coefficient, molar refraction, conductivity study.

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### V1.1. Introduction

Ionic liquids (ILs) are organic solvents that are liquids at or near room temperature in their pure state. They have been widely used in a number of fields in both academia and industry and exhibit many useful advantages such as a low melting point (<373 K), are liquid over a wide temperature range, and have suitable viscosity, thermal stability, and the ability to dissolve a variety of chemicals, and most importantly, negligible vapour pressure [1,2]. Ionic liquids have been proposed as green and benign replacements for traditional volatile organic solvents, and a rising number of applications in the fields of catalysis, chemical reactions, separations, electrochemistry, Nano-science and biosciences far studied[3,4].

Vitamin C, which is also known as L-ascorbic acid is highly polar and readily soluble in water. Vitamin C can help to prevent and treat scurvy and the common cold. It is essential for the synthesis of collagen, neurotransmitters and creatinine [5]. Due to the great importance of vitamin C in human beings, the volumetric and viscometric investigation of the solutes has gained

increased significance in several areas of analytical chemistry such as pharmaceutical and food applications. As the body fluid is always circulating, it is interesting to study the transport properties of vitamins in aqueous solutions at different temperatures. Water is a very simple molecule but very complicated to understand especially when it is mixed with other solutes. So, it was believed to study the effect of dissolution of L-ascorbic acid on the structure of aqueous ionic liquid medium at different temperatures.

Measurements of density, viscosity and refractive index, conductivity of aqueous IL solution of L-ascorbic have not been made over significant temperature and concentration ranges. These measurements are important for elucidation of ion-solvent, ion-ion and solvent-solvent interactions in aqueous ternary ( $\text{H}_2\text{O} + \text{IL} + \text{L-ascorbic acid}$ ) systems. The nature and degree of molecular interactions in different solutions depend upon the nature of the medium, extent of solvation taking place in solution and also the structure and size of the solute molecule [6-10].

Therefore, in present study we have endeavoured to make ascertain nature of interaction of solute itself (L-ascorbic acid) and with co-solute 1-butylpyridinium bromide (IL) in  $w_1=0.001$ , 0.003 and 0.005 mass fraction of aqueous medium at different temperatures (298.15-313.15)K with 5 interval to explain various noncovalent interactions prevailing in the ternary systems under investigation.

## V1.2. Experimental section

### V1.2.1 Source and purity of materials

1-butylpyridinium bromide and L-ascorbic acid were purchased from Sigma-Aldrich. The mass fractions purity of both was  $\geq 0.99$ . The reagents were always placed in the desiccators over  $\text{P}_2\text{O}_5$  to keep them in dry atmosphere. These chemicals were used as received without further purification. The provenance and purity of the chemical used has been depicted in table 1.

### V1.2.2 Apparatus and procedure

Solubility of the 1-butylpyridinium bromide and L-ascorbic acid in water (deionised, doubly distilled water) has been checked surely, prior to start of the experimental work and perceived that L-ascorbic acid is soluble in all proportion of aqueous IL solution. The mother solutions of L-ascorbic acid were prepared by mass (Mettler Toledo AG-285 with uncertainty 0.0003g) and then the working solutions (six sets) were prepared by mass dilution. The conversion of molarity into molality [11] has been done using experimental density values of respective solutions.

The densities ( $\rho$ ) of the experimental solutions were measured by using of (DMA 4500M) vibrating u-tube Anton Paar digital density meter with a precision of  $\pm 0.00005 \text{ g.cm}^{-3}$  maintained

at  $\pm 0.01$  K of the desired temperature. The calibration was carried out by passing deionised, triply distilled water and dry air [12].

A Brookfield DV-III Ultra Programmable Rheometer with fitted spindle size-42 is used to measure the viscosity ( $\eta$ ). The detail description has already been described earlier [13].

Refractive index ( $n_D$ ) was measured with the help of a Digital Refractometer Mettler Toledo instrument. The light source was LED,  $\lambda=589.3\text{nm}$ . The refractometer was calibrated twice using distilled water and after every few measurements calibration was checked. [14]. The uncertainty of refractive index measurement was  $\pm 0.0002$  units.

Measurements of conductivity were carried out in a Systronics-308 conductivity meter (accuracy  $\pm 0.01\%$ ) using a dip-type dipping conductivity cell, CD-10, having a cell constant of approximately  $(0.1 \pm 0.001) \text{cm}^{-1}$ . Measurements of experimental solutions were completed in a water bath maintained within  $T = (298.15 \pm 0.01) \text{K}$  [15].

### V1.3. Result and Discussion

The physical parameters of binary mixtures in different mass fractions ( $w_1=0.001, 0.003, 0.005$ ) of aqueous ionic liquid (IL) solutions at five different temperatures (293.15K, 298.15K, 303.15K, 308.15K and 313.15K) and at 1.013 bar have been reported in table 2. The experimental measured values of density and viscosity of L-ascorbic acid (AA) as a function of concentration (molality), in different mass fractions of aqueous ionic liquid (IL) mixture at above mentioned temperatures have been listed in **Table 3**.

#### V1.3.1 Apparent molar volume

Volumetric properties, like, apparent molar volume ( $\varphi_V$ ) and limiting apparent molar volume ( $\varphi_V^0$ ) contemplate significant tools for understanding of interactions taking place in solution systems. The apparent molar volume can be regarded to be the sum of the geometric volume of the central solute molecule and changes in the solvent volume due to its interaction with the solute around the peripheral or co-sphere. Therefore, the apparent molar volumes ( $\varphi_V$ ) have been determined from the solutions densities using the suitable equation [14] and the values are given in **Table 4**.

$$\varphi_V = M/\rho - 1000 (\rho - \rho_0)/m\rho\rho_0 \quad (1)$$

Where  $M$  is the molar mass of the L-ascorbic acid,  $m$  is the molality of the solution,  $\rho$  and  $\rho_0$  are the density of the solution and aqueous ionic liquid mixture respectively.

The values of ( $\varphi_V$ ) are positive and large for all the systems, signifying strong solute-co-solute interactions. The apparent molar volumes ( $\varphi_V$ ) are found to decrease with increasing concentration (molality,  $m$ ) of ascorbic acid in same mass fraction of aqueous ionic liquid at same

temperature. It is also found that apparent molar volumes ( $\varphi_V$ ) increase with both increasing temperature as well as mass fraction of aqueous IL solution and varied with  $\sqrt{m}$  and could be least-squares fitted to the extended Masson equation [16] from where limiting molar volume,  $\varphi_V^0$  (infinite dilution partial molar volume) have been estimated and the values have been represented in **Table 5**.

$$\varphi_V = \varphi_V^0 + S_V^* \sqrt{m} \quad (2)$$

$\varphi_V^0$  is the apparent molar volume at infinite dilution,  $S_V^*$  is the experimental slope. At infinite dilution solute molecule is surrounded only by the solvent molecules and remains infinite distant from each other. Consequently, that  $\varphi_V^0$  is unaffected by itself interaction of ascorbic acid molecules and it is a measure only of the solute-co-solute (AA-IL) interaction.

A scrutiny of **Table 5** shows that  $\varphi_V^0$  are large and positive for all L-ascorbic acid at all the studied temperatures, suggesting the presence of strong solute-co-solute interaction (scheme 1). Comparing  $\varphi_V^0$  with  $S_V^*$  values show that the magnitude of  $\varphi_V^0$  is greater than  $S_V^*$ , suggesting that solute-co-solute interactions predominates over itself interaction of solute molecules in all solutions at all studied temperatures. Moreover,  $S_V^*$  values are negative at all studied temperatures indicates force of itself interaction of ascorbic acid molecules is very poor.

The variation of  $\varphi_V^0$  with temperature are fitted to a polynomial of the following

$$\varphi_V^0 = a_0 + a_1 T + a_2 T^2 \quad (3)$$

Where  $T$  is the temperature in K and  $a_0$ ,  $a_1$  and  $a_2$  are the empirical coefficients depending on the solute, mass fraction of co solute IL. Values of coefficients of the above equation for the in aqueous IL mixtures are reported in **Table 6**.

The limiting apparent molar expansibilities,  $\varphi_E^0$ , can be evaluated by the following equation,

$$\varphi_E^0 = (\delta\varphi_V^0/\delta T)_P = a_1 + 2a_2 T \quad (4)$$

The limiting apparent molar expansibilities,  $\varphi_E^0$ , change in magnitude with the change of temperature. The values of  $\varphi_E^0$  for different solutions of studied L-ascorbic acid at ( $T=293.15\text{K}$  to  $313.15\text{K}$ ) are reported in **Table 7**.

All the values of  $\varphi_E^0$  shown in the **Table 7** are positive for L-ascorbic acid in aqueous IL and studied temperature. This fact helps to explain the absence of caging or packing effect for the IL in solution [17].

The long-range structure-making and breaking capacity of the solute in mixed system can be determined by examining the sign of  $(\delta\varphi_E^0/\delta T)_P$  developed by Hepler[18].

$$(\delta\varphi_E^0/\delta T)_P = (\delta^2\varphi_V^0/\delta T^2)_P = 2a_2 \quad (5)$$

The positive sign or small negative of  $(\delta\varphi_E^0/\delta T)_P$  signifies the molecule is a structure-maker; otherwise, it is a structure-breaker [19]. The perusal of table 6 shows that,  $(\delta\varphi_E^0/\delta T)_P$  values of ascorbic acid are all positive under investigation. It shows the more symmetric rearrangement of the interacting molecules (AA and IL) with the formation of H-bonding, van der Waal forces, dipole-dipole interactions etc. This symmetric arrangement is signifying the molecules of ascorbic acid and IL is interacting with structure-making tendency in all of the studied solution systems. The **Table 6** also showing the positively magnitude of  $(\delta\varphi_E^0/\delta T)_P$  values in of L-ascorbic acid is depicting this structure-making tendency.

### V1.3.2 Viscosity

The experimental viscosity data for studied systems are listed in **Table 3**. The relative viscosity ( $\eta_r$ ) has been calculated using extended Jones-Dole equation [20] for non-electrolytes.

$$(\eta/\eta_0 - 1)/\sqrt{m} = (\eta_r - 1)/\sqrt{m} = A + B \cdot \sqrt{m} \quad (6)$$

Where  $\eta_r = \eta/\eta_0$  is the relative viscosity,  $\eta$  and  $\eta_0$  are the viscosities of ternary solutions (AA + IL) and solvent (aqueous IL) respectively and  $m$  is the molality of L-Ascorbic acid in ternary solutions. Where  $A$  is known as Falkenhagen coefficient [21] as it is determined by the ionic attraction theory of Falkenhagen-Vernon and  $B$  is empirical constants known as viscosity  $B$ - coefficients, which are specifying to the interaction of solute itself and/or with co solute molecules respectively. The values of  $A$ -and  $B$ -coefficients are estimated by least-square polynomial method by plotting  $(\eta_r - 1)/\sqrt{m}$  against  $\sqrt{m}$  with second order and reported in **Table 4**. It is observed from table 4 the values of the  $A$ -coefficient are found to decrease with increase in temperature. This fact indicates the presence of very weak solute-solute interaction and also in excellent agreement with those obtained from  $S_V^*$  values.

The valuable information about the solvation of the solvated solutes and their effects on the structure of the co solute IL in the local vicinity of the solute (L-ascorbic acid) molecules in solutions has been obtained from viscosity  $B$ -coefficient [22]. It is found from table 4; the values of  $B$ -coefficient are positive and much higher than  $A$ -coefficient which signifies solute-co solute interaction is dominant over solute-solute and co-solute-co-solute interaction. It is also observed that the positive magnitude of viscosity  $B$ -coefficient increases with increasing temperature and also increases with an increase in mass fraction of aqueous IL which suggests that solute-co-solute interaction is strengthened with rise in temperature as well as mass fraction of aqueous IL mixture. These results are in good agreement with those obtained from limiting apparent molar volume  $\varphi_V^0$  values.

It is observed from **Table 4** that the values of the  $B$ -coefficient of ascorbic acid increases with temperature, i.e., the  $dB/dT$  values are positive. From table 8, the small positive  $dB/dT$  values for the L-ascorbic acid behaves almost as structure-maker.

Furthermore, it is attractive to observe that there is linear correlation between viscosity  $B$ -coefficients of the studied L-ascorbic acid with the limiting apparent molar volumes ( $\varphi_V^0$ ) in different mass fraction of aqueous IL solutions. From the above fact it means

$$B = A_1 + A_2 \varphi_V^0 \quad (7)$$

The coefficients  $A_1$  and  $A_2$  are listed in table 8. As both viscosities  $B$ -coefficient and limiting apparent molar volumes define the solute-solvent interaction in solution. The linear variation of viscosity  $B$ -coefficient and limiting apparent molar volume ( $\varphi_V^0$ ) reflects the positive slope (or  $A_2$ ).

It is evident from this study, that there is a strong interaction between L-ascorbic acid and IL and it becomes stronger with rise in temperature. As molecules of L-ascorbic acid are engaged with the IL molecules, the interaction among the IL molecules becomes less effective. We have obtained the derived parameters like, limiting apparent molar volume ( $\varphi_V^0$ ), viscosity  $B$ -coefficient by interpolation and presented in table 5. The positive and significant magnitude of  $\varphi_V^0$  and  $B$ -coefficient from **Table 5** clearly indicates that the limiting apparent molar volume ( $\varphi_V^0$ ), viscosity  $B$ -coefficient is increases with increasing mass fraction of IL, which indicates the positive effect of interaction of ascorbic acid with IL

### V1.3.3 Refractive Index

The measurement of refractive index is also an appropriate method for inspecting the molecular interaction present in solution. The molar refraction ( $R_M$ ) can be appraised from the Lorentz-Lorenz relation [23]. The refractive index of a substance is defined as the ratio  $c/c_0$ , where  $c$  and  $c_0$  is the velocity of light in the medium and in vacuum respectively. Stated more simply that the refractive index of a compound describes its capability to refract light as it passes from one medium to another and thus, the higher the refractive index of a compound, the more the light is refracted [24]. As stated by Deetlefs et al. [25] the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser. Hence, a perusal of **Table 9** and **Table 10** we found that the refractive index and the molar refraction are higher for the studied ascorbic acid and in all the mass fraction of aqueous IL, indicating to the fact that the molecules are more tightly packed in the solution.

The Limiting molar refraction ( $R_M^0$ ) estimated from the following equation (14) and presented in **Table 10**.

$$R_M = R_M^0 + R_S \sqrt{m} \quad (8)$$

Accordingly, we found that the higher values of refractive index and  $R_M^0$  which representing the fact that the molecules of ascorbic acid and are more tightly packed and greater solute-solvent interaction with IL molecules than solute solvent interaction. This is also in good agreement with the results obtained from apparent molar volume and viscosity  $B$ -coefficients discussed above.

#### V1.3.4 Conductivity Study

The conductivity study of the L-ascorbic acid for the interaction (solute – co-solute) in the aqueous solution of IL has been done at five different temperatures. Transport phenomena, molecular and ionic interaction in the ternary system gives some valuable information [26]. The specific conductivities ( $k$ ) of aqueous IL solution has been monitored with increasing the concentration of L-ascorbic acid at five different temperatures and Tabulated in **Table 11**. Consequently, it has been observed that molar conductivity ( $\Lambda$ ) values increases with increase in temperatures and gradual addition of L-ascorbic acid to the IL solution causes a continuous decrease in molar conductivity of the solution. The mobility of the ionic species in solution playing the important role, in spite of growing number of ionic species with added L-ascorbic acid solution, as a result the moral conductivity decreases [27, 28]. It may be due to the growing of solute-solvent interaction governed by the dipole-dipole, ion-dipole and hydrophobic – hydrophobic interaction in solution mixtures between the solute and solvent molecules.

#### V1.4. Conclusion

In the summary of this study, that there is a strong interaction between L-ascorbic and IL and it becomes stronger with rise in temperature. As molecules of L-ascorbic and IL have engaged each other, solute-co solute interaction is much greater than the solute-solute and solvent-solvent interactions in the ternary system.

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## Tables

**Table 1.** Source and purity of the chemicals

| Chemical name             | Source        | mass fraction<br>purity | Purification<br>Method |
|---------------------------|---------------|-------------------------|------------------------|
| 1-butylpyridinium bromide | Sigma-Aldrich | $\geq 0.99$             | Used as procured       |
| L-ascorbic acid           | Sigma-Aldrich | $\geq 0.99$             | Used as procured       |

**Table 2.** Experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and refractive index ( $n_D$ ) at various temperature and at pressure 1.013 bar of different mass fraction ( $w_1$ ) of aq. IL mixtures\*

| Aq. IL<br>Mixture ( $w_1$ ) | Temperature<br>/K | $\rho \times 10^{-3}$<br>/kg·m <sup>-3</sup> | $\eta$<br>/mP·s | $n_D$  |
|-----------------------------|-------------------|--|-----------------|--------|
| 0.001                       | 293.15            | 0.399890                                     | 1.130           | 1.3322 |
|                             | 298.15            | 0.99789                                      | 1.022           | 1.3323 |
|                             | 303.15            | 0.99650                                      | 0.924           | 1.3322 |
|                             | 308.15            | 0.99496                                      | 0.855           | 1.3321 |
|                             | 313.15            | 0.99321                                      | 0.803           | 1.3320 |
| 0.003                       | 293.15            | 0.99814                                      | 1.132           | 1.3324 |
|                             | 298.15            | 0.99710                                      | 1.024           | 1.3324 |
|                             | 303.15            | 0.99658                                      | 0.933           | 1.3323 |
|                             | 308.15            | 0.99525                                      | 0.864           | 1.3322 |
|                             | 313.015           | 0.99340                                      | 0.807           | 1.3321 |
| 0.005                       | 293.15            | 0.99320                                      | 1.141           | 1.3325 |
|                             | 298.15            | 0.99828                                      | 1.029           | 1.3325 |
|                             | 303.15            | 0.99650                                      | 0.937           | 1.3324 |
|                             | 308.15            | 0.99534                                      | 0.869           | 1.3323 |
|                             | 313.15            | 0.99243                                      | 0.813           | 1.3322 |

\*Standard uncertainties  $u$  are:  $u(\rho) = 0.002 \text{ kg}\cdot\text{m}^{-3}$ ,  $u(\eta) = 0.02 \text{ mP}\cdot\text{s}$ ,  $u(n_D) = 0.0002$  and  $u(T) = 0.01\text{K}$ , (0.68 level of confidence)

**Table 3.** Experimental values of density ( $\rho$ ) and viscosity ( $\eta$ ), L-ascorbic acid in different mass fractions of aqueous IL acid mixture ( $w_1$ ) at five different temperatures and at pressure 1.013 bar\*

| $^a m$<br>/mol·kg <sup>-1</sup> | $\rho \times 10^{-3}$<br>/kg·m <sup>-3</sup> | $\eta$<br>/mP·s | $^a m$<br>/mol·kg <sup>-1</sup> | $\rho \times 10^{-3}$<br>/kg·m <sup>-3</sup> | $\eta$<br>/mP·s | $^a m$<br>/mol·kg <sup>-1</sup> | $\rho \times 10^{-3}$<br>/kg·m <sup>-3</sup> | $\eta$<br>/mP·s |
|---------------------------------|--|-----------------|---------------------------------|--|-----------------|---------------------------------|--|-----------------|
|                                 | $w_1=0.001$                                  |                 |                                 | $w_1=0.003$                                  |                 |                                 | $w_1=0.005$                                  |                 |
| T =                             | 293.15 K                                     |                 |                                 | 293.15 K                                     |                 |                                 | 293.15 K                                     |                 |
| 0.010                           | 0.99905                                      | 1.136           | 0.010                           | 0.99916                                      | 1.138           | 0.010                           | 0.99943                                      | 1.145           |
| 0.025                           | 1.00005                                      | 1.141           | 0.025                           | 1.00016                                      | 1.141           | 0.025                           | 1.00022                                      | 1.151           |
| 0.040                           | 1.00103                                      | 1.148           | 0.040                           | 1.00118                                      | 1.148           | 0.040                           | 1.00125                                      | 1.157           |
| 0.055                           | 1.00209                                      | 1.152           | 0.055                           | 1.00223                                      | 1.152           | 0.055                           | 1.00231                                      | 1.162           |
| 0.070                           | 1.00317                                      | 1.158           | 0.070                           | 1.00330                                      | 1.158           | 0.070                           | 1.00333                                      | 1.166           |
| 0.085                           | 1.00415                                      | 1.164           | 0.085                           | 1.00432                                      | 1.166           | 0.085                           | 1.00435                                      | 1.173           |
| T =                             | 298.15 K                                     |                 |                                 | 298.15 K                                     |                 |                                 | 298.15 K                                     |                 |
| 0.010                           | 0.99798                                      | 1.028           | 0.010                           | 0.99824                                      | 1.029           | 0.010                           | 0.99837                                      | 1.033           |
| 0.025                           | 0.99887                                      | 1.033           | 0.025                           | 0.99899                                      | 1.034           | 0.025                           | 0.99915                                      | 1.038           |
| 0.040                           | 0.99988                                      | 1.038           | 0.040                           | 0.99997                                      | 1.041           | 0.040                           | 1.00005                                      | 1.045           |
| 0.055                           | 1.0009                                       | 1.045           | 0.055                           | 1.00102                                      | 1.046           | 0.055                           | 1.00111                                      | 1.052           |
| 0.070                           | 1.00197                                      | 1.050           | 0.070                           | 1.00208                                      | 1.052           | 0.070                           | 1.00223                                      | 1.056           |
| 0.085                           | 1.00298                                      | 1.057           | 0.085                           | 1.00316                                      | 1.058           | 0.085                           | 1.00342                                      | 1.062           |
| T =                             | 303.15 K                                     |                 |                                 | 303.15 K                                     |                 |                                 | 303.15 K                                     |                 |
| 0.010                           | 0.99659                                      | 0.930           | 0.010                           | 0.99666                                      | 0.938           | 0.010                           | 0.99676                                      | 0.941           |
| 0.025                           | 0.99746                                      | 0.936           | 0.025                           | 0.9975                                       | 0.943           | 0.025                           | 0.99757                                      | 0.946           |
| 0.040                           | 0.99847                                      | 0.941           | 0.040                           | 0.99857                                      | 0.948           | 0.040                           | 0.9986                                       | 0.952           |
| 0.055                           | 0.99948                                      | 0.948           | 0.055                           | 0.99959                                      | 0.953           | 0.055                           | 0.99968                                      | 0.958           |
| 0.070                           | 1.00053                                      | 0.954           | 0.070                           | 1.00075                                      | 0.962           | 0.070                           | 1.00073                                      | 0.964           |
| 0.085                           | 1.00152                                      | 0.962           | 0.085                           | 1.00084                                      | 0.968           | 0.085                           | 1.00089                                      | 0.971           |
| T =                             | 303.15 K                                     |                 |                                 | 308.15 K                                     |                 |                                 | 308.15 K                                     |                 |
| 0.010                           | 0.99503                                      | 0.861           | 0.010                           | 0.99529                                      | 0.869           | 0.010                           | 0.99538                                      | 0.871           |
| 0.025                           | 0.99584                                      | 0.866           | 0.025                           | 0.99599                                      | 0.874           | 0.025                           | 0.996  | 0.877           |
| 0.040                           | 0.99683                                      | 0.871           | 0.040                           | 0.99696                                      | 0.880           | 0.040                           | 0.99703                                      | 0.882           |
| 0.055                           | 0.99789                                      | 0.875           | 0.055                           | 0.99797                                      | 0.886           | 0.055                           | 0.99808                                      | 0.888           |
| 0.070                           | 0.99892                                      | 0.885           | 0.070                           | 0.99908                                      | 0.894           | 0.070                           | 0.99928                                      | 0.896           |
| 0.085                           | 0.99991                                      | 0.892           | 0.085                           | 1.00013                                      | 0.901           | 0.085                           | 1.00038                                      | 0.903           |
| T =                             | 313.15K                                      |                 |                                 | 313.15K                                      |                 |                                 | 313.15K                                      |                 |
| 0.010                           | 0.99326                                      | 0.809           | 0.010                           | 0.99344                                      | 0.812           | 0.010                           | 0.99346                                      | 0.817           |
| 0.025                           | 0.99404                                      | 0.814           | 0.025                           | 0.99408                                      | 0.817           | 0.025                           | 0.99411                                      | 0.823           |
| 0.040                           | 0.99502                                      | 0.820           | 0.040                           | 0.99515                                      | 0.822           | 0.040                           | 0.99519                                      | 0.829           |
| 0.055                           | 0.99605                                      | 0.826           | 0.055                           | 0.99613                                      | 0.828           | 0.055                           | 0.99624                                      | 0.836           |
| 0.070                           | 0.99708                                      | 0.833           | 0.070                           | 0.99722                                      | 0.836           | 0.070                           | 0.99735                                      | 0.844           |
| 0.085                           | 0.99807                                      | 0.842           | 0.085                           | 0.99832                                      | 0.844           | 0.085                           | 0.99847                                      | 0.850           |

\*Standard uncertainties  $u$  are:  $u(\rho) = 0.00002 \text{ kg}\cdot\text{m}^{-3}$ ,  $u(\eta) = 0.02 \text{ mP}\cdot\text{s}$  and  $u(T) = 0.01 \text{ K}$   
(0.68 level of confidence)

<sup>a</sup> molality has been expressed per kg (IL + water) solvent mixture

**Table 4.** Apparent molar volume ( $\varphi_V$ ) and  $(\eta_r - I)/\sqrt{m}$  of L-Ascorbic acid in different mass fraction ( $w_1$ ) of aqueous IL mixtures at five different temperatures \*

| <sup>a</sup> molality<br>/mol·kg <sup>-1</sup> | $\varphi_V \times 10^6$<br>/m <sup>3</sup> mol <sup>-1</sup> | $(\eta_r - I)/\sqrt{m}$<br>/kg <sup>1/2</sup> mol <sup>-1/2</sup> | <sup>a</sup> molality<br>/mol·kg <sup>-1</sup> | $\varphi_V \times 10^6$<br>/m <sup>3</sup> mol <sup>-1</sup> | $(\eta_r - I)/\sqrt{m}$<br>/kg <sup>1/2</sup> mol <sup>-1/2</sup> | <sup>a</sup> molality<br>/mol·kg <sup>-1</sup> | $\varphi_V \times 10^6$<br>/m <sup>3</sup> mol <sup>-1</sup> | $(\eta_r - I)/\sqrt{m}$<br>/kg <sup>1/2</sup> mol <sup>-1/2</sup> |
|--|--|---|--|--|---|--|--|---|
| w <sub>1</sub> =0.001                          |  |   | w <sub>1</sub> =0.003                          |  |   | w <sub>1</sub> =0.005                          |  |   |
| T = 293.15 K                                   |  |   | T = 293.15 K                                   |  |   | T = 293.15 K                                   |  |   |
| 0.010  | 161.3074   | 0.10  | 0.010  | 164.2890   | 0.10  | 0.010  | 165.2465   | 0.10  |
| 0.025  | 130.2733   | 0.15  | 0.025  | 131.4611   | 0.15  | 0.025  | 140.2315   | 0.15  |
| 0.040  | 123.0157   | 0.20  | 0.040  | 122.7562   | 0.20  | 0.040  | 127.9780   | 0.20  |
| 0.055  | 118.2601   | 0.23  | 0.055  | 118.2516   | 0.23  | 0.055  | 121.8612   | 0.23  |
| 0.070  | 115.2568   | 0.26  | 0.070  | 115.3915   | 0.26  | 0.070  | 118.9343   | 0.26  |
| 0.085  | 114.4912   | 0.29  | 0.085  | 114.1324   | 0.29  | 0.085  | 117.0449   | 0.29  |
| T = 298.15 K                                   |  |   | T = 298.15 K                                   |  |   | T = 298.15 K                                   |  |   |
| 0.010  | 165.4707   | 0.10  | 0.010  | 166.4314   | 0.10  | 0.010  | 167.4118   | 0.10  |
| 0.025  | 136.3732   | 0.15  | 0.025  | 142.3587   | 0.15  | 0.025  | 142.2825   | 0.15  |
| 0.040  | 126.0911   | 0.20  | 0.040  | 130.5747   | 0.20  | 0.040  | 130.2784   | 0.20  |
| 0.055  | 121.2318   | 0.23  | 0.055  | 123.9409   | 0.23  | 0.055  | 123.0563   | 0.23  |
| 0.070  | 117.7392   | 0.26  | 0.070  | 120.0063   | 0.26  | 0.070  | 117.9590   | 0.26  |
| 0.085  | 116.1897   | 0.29  | 0.085  | 117.2309   | 0.29  | 0.085  | 113.8659   | 0.29  |
| T = 303.15 K                                   |  |   | T = 303.15 K                                   |  |   | T = 303.15 K                                   |  |   |
| 0.010  | 167.6947   | 0.10  | 0.010  | 168.6877   | 0.10  | 0.010  | 171.6834   | 0.10  |
| 0.025  | 138.1137   | 0.15  | 0.025  | 139.7137   | 0.15  | 0.025  | 140.1794   | 0.15  |
| 0.040  | 127.1993   | 0.20  | 0.040  | 126.6911   | 0.20  | 0.040  | 127.1490   | 0.20  |
| 0.055  | 122.2345   | 0.23  | 0.055  | 121.6820   | 0.23  | 0.055  | 120.3674   | 0.23  |
| 0.070  | 118.8225   | 0.26  | 0.070  | 116.8140   | 0.26  | 0.070  | 116.7937   | 0.26  |
| 0.085  | 117.3267   | 0.29  | 0.085  | 114.0258   | 0.29  | 0.085  | 112.1710   | 0.29  |
| T = 308.15 K                                   |  |   | T = 308.15 K                                   |  |   | T = 308.15 K                                   |  |   |
| 0.010  | 169.9583   | 0.10  | 0.010  | 172.9363   | 0.10  | 0.010  | 172.9211   | 0.10  |
| 0.025  | 141.4943   | 0.15  | 0.025  | 147.1081   | 0.15  | 0.025  | 150.3231   | 0.15  |
| 0.040  | 129.8377   | 0.20  | 0.040  | 133.8415   | 0.20  | 0.040  | 134.3368   | 0.20  |
| 0.055  | 123.2543   | 0.23  | 0.055  | 127.0749   | 0.23  | 0.055  | 126.7021   | 0.23  |
| 0.070  | 119.9223   | 0.26  | 0.070  | 121.7701   | 0.26  | 0.070  | 120.1852   | 0.26  |
| 0.085  | 118.2437   | 0.29  | 0.085  | 119.0530   | 0.29  | 0.085  | 117.1584   | 0.29  |
| T=313.15K                                      |  |   | T=313.15K                                      |  |   | T=313.15K                                      |  |   |
| 0.010  | 172.2706   | 0.10  | 0.010  | 173.2509   | 0.10  | 0.010  | 174.2580   | 0.10  |
| 0.025  | 143.7050   | 0.15  | 0.025  | 149.7550   | 0.15  | 0.025  | 149.7513   | 0.15  |
| 0.040  | 131.4999   | 0.20  | 0.040  | 132.9996   | 0.20  | 0.040  | 132.7442   | 0.20  |
| 0.055  | 125.0295   | 0.23  | 0.055  | 127.0351   | 0.23  | 0.055  | 125.5640   | 0.23  |
| 0.070  | 121.3304   | 0.26  | 0.070  | 122.0384   | 0.26  | 0.070  | 120.5955   | 0.26  |
| 0.085  | 119.4161   | 0.29  | 0.085  | 118.6930   | 0.29  | 0.085  | 117.2690   | 0.29  |

\*Standard uncertainties  $u$  are:  $u(T) = 0.01\text{K}$ , the accuracy of  $\varphi_V$  is  $1.01 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$  and  $(\eta_r - I)/\sqrt{m}$  is  $0.002 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  (0.68 level of confidence)

<sup>a</sup> molality has been expressed per kg of (IL + water) solvent mixture

**Table 5.** Limiting apparent molar volume ( $\varphi_V^0$ ), experimental slope ( $S_V^*$ ), viscosity  $A$ - and  $B$ -coefficient of L-ascorbic acid in different mass fraction ( $w_I$ ) of aqueous IL mixtures at five different temperatures\*

| Mass fraction ( $w_I$ ) | T /K   | $\varphi_V^0 \times 10^6$<br>/m <sup>3</sup> mol <sup>-1</sup> | $S_V^* \times 10^6$<br>/m <sup>3</sup> mol <sup>-3/2</sup> kg <sup>1/2</sup> | $B$<br>/kg mol <sup>-1</sup> | $A$<br>/kg <sup>1/2</sup> mol <sup>-1/2</sup> |
|-------------------------|--------|--|--|------------------------------|---|
| 0.001                   | 293.15 | 174.80   | -228.31  | 0.52                         | 0.03  |
|                         | 298.15 | 181.69   | -244.93  | 0.58                         | 0.05  |
|                         | 303.15 | 184.34   | -251.01  | 0.64                         | 0.02  |
|                         | 308.15 | 188.46   | -261.69  | 0.73                         | 0.04  |
|                         | 313.15 | 191.45   | -267.62  | 0.78                         | 0.01  |
| 0.003                   | 293.15 | 178.73   | -244.21  | 0.63                         | 0.01  |
|                         | 298.15 | 185.87   | -251.03  | 0.69                         | 0.03  |
|                         | 303.15 | 188.56   | -274.23  | 0.76                         | 0.05  |
|                         | 308.15 | 192.86   | -276.06  | 0.81                         | 0.02  |
|                         | 313.15 | 195.14   | -283.01  | 0.88                         | 0.03  |
| 0.005                   | 293.15 | 183.3  | -245.13  | 0.71                         | 0.03  |
|                         | 298.15 | 189.22   | -271.58  | 0.77                         | 0.01  |
|                         | 303.15 | 193.16   | -295.63  | 0.83                         | 0.04  |
|                         | 308.15 | 198.09   | -292.71  | 0.93                         | 0.01  |
|                         | 313.15 | 198.68   | -296.67  | 0.99                         | 0.05  |

\*Standard uncertainties values of  $u$  are:  $u(T) = 0.01\text{K}$

**Table 6.** Values of various coefficients and standard deviation of equation-3 for L-ascorbic acid in different aqueous IL solutions\*

| Aqueous IL<br>Mixture ( $w_I$ ) | $a_0 \times 10^6$<br>/m <sup>3</sup> mol <sup>-1</sup> | $a_1 \times 10^6$<br>/ m <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> | $a_2 \times 10^6$<br>/ m <sup>3</sup> mol <sup>-1</sup> K <sup>-2</sup> | $(\delta\varphi_E^0/\delta T)_P \times 10^6$<br>/ m <sup>3</sup> mol <sup>-1</sup> K <sup>-2</sup> |
|---------------------------------|--|---|---|--|
| 0.001                           | -1720  | 11.76   | -0.018  | -0.03  |
| 0.003                           | -2181.40   | 14.84   | -0.023  | -0.02  |
| 0.005                           | -2585.5  | 17.54   | -0.027  | -0.05  |
| Average standard<br>deviation   | 2.1  | 0.001   | 0.0002  | 0.0001   |

**Table 7.** Limiting apparent molar expansibilities ( $\phi_E^0$ ) for L-ascorbic acid in different mass fraction of aqueous IL ( $w_I$ ) at different temperature

| Aqueous IL Mixture ( $w_I$ ) | $\phi_E^0 \times 10^6 / \text{m}^3 \text{mol}^{-1} \text{K}^{-1}$ |         |         |         |         |
|------------------------------|---|---------|---------|---------|---------|
| T/ K                         | 293.15  | 298.15  | 303.15  | 308.15  | 313.15  |
| 0.001                        | 1.15497   | 0.97397 | 0.79297 | 0.61197 | 0.43097 |
| 0.003                        | 1.24284   | 1.01084 | 0.77884 | 0.54684 | 0.31484 |
| 0.005                        | 1.36212   | 1.08612 | 0.81012 | 0.53412 | 0.25812 |
| Average standard Deviation   | 0.003   | 0.003   | 0.002   |         |         |

**Table 8.** Values of  $dB/dT$ ,  $A_1$ ,  $A_2$  coefficients for the L-Ascorbic acid in different mass fraction of aqueous IL acid ( $w_I$ ) at studied temperatures\*

| Aqueous IL Mixture ( $w_I$ ) | $dB/dT$ | $A_1$  | $A_2$ |
|------------------------------|---------|--------|-------|
| 0.001                        | 0.043   | -6.943 | 0.023 |
| 0.002                        | 0.028   | -7.869 | 0.024 |
| 0.003                        | 0.039   | -8.573 | 0.039 |
| Average standard deviation   | 0.001   | 0.003  | 0.002 |

\*Standard uncertainties values of  $u$  are:  $u(T) = 0.01\text{K}$

**Table 9.** Refractive index ( $n_D$ ) and molar refraction ( $R_M$ ) of L-ascorbic acid in different mass fraction of aqueous solutions at different temperatures and at pressure 1.013 bar\*

| $a$<br>molality<br>/mol·kg <sup>-1</sup> | $n_D$     | $R_M \times 10^6$<br>/ m <sup>3</sup> mol <sup>-1</sup> | $a$<br>molality<br>/mol·kg <sup>-1</sup> | $n_D$     | $R_M \times 10^6$<br>/ m <sup>3</sup> mol <sup>-1</sup> | $a$<br>molality<br>/mol·kg <sup>-1</sup> | $n_D$     | $R_M \times 10^6$<br>/ m <sup>3</sup> mol <sup>-1</sup> |
|--|-----------|---|--|-----------|---|--|-----------|---|
|  | w1=0.001  |   |  | w1=0.003  |   |  | w1=0.005  |   |
|  | T=293.15K |   |  | T=293.15K |   |  | T=293.15K |   |
| 0.010                                    | 1.3326    | 36.2241   | 0.010                                    | 1.3328    | 36.2398   | 0.010                                    | 1.3331    | 36.2597   |
| 0.025                                    | 1.3327    | 36.1977   | 0.025                                    | 1.3329    | 36.2135   | 0.025                                    | 1.333     | 36.2212   |
| 0.040                                    | 1.3329    | 36.1820   | 0.040                                    | 1.333     | 36.1864   | 0.040                                    | 1.3331    | 36.1938   |
| 0.055                                    | 1.3331    | 36.1634   | 0.055                                    | 1.3332    | 36.1682   | 0.055                                    | 1.3333    | 36.1752   |
| 0.070                                    | 1.3333    | 36.1442   | 0.070                                    | 1.3334    | 36.1493   | 0.070                                    | 1.3336    | 36.1679   |
| 0.085                                    | 1.3336    | 36.1384   | 0.085                                    | 1.3337    | 36.1421   | 0.085                                    | 1.3338    | 36.1509   |
|  | T=298.15K |   |  | T=298.15K |   |  | T=298.15K |   |

| <sup>a</sup><br>molality<br>/mol·kg <sup>-1</sup> | <i>n<sub>D</sub></i> | <i>R<sub>M</sub></i> ×10 <sup>6</sup><br>/ m <sup>3</sup> mol <sup>-1</sup> | <sup>a</sup><br>molality<br>/mol·kg <sup>-1</sup> | <i>n<sub>D</sub></i> | <i>R<sub>M</sub></i> ×10 <sup>6</sup><br>/ m <sup>3</sup> mol <sup>-1</sup> | <sup>a</sup><br>molality<br>/mol·kg <sup>-1</sup> | <i>n<sub>D</sub></i> | <i>R<sub>M</sub></i> ×10 <sup>6</sup><br>/ m <sup>3</sup> mol <sup>-1</sup> |
|---|----------------------|---|---|----------------------|---|---|----------------------|---|
| 0.010   | 1.3325               | 36.2530   | 0.010   | 1.3327               | 36.2633   | 0.010   | 1.3329               | 36.2784   |
| 0.025   | 1.3327               | 36.2405   | 0.025   | 1.3328               | 36.2460   | 0.025   | 1.333                | 36.2600   |
| 0.040   | 1.3329               | 36.2236   | 0.040   | 1.333                | 36.2302   | 0.040   | 1.3332               | 36.2471   |
| 0.055   | 1.3331               | 36.2064   | 0.055   | 1.3332               | 36.2120   | 0.055   | 1.3333               | 36.2186   |
| 0.070   | 1.3333               | 36.1875   | 0.070   | 1.3334               | 36.1934   | 0.070   | 1.3335               | 36.1978   |
| 0.085   | 1.3335               | 36.1707   | 0.085   | 1.3336               | 36.1741   | 0.085   | 1.3337               | 36.1745   |
|   | T=303.15K            |   |   | T=303.15K            |   |   | T=303.15K            |   |
| 0.010   | 1.3324               | 36.2936   | 0.010   | 1.3326               | 36.3109   | 0.010   | 1.3328               | 36.3271   |
| 0.025   | 1.3325               | 36.2719   | 0.025   | 1.3327               | 36.2902   | 0.025   | 1.3329               | 36.3075   |
| 0.040   | 1.3327               | 36.2550   | 0.040   | 1.3329               | 36.2711   | 0.040   | 1.3331               | 36.2898   |
| 0.055   | 1.3330               | 36.2480   | 0.055   | 1.333                | 36.2440   | 0.055   | 1.3332               | 36.2605   |
| 0.070   | 1.3332               | 36.2297   | 0.070   | 1.3334               | 36.2415   | 0.070   | 1.3334               | 36.2422   |
| 0.085   | 1.3334               | 36.2136   | 0.085   | 1.3336               | 36.2203   | 0.085   | 1.3337               | 36.2265   |
|   | T=308.15K            |   |   | T=308.15K            |   |   | T=308.15K            |   |
| 0.010   | 1.3322               | 36.3307   | 0.010   | 1.3324               | 36.3410   | 0.010   | 1.3326               | 36.3576   |
| 0.025   | 1.3323               | 36.3111   | 0.025   | 1.3325               | 36.3254   | 0.025   | 1.3327               | 36.3449   |
| 0.040   | 1.3326               | 36.3047   | 0.040   | 1.3327               | 36.3099   | 0.040   | 1.3329               | 36.3272   |
| 0.055   | 1.3328               | 36.2860   | 0.055   | 1.333                | 36.3028   | 0.055   | 1.3331               | 36.3087   |
| 0.070   | 1.333                | 36.2683   | 0.070   | 1.3332               | 36.2823   | 0.070   | 1.3333               | 36.2849   |
| 0.085   | 1.3333               | 36.2620   | 0.085   | 1.3334               | 36.2639   | 0.085   | 1.3335               | 36.2647   |
|   | T=313.15K            |   |   | T=313.15K            |   |   | T=313.15K            |   |
| 0.010   | 1.3320               | 36.3755   | 0.010   | 1.3321               | 36.3789   | 0.010   | 1.3322               | 36.3881   |
| 0.025   | 1.3321               | 36.3569   | 0.025   | 1.3322               | 36.3654   | 0.025   | 1.3323               | 36.3742   |
| 0.040   | 1.3324               | 36.3509   | 0.040   | 1.3325               | 36.3561   | 0.040   | 1.3325               | 36.3546   |
| 0.055   | 1.3326               | 36.3332   | 0.055   | 1.3327               | 36.3402   | 0.055   | 1.3328               | 36.3461   |
| 0.070   | 1.3329               | 36.3253   | 0.070   | 1.333                | 36.3301   | 0.070   | 1.3331               | 36.3353   |
| 0.085   | 1.3332               | 36.3190   | 0.085   | 1.3333               | 36.3198   | 0.085   | 1.3334               | 36.3242   |

\*Standard uncertainties *u* are: *u* (*n<sub>D</sub>*) =0.02 and *u* (*T*) =0.01K (0.68 level of confidence)

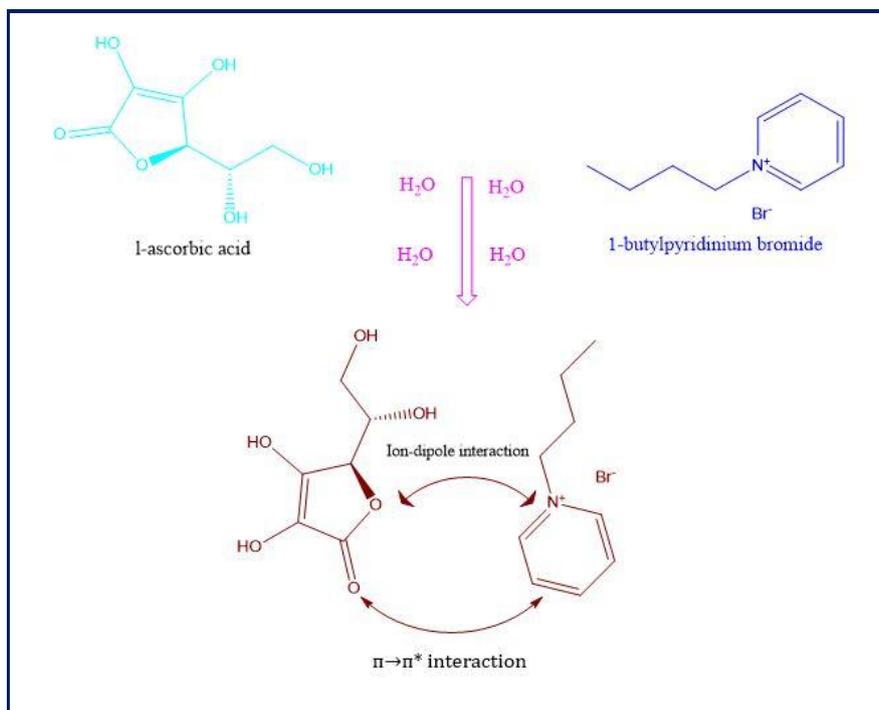
<sup>a</sup> molality has been expressed per kilogram of (IL + water) solvent mixture

**Table 10.** Limiting molar refraction (*R<sub>M</sub><sup>0</sup>*) of L-ascorbic acid in different temperatures and in different mass fraction of aqueous IL solutions at pressure 1.013 bar \*

| Aq. IL<br>mixtures(w1) | <i>R<sub>M</sub><sup>0</sup></i> ×10 <sup>6</sup><br>/ m <sup>3</sup> mol <sup>-1</sup> |         |         |         |         |
|------------------------|---|---------|---------|---------|---------|
|                        | 293.15K   | 298.15K | 303.15K | 308.15K | 313.15K |
| 0.001                  | 36.27   | 36.30   | 36.33   | 36.37   | 36.40   |
| 0.003                  | 36.29   | 36.31   | 36.36   | 36.38   | 36.41   |
| 0.005                  | 36.31   | 36.34   | 36.38   | 36.41   | 36.42   |

**Table 11.** Specific conductivity (k) of L-ascorbic acid in different temperatures and in different mass fraction of aqueous IL solutions at pressure 1.013 bar \*

| Added L-Ascorbic acid | Total volume | Conc. L-ascorbic acid solution | Specific Conductivity/<br>mS cm-1 |      |      |         |         |
|-----------------------|--------------|--------------------------------|-----------------------------------|------|------|---------|---------|
|                       |              |                                | /mL                               | /mL  | /mM  | 293.15K | 298.15K |
| 0                     | 10           | 0.001                          | 0.11                              | 0.14 | 0.15 | 0.22    | 0.23    |
| 1                     | 11           | 0.003                          | 0.37                              | 0.41 | 0.42 | 0.44    | 0.39    |
| 2                     | 12           | 0.003                          | 0.47                              | 0.44 | 0.47 | 0.48    | 0.50    |
| 3                     | 13           | 0.004                          | 0.53                              | 0.48 | 0.50 | 0.49    | 0.57    |
| 4                     | 14           | 0.004                          | 0.57                              | 0.49 | 0.61 | 0.51    | 0.63    |
| 5                     | 15           | 0.005                          | 0.61                              | 0.51 | 0.66 | 0.55    | 0.67    |
| 6                     | 16           | 0.005                          | 0.64                              | 0.53 | 0.67 | 0.60    | 0.69    |
| 7                     | 17           | 0.005                          | 0.67                              | 0.54 | 0.71 | 0.65    | 0.73    |
| 8                     | 18           | 0.006                          | 0.69                              | 0.59 | 0.74 | 0.69    | 0.74    |
| 9                     | 19           | 0.006                          | 0.70                              | 0.62 | 0.76 | 0.74    | 0.76    |
| 10                    | 20           | 0.006                          | 0.72                              | 0.63 | 0.78 | 0.76    | 0.78    |
| 11                    | 21           | 0.007                          | 0.73                              | 0.64 | 0.79 | 0.77    | 0.79    |
| 12                    | 22           | 0.007                          | 0.74                              | 0.66 | 0.80 | 0.78    | 0.79    |
| 13                    | 23           | 0.007                          | 0.76                              | 0.68 | 0.82 | 0.79    | 0.80    |
| 14                    | 24           | 0.007                          | 0.77                              | 0.69 | 0.82 | 0.79    | 0.82    |
| 15                    | 25           | 0.007                          | 0.78                              | 0.70 | 0.83 | 0.80    | 0.83    |
| 16                    | 26           | 0.007                          | 0.78                              | 0.72 | 0.85 | 0.81    | 0.85    |
| 17                    | 27           | 0.007                          | 0.79                              | 0.73 | 0.85 | 0.85    | 0.86    |
| 18                    | 28           | 0.008                          | 0.80                              | 0.74 | 0.85 | 0.86    | 0.87    |
| 19                    | 29           | 0.008                          | 0.81                              | 0.75 | 0.86 | 0.87    | 0.88    |
| 20                    | 30           | 0.008                          | 0.81                              | 0.78 | 0.87 | 0.88    | 0.90    |

Schemes**Scheme1. Plausible solute-co solute interaction.**

## CHAPTER-VII

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### **SUBSISTENCE OF ASSORTED MOLECULAR INTERACTIONS OF SUBSTANTIAL AMINO ACIDS PREVALENT IN AQUEOUS SOLUTIONS OF IONIC LIQUID (TBMS) PROBED BY EXPERIMENTAL AND COMPUTATIONAL INVESTIGATIONS**

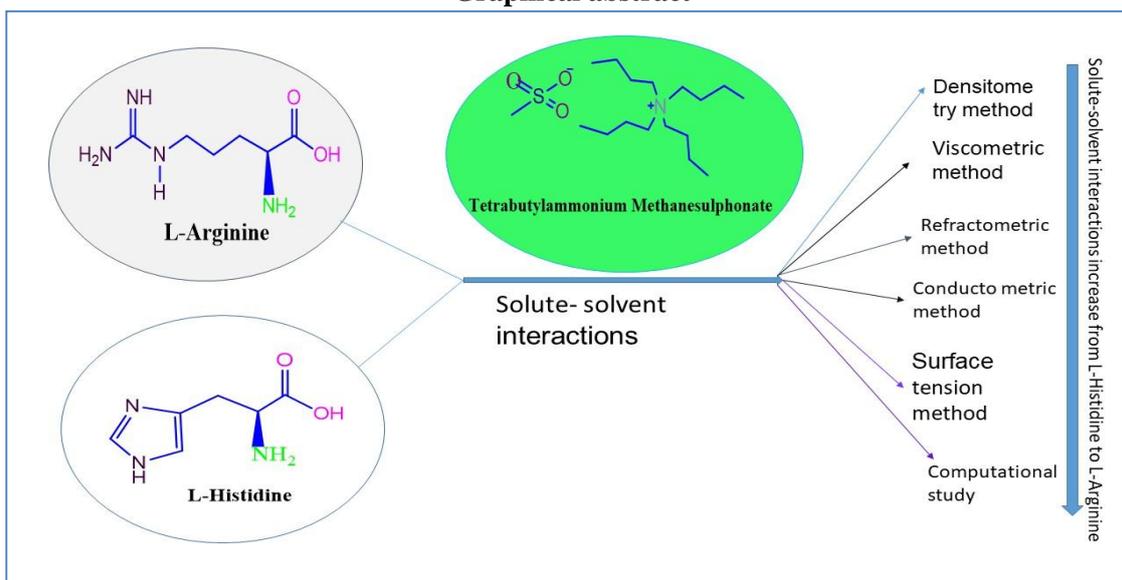
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#### **ABSTRACT:**

Solution behaviour prevailing in L-Arginine and L-Histidine in aqueous Tetrabutylammonium methanesulphonate (TBMS) has been studied to investigate the mode of interactions by means of density ( $\rho$ ), viscosity ( $\eta$ ), surface tension ( $\sigma$ ), refractive index ( $n_D$ ) and electrolytic conductivity at three different temperatures. The nature of interactions occurring in the solutions have been elucidated on the basis of apparent molar volume ( $\Phi_v^0$ ), limiting molar expansivities ( $\Phi_E^0$ ), viscosity *A*- and *B*- coefficients, molar refraction ( $R_M$ ) and concentration measurements. Molar conductance ( $\Lambda$ ), as well as specific conductance ( $\kappa$ ), obtained, so, describe the nature of solute-solute and solute-solvent interactions in the solution mixtures. Using Gaussian 09W quantum chemical package, optimum energies with the optimised geometries of molecular assembly for (TBMS+L-Arginine) and (TBMS+L-Histidine) systems and also critical micelle concentration (CMC) values were calculated and found supportive to the practical outcomes that show the solute-solvent interactions prevailing between the TBMS (IL) and amino acids; L-Arginine and L-Histidine are dominant over the solute-solute interactions. Furthermore, L-Arginine shows a higher extent of interaction that is also influenced by the concentrations and temperatures in comparison to L-Histidine in aqueous IL solutions. The theoretical observations of the study determining  $\Delta\mu_1^{0\ddagger}$ ,  $\Delta\mu_2^{0\ddagger}$ ,  $\Delta H^{0\ddagger}$ , and  $T\Delta S^{0\ddagger}$  also imply the presence of strong interactions in the systems. The various types of interactions between amino acids which are the protein backbone, in presence of ionic liquids would develop a many-dimensional challenge in the field of solution chemistry. Studies of such systems could be advanced further using the correlated outcomes of the investigation.

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## Graphical abstract



## 1. Introduction

It is well recognized that the reaction medium plays a significant role in the determination of the reactivity reflected in thermodynamic, transport and spectral properties [1]. Gaining perception in the mechanism of such types of interactions, studies on thermodynamic and transport properties concerning one or more solutes in different mixed solvent systems are greatly useful. Experimental studies on apparent molar volume, the viscosity of electrolytes and the temperature of solutions have been employed as a function of reviewing ion-ion and ion-solvent interactions [2]. The outcome of a number of workers [3] is that the accumulation of an electrolyte could disrupt or construct the structure of a liquid system. The accretion of solutes to a solution of electrolyte makes happen a variation in ion's solvation and often cause an enormous change in the reactivity of dissolved electrolytes present in the studied systems. The Physico-chemical property; viscosity of a liquid depending upon the intermolecular forces as well as structural features of the liquid can be inferred at different concentrations and temperatures of the solutions.

Since, ionic liquids comprise respective ions that could be available for the different types of interactions with susceptible solutes present in the systems under investigation, the Physico-chemical study of such systems provides a scope to investigate possible solute-solute and solute-solvent interactions for a wide range of solutes in a series of ionic liquids to determine the possibility of these solutes along with the definite solvents for general applications in chemistry and technology. The distinctive properties and uses of ionic liquids have made it possible for a new revolution in the field of materials sciences [4]. Presently, the importance of various studies on ionic liquids has developed in the way of pharmaceuticals and life sciences. In a review, Egorova et al. proposed that biochemical applications of ionic liquids will be the

most important research area in the near future [5]. Thus, ionic liquids are considerable of much attention in the field of sustainable chemical engineering, green chemistry, advanced material sciences etc.

The Physico-chemical properties of amino acids in various aqueous solutions are noteworthy to recognize the nature of interactions for understanding the characteristics of the chemical and biological systems. The stabilization of instinctive conformation of proteins is accompanied by various molecular interactions [6] like solute–solute, solute-solvent and solvent-solvent interactions.

L-Arginine is utilized by the cells of the immune system where the enzyme inducible NOS generates nitric oxide for cell signalling; oxidative bactericidal activities [7]. It is helpful to diminish infection rates, specifically in conditions that compromise immune function for example surgical procedures or precarious ailments [8]. On the other hand, L-Histidine is a nutritionally crucial amino acid with distinctive biochemical and physiological properties that have generated a good theoretical rationale to suggest the use of Histidine as a nutritional supplement in a wide range of circumstances. Primarily it was exposed to treat the patients with anaemia and rheumatoid arthritis having chronic renal failure [9].

Environmental characteristics in addition to “green chemistry” have attracted the attention of researchers on the usage of renewable raw resources for the designing and producing of ionic liquids. Therefore, in contemporary years, ionic liquids have been produced from amino acids, sugars, and terpenes [10]. Amino acid ionic liquids have a great hydrogen bonding capability convenient for dissolution of biomaterials for example DNA, cellulose, and different other carbohydrates [11]. This hydrogen bonding formation ability enhances its use as chiral solvents and substances for dissolution and stabilization of biomolecules like nucleic acids, cellulose, carbohydrates etc. in medicinal chemistry, synthetic chemistry along with pharmaceutical chemistry [12]. Specifically, in industrial and pharmaceutical chemistry, ionic liquids along with amino acids have many diverse applications, for example, an intermediate in the production of peptides, chiral solvents as well as absorbents for acid gases [13].

Quaternary ammonium-based ionic liquids may perhaps attract indeed the negatively charged constituents like bacterial proteins and successively gets denatured as a consequence of disorganization in the protein chain caused by the positive charge on the nitrogen atom. There are extensive volumetric and viscometric research works on amino acids in aqueous electrolyte solutions [14]. Accordingly, the study of the Physico-chemical properties of amino acids in aqueous solutions of ionic liquids will be very convenient for the procurement of information about several types of interactions taking place in these solutions, which are mostly hydrophobic

and electrostatic in nature. That eventually provide significant information about the insight into the conformational stability and unfolding activities of globular proteins.

Moreover, research works on solubility and stability of amino acids in the occurrence of ammonium-based ionic liquids are existing [15] but the study on Physico-chemical properties of amino acids in aqueous solutions of ammonium-based ionic liquids with respect to concentration and temperature are inadequate. Thus, with the aim to realize the actions of amino acids in ionic liquids and with the purpose of understanding the solvation behaviour of amino acids [16], we have tried to report herein Physico-chemical characteristics of L-Arginine and L-Histidine in aqueous Tetrabutylammonium methanesulphonate solution at temperatures 298.15 K, 303.15 K and 308.15 K. Several derived thermodynamic parameters such as density, viscosity, refractive index, surface tension, conductance study and also quantum chemical calculations have been considered to study the solvation behaviour in terms of Physico-chemical characteristics along with the effect of molality and temperatures on the interactions present in the solutions of amino acids; L-Arginine and L-Histidine of different concentration in aqueous Tetrabutylammonium methanesulphonate (TBMS) solution of 0.001 mole/kg, 0.003 mole/kg and 0.005 mole/kg. In this regard, different thermodynamic parameters i.e. apparent molar volume ( $\Phi_v$ ), limiting apparent molar volume ( $\Phi_v^0$ ), limiting molar expansivities ( $\Phi_E^0$ ), Surface tension ( $\sigma$ ), refractive index ( $n_D$ ), molar refraction ( $R_M$ ), Molar conductance ( $A$ ), specific conductance ( $\kappa$ ), viscosity A-, B-coefficients also temperature derivative of  $B$ ;  $dB/dT$ ;  $\Delta\mu_1^{0\neq}$ ,  $\Delta\mu_2^{0\neq}$ ,  $\Delta H^{0\neq}$ , and  $T\Delta S^{0\neq}$ , critical micelle concentration (CMC) values have been determined and analysed accordingly to understand more noticeably the interactions taking place in the studied solution mixtures.

## 2. Experimental Section

### 2.1 Source and Purity of Samples

Materials used in this work; Tetrabutylammonium methanesulphonate,  $C_{17}H_{39}NO_3S$  (M.W. 337.6 g/mole) and amino acids, L-Arginine,  $C_6H_{14}N_4O_2$  (M.W. 174.204 g/mole) and L-Histidine,  $C_6H_9N_3O_2$  (M.W. 155.1546 g/mole) of purest grade were obtained from Sigma Aldrich Germany, SRL India and TLC Japan, respectively and was used as bought. The mass purity of studied IL was  $\geq 0.98$  and for studied amino acids were  $\geq 0.99$ . Amino acids and IL were dried in a vacuum desiccator over anhydrous  $CaCl_2$  for a minimum of 72 hours at room temperature and these were taken under consideration for the experiment without further purification. The amount of water content in IL (TBMS) was evaluated by Karl Fischer Titrator at approximately 0.05% (w%). A small amount of water has been considered for the preparations of stock solutions. To prepare the solutions, doubly distilled deionized water with a conductivity of approximately  $0.7 \mu S \cdot cm^{-1}$  was used. The specifications of chemicals used in this work are described in **Table 1**.

## 2.2 Apparatus and Procedure

To measure the densities ( $\rho$ ) of experimental aqueous systems and the solutions of different concentrations at the different experimental temperatures, vibrating-tube Anton Paar Density-Meter (DMA 4500M) was used. The overall uncertainty in density was found to be in the range of  $\pm 0.00093 \text{ g.cm}^{-3}$ . The instrument was calibrated by doubly distilled deionized degassed water and bypassing hot dry air [17]. The temperature was maintained within the range  $\pm 0.01 \text{ K}$  with the help of an automatic built-in Peltier device.

Measurement of viscosities of the prepared solutions ( $\eta$ ) under experiment was carried out by Brookfield DV-III Ultra Programmable Rheometer having a spindle size-42 with an accuracy of  $\pm 1\%$ . The specifics about the viscometer have already been illustrated previously [18]. The instrument was calibrated using known viscosities of water and aqueous solutions of  $\text{CaCl}_2$  by means of reference [19]. Prior to each investigation, calibration was done to avoid any unwanted errors. Brookfield Digital TC-500 temperature thermostat bath was used to maintain the experimental temperatures of the solutions.

Refractive indices of the experimental solutions were measured with the help of a Digital Refractometer Mettler Toledo with a light-emitting diode (LED). The accuracy for the refractive index measurement was almost  $\pm 0.0002$  units. The refractometer was calibrated twice with distilled water before the measurement of the refractive indices of prepared solutions. The calibration of the instrument was repeated after a few seconds of each experiment [20]. The light source used was a light-emitting diode,  $\lambda = 589.3 \text{ nm}$ . The temperature of the experimental solutions was retained throughout the experiment in a Brookfield Digital TC-500 Thermostatic water bath.

Specific conductivity of the solutions was measured through Systronics- 308 conductivity meter of working frequency  $1 \text{ kHz}$  with an accuracy of  $\pm 1\%$ . The cell constant was carried out using freshly prepared  $0.01 \text{ M}$  aqueous  $\text{KCl}$  solution [21] and it was maintained within the range  $0.09\text{--}1.00 \text{ cm}^{-1}$  during the experiment. All the solutions were placed in a dip-type immersion conductivity (CD-10) cell with a cell constant of about  $(0.1 \pm 0.001) \text{ cm}^{-1}$ . The cell was attached to a temperature-controlled water bath to sustain the investigational temperature. The cell constant was decided by means of the technique as suggested by Lind et al. [22].

To minimize any loss due to evaporation, sufficient precautions were taken in the course of the actual measurements. Mettler AG-285 electronic balance with a precision of  $\pm 0.01 \text{ mg}$  was used for mass measurements to prepare stock solutions. After preparation of stock solutions of ionic liquid and amino acids were further used to prepare different concentration sets by proper dilution. Experimental density values were used to convert molarity into molality and the combined standard uncertainty according to mass purity was assessed as  $\pm 0.0071 \text{ mol. kg}^{-1}$ .

K9 digital Tensiometer (KrussGmbH, Hamburg, Germany) instrument was used to determine the surface tension of different concentrations of mixed and pure experimental solutions. The accuracy of the instrument was  $\pm 0.3 \text{ mN/m}$ . For the determination of surface tension the platinum ring detachment technique was used. The calibration of the K9 digital Tensiometer was carried out with doubly distilled water and the calibration value of surface tension was found to be  $71.6 \text{ mN/m}$  which is in good agreement with the literature values of surface tension ( $71.99 \pm 0.05$ ). This tensiometer is a very good precision instrument that contains a solid and vibration-free base. This instrument puts on such a place that same demand on its neighbour as a laboratory balance with a resolution of  $0.1 \text{ mg}$ . In addition, a clean and dust-free atmosphere is needed for the measurements of surface tension.

Theoretical i.e. Ab-initio calculations were executed through Gaussian09W quantum chemical package [23].

### 3. Results and Discussion

Experimental values of density ( $\rho$ ), viscosity ( $\eta$ ), molar refraction ( $^R_M$ ) of different molality ( $m$ ) of aqueous TBMS solution at  $298.15 \text{ K}$ ,  $303.15 \text{ K}$  and  $308.15 \text{ K}$  are presented in **Table S1**. **Table S2** provides the experimental values of refractive index ( $n_D$ ), specific conductance ( $\kappa$ ) and surface tension ( $\sigma$ ) of different aqueous ionic liquid solutions of TBMS at temperatures  $298.15 \text{ K}$ ,  $303.15 \text{ K}$  and  $308.15 \text{ K}$ .

#### 3.1. Apparent Molar Volume

Here, we present information occurring the chemistry of ionic liquid interactions with amino acids in an aqueous solution that has been obtained from the apparent molar volume ( $\Phi_v$ ), limiting apparent molar volume ( $\Phi_v^0$ ) and experimental slope ( $S_v^*$ ) of amino acid in an aqueous solution of ionic liquid. All the three parameters governed by the solvent environment surrounding solute molecules, give the information that relates to the structural penalties of solute-solvent interactions. The experimental values of density ( $\rho$ ) at  $0.001$ ,  $0.003$  and  $0.005$  mole/kg concentrations of an aqueous ionic liquid solution of TBMS at  $298.15 \text{ K}$ ,  $303.15 \text{ K}$  and  $308.15 \text{ K}$  for different concentrations of L-Arginine and L-Histidine solutions have been represented in Table S3. Table S4 provides the apparent molar volume ( $\Phi_v$ ) of L-Arginine and L-Histidine solution, respectively in ( $0.001$ ,  $0.003$ ,  $0.005$ ) mole/kg aqueous ionic liquid (TBMS) solution at temperatures  $298.15 \text{ K}$ ,  $303.15 \text{ K}$  and  $308.15 \text{ K}$ . This apparent molar volume is the summation of the geometric volume of the central solute molecule and deviations in the solvent volume owing to interaction with the solute nearby the periphery or co-sphere. The apparent molar volumes were calculated from the solution densities (**Table S3**) of the solutions using the following equation [24].

$$\Phi_v = M / \rho_0 - (\rho - \rho_0) / m \rho \rho_0 \quad (1)$$

where M stands for the molar mass of the solute, m signifies the molality of the solution,  $\rho$  and  $\rho_0$  imply the densities of the solution and solvent respectively. The  $\Phi_v$  values are positive and get decrease with the intensification of the concentration (molality, m) of (L-Arginine + TBMS + H<sub>2</sub>O) and (L-Histidine + TBMS + H<sub>2</sub>O) solutions. Conversely,  $\Phi_v$  values increase with the increase in temperature at all the concentrations of L-Arginine and L-Histidine as well. The experimental values of  $\Phi_v$  also increase with an increase in mass fraction of the aqueous TBMS solution accordingly. It was further observed that L-Arginine have  $\Phi_v$  values higher than that of L-Histidine.

The limiting apparent molar volumes ( $\Phi_v^0$ ), i.e. apparent molar volume at infinite dilution were determined using a least-squares fitting linear method as the plots of  $\Phi_v$  versus square root of the molar concentration,  $\sqrt{m}$  using the Masson equation as follows [23] to analyse the different interactions taking place in the solutions:

$$\Phi_v = \Phi_v^0 + S_v^* \sqrt{m} \quad (2)$$

where  $\Phi_v^0$ , the limiting apparent molar volume at infinite dilution which shows the existence of interactions between solute-solvent and  $S_v^*$  stands for the experimental slope which gives the information about the nature of interactions between the solute molecules. **Table 2** represents the values of limiting apparent molar volumes ( $\Phi_v^0$ ) and experimental slopes ( $S_v^*$ ) of L-Arginine and L-Histidine solutions, respectively in ionic liquid TBMS at experimental temperatures.

**Figure 1 & 2** implies the variation of  $\Phi_v^0$  values of L-Arginine and L-Histidine solutions, respectively at 0.001, 0.003 and 0.005 (mole/kg), mass fraction of the ionic liquid TBMS and as a function of temperature. The positive  $\Phi_v^0$  values seem to increase with an increase in temperature as with the increase in the concentration of TBMS for both the amino acids. However,  $S_v^*$  values are negative for all the solutions and decrease with the rise in temperature and also with the increase in the concentration of the ionic liquid. Experimental data also reveal that L-Histidine has lower  $\Phi_v^0$  but higher  $S_v^*$  values in comparison to L-Arginine.

Positive  $\Phi_v^0$  values for all of the studied solvent mixtures show the presence of solute-solvent interactions. The order of solute-solvent interaction is (TBMS+L-Arg > TBMS+L-His) as represented in **Figures 1 & 2**. At infinite dilution, each solute molecule seems to be surrounded only by solvent molecules and keeps indefinitely distant from each other resulting in a greater extent of solute-solvent interaction rather than solute-solute interaction. Again the dipole-dipole interactions taking place in the solution phase that explains the above-mentioned order of interactions (solute-solvent), since higher the dipole-dipole interactions which suggested the

lower values of  $\Phi_r$  as well as  $\Phi_r^0$ . Theoretically, the dipole moment of TBMS, L-Arg, L-His were calculated with the help of the Gaussian 09 quantum chemical package are listed in **Table 12**.

A review of **Table 2** indicates that the positive  $\Phi_r^0$  values are maximum for L-Arginine in case of 0.005 m aqueous ionic liquid solution of TBMS at 308.15 K signifying utmost solute-solvent interaction and minimum for L-Histidine in case of 0.001 mole/kg aqueous ionic liquid solution at 298.15 K, suggesting the least solute-solvent interaction which was quite similar with some previous literature values [25]. This is perhaps owing to the release of a number of solvent molecules from unfastened solvation layers in the course of the solute-solvent interactions [26]. The higher  $\Phi_r^0$  values of L-Arginine specifies its more interaction with TBMS than that of L-Histidine under experimental conditions. Further, the  $S_r^*$  values point toward the extent of solute-solute interaction taking place in the mixture of solutions. The values of  $S_r^*$  are negative for all the experimental solutions which were in good agreement with the previous literature values [14, 25]. The higher values of  $S_r^*$  in L-Histidine seem to be the presence of interaction among itself to a greater extent in comparison to L-Arginine in respect of all the experimental conditions. This may be due to the presence of the imidazole side chain in the skeletal structure of L-Histidine as depicted by their molecular structures in **Scheme 1**.

Comparing the magnitude of  $\Phi_r^0$  and  $S_r^*$  values quantitatively, it was observed that  $\Phi_r^0$  values are much greater in magnitude than  $S_r^*$  values for all the experimental solutions and under all conditions. This recommends, the occurrence of stronger solute-solvent interactions and weaker solute-solute interactions in all the solutions [27-28]. There may be the effect of hydrophobic hydration or the caging effect of water molecules present in the solution mixtures [29] resulting in hydrophobic interactions occurring in amino acids that cause volume contractions. Thus the values of  $S_r^*$  given in **Table 2**, provides useful information about solute-solute interactions [30]. The positive sign of the slope specifies interactions between the hydrophilic groups in solution, while the negative sign leads to the hydrophobic cospheres as described by Hedwig [31]. Here the values of  $S_r^*$  are negative indicating weak solute-solute interactions. The same trend was observed by Harsh Kumar et al. [32].

Through **Scheme 3** the plausible molecular interactions occurring in the ionic liquid with two amino acids may be interpreted.

The temperature dependence of  $\Phi_r^0$ , studied here in the solution mixture from 298.15 K to 308.15 K at the interval of 5 K of temperature can be expressed by the following polynomial equation [33] as follows:

$$\Phi_r^0 = a_0 + a_1 T + a_2 T^2 \quad (3)$$

Where  $T$  is the temperature in Kelvin scale. The values of coefficients  $a_0$ ,  $a_1$  and  $a_2$  are three empirical coefficients depending on the nature of the solute and mass fraction ( $W$ ) of solvent at (298.15, 303.15 and 308.15) K. The empirical coefficient values ( $a_0$ ,  $a_1$  and  $a_2$ ) of L-Arginine and L-Histidine solution in different concentration (0.001, 0.003, 0.005) mole/kg of the TBMS at 298.15 K, 303.15 K and 308.15 K are recorded in **Table 3**.

Partial molar volume of transfer at infinite dilution is calculated using eq. 4 as given below and represented in **Table S5**.

$$\Delta\Phi_v^0 = \Phi_v^0(\text{in aqueous IL}) - \Phi_v^0(\text{in water}) \quad (4)$$

The obtained values of partial molar volume of transfer at infinite dilution are all positive and increase with an increase in the concentration of ionic liquid. The co-sphere overlap model plays a dynamic role in defining the nature of interactions occurring in the system. In fact, there are three discrete forms of interactions between TBMS+L-Arg and TBMS+L-His in view of the Cosphere overlap model [34-35]. (i) ion-ion interactions between  $\text{COO}^-$  group of amino acids with  $[\text{N}^+]$  part of TBMS and  $-\text{NH}_3^+$  groups of the amino acids with the negative part ( $\text{CH}_3\text{SO}_3^-$ ) of TBMS; (ii) ion-hydrophobic interactions between the  $-\text{NH}_3^+$  or  $\text{COO}^-$  of amino acids and hydrophobic portion (alkyl part) of IL TBMS; (iii) H-bonding interaction between the negative part ( $\text{CH}_3\text{SO}_3^-$ ) of the IL, one (N-H) part of the imidazole ring and hydrogens attached with N in the amino acids and (iv) hydrophobic-hydrophobic interactions between the hydrophobic parts of the amino acids and alkyl part of TBMS that may be more operative in the present analysis. A negative value of transfer volume is approved by ion-hydrophobic interactions and hydrophobic-hydrophobic interactions while ion-hydrophilic and hydrophilic-hydrophilic interactions demonstrate reverse contributions toward  $\Delta\Phi_v^0$  values. The accumulation of co-solutes to the aqueous solution of ionic liquids rescinds the cage structure of solvent and solute. In the present system, the ion-ion interactions prevail to a greater extent than the hydrophobic-hydrophilic and hydrophobic-hydrophobic interactions resulting in a positive change in volumes. Thus the positive transfer values reproduce the strong ion-ion interactions of amino acids with ionic liquids.

$$\Phi_E^0 = (\delta\Phi_v^0 / \delta T)_{P=0} = a_1 + 2a_2T \quad (5)$$

The values of  $\Phi_E^0$ , assess the extent of long-range structure-making or structure breaking potential of a solute in a solution mixture. The values of  $\Phi_E^0$  for the studied solution mixtures at (298.15, 308.15, and 318.15) K are recorded in **Table 4**.

The positive  $\Phi_E^0$  values except for a little negative value for 0.005 mole/kg IL solution of L-Histidine, for all of the examined solutions at all the temperatures, suggest that expansivities of all the experimental solutions are greater than that of the pure solvent. Also, it has been

observed that the  $\Phi_E^0$  values of the solutions are getting decreased with increase in temperature which indicates that some water molecules may be removed free from the hydration layers by increasing the temperature resulting in the increase of the solution volume faster to some extent than that of the pure solvent [36]. Also, positive  $\Phi_E^0$  values suggest the absence of caging or packing effect in the investigated solutions at all the temperatures.

The solute-solvent interaction may cause structure break or synergistic structure make. In this regard, Hepler developed a way to inspect the nature of the solute-solvent interaction going on in the solution phase [37]. According to Hepler opinion,  $(\delta\Phi_E^0/\delta T)_P$  values determine whether the interaction is structure breaker or structure maker [38].

$$(\delta\Phi_E^0/\delta T)_P = (\delta^2\Phi_V^0/\delta T^2)_P = 2a_2 \quad (6)$$

In general, negative and small positive  $(\delta\Phi_E^0/\delta T)_P$  values intensely show structure-breaking more willingly than structure-making interaction. In our case, the negative values recorded in **Table 4** respectively for L-Arginine and L-Histidine solutions in IL (TBMS) at 298.15 K, 303.15 K and 308.15 K temperatures endorse that the solute-solvent interaction acts as a structure-breaker. Thus all in the solutions, both the amino acids (solutes) are undoubtedly structure-breakers and result in disruption of the solvent structure with increasing solute-solvent interactions.

### 3.2. Viscosity

In the case of aqueous electrolytic solutions, the extent of ionic hydration [39] as well as structural interactions [40-41] within the ionic hydration cospheres [42] can be exposed by reviewing the viscosity coefficient with changing concentration and also the temperature of the aqueous solution. **Table S6** and **Table S7** provide viscosity ( $\eta$ ) values of L-Arginine and L-Histidine in aqueous ionic liquid solution which were in good agreement with the earlier literature values [14, 25] at temperatures 298.15 K, 303.15 K and 303.15 K respectively. The experimental results indicate that the viscosity of all the studied solutions increases with increasing the molality of IL solutions. Sarkar et al. also studied on Physico-chemical properties of TBMS [43]. This may be due to the increasing number of collisions taking place among the molecules with the increase in molality of the ionic liquid causing a loss of kinetic energy, the molecules are likely to be disposed to stick together with increasing viscosity.

Viscosity data obtained were studied with the help of the Jones-Dole equation [44].

$$\eta_r = \eta/\eta^0 = 1 + A\sqrt{c} + Bc \quad (7)$$

Where  $\eta$  and  $\eta^0$  signify viscosities of solution and solvent respectively,  $c$  stands for the concentration of the solution in molality. Experimental Values of  $(\eta/\eta^0 - 1)/\sqrt{m}$  for all the studied solution mixtures in 0.001, 0.003 and 0.005 mole/kg aqueous IL solution at temperatures 298.15 K, 303.15 K and 303.15 K have been represented in **Table S6** and **Table S7**.

The experimental values of  $(\eta/\eta^0 - 1)/\sqrt{m}$  are positive and increase with increasing concentration of both the amino acids in solutions and also with increasing temperature from 298.15 K to 308.15 K. Further, the  $(\eta/\eta^0 - 1)/\sqrt{m}$  values seem to be increased with the concentration of aqueous IL (TBMS) solution from 0.001 mole/kg to 0.005 mole/kg accordingly.

Rearranging the above Equation (7) following equation is obtained:

$$(\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \quad (8)$$

In the above equation, viscosity  $A$ -coefficient is a constant, also recognized as Falkenhagen coefficient [45] signifying long-range coulombic forces representing the solute-solute interaction and a weak solute-solute interaction (amino acid-amino acid) in solution mixtures as also observed from previous investigations. The  $B$ -coefficient is an adjustable parameter in this equation, which determines the extent of the effective hydrodynamic volume and reveals the solute-solvent interactions [46]. It is governed by the size and shapes effect of solute as well as structural effect persuaded by solute-solvent interaction as also happened in the present study that the viscosity  $B$ -coefficient values are positive in all conditions and quite greater than the  $A$ -coefficient indicating dominancy of the solute-solvent interaction over the solute-solute interaction. The viscosity  $B$ -coefficient seems to be increased with increasing temperature and also mass fraction of aqueous TBMS mixture implying that the solute-solvent interaction is developing with increasing mass fraction of TBMS mixture along with the temperature. In relation to the Jones-Dole equation the values of viscosity  $A$ - and  $B$ -coefficients obtained by linear least-square analysis from the plots of  $(\eta_r - 1)/\sqrt{c}$  vs  $\sqrt{c}$ , are reported in Table 5 for L-Arginine and L-Histidine solutions at temperatures 298.15 K, 303.15 K and 303.15 K. **Figure 3** and **Figure 4** show the variation of  $B$  values of L-Arginine and L-Histidine respectively against 0.001, 0.003 and 0.005 mole/kg IL solutions as a function of temperature whereas, Figure S1 and Figure S2 represent the variation of viscosity  $B$ -coefficient of L-Arginine and L-Histidine against temperature in different concentration of IL respectively.

**Table 5** show that the viscosity  $B$ -coefficient are positive for all the studied solutions signifying the existence of strong solute-solvent interactions that strengthen with an increase in the solvent viscosity value, which also supports the results obtained from  $\Phi_r^0$  values described before. Conversely, the negative values of the viscosity  $A$ -coefficient for most of the cases are smaller in comparison to viscosity  $B$ -coefficients thereby, indicating solute-solvent interactions are prominent over the solute-solute interactions. These outcomes specify the presence of very

weak solute–solute interactions in the solutions which also qualify with the results obtained from  $S_r^*$  values. The solute-solvent interaction obtained from the viscosity  $B$ -coefficient which were in good agreement with the former literature values [14, 21-25] takes place into the local vicinity of the solute molecules in the solution mixtures. The higher  $B$ -coefficient values for higher viscosity values is due to the solvated solute molecules associated by the solvent molecules all around because of the formation of an associated molecule by solute-solvent interactions [47]. Again, here the solute-solvent interactions are getting more strengthened with the increasing temperatures and also with the concentration of the IL solutions with more interaction between L-Arginine and aqueous IL solutions. The  $B$ -values of L-Arginine in aqueous TBMS solution in all respects are much larger than that for L-Histidine that signifying a greater solute-solvent interaction prevails in L-Arginine and aqueous TBMS solution. These consequences are comparable to those achieved from  $\Phi_r^0$  values.

Further, extensive study of the viscosity  $B$ -coefficient shows that the first derivative of  $B$ -coefficient over temperature is a measure of viscosity  $B$ -coefficient in visualizing the nature of solute-solvent interaction as structure-breaker or structure-maker. The  $dB/dT$  values determine the measure of activation energy necessary for the viscous flow in the solution. The measure of  $dB/dT$  is more indicative of the structure making or structure breaking ability than the sign or magnitude of the  $B$ -coefficient [48-49]. **Table 5** represent the values viscosity  $B$ -coefficients of L-Arginine and L-Histidine solutions along with the values of  $dB/dT$  at 0.001, 0.003 and 0.005 mole/kg solution of IL at (298.15, 303.15 and 308.15) K. The small positive values of  $dB/dT$  for all the experimental solutions designate about the structure-breaker effect of the L-Arginine and also L-Histidine in the aqueous ionic liquid solution of TBMS. The  $dB/dT$  theory as in Eyring's viscosity theory [50], indicates the negative value of  $dB/dT$  resembles the presence of higher energy of activation for viscous flow in solution rather than in pure solvent.

Overall, positive  $B$ -coefficient values suggest kosmotropes because strongly and firmly hydrated solutes exhibit a greater improvement in viscosity with concentration, while negative  $B$ -coefficients suggest chaotropes for weakly and feebly hydrated solutes [51]. In contrast, viscosity  $B$ -coefficients may not be evocative all the cases, predominantly for large hydrophobic components but the sign and magnitude of the  $B$ -coefficient, the values of is a superior indicator of the degree of structure-making or breaking potential [52-53]. The ratio of  $(B/\Phi_r^0)$  which has a high value [54] indicates that the primary solvation shell is formed.

According to **Table 5** and **Table 6**,  $B$ -coefficients for both the amino acids increase with temperature (positive  $dB/dT$ ) and also the high value of the ratio  $(B/\Phi_r^0)$  signifying the construction of a primary solvation shell as structure-disruptor.

Eyring and co-workers [50], show that the free energy of activation,  $\Delta\mu_1^{0\#}$  per mole of the solvent of viscous flow can be determined using the equation as follows:

$$\eta_0 = \frac{hN}{V_1^0} \exp\left(\frac{\Delta\mu_1^{0\#}}{RT}\right) \quad (9)$$

where  $h$  means Planck's constant,  $N_A$  represents Avogadro's number and  $V_1^0$  indicates the solvent's partial molar volume. This can be reorganized as the equation (10)

$$\Delta\mu_1^{0\#} = RT \ln(\eta_0 V_1^0 / hN_A) \quad (10)$$

If Equations. (8) as well as (10) [55-56] are followed, then the following equation can be obtained

$$B = (V_1^0 - V_2^0) / 1000 + V_1^0 (\Delta\mu_1^{0\#} - \Delta\mu_2^{0\#}) / 1000 RT \quad (11)$$

where  $V_2^0$  is limiting partial molar volume ( $\Phi_r^0$ ) of the solute present,  $\Delta\mu_2^{0\#}$  denotes ionic activation energy per mole of solute at infinite dilution. From the equation. (11), the following equation can be get

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + \frac{RT}{V_1^0} [B - (V_1^0 - V_2^0)] \quad (12)$$

**Table 7** shows that the  $\Delta\mu_2^{0\#}$  values are all positive and much higher than  $\Delta\mu_1^{0\#}$  representing that in the ground state, the interaction between the amino acids and the aqueous TBMS mixture is stronger than that in the transition state. The entropy for activation,  $\Delta S_2^{0\#}$  [57] of the experimental solution mixtures has been calculated using the following equation

$$d(\Delta\mu_2^{0\#}) / dt = - \Delta S_2^{0\#} \quad (13)$$

Using the least-squares method, the value of  $\Delta S_2^{0\#}$  has been obtained from the negative slope of the plots of  $\Delta\mu_2^{0\#}$  versus T.

Enthalpy of activation,  $\Delta H_2^{0\#}$  [57] has been calculated from the following relation

$$\Delta H_2^{0\#} = \Delta\mu_2^{0\#} + T \Delta S_2^{0\#} \quad (14)$$

Values of  $\Delta S_2^{0\#}$  and  $\Delta H_2^{0\#}$  are also represented in **Table 7** which displays that the value of  $\Delta\mu_2^{0\#}$  depends on the viscosity coefficients and the terms  $(V_1^0 - V_2^0)$ .  $\Delta\mu_2^{0\#}$  is the variation in free energy of activation of viscous flow per mole of aqueous amino acid solutions in presence of ionic liquid TBMS. The transition state theory states that the solvent molecules should pass through the viscous transition state. In view of Feakins et al. [55], if  $\Delta\mu_2^{0\#} > \Delta\mu_1^{0\#}$  for positive viscosity B-coefficient that indicates greater solute-solvent interactions resulting in the formation of the transition state followed by breaking and altering the intermolecular forces prevailing in the solvent structure of the medium [57-58]. Further positive values of  $\Delta S_2^{0\#}$  and  $\Delta H_2^{0\#}$  suggest that the formation of the transition state is associated with bond-breaking and rising accordingly.

However, any specific mechanism in this context is quite difficult to develop though the disordered state of the slip-plane may be proposed [57]. Finally, according to Feakins et al. model, as  $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$  both the amino acids performs as structure breakers that again supports the  $dB/dT$  characteristics in an aqueous TBMS mixture.

### 3.3. Refractive Index

Optical Data of the refractive index of the experimental solutions provide important information regarding molecular interactions in terms of molecular structures in the solutions. Refractive index signifies the speed of light which with increasing concentration due to interactions among the components of a system value also increase. The refractive index of a solution mixture can be interrelated by the application of a composition-dependent polynomial equation and molar refraction;  $^R_M$  in solution.

The molar refraction  $^R_M$  can be estimated from the Lorentz–Lorenz relation as follows [59]:

$$^R_M = \{(n_D^2 - 1) / (n_D^2 + 2)\}(M/\rho) \quad (15)$$

where  $^R_M$ ,  $n_D$ ,  $M$  and  $\rho$  stand for the molar refraction, the refractive index, the molar mass and the density of the solution, respectively. The refractive index of a substance refers to its ability to refract light as it travels from one medium to another and consequently, the higher the refractive index of a system, the more the light gets refracted [60]. It can simultaneously measure the compactness of that system involved in my research work. Further, as opined by Deetlefs et al. the refractive index of a substance is higher when its molecules are more strongly packed or generally while the substance is denser [61].

**Table S8** and **Table S9** represent the experimental values of refractive index ( $n_D$ ) and molar refraction ( $^R_M$ ) of L-Arginine and L-Histidine in different concentrations (0.001, 0.003 and 0.005 mole/kg) of aqueous IL; Tetrabutylammonium methanesulphonate at temperatures 298.15 K, 303.15 K and 308.15 K, respectively.

From the experimental values of refractive index ( $n_D$ ) and molar refraction ( $^R_M$ ), it has been observed that refractive index ( $n_D$ ) values for all the solutions decrease with increasing temperature whereas molar refraction ( $^R_M$ ) values show the opposite trend with increasing temperature. But, both the parameters ( $n_D$ ) and ( $^R_M$ ) display an increasing trend with an increase in the concentration of L-Arginine and L-Histidine and also the concentration of ionic liquid solutions. Again, L-Arginine shows higher values of refractive index ( $n_D$ ) than L-Histidine. This result is in good agreement with the volumetric and viscometric results obtained earlier. Analysis of the data from **Table S2** and **Table 8** enables us to draw the sequence of compactness of the systems indicating that the molecules are more tightly packed in the solution mixture of L-

Arginine. Therefore, the higher refractive index values for the L-Arginine indicate the presence of more tightly packed molecules in the solution. The following is the sequence of compactness of the two systems in the solution phase; (TBMS+L-Arg) > (TBMS+L-His) [25].

The limiting molar refraction, ( $R_M^0$ ) listed in Table 8 can be determined from the following equation-

$$R_M = R_M^0 + R_S \sqrt{m} \quad (16)$$

where 'm' is the molality of solution and  $R_M^0$  is the limiting molar refraction that suggests solute-solvent interaction. This study of limiting molar refraction operates as an informative parameter for studying the molecular interaction that takes place in the solution. **Figure 5** show a gradual increase in the values of  $R_M^0$  with the rise in the concentration of co-solvent and temperature that also supports the fact that here the solute-solvent interaction dominates over solute-solute interactions and is reinforced with an increase in temperature and also the mass fraction of aqueous TBMS mixture. The  $R_M^0$  values of L-Arginine in aqueous TBMS solution are much higher than that for L-Histidine, representing a greater extent of solute-solvent interaction prevailing in L-Arginine that were found to be similar remarks as assessed from apparent molar volume and viscosity B-coefficients mentioned earlier.

### 3.4 Electrical Conductance

The nature of solute-solvent interactions and the structure making or structure breaking tendency of components in a given solvent can be assumed with the help of an electrical conductance study. The conductance study of the interaction (solute-solvent) between L-Arginine and L- Histidine with the aqueous solution of ILs, BTAMS has been performed at three different temperatures. The advantage of this study is that this measurement provides information about the interaction and transport phenomena of the (L-Arg + ILs + H<sub>2</sub>O) and (L-His + ILs + H<sub>2</sub>O) ternary systems [62]. Experimental values of specific conductance ( $\kappa$ ) of different molality of aqueous IL(TBMS) solution at 298.15 K, 303.15 K and 308.15 K are represented in **Table S10**. Such a type of investigation was also done by Sarkar et al. [44]. The specific conductance ( $\kappa$ ) values increase with increasing temperature and also with the increase in the concentration of aqueous IL solution and the solutions of L-Arginine and L-Histidine. However, the molar conductance ( $\Lambda$ ) values as reported in **Table 9**, decrease with the increasing concentration of L-Arginine and L-Histidine solutions. On the other hand, solutions of L-Histidine have higher molar conductance ( $\Lambda$ ) values in comparison to that of L-Arginine under all experimental conditions.

**Figure 6** and **Figure 7** provide the variation of molar conductance ( $\Lambda$ ) with different concentrations of amino acids, L-Arginine and L-Histidine in aqueous (0.001, 0.003, 0.005)m of IL (TBMS) solution at different temperature 298.15 K, 303.15 K and 308.15 K respectively.

The molar conductance ( $\Lambda$ ) is obtained from the values of specific conductance ( $\kappa$ ) with the help of the following equation [41]:

$$\Lambda = (1000\kappa) / C \quad (17)$$

Linear conductivity curves ( $\Lambda$  vs.  $C$ ) were estimated for the amino acids; L-Arginine and L-Histidine in IL solutions and extrapolation of  $\sqrt{C} = 0$  were used to calculate the limiting molar conductance. It has been observed that  $\Lambda$  value increases with increasing temperature for every experimental system and with increasing concentration of amino acids as well as IL (TBMS) solutions. While gradual addition of either L-Arginine or L-Histidine to ILs solution causes a constant decrease in molar conductance values. Here, the mobility of the ions present in solution plays the principal role, despite developing ionic substances on the addition of aqueous L-Arginine or L-Histidine solution [63] showing the decreasing trend of molar conductance values. It may be caused by the solute-solvent interaction governed by the ion-hydrophilic, ion hydrophobic as well as hydrophobic-hydrophobic interaction occurring in the solution mixtures. The development of the molecular association, therefore, forces the ionic substances to be less mobile indicating such conductivity results of the present study. Thus, the conductometric study also supports the observation obtained from the investigation of density, viscosity, refractive index and surface tension as well.

Furthermore, in order to investigate the critical micelle concentration (CMC) value of studied ionic liquid TBMS and the amino acids under experiment, we have made systematic measurements of electrical conductance. The different concentrations, 0.001, 0.003, 0.005 molality/mol.kg<sup>-1</sup> of TBMS solutions are stepwise added for the measurement of the conductance in a fixed amount of amino acids (0.01 mol/kg, 20 mL) at different temperatures. The conductivity data in this regard are listed in **Table S11-S13** and **S14-S16** and the plots related to it are shown in Figure S3, S4, S5. From the figures, it is clear that there is present a sharp breakpoint in each case in different temperatures and concentrations that are summarized in Table 10. Thus the CMC value so obtained are of good agreement with the former study and reveals that the solute-solvent interactions are predominating over solute-solute interaction in the case of TBMS+L-Arginine than TBMS+L-Histidine in each concentration and temperature.

### 3.5 Surface Tension

The investigation of surface tension is of great importance in many scientific and technological fields. As an important parameter, surface tension is the unique most available experimental parameter that designates the thermodynamic features and provides information about the internal structure of the studied liquid systems. From **Table 11** and also **Figure 8** and **9**, it is observed that with increasing the concentration of ionic liquid in water the surface tension decreases because the molecules of the ionic liquid can get aggregates in water [64].

However, when the addition of amino acid takes place into the ionic liquid solution, the solute molecule can interact with ionic liquid and aggregation of ionic liquid decreases, as a result the surface tension gradually increases. The Tetra butylammonium methanesulphonate (IL) has a long butyl chain, so it can easily aggregate in water with increasing the concentration of ionic liquid, therefore, the surface tension generally decreases but with the addition of L-Arginine and L-Histidine in the ionic liquid mixture, the surface tension increases due to the inward pull of the solute molecules (L-Arginine, L-Histidine) from the surface by the bulk molecules (Ionic liquid). The inward pull of solute molecules depends upon the interaction between the L-Arginine and L-Histidine with the ionic liquid mixture [65]. The values obtained from the surface tension measurement, it was observed that the surface tension of the solution mixtures of L-Arginine is greater than the L-Histidine solution, which indicates the higher inward pull taking place in the case of L-Arginine solution mixture and can be illustrated by the interaction between zwitterionic groups of amino acids and a polar solvent, therefore, the solute-solvent interaction is more prominent in L-Arginine solution than that of L-Histidine solution.

### 3.6 Gaussian 09W Quantum Chemical Calculation: Theoretical basis of the Interaction

Theoretically, this field is very much important. For applying in quantum, mechanical calculation there is no use or maintenance sequence of configurations and no straight use of known structure. The main idea is to establish a realistic function that replicates the physical forces and chemical contacts. UB3YLP function is used for the calculation. Diffused basic functions are found to be effective in describing the weak interaction associated with the atoms in molecules. For this purpose, we have used a basis set 6-311G (d) for an exact description of performing weak interaction prevail in the transition structures.

This calculation has been carried out through Gaussian 09W quantum chemical package. The quantum mechanical calculations of optimum energy estimate the extent of  $O \cdots N \cdots O$ ,  $C=O \cdots O - H$  interactions. Such interaction involving in L-Arginine and L-Histidine cluster in the sphere of ionic liquid [66] the aforesaid statements were well thought out in our present work. We depicted the molecular assembly between the  $L-Arg \cdots IL(1)$  and  $L-His \cdots IL(1)$  through quantum chemical calculations which support the existence of such type of cluster. The calculated theoretical value through Gaussian 09w quantum mechanical tools that support the above results obtained from different types of experimental parameters in the manuscript. The several properties of different systems in computational technique are summarized in **Table 12**.

The extent of stabilization energy of pure and as well as their molecular assembly can be evaluated by optimization energy value. While the formation of molecular gather is assorted by the solute-solvent interaction in the solution phase. The value of optimization energy can explain the possibility of higher solute-solvent interaction. More minimization of optimization energy, higher is the solute-solvent interaction associated with the atmos. Prominent solute-solvent

interaction is observed in (TBMS+L-Arg+H<sub>2</sub>O) system over (TBMS+L-His+H<sub>2</sub>O) system and discussed here with especially in consort with the optimum geometry of the system depicted in **Scheme 2**.

The solute molecule surrounded by solvent molecule by non-covalent interaction can also be explained on the basis of thermodynamics [67].

#### 4. Conclusion

The aim of the present paper was to establish the nature of solute-solute and solute-solvent interactions in the solutions of TBMS + amino acid systems of several concentrations and temperatures for chemical and technological applications. The investigation of Physico-chemical parameters through density, viscosity, refractive index, surface tension and conductance study refers to the mode of interactions taking place in the amino acids; L-Arginine and L-Histidine in ionic liquid solutions of TBMS at different concentrations as well as different temperatures. In the present study, all the parameters were interpreted in terms of solute-solute and solute-solvent interactions occurring among the various components of the experimental solution mixtures. Analysis of apparent molar volume, limiting apparent molar volume, molar refraction, limiting molar refraction, viscosity B coefficient and surface tension signify the solute-solvent interaction is predominant over solute-solute interaction. The  $(\delta\Phi_E^0/\delta T)_P$  and  $(dB/dT)$  values have been considered to illustrate the facts that, the solute-solvent interaction is significantly structure breaking which is further established by Hepler's constant values. From the study of the investigated solutions presence of strong solute-solvent interaction was observed and also supposed to be more effective and predominant than the solute-solute interaction occurring in experimental systems. Amino acid L-Histidine fused with the imidazole ring undergoes a lower degree of interactions in the presence of ionic liquid (TBMS) as compared to L-Arginine. Surface tension indicated the starring role of the hydrophilic and hydrophobic character of solutes in molecular interactions with TBMS in aqueous solutions. Again, conductance data also recommends the mode of interactions going on between the solute and solvent thereby the presence of mobility in the solution phase. Ultimately, strong hydrophobic-hydrophobic interactions are playing an important role too. Furthermore, electrostatic and hydrophobic interactions are more predominant for the L-Arginine-TBMS system, associating the experimental outcomes. The experiment definitely would provide for a more inclusive understanding of such systems to a large extent.

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### CRedit author statement

Mahendra Nath Roy: Conceptualization, Resources, Supervision

Sukdev Majumder: Investigation, Data curation, Tabulation, Formal analysis

Lovely Sarkar: Formal analysis, Writing-Original Draft

Modhusudan Mondal: Writing-Review and Editing

Debadrita Roy: Writing-Review and Editing

Kanak Roy: Writing-Review and Editing

Abhinath Barman: Writing-Review and Editing

Nitish Roy: Writing-Review and Editing

## Tables

**Table 1.** Specification of chemical samples.

| SL. No. | Name of Chemicals and their IUPAC name   | CAS NO.    | Supplier      | <sup>b</sup> Purity of Mass Fraction | <sup>a</sup> Water Contain (w%) | Molar mass(g/mole) |
|---------|--|------------|---------------|--------------------------------------|---------------------------------|--------------------|
| 1       | Tetrabutylammonium Methanesulphonate (C <sub>17</sub> H <sub>39</sub> NO <sub>3</sub> S)<br>methanesulfonate;tetrabutylazanium | 65411-49-6 | Sigma Aldrich | ≥ 0.98                               | ~0.05%                          | 337.6              |
| 2       | L-Arginine (C <sub>6</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> )<br>(S)-2-Amino-5-guanidinopentanoic acid            | 74-79-3    | SRL           | ≥0.99                                | –                               | 174.204            |
| 3       | L-Histidine (C <sub>6</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub> )<br>(2S)-2-amino-3-(1H-imidazol-5-yl)propanoic acid  | 71-00-1    | TLC           | ≥0.99                                | –                               | 155.1546           |

<sup>a</sup>The (w%) of water in TBMS(IL) are measured by using the Karl–Fischer Titrator.

<sup>b</sup>amino acids and IL are dried in a vacuum desiccator minimum of 72 hours over anhydrous CaCl<sub>2</sub>.

All chemicals are taken without further purification.

**Table 2.** Limiting apparent molar volumes ( $\Phi_v^0$ ) and Experimental slopes ( $S_v^*$ ) of (L-ARGININE+TBMS+H<sub>2</sub>O) and (L-HISTIDINE+TBMS+H<sub>2</sub>O) systems in aqueous solutions of (0.001, 0.003, 0.005) m IL (TBMS) at 298.15 K, 303.15 K, 308.15 K at atmospheric pressure 0.1MPa.

| Temperature/<br>(K)                      | $\Phi_v^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$ | $S_v^* \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-3/2} \cdot \text{kg}^{1/2})$ | $\Phi_v^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$ | $S_v^* \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-3/2} \cdot \text{kg}^{1/2})$ |
|--|---|--|---|--|
| (L-ARGININE+TBMS+H <sub>2</sub> O)system |   | (L-Histidine+TBMS +H <sub>2</sub> O)system                                       |   |  |
| 0.001mL/mol.kg <sup>-1</sup>             |   |  |   |  |
| 298.15K                                  | 127.46±0.02   | -9.85±0.01   | 103.20 ±0.01  | -7.74 ±0.01  |
| 303.15K                                  | 129.28±0.01   | -16.00±0.01  | 104.76 ±0.00  | -11.99±0.03  |
| 308.15K                                  | 130.59±0.01   | -17.12±0.01  | 106.09 ±0.00  | -14.24±0.01  |
| 0.003mL/ mol.kg <sup>-1</sup>            |   |  |   |  |
| 298.15K                                  | 130.63±0.02   | -20.11±0.03  | 105.92±0.01   | -15.50±0.01  |
| 303.15K                                  | 133.87±0.02   | -28.65±0.01  | 107.71±0.00   | -19.00±.00   |
| 308.15K                                  | 136.06±0.01   | -33.40±0.01  | 108.92±0.01   | -20.67±0.02  |
| 0.005mL/ mol.kg <sup>-1</sup>            |   |  |   |  |
| 298.15K                                  | 131.74±0.01   | -23.16±0.02  | 107.17±0.00   | -18.03±0.01  |
| 303.15K                                  | 135.53±0.00   | -32.65±0.03  | 109.15±0.00   | -26.92±0.01  |
| 308.15K                                  | 137.36±0.03   | -38.42±0.04  | 109.75±0.00   | -28.10±0.00  |

\*Standard uncertainties values of u are:  $u(T) = \pm 0.01\text{K}$  (0.68 level of confidence), #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{ mol kg}^{-1}$ . \*molality has been expressed per kg of (TBMS + water) solvent mixture. \* Standard uncertainty in pressure  $u(P) = \pm 0.01 \text{ MPa}$ .

**Table 3.** Empirical coefficient values ( $a_0$ ,  $a_1$  and  $a_2$ ) of L-Arginine & L-Histidine in different concentrations (0.001, 0.003, 0.005)m in aqueous IL (TBMS) solutions at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

| Molality<br>of IL<br>/mol.kg <sup>-1</sup> | $a_0 \times 10^6 / \text{m}^3 \text{mol}^{-1}$ | $a_1 \times 10^6 / \text{m}^3 \text{mol}^{-1} \text{K}^{-1}$ | $a_2 \times 10^6 / \text{m}^3 \text{mol}^{-1} \text{K}^{-2}$ | $a_0 \times 10^6 / \text{m}^3 \text{mol}^{-1}$ | $a_1 \times 10^6 / \text{m}^3 \text{mol}^{-1} \text{K}^{-1}$ | $a_2 \times 10^6 / \text{m}^3 \text{mol}^{-1} \text{K}^{-2}$ |
|--|--|--|--|--|--|--|
| 0.001                                      | -902.99  | 6.4973   | -0.0102  | -405.59  | 3.078  | -0.0046  |
| 0.003                                      | -1960.6  | 13.275   | -0.0210  | -1049.3  | 7.3331   | -0.0116  |
| 0.005                                      | -3637.3  | 24.329   | -0.0392  | -2505.5  | 16.992   | -0.0276  |

\*Standard uncertainties values of u are:  $u(T) = \pm 0.01\text{K}$ , Standard uncertainty in pressure  $u(P) = \pm 0.01 \text{ MPa}$  \*molality has been expressed per kg of (TBMS + water) solvent mixture. \*#Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{ mol kg}^{-1}$ .

**Table 4.** Values of limiting molar expansivities  $\Phi_E^0$  &  $(\delta\Phi_E^0/\delta T)_P$  of L-Arginine and L-Histidine of different concentrations (0.001, 0.003, 0.005) m in aqueous IL (TBMS) solutions at different temperature and pressure 0.1MPa

| Molality of IL/ mol.kg-1 | $\Phi_E^0 \times 10^6$<br>/m <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> |         |         | $(\delta\Phi_E^0/\delta T)_P \times 10^6$ /m <sup>3</sup> mol <sup>-1</sup> K <sup>-2</sup> | $\Phi_E^0 \times 10^6$<br>/m <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> |         |          | $(\delta\Phi_E^0/\delta T)_P \times 10^6$ /m <sup>3</sup> mol <sup>-1</sup> K <sup>-2</sup> |
|--------------------------|---|---------|---------|---|---|---------|----------|---|
|                          | 298.15K   | 303.15K | 308.15K |   | 298.15K   | 303.15K | 308.15K  |   |
| 0.001                    | 0.41504   | 0.31304 | 0.21104 | -0.0204   | 0.33502   | 0.28902 | 0.24302  | -0.0092   |
| 0.003                    | 0.7527  | 0.5427  | 0.3327  | -0.0420   | 0.41602   | 0.30002 | 0.18402  | -0.0232   |
| 0.005                    | 0.95404   | 0.56204 | 0.17004 | -0.0784   | 0.53412   | 0.25812 | -0.01788 | -0.0552   |

\*Standard uncertainties values of u are: u (T) = ±0.01K, \* Standard uncertainty in pressure u (P) = ± 0.01 MPa. \*molality has been expressed per kg of (TBMS + water) solvent mixture. \* #Combined standard uncertainties in molality according to stated purity u(m) = ±0.0092 mol kg<sup>-1</sup>.

**Table 5.** Viscosity B-coefficients, A-coefficients of (L-ARGININE+TBMS+H<sub>2</sub>O) and L-HISTIDINE+TBMS+H<sub>2</sub>O) systems along with dB/dT values in aqueous IL(TBMS) solutions of different concentrations (0.001,0.003,0.005)m at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

| Temperature (K)                     | 0.001mIL/ mol.kg-1                        |                           | 0.003mIL/ mol.kg-1                        |                           | 0.005mIL/ mol.kg-1                        |                           | dB/dT |
|-------------------------------------|---|---------------------------|---|---------------------------|---|---------------------------|-------|
|                                     | B (kg <sup>1/2</sup> mol <sup>1/2</sup> ) | A (kg.mol <sup>-1</sup> ) | B (kg <sup>1/2</sup> mol <sup>1/2</sup> ) | A (kg.mol <sup>-1</sup> ) | B (kg <sup>1/2</sup> mol <sup>1/2</sup> ) | A (kg.mol <sup>-1</sup> ) |       |
| (L-ARGININE+TBMS+H <sub>2</sub> O)  |   |                           |   |                           |   |                           |       |
| 298.15                              | 0.632±0.013                               | 0.026                     | 0.707±0.012                               | 0.025                     | 0.819±0.014                               | 0.024                     | 0.027 |
| 303.15                              | 0.816±0.013                               | 0.024                     | 0.888±0.012                               | 0.024                     | 0.971±0.014                               | 0.023                     | 0.029 |
| 308.15                              | 0.904±0.013                               | 0.023                     | 0.999±0.012                               | 0.022                     | 1.116±0.014                               | 0.017                     | 0.029 |
| (L-HISTIDINE+TBMS+H <sub>2</sub> O) |   |                           |   |                           |   |                           |       |
| 298.15                              | 0.467±0.011                               | 0.033                     | 0.572±0.012                               | 0.032                     | 0.662±0.013                               | 0.031                     | 0.019 |
| 303.15                              | 0.580±0.011                               | 0.032                     | 0.671±0.012                               | 0.028                     | 0.757±0.013                               | 0.025                     | 0.020 |
| 308.15                              | 0.658±0.011                               | 0.026                     | 0.769±0.012                               | 0.026                     | 0.874±0.013                               | 0.019                     | 0.021 |

\*Standard uncertainties values of u are: u (T) = ±0.01K (0.68 level of confidence), Falkenhagen coefficient (A), Viscosity B-Coefficients (B) are given in the parentheses. \*Standard uncertainty in pressure u (P) = 0.01 MPa \*molality has been expressed per kg of (TBMS + water) solvent mixture. \* #Combined standard uncertainties in molality according to stated purity u(m) = ±0.0092 mol kg<sup>-1</sup>.

**Table 6.** Values of  $(B/\Phi_v^0)$  for L-Arginine and L-Histidine in different concentrations of aqueous TBMS (IL) solutions at different temperature and atmospheric pressure 0.1MPa.

| Temperature (K) | $B / \Phi_v^0$      |        |        | $B / \Phi_v^0$       |        |        |
|-----------------|---------------------|--------|--------|----------------------|--------|--------|
|                 | 0.001m              | 0.003m | 0.005m | 0.001m               | 0.003m | 0.005m |
|                 | L-ARGININE+ aq.TBMS |        |        | L-HISTIDINE +aq.TBMS |        |        |
| 298.15          | 4.960               | 5.415  | 6.218  | 4.527                | 5.401  | 6.178  |
| 303.15          | 6.312               | 6.640  | 7.169  | 5.659                | 6.237  | 6.940  |
| 308.15          | 6.927               | 7.348  | 8.129  | 6.139                | 7.062  | 7.963  |

<sup>a</sup>Mass fractions of TBMS in aqueous solution; #Standard uncertainty in molality u (m) = ±0.0001mol kg<sup>-1</sup>. \*Standard uncertainty in temperature u (T) = ± 0.01 K. \*Standard uncertainty in pressure u (P) = ± 0.01MPa \*molality has been expressed per kg of (TBMS + water) solvent mixture. \* #Combined standard uncertainties in molality according to stated purity u(m) = ±0.0092 mol kg<sup>-1</sup>.

**Table 7.** Values of  $(V_1^0 - V_2^0)$ ,  $\Delta\mu_1^{0\#}$ ,  $\Delta\mu_2^{0\#}$ ,  $T\Delta S_2^{0\#}$ ,  $\Delta H_2^{0\#}$  for L-Arginine and L-Histidine in different concentrations of an aqueous solution of IL(TBMS) mixture at different temperatures and atmospheric pressure 0.1MPa.

| Parameters                      | 0.001mL/<br>mol.kg <sup>-1</sup> |          |          | 0.003mL/<br>mol.kg <sup>-1</sup> |         |         | 0.005mL<br>mol.kg <sup>-1</sup> |         |         |
|---------------------------------|----------------------------------|----------|----------|----------------------------------|---------|---------|---------------------------------|---------|---------|
|                                 | T=298.15K                        | 303.15K  | 308.15K  | T=298.15K                        | 303.15K | 308.15K | 298.15K                         | 303.15K | 308.15K |
| L-Arginine                      |                                  |          |          |                                  |         |         |                                 |         |         |
| $(V_1^0 - V_2^0)/m^3.mol^{-1}$  | -109.457                         | -111.277 | -112.587 | -112.62                          | -115.86 | -118.05 | -113.72                         | -117.51 | -119.34 |
| $\Delta\mu_1^{0\#}/KJ.mol^{-1}$ | 9.39                             | 9.39     | 9.35     | 9.47                             | 9.41    | 9.37    | 9.51                            | 9.43    | 9.44    |
| $\Delta\mu_2^{0\#}/KJ.mol^{-1}$ | 111.53                           | 140.08   | 154.10   | 122.35                           | 150.04  | 168.41  | 137.89                          | 161.83  | 185.22  |
| $T\Delta S_2^{0\#}/KJ.mol^{-1}$ | 1260.13                          | 1282.74  | 1302.39  | 1373.30                          | 1396.34 | 1419.37 | 1411.35                         | 1435.02 | 1458.69 |
| $\Delta H_2^{0\#}/KJ.mol^{-1}$  | 1371.66                          | 1422.82  | 1456.50  | 1495.66                          | 1546.38 | 1587.78 | 1549.23                         | 1596.88 | 1643.91 |
| L-Histidine                     |                                  |          |          |                                  |         |         |                                 |         |         |
| $(V_1^0 - V_2^0)/m^3.mol^{-1}$  | -85.19                           | -86.75   | -88.08   | -87.91                           | -89.70  | -90.91  | -89.15                          | -91.13  | -91.73  |
| $\Delta\mu_1^{0\#}/KJ.mol^{-1}$ | 9.39                             | 9.33     | 9.35     | 9.47                             | 9.41    | 9.37    | 9.51                            | 9.43    | 9.35    |
| $\Delta\mu_2^{0\#}/KJ.mol^{-1}$ | 86.83                            | 102.73   | 115.53   | 100.32                           | 116.01  | 131.74  | 112.91                          | 128.20  | 146.71  |
| $T\Delta S_2^{0\#}/KJ.mol^{-1}$ | 855.63                           | 869.98   | 884.32   | 936.79                           | 952.50  | 968.20  | 1007.96                         | 1024.86 | 1041.76 |
| $\Delta H_2^{0\#}/KJ.mol^{-1}$  | 942.46                           | 972.71   | 999.86   | 1037.11                          | 1068.50 | 1099.96 | 112.87                          | 1153.05 | 1188.48 |

<sup>m</sup>different concentrations of TBMS in aqueous solution; \*Standard uncertainty in temperature u (T) = ± 0.01 K. \*Standard uncertainty in pressure u (P) = ± 0.01 MPa \*molality has been expressed per kg of (TBMS + water) solvent mixture. \*#Combined standard uncertainties in molality according to stated purity u(m) = ± 0.0092 mol kg<sup>-1</sup>.

**Table 8.** Limiting molar refraction ( $R_M^0$ ) of L-Arginine and L-Histidine in aqueous ionic liquid IL (TBMS) solutions of different concentrations, (0.001, 0.003, 0.005) m at different temperature and atmospheric pressure 0.1MPa.

| Temperature/K                       | 298.15 K     | 303.15 K     | 308.15 K     |
|-------------------------------------|--------------|--------------|--------------|
| Molality of IL/mol.kg <sup>-1</sup> |              |              |              |
| L-ARGININE+aq.TBMS                  |              |              |              |
| 0.001                               | 35.856±0.028 | 35.877±0.027 | 35.920±0.027 |
| 0.003                               | 35.884±0.027 | 35.904±0.027 | 35.946±0.028 |
| 0.005                               | 35.902±0.027 | 35.929±0.028 | 35.972±0.028 |
| L-HISTIDINE+aq.TBMS                 |              |              |              |
| 0.001                               | 31.870±0.042 | 31.897±0.039 | 31.944±0.042 |
| 0.003                               | 31.886±0.039 | 31.911±0.039 | 31.957±0.039 |
| 0.005                               | 31.919±0.042 | 31.944±0.042 | 31.992±0.042 |

\*Standard errors for limiting molar refraction ( $R_M^0$ ) are given in their parenthesis. \*Standard uncertainties values of u are: u (T) = ± 0.01K (0.68 level of confidence), \*Standard uncertainty in pressure u (P) = ± 0.01 MPa \*molality has been expressed per kg of (TBMS + water) solvent mixture. \*#Combined standard uncertainties in molality according to stated purity u(m) = ± 0.0092 mol kg<sup>-1</sup>.

**Table 9.** Molar conductance ( $\Lambda$ ) of L-Arginine and L-Histidine in aqueous IL (TBMS) solution of different concentrations, (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

| Molality(m)<br>/mol.kg <sup>-1</sup> | $\Lambda$<br>/S.cm <sup>2</sup> .mol <sup>-1</sup> | Molality(m)<br>/mol.kg <sup>-1</sup> | $\Lambda$<br>/S.cm <sup>2</sup> .mol <sup>-1</sup> | Molality(m)<br>/mol.kg <sup>-1</sup> | $\Lambda$<br>/S.cm <sup>2</sup> .mol <sup>-1</sup> |
|--------------------------------------|--|--------------------------------------|--|--------------------------------------|--|
|                                      | 298.15K  |                                      | 303.15K  |                                      | 308.15K  |
| L-ARGININE+aq.TBMS                   |  |                                      |  |                                      |  |
| 0.001mL/ mol.kg <sup>-1</sup>        |  |                                      |  |                                      |  |
| 0.01004                              | 8.300±0.001  | 0.01005                              | 9.100±0.003  | 0.01007                              | 10.100±0.002                                       |
| 0.02515                              | 4.520±0.002  | 0.02518                              | 4.800±0.001  | 0.02523                              | 5.160±0.004  |
| 0.04032                              | 3.525±0.001  | 0.04037                              | 3.750±0.004  | 0.04044                              | 4.025±0.001  |
| 0.05554                              | 2.890±0.004  | 0.05562                              | 3.090±0.003  | 0.05572                              | 3.327±0.001  |
| 0.07082                              | 2.571±0.005  | 0.07092                              | 2.771±0.001  | 0.07105                              | 2.985±0.003  |
| 0.08616                              | 2.470±0.001  | 0.08628                              | 2.635±0.001  | 0.08644                              | 2.835±0.006  |

| 0.003mIL/ mol.kg <sup>-1</sup> |              |         |              |         |              |
|--------------------------------|--------------|---------|--------------|---------|--------------|
| 0.01004                        | 11.000±0.001 | 0.01005 | 11.700±0.001 | 0.01007 | 12.400±0.001 |
| 0.02515                        | 5.200±0.004  | 0.02518 | 5.920±0.007  | 0.02523 | 6.240±0.004  |
| 0.04031                        | 4.250±0.002  | 0.04037 | 4.450±0.001  | 0.04044 | 4.700±0.003  |
| 0.05554                        | 3.363±0.003  | 0.05562 | 93.454±0.005 | 0.05572 | 3.727±0.001  |
| 0.07082                        | 3.057±0.008  | 0.07092 | 3.214±0.005  | 0.07104 | 3.357±0.001  |
| 0.08615                        | 2.929±0.001  | 0.08628 | 3.152±0.002  | 0.08643 | 3.294±0.001  |
| 0.005mIL/ mol.kg <sup>-1</sup> |              |         |              |         |              |
| 0.01004                        | 13.600±0.003 | 0.01005 | 14.800±0.005 | 0.01007 | 17.500±0.001 |
| 0.02515                        | 6.480±0.001  | 0.02518 | 8.120±0.001  | 0.02522 | 8.560±0.007  |
| 0.04031                        | 4.725±0.002  | 0.04037 | 5.350±0.001  | 0.04044 | 5.650±0.001  |
| 0.05554                        | 3.909±0.001  | 0.05561 | 4.400±0.003  | 0.05571 | 4.654±0.002  |
| 0.07082                        | 3.357±0.002  | 0.07091 | 3.928±0.001  | 0.07104 | 4.028±0.001  |
| 0.08615                        | 3.117±0.002  | 0.08627 | 3.705±0.002  | 0.08642 | 3.800±0.004  |
| L-HISTIDINE+aq.TBMS            |              |         |              |         |              |
| 0.001mIL/ mol.kg <sup>-1</sup> |              |         |              |         |              |
| 0.01003                        | 12.600±0.001 | 0.01005 | 13.600±0.008 | 0.01007 | 14.800±0.004 |
| 0.02513                        | 5.480±0.001  | 0.02517 | 6.120±0.001  | 0.02518 | 6.720±0.0001 |
| 0.04028                        | 4.275±0.001  | 0.04033 | 4.550±0.002  | 0.04041 | 4.800±0.001  |
| 0.05547                        | 7.45±0.001   | 0.05549 | 3.600±0.005  | 0.05564 | 3.854±0.003  |
| 0.07070                        | 3.290±0.001  | 0.07080 | 3.242±0.001  | 0.07093 | 3.414±0.001  |
| 0.08598                        | 3.171±0.001  | 0.08610 | 3.223±0.003  | 0.08626 | 3.352±0.002  |
| 0.003mIL/ mol.kg <sup>-1</sup> |              |         |              |         |              |
| 0.01003                        | 15.500±0.007 | 0.01005 | 16.600±0.003 | 0.01007 | 17.600±0.004 |
| 0.02513                        | 6.920±0.010  | 0.02517 | 7.440±0.001  | 0.02521 | 8.040±0.001  |
| 0.04028                        | 4.950±0.002  | 0.04033 | 5.175±0.005  | 0.04040 | 5.675±0.007  |
| 0.05554                        | 4.036±0.002  | 0.05540 | 4.272±0.002  | 0.05564 | 4.472±0.001  |
| 0.07070                        | 3.657±0.003  | 0.07080 | 3.957±0.001  | 0.07093 | 4.071±0.002  |
| 0.08598                        | 3.470±0.004  | 0.08610 | 3.705±0.007  | 0.08626 | 3.952±0.001  |
| 0.005mIL/ mol.kg <sup>-1</sup> |              |         |              |         |              |
| 0.01003                        | 18.600±0.001 | 0.01005 | 19.400±0.003 | 0.01006 | 20.800±0.001 |
| 0.02513                        | 8.760±0.002  | 0.02516 | 8.960±0.001  | 0.02521 | 9.320±0.003  |
| 0.04027                        | 6.200±0.001  | 0.04033 | 6.475±0.002  | 0.04040 | 6.575±0.001  |
| 0.05546                        | 4.890±0.006  | 0.05553 | 5.363±0.001  | 0.05563 | 5.636±0.004  |
| 0.07070                        | 4.542±0.001  | 0.07079 | 4.671±0.004  | 0.07091 | 4.785±0.001  |
| 0.08598                        | 4.070±0.001  | 0.08609 | 4.188±0.003  | 0.08623 | 4.305±0.005  |

\*Standard errors in molar conductivity  $\Lambda / S.cm^2.mol^{-1}$  is given in their parenthesis.  $(T) = \pm 0.01K$  (0.68 level of confidence) and pressure  $u (P) = 0.01 MPa$  \*molality has been expressed per kg of (TBMS + water) solvent mixture. \*#Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 mol kg^{-1}$ .

**Table 10.** CMC values of L-Arginine and L-Histidine in different concentrations( 0.001, 0.003, 0.005)m aqueous solutions of TBMS at different temperatures at atmospheric pressure 0.1MPa.

| Molality/m of IL | Temperatures | Con. of L-Arginine(mole/kg) from conductance | CMC break point from conductance(mL) | Con. of L-Histidine(mole/kg) from conductance | CMC break point from conductance(mL) |
|------------------|--------------|--|--------------------------------------|---|--------------------------------------|
| 0.001            | 298.15K      | 0.00514                                      | 38.90                                | 0.00510                                       | 39.15                                |
| 0.001            | 303.15K      | 0.00580                                      | 34.42                                | 0.00567                                       | 35.25                                |
| 0.001            | 308.15K      | 0.00614                                      | 32.56                                | 0.00585                                       | 34.48                                |
| 0.003            | 298.15K      | 0.00619                                      | 32.27                                | 0.00567                                       | 35.12                                |
| 0.003            | 303.15K      | 0.00640                                      | 31.22                                | 0.00593                                       | 33.72                                |
| 0.003            | 308.15K      | 0.00664                                      | 30.11                                | 0.00580                                       | 34.48                                |
| 0.005            | 298.15K      | 0.00684                                      | 29.23                                | 0.00669                                       | 29.87                                |
| 0.005            | 303.15K      | 0.00664                                      | 30.11                                | 0.00607                                       | 32.92                                |
| 0.005            | 308.15K      | 0.00718                                      | 27.87                                | 0.00681                                       | 29.36                                |

\*Standard uncertainty of CMC (u): $\pm 0.01$ , \*Standard uncertainty in pressure u (P)=  $\pm 0.01$ MPa  
 \*molality has been expressed per kg of (TBMS + water) solvent mixture. \*#Combined standard uncertainties in molality according to stated purity u(m) = $\pm 0.0092$  mol kg<sup>-1</sup>.

**Table 11.** Surface tension ( $\sigma$ ) of L-Arginine and L-Histidine of different molality at 298.15 K in different concentrations(0.001, 0.003, 0.005) m of IL (TBMS) solutions and at atmospheric pressure 0.1MPa.

| Molality(m) /mol.kg <sup>-1</sup> | $\sigma$ (mN/m) | Molality(m) /mol.kg <sup>-1</sup> | $\sigma$ (mN/m) | Molality(m) /mol.kg <sup>-1</sup> | $\sigma$ (mN/m)   |
|-----------------------------------|-----------------|-----------------------------------|-----------------|-----------------------------------|-------------------|
| L-ARGININE+aq.TBMS                |                 |                                   |                 |                                   |                   |
| 0.001mIL/ mol.kg <sup>-1</sup>    |                 | 0.003mIL/ mol.kg <sup>-1</sup>    |                 | 0.005mIL/ mol.kg <sup>-1</sup>    |                   |
| 0.01004                           | 62.7 $\pm$ 0.01 | 0.01004                           | 61.2 $\pm$ 0.02 | 0.01004                           | 59.8 $\pm$ 0.03   |
| 0.02515                           | 63.6 $\pm$ 0.01 | 0.02515                           | 62.0 $\pm$ 0.02 | 0.02515                           | 60.5 $\pm$ 0.03   |
| 0.04032                           | 64.6 $\pm$ 0.01 | 0.04031                           | 62.9 $\pm$ 0.02 | 0.04032                           | 61.4 $\pm$ 0.03   |
| 0.05540                           | 65.3 $\pm$ 0.01 | 0.05554                           | 63.6 $\pm$ 0.02 | 0.05554                           | 62.3 $\pm$ 0.03   |
| 0.07082                           | 66.3 $\pm$ 0.01 | 0.07082                           | 64.3 $\pm$ 0.02 | 0.07082                           | 63.1 $\pm$ 0.03   |
| 0.08616                           | 66.9 $\pm$ 0.01 | 0.08615                           | 65.1 $\pm$ 0.02 | 0.08616                           | 63.9 $\pm$ 0.03   |
| L-HISTIDINE+aq.TBMS               |                 |                                   |                 |                                   |                   |
| 0.001mIL/ mol.kg <sup>-1</sup>    |                 | 0.003mIL/ mol.kg <sup>-1</sup>    |                 | 0.005mIL/ mol.kg <sup>-1</sup>    |                   |
| 0.01003                           | 60.9 $\pm$ 0.02 | 0.01003                           | 57.8 $\pm$ 0.01 | 0.01003                           | 55.7 $\pm$ 0.01   |
| 0.02513                           | 61.6 $\pm$ 0.02 | 0.02513                           | 58.3 $\pm$ 0.01 | 0.02513                           | 56.6.3 $\pm$ 0.01 |
| 0.04028                           | 62.2 $\pm$ 0.02 | 0.04028                           | 59.3 $\pm$ 0.01 | 0.04027                           | 57.8.1 $\pm$ 0.01 |
| 0.05547                           | 63.3 $\pm$ 0.02 | 0.05547                           | 60.2 $\pm$ 0.01 | 0.05546                           | 58.6 $\pm$ 0.01   |
| 0.07070                           | 64.1 $\pm$ 0.02 | 0.07070                           | 61.3 $\pm$ 0.01 | 0.07070                           | 59.9 $\pm$ 0.01   |
| 0.08598                           | 64.6 $\pm$ 0.02 | 0.08598                           | 62.7 $\pm$ 0.01 | 0.08598                           | 61.2 $\pm$ 0.01   |

\*Standard uncertainties u ( $\sigma$ )= ( $\pm 0.03$ mN/m) \*Standard uncertainty in pressure u (P) = $\pm 0.01$  MPa and u (T) =  $\pm 0.01$ K (0.68 level of confidence). \*molality has been expressed per kg of (TBMS + water) solvent mixture. \*#Combined standard uncertainties in molality according to stated purity u(m) = $\pm 0.0092$  mol kg<sup>-1</sup>.

**Table 12.** Optimizations Energy of pure TBMS, L-ARG, L-HIS and (TBMS+L-ARG), (TBMS+L-HIS) systems using appropriate methodology and 6-311G (d) basis set.

| System       | Calculation method | Basis set  | Optimization energy(a.u) | Dipole moment(D) |
|--------------|--------------------|------------|--------------------------|------------------|
| TBMS         | UB3LYP             | 6-311G (d) | -1350.3115               | 13.9546          |
| L-ARG        | UB3LYP             | 6-311G (d) | -606.49617               | 3.5197           |
| L-HIS        | UB3LYP             | 6-311G (d) | -549.92985               | 5.9015           |
| (TBMS+L-ARG) | UB3LYP             | 6-311G (d) | -1236.6553               | 14.4551          |
| (TBMS+L-HIS) | UB3LYP             | 6-311G (d) | -1143.2869               | 15.5051          |

## Supporting Information

### Tables

**Table S1.** Experimental values of density ( $\rho$ ), viscosity ( $\eta$ ), molar refraction ( $^R_M$ ) of different concentrations (0.001, 0.003, 0.005) m of aqueous solvent (TBMS) solutions at 298.15 K, 303.15 K, 308.15 K at atmospheric pressure 0.1MPa.

| Aqueous solvent<br>Molality/mol.kg <sup>-1</sup> | 298.15 K     | 303.15 K     | 308.15 K     |
|--|--------------|--------------|--------------|
| $\rho(\text{g/cm}^3)$                            |              |              |              |
| 0.001  | 0.99706      | 0.99570      | 0.99395      |
| 0.003  | 0.99713      | 0.99580      | 0.99408      |
| 0.005  | 0.99719      | 0.99589      | 0.99420      |
| $\eta/\text{mPa.s}$                              |              |              |              |
| 0.001  | 0.981±0.011  | 0.899±0.011  | 0.854±0.011  |
| 0.003  | 1.013±0.011  | 0.93±0.011   | 0.860±0.011  |
| 0.005  | 1.028±0.011  | 0.936±0.011  | 0.884±0.011  |
| $^R_M$   |              |              |              |
| 0.001  | 35.839±0.018 | 35.858±0.018 | 35.901±0.018 |
| 0.003  | 35.844±0.018 | 35.87±0.018  | 35.897±0.018 |
| 0.005  | 35.869±0.018 | 35.91±0.018  | 35.917±0.018 |

# Overall standard uncertainties  $u$  are:  $u(\rho) = \pm 0.00093 \text{ g.cm}^{-3}$ ,  $u(n_D) = \pm 0.0002$  and  $u(T) = \pm 0.01 \text{ K}$ , (0.68 level of confidence), \*Standard error in molar refraction ( $^R_M$ ) and refractive index ( $\eta/\text{mPa.s}$ ) is in their parenthesis, #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{ mol kg}^{-1}$ . Standard uncertainty in pressure  $u(P) = \pm 0.01 \text{ MPa}$

**Table S2.** Experimental values of refractive index ( $n_D$ ), sp. conductance ( $\kappa$ ), surface tension ( $\sigma$ ) of different concentrations (0.001, 0.003, 0.005) m of aqueous solvent (TBMS) solution at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

| Aqueous solvent<br>Molality/mol.kg-1 | $n_D$       |             |             | $\sigma$ (mN/m) |
|--------------------------------------|-------------|-------------|-------------|-----------------|
|                                      | 298.15K     | 303.15K     | 308.15K     | 298.15K         |
| 0.001                                | 1.3322      | 1.3319      | 1.3315      | 64.7            |
| 0.003                                | 1.3323      | 1.3318      | 1.3317      | 63.6            |
| 0.005                                | 1.3325      | 1.3322      | 1.3319      | 60.6            |
| $\kappa$ (ms/cm)                     |             |             |             |                 |
| 0.001                                | 0.102±0.013 | 0.115±0.010 | 0.120±0.014 |                 |
| 0.003                                | 0.170±0.009 | 0.192±0.017 | 0.213±0.009 |                 |
| 0.005                                | 0.250±0.012 | 0.270±0.011 | 0.303±0.014 |                 |

\*Standard Uncertainties ( $u$ ) are :  $u(n_D) = \pm 0.0002$ ,  $u(\kappa) = \pm 0.01 (\text{mScm}^{-1})$   $u(\sigma) = 0.3 \text{ mN/m}$

\*Standard uncertainty in pressure  $u(P) = \pm 0.01 \text{ MPa}$  \*molality has been expressed per kg of (TBMS + water) solvent mixture. \* #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{ mol kg}^{-1}$ .

**Table S3.** Density ( $\rho$ ) of (L-ARGININE+TBMS+H<sub>2</sub>O) and (L-HISTIDINE+TBMS+H<sub>2</sub>O) systems in aqueous TBMS solutions of different concentrations (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K and 308.15 K and at atmospheric pressure 0.1MPa.

| Molality(m)<br>/mol.kg <sup>-1</sup> | Density( $\rho$ )<br>g/cm <sup>3</sup> | Molality(m)<br>/mol.kg <sup>-1</sup> | Density( $\rho$ )<br>g/cm <sup>3</sup> | Molality(m)<br>/mol.kg <sup>-1</sup> | Density( $\rho$ )<br>g/cm <sup>3</sup> |
|--------------------------------------|--|--------------------------------------|--|--------------------------------------|--|
|                                      | 298.15K                                |                                      | 303.15K                                |                                      | 308.15K                                |
| (L-ARGININE+ aq.TBMS)                |  |                                      |  |                                      |  |
| 0.001m/mol.kg <sup>-1</sup>          |  |                                      |  |                                      |  |
| 0.01004                              | 0.99754                                | 0.01005                              | 0.99617                                | 0.01007                              | 0.99441                                |
| 0.02515                              | 0.99828                                | 0.02518                              | 0.99690                                | 0.02523                              | 0.99513                                |
| 0.04032                              | 0.99902                                | 0.04037                              | 0.99765                                | 0.04044                              | 0.99587                                |
| 0.05554                              | 0.99979                                | 0.05562                              | 0.99842                                | 0.05572                              | 0.99661                                |
| 0.07082                              | 1.00054                                | 0.07092                              | 0.99918                                | 0.07105                              | 0.99737                                |
| 0.08616                              | 1.00130                                | 0.08628                              | 0.99995                                | 0.08644                              | 0.99815                                |
| 0.003mL/mol.kg <sup>-1</sup>         |  |                                      |  |                                      |  |
| 0.01004                              | 0.99759                                | 0.01005                              | 0.99624                                | 0.01007                              | 0.99450                                |
| 0.02515                              | 0.99830                                | 0.02518                              | 0.99692                                | 0.02523                              | 0.99519                                |
| 0.04031                              | 0.99906                                | 0.04037                              | 0.99767                                | 0.04044                              | 0.99592                                |
| 0.05554                              | 0.99982                                | 0.05562                              | 0.99844                                | 0.05572                              | 0.99665                                |
| 0.07082                              | 1.00058                                | 0.07092                              | 0.99920                                | 0.07104                              | 0.99743                                |
| 0.08615                              | 1.00135                                | 0.08628                              | 0.99997                                | 0.08643                              | 0.99820                                |
| 0.005mL/mol.kg <sup>-1</sup>         |  |                                      |  |                                      |  |
| 0.01004                              | 0.99764                                | 0.01005                              | 0.99631                                | 0.01007                              | 0.99461                                |
| 0.02515                              | 0.99835                                | 0.02518                              | 0.99701                                | 0.02522                              | 0.99530                                |
| 0.04031                              | 0.99910                                | 0.04037                              | 0.99774                                | 0.04044                              | 0.99603                                |
| 0.05554                              | 0.99986                                | 0.05561                              | 0.99849                                | 0.05571                              | 0.99678                                |
| 0.07082                              | 1.00062                                | 0.07091                              | 0.99925                                | 0.07104                              | 0.99754                                |
| 0.08615                              | 1.00138                                | 0.08627                              | 1.00000                                | 0.08642                              | 0.99832                                |
| L-HISTIDINE+aq.TBMS                  |  |                                      |  |                                      |  |
| 0.001mL/mol.kg <sup>-1</sup>         |  |                                      |  |                                      |  |
| 0.01003                              | 0.99759                                | 0.01005                              | 0.99622                                | 0.01007                              | 0.99446                                |
| 0.02513                              | 0.9984                                 | 0.02517                              | 0.99702                                | 0.02518                              | 0.99525                                |
| 0.04028                              | 0.99921                                | 0.04033                              | 0.99783                                | 0.04041                              | 0.99606                                |
| 0.05547                              | 1.00003                                | 0.05549                              | 0.99865                                | 0.05564                              | 0.99687                                |
| 0.07070                              | 1.00086                                | 0.07080                              | 0.99948                                | 0.07093                              | 0.99769                                |
| 0.08598                              | 1.0017                                 | 0.08610                              | 1.00032                                | 0.08626                              | 0.99852                                |
| 0.003mL/mol.kg <sup>-1</sup>         |  |                                      |  |                                      |  |
| 0.01003                              | 0.99764                                | 0.01005                              | 0.99630                                | 0.01007                              | 0.99457                                |
| 0.02513                              | 0.99843                                | 0.02517                              | 0.99707                                | 0.02521                              | 0.99533                                |
| 0.04028                              | 0.99924                                | 0.04033                              | 0.99786                                | 0.04040                              | 0.99612                                |
| 0.05554                              | 1.00006                                | 0.05540                              | 0.99867                                | 0.05564                              | 0.99693                                |
| 0.07070                              | 1.00088                                | 0.07080                              | 0.99951                                | 0.07093                              | 0.99775                                |
| 0.08598                              | 1.00172                                | 0.08610                              | 1.00036                                | 0.08626                              | 0.99857                                |
| 0.005mL/mol.kg <sup>-1</sup>         |  |                                      |  |                                      |  |
| 0.01003                              | 0.99769                                | 0.01005                              | 0.99641                                | 0.01006                              | 0.99469                                |
| 0.02513                              | 0.99847                                | 0.02516                              | 0.99719                                | 0.02521                              | 0.99546                                |
| 0.04027                              | 0.99927                                | 0.04033                              | 0.99800                                | 0.04040                              | 0.99626                                |
| 0.05546                              | 1.00008                                | 0.05553                              | 0.99882                                | 0.05563                              | 0.99709                                |
| 0.07070                              | 1.00090                                | 0.07079                              | 0.99967                                | 0.07091                              | 0.99795                                |
| 0.08598                              | 1.00174                                | 0.08609                              | 1.00053                                | 0.08623                              | 0.99882                                |

#Overall Standard uncertainties  $u$  are:  $u(\rho) = 0.00093 \text{ g/cm}^3$ ,  $u(T) = \pm 0.01 \text{ K}$ , (0.68 level of confidence). #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{ mol kg}^{-1}$ . \*Standard uncertainty in pressure  $u(P) = \pm 0.01 \text{ MPa}$

**Table S4.** Apparent Molar volume ( $\Phi_v$ ) of (L-ARGININE+TBMS+H<sub>2</sub>O) and (L-HIS TIDINE+TBMS+H<sub>2</sub>O) systems in aqueous IL (TBMS) of different concentrations (0.00, 0.003, 0.005) m mass fractions,  $W_1=0.001, 0003, 0.005$  at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

| Molality(m)<br>/mol.kg <sup>-1</sup> | $\Phi_v \times 10^6$<br>(m <sup>3</sup> . mol <sup>-1</sup> ) | Molality(m)<br>/mol.kg <sup>-1</sup> | $\Phi_v \times 10^6$<br>(m <sup>3</sup> . mol <sup>-1</sup> ) | Molality(m)<br>/mol.kg <sup>-1</sup> | $\Phi_v \times 10^6$<br>(m <sup>3</sup> . mol <sup>-1</sup> ) |
|--------------------------------------|---|--------------------------------------|---|--------------------------------------|---|
|                                      | 298.15K   |                                      | 303.15K   |                                      | 308.15K   |
| (L-ARGININE+ aq.TBMS)                |   |                                      |   |                                      |   |
| 0.001mL/mol.kg-1                     |   |                                      |   |                                      |   |
| 0.01004                              | 126.57±0.02   | 0.01005                              | 127.75±0.02   | 0.01007                              | 128.98±0.02   |
| 0.02515                              | 125.77±0.02   | 0.02518                              | 126.74±0.02   | 0.02523                              | 127.77±0.02   |
| 0.04032                              | 125.57±0.02   | 0.04037                              | 125.99±0.02   | 0.04044                              | 126.97±0.02   |
| 0.05554                              | 124.93±0.02   | 0.05562                              | 125.28±0.02   | 0.05572                              | 126.60±0.02   |
| 0.07082                              | 124.85±0.02   | 0.07092                              | 125.02±0.02   | 0.07105                              | 126.10±0.02   |
| 0.08616                              | 124.68±0.02   | 0.08628                              | 124.74±0.02   | 0.08644                              | 125.55±0.02   |
| 0.003mL/mol.kg-1                     |   |                                      |   |                                      |   |
| 0.01004                              | 128.57±0.02   | 0.01005                              | 130.75±0.02   | 0.01007                              | 132.99±0.02   |
| 0.02515                              | 127.77±0.02   | 0.02518                              | 129.94±0.02   | 0.02523                              | 130.57±0.02   |
| 0.04031                              | 126.31±0.02   | 0.04037                              | 127.99±0.02   | 0.04044                              | 128.96±0.02   |
| 0.05554                              | 125.65±0.02   | 0.05562                              | 126.73±0.02   | 0.05572                              | 128.23±0.02   |
| 0.07082                              | 125.27±0.02   | 0.07092                              | 126.16±0.02   | 0.07104                              | 127.09±0.02   |
| 0.08615                              | 124.91±0.02   | 0.08628                              | 125.67±0.02   | 0.08643                              | 126.48±0.02   |
| 0.005mL/mol.kg-1                     |   |                                      |   |                                      |   |
| 0.01004                              | 129.56±0.02   | 0.01005                              | 132.74±0.02   | 0.01007                              | 133.98±0.02   |
| 0.02515                              | 128.16±0.02   | 0.02518                              | 129.93±0.02   | 0.02522                              | 130.96±0.02   |
| 0.04031                              | 126.81±0.02   | 0.04037                              | 128.48±0.02   | 0.04044                              | 129.20±0.02   |
| 0.05554                              | 126.01±0.02   | 0.05561                              | 127.45±0.02   | 0.05571                              | 128.03±0.02   |
| 0.07082                              | 125.55±0.02   | 0.07091                              | 126.72±0.02   | 0.07104                              | 127.22±0.02   |
| 0.08615                              | 125.26±0.02   | 0.08627                              | 126.37±0.02   | 0.08642                              | 126.46±0.02   |
| L-HISTIDINE+aq.TBMS                  |   |                                      |   |                                      |   |
| 0.001mL/mol.kg-1                     |   |                                      |   |                                      |   |
| 0.01003                              | 102.45±0.01   | 0.01005                              | 103.59±0.01   | 0.01007                              | 104.78±0.01   |
| 0.02513                              | 101.85±0.01   | 0.02517                              | 102.79±0.01   | 0.02518                              | 103.78±0.01   |
| 0.04028                              | 101.70±0.01   | 0.04033                              | 102.34±0.01   | 0.04041                              | 103.02±0.01   |
| 0.05547                              | 101.45±0.01   | 0.05549                              | 101.95±0.01   | 0.05564                              | 102.68±0.01   |
| 0.07070                              | 101.16±0.01   | 0.07080                              | 101.59±0.01   | 0.07093                              | 102.34±0.01   |
| 0.08598                              | 100.86±0.01   | 0.08610                              | 101.23±0.01   | 0.08626                              | 102.00±0.01   |
| 0.003mL/mol.kg-1                     |   |                                      |   |                                      |   |
| 0.01003                              | 104.45±0.01   | 0.01005                              | 105.59±0.01   | 0.01007                              | 106.78±0.01   |
| 0.02513                              | 103.45±0.01   | 0.02517                              | 104.79±0.01   | 0.02521                              | 105.78±0.01   |
| 0.04028                              | 102.69±0.01   | 0.04033                              | 104.09±0.01   | 0.04040                              | 104.77±0.01   |
| 0.05554                              | 102.17±0.01   | 0.05540                              | 103.40±0.01   | 0.05564                              | 103.95±0.01   |
| 0.07070                              | 101.87±0.01   | 0.07080                              | 102.58±0.01   | 0.07093                              | 103.33±0.01   |
| 0.08598                              | 101.44±0.01   | 0.08610                              | 101.93±0.01   | 0.08626                              | 102.93±0.01   |
| 0.005mL/mol.kg-1                     |   |                                      |   |                                      |   |
| 0.01003                              | 105.45±0.01   | 0.01005                              | 106.58±0.01   | 0.01006                              | 106.77±0.01   |
| 0.02513                              | 104.24±0.01   | 0.02516                              | 104.78±0.01   | 0.02521                              | 105.36±0.01   |
| 0.04027                              | 103.44±0.01   | 0.04033                              | 103.57±0.01   | 0.04040                              | 104.25±0.01   |
| 0.05546                              | 102.89±0.01   | 0.05553                              | 102.84±0.01   | 0.05563                              | 103.20±0.01   |
| 0.07070                              | 102.44±0.01   | 0.07079                              | 101.99±0.01   | 0.07091                              | 102.17±0.01   |
| 0.08598                              | 101.91±0.01   | 0.08609                              | 101.33±0.01   | 0.08623                              | 101.38±0.01   |

\*Standard uncertainties  $u$  are:  $u(T) = \pm 0.01\text{K}$ , (0.68 level of confidence), \*molality has been expressed per kg of (TBMS + water) solvent mixture. #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{ mol kg}^{-1}$  (0.68 level of confidence). Standard uncertainty in pressure  $u(P) = \pm 0.01 \text{ MPa}$

**Table S5.** Volume transfer/ $\Delta\Phi_v^0$  for L-Arginine and L-Histidine in aqueous solutions of (0.001, 0.003, 0.005) m IL (TBMS) at 298.15 K, 303.15 K, 308.15 K at atmospheric pressure 0.1MPa.

| Temperature/<br>(K)           | $\Delta\Phi_v^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$ | $\Delta\Phi_v^0 \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$ |
|-------------------------------|---|---|
|                               | L-Arginine  | L-Histidine   |
| 0.001 mL/mol.kg <sup>-1</sup> |   |   |
| 298.15K                       | 0.592   | 0.481   |
| 303.15K                       | 0.572   | 0.477   |
| 308.15K                       | 0.537   | 0.451   |
| 0.003 mL/mol.kg <sup>-1</sup> |   |   |
| 298.15K                       | 1.085   | 0.856   |
| 303.15K                       | 1.038   | 0.832   |
| 308.15K                       | 0.989   | 0.802   |
| 0.005 mL/mol.kg <sup>-1</sup> |   |   |
| 298.15K                       | 1.510   | 1.094   |
| 303.15K                       | 1.401   | 0.998   |
| 308.15K                       | 1.198   | 0.935   |

\*Standard uncertainties values of  $u$  are:  $u(T) = \pm 0.01\text{K}$  (0.68 level of confidence), #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{ mol kg}^{-1}$ . \*molality has been expressed per kg of (TBMS + water) solvent mixture. \* Standard uncertainty in pressure  $u(P) = \pm 0.01\text{MPa}$ .

**Table S6.** Viscosity ( $\eta$ ) and  $(\eta/\eta^0 - 1)/\sqrt{m}$  of (L-ARGININE+TBMS+H<sub>2</sub>O) in aqueous IL (TBMS) of different concentrations (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

| Molality( $m$ )<br>/ mol.kg <sup>-1</sup> | $\eta$ (mPa.s) | Molality( $m$ )<br>/ mol.kg <sup>-1</sup> | $\eta$ (mPa.s) | Molality( $m$ )<br>/ mol.kg <sup>-1</sup> | $\eta$ (mPa.s) |
|---|----------------|---|----------------|---|----------------|
|   | 298.15K        |   | 303.15K        |   | 308.15K        |
| (L-ARGININE+TBMS+H <sub>2</sub> O)        |                |   |                |   |                |
| 0.001mL/mol.kg <sup>-1</sup>              |                |   |                |   |                |
| 0.01004                                   | 1.006±0.011    | 0.01005                                   | 0.912±0.011    | 0.01007                                   | 0.873±0.011    |
| 0.02515                                   | 1.017±0.011    | 0.02518                                   | 0.923±0.011    | 0.02523                                   | 0.886±0.011    |
| 0.04032                                   | 1.028±0.011    | 0.04037                                   | 0.936±0.011    | 0.04044                                   | 0.898±0.011    |
| 0.05554                                   | 1.038±0.011    | 0.05562                                   | 0.949±0.011    | 0.05572                                   | 0.911±0.011    |
| 0.07082                                   | 1.049±0.011    | 0.07092                                   | 0.960±0.011    | 0.07105                                   | 0.923±0.011    |
| 0.08616                                   | 1.059±0.011    | 0.08628                                   | 0.972±0.011    | 0.08644                                   | 0.937±0.011    |
| 0.003mL/mol.kg <sup>-1</sup>              |                |   |                |   |                |
| 0.01004                                   | 1.022±0.011    | 0.01005                                   | 0.941±0.011    | 0.01007                                   | 0.877±0.011    |
| 0.02515                                   | 1.034±0.011    | 0.02518                                   | 0.954±0.011    | 0.02523                                   | 0.890±0.011    |
| 0.04031                                   | 1.046±0.011    | 0.04037                                   | 0.967±0.011    | 0.04044                                   | 0.905±0.011    |
| 0.05554                                   | 1.057±0.011    | 0.05562                                   | 0.980±0.011    | 0.05572                                   | 0.918±0.011    |
| 0.07082                                   | 1.070±0.011    | 0.07092                                   | 0.995±0.011    | 0.07104                                   | 0.933±0.011    |
| 0.08615                                   | 1.082±0.011    | 0.08628                                   | 1.009±0.011    | 0.08643                                   | 0.947±0.011    |
| 0.005mL/mol.kg <sup>-1</sup>              |                |   |                |   |                |
| 0.01004                                   | 1.034±0.011    | 0.01005                                   | 0.958±0.011    | 0.01007                                   | 0.907±0.011    |
| 0.02515                                   | 1.048±0.011    | 0.02518                                   | 0.972±0.011    | 0.02522                                   | 0.922±0.011    |
| 0.04031                                   | 1.062±0.011    | 0.04037                                   | 0.987±0.011    | 0.04044                                   | 0.938±0.011    |
| 0.05554                                   | 1.075±0.011    | 0.05561                                   | 1.002±0.011    | 0.05571                                   | 0.954±0.011    |
| 0.07082                                   | 1.089±0.011    | 0.07091                                   | 1.017±0.011    | 0.07104                                   | 0.969±0.011    |
| 0.08615                                   | 1.103±0.011    | 0.08627                                   | 1.033±0.011    | 0.08642                                   | 0.987±0.011    |

|                              | $(\eta/\eta^0-1)/\sqrt{m}/$<br>$\text{kg}^{1/2}\text{mol}^{-1/2}$ |         | $(\eta/\eta^0-1)/\sqrt{m}/$<br>$\text{kg}^{1/2}\text{mol}^{-1/2}$ |         | $(\eta/\eta^0-1)/\sqrt{m}/$<br>$\text{kg}^{1/2}\text{mol}^{-1/2}$ |
|------------------------------|---|---------|---|---------|---|
| 0.001mL/mol.kg <sup>-1</sup> |   |         |   |         |   |
| 0.01004                      | 0.090±0.002   | 0.01005 | 0.111±0.003   | 0.01007 | 0.115±0.002   |
| 0.02515                      | 0.126±0.002   | 0.02518 | 0.147±0.004   | 0.02523 | 0.168±0.002   |
| 0.04032                      | 0.155±0.002   | 0.04037 | 0.188±0.004   | 0.04044 | 0.202±0.004   |
| 0.05554                      | 0.174±0.003   | 0.05562 | 0.221±0.004   | 0.05572 | 0.236±0.005   |
| 0.07082                      | 0.196±0.004   | 0.07092 | 0.241±0.005   | 0.07105 | 0.263±0.005   |
| 0.08616                      | 0.212±0.004   | 0.08628 | 0.264±0.005   | 0.08644 | 0.292±0.006   |
| 0.003mL/mol.kg <sup>-1</sup> |   |         |   |         |   |
| 0.01004                      | 0.099±0.003   | 0.01005 | 0.118±0.004   | 0.01007 | 0.127±0.003   |
| 0.02515                      | 0.137±0.003   | 0.02518 | 0.163±0.004   | 0.02523 | 0.175±0.004   |
| 0.04031                      | 0.167±0.004   | 0.04037 | 0.198±0.004   | 0.04044 | 0.224±0.005   |
| 0.05554                      | 0.189±0.003   | 0.05562 | 0.229±0.005   | 0.05572 | 0.255±0.005   |
| 0.07082                      | 0.215±0.003   | 0.07092 | 0.262±0.006   | 0.07104 | 0.290±0.006   |
| 0.08615                      | 0.236±0.005   | 0.08628 | 0.289±0.004   | 0.08643 | 0.318±0.006   |
| 0.005mL/mol.kg <sup>-1</sup> |   |         |   |         |   |
| 0.01004                      | 0.107±0.005   | 0.01005 | 0.127±0.005   | 0.01007 | 0.134±0.006   |
| 0.02515                      | 0.154±0.005   | 0.02518 | 0.173±0.006   | 0.02522 | 0.190±0.006   |
| 0.04031                      | 0.190±0.006   | 0.04037 | 0.216±0.006   | 0.04044 | 0.239±0.006   |
| 0.05554                      | 0.216±0.006   | 0.05561 | 0.252±0.006   | 0.05571 | 0.280±0.007   |
| 0.07082                      | 0.242±0.007   | 0.07091 | 0.282±0.007   | 0.07104 | 0.312±0.008   |
| 0.08615                      | 0.266±0.005   | 0.08627 | 0.313±0.007   | 0.08642 | 0.350±0.009   |

\*Standard uncertainties  $u$  are:  $u(T) = \pm 0.01\text{K}$ , (0.68 level of confidence), \*molality has been expressed per kg of (TBMS + water) solvent mixture. Standard errors in  $(\eta)$  and  $u(\eta_r-1)/\sqrt{m}$  is given in the parenthesis #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{ mol kg}^{-1}$  (0.68 level of confidence). Standard uncertainty in pressure  $u(P) = \pm 0.01 \text{ MPa}$

**Table S7.** Viscosity ( $\eta$ ) and  $(\eta/\eta^0-1)/\sqrt{m}$  of (L-HISTIDINE+TBMS+H<sub>2</sub>O) system in aqueous IL (TBMS) of different concentrations (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K, 308.15 K and at atmospheric pressure 0.1MPa.

| Molality( $m$ )<br>/ mol.kg <sup>-1</sup> | $\eta$ (mPa.s) | Molality( $m$ )<br>/ mol.kg <sup>-1</sup> | $\eta$ (mPa.s) | Molality( $m$ )<br>/ mol.kg <sup>-1</sup> | $\eta$ (mPa.s) |
|---|----------------|---|----------------|---|----------------|
|   | 298.15K        |   | 303.15K        |   | 308.15K        |
| (L-HISTIDINE+TBMS+H <sub>2</sub> O)       |                |   |                |   |                |
| 0.001mL/mol.kg <sup>-1</sup>              |                |   |                |   |                |
| 0.01003                                   | 1.005±0.011    | 0.01005                                   | 0.910±0.011    | 0.01007                                   | 0.871±0.011    |
| 0.02513                                   | 1.014±0.011    | 0.02517                                   | 0.920±0.011    | 0.02518                                   | 0.881±0.011    |
| 0.04028                                   | 1.024±0.011    | 0.04033                                   | 0.929±0.011    | 0.04041                                   | 0.891±0.011    |
| 0.05547                                   | 1.031±0.011    | 0.05549                                   | 0.938±0.011    | 0.05564                                   | 0.900±0.011    |
| 0.07070                                   | 1.038±0.011    | 0.07080                                   | 0.947±0.011    | 0.07093                                   | 0.909±0.011    |
| 0.08598                                   | 1.047±0.011    | 0.08610                                   | 0.955±0.011    | 0.08626                                   | 0.919±0.011    |
| 0.003mL/mol.kg <sup>-1</sup>              |                |   |                |   |                |
| 0.01003                                   | 1.021±0.011    | 0.01005                                   | 0.939±0.011    | 0.01007                                   | 0.875±0.011    |
| 0.02513                                   | 1.032±0.011    | 0.02517                                   | 0.950±0.011    | 0.02521                                   | 0.886±0.011    |
| 0.04028                                   | 1.042±0.011    | 0.04033                                   | 0.960±0.011    | 0.04040                                   | 0.898±0.011    |
| 0.05554                                   | 1.052±0.011    | 0.05540                                   | 0.971±0.011    | 0.05564                                   | 0.908±0.011    |
| 0.07070                                   | 1.062±0.011    | 0.07080                                   | 0.981±0.011    | 0.07093                                   | 0.919±0.011    |
| 0.08598                                   | 1.071±0.011    | 0.08610                                   | 0.992±0.011    | 0.08626                                   | 0.930±0.011    |
| 0.005mL/mol.kg <sup>-1</sup>              |                |   |                |   |                |
| 0.01003                                   | 1.033±0.011    | 0.01005                                   | 0.956±0.011    | 0.01006                                   | 0.905±0.011    |
| 0.02513                                   | 1.045±0.011    | 0.02516                                   | 0.968±0.011    | 0.02521                                   | 0.917±0.011    |

|                              |   |         |   |         |   |
|------------------------------|---|---------|---|---------|---|
| 0.04027                      | 1.057±0.011   | 0.04033 | 0.980±0.011   | 0.04040 | 0.930±0.011   |
| 0.05546                      | 1.068±0.011   | 0.05553 | 0.992±0.011   | 0.05563 | 0.942±0.011   |
| 0.07070                      | 1.079±0.011   | 0.07079 | 1.004±0.011   | 0.07091 | 0.956±0.011   |
| 0.08598                      | 1.091±0.011   | 0.08609 | 1.017±0.011   | 0.08623 | 0.968±0.011   |
|                              | $(\eta/\eta^{\circ}-1)/\sqrt{m}/$<br>$\text{kg}^{1/2}\text{mol}^{-1/2}$ |         | $(\eta/\eta^{\circ}-1)/\sqrt{m}/$<br>$\text{kg}^{1/2}\text{mol}^{-1/2}$ |         | $(\eta/\eta^{\circ}-1)/\sqrt{m}/$<br>$\text{kg}^{1/2}\text{mol}^{-1/2}$ |
| 0.001mL/mol.kg <sup>-1</sup> |   |         |   |         |   |
| 0.01003                      | 0.080±0.002   | 0.01005 | 0.088±0.003   | 0.01007 | 0.092±0.006   |
| 0.02513                      | 0.108±0.002   | 0.02517 | 0.126±0.002   | 0.02518 | 0.131±0.004   |
| 0.04028                      | 0.131±0.002   | 0.04033 | 0.149±0.002   | 0.04041 | 0.160±0.006   |
| 0.05547                      | 0.145±0.003   | 0.05549 | 0.169±0.002   | 0.05564 | 0.182±0.004   |
| 0.07070                      | 0.155±0.003   | 0.07080 | 0.187±0.004   | 0.07093 | 0.200±0.006   |
| 0.08598                      | 0.171±0.003   | 0.08610 | 0.200±0.006   | 0.08626 | 0.221±0.002   |
| 0.003mL/mol.kg <sup>-1</sup> |   |         |   |         |   |
| 0.01003                      | 0.089±0.002   | 0.01005 | 0.097±0.005   | 0.01007 | 0.104±0.006   |
| 0.02513                      | 0.125±0.003   | 0.02517 | 0.136±0.002   | 0.02521 | 0.146±0.003   |
| 0.04028                      | 0.148±0.003   | 0.04033 | 0.161±0.002   | 0.04040 | 0.184±0.002   |
| 0.05554                      | 0.168±0.002   | 0.05540 | 0.187±0.002   | 0.05564 | 0.206±0.004   |
| 0.07070                      | 0.186±0.004   | 0.07080 | 0.206±0.003   | 0.07093 | 0.230±0.003   |
| 0.08598                      | 0.199±0.004   | 0.08610 | 0.227±0.004   | 0.08626 | 0.252±0.003   |
| 0.005mL/mol.kg <sup>-1</sup> |   |         |   |         |   |
| 0.01003                      | 0.098±0.004   | 0.01005 | 0.106±0.005   | 0.01006 | 0.111±0.005   |
| 0.02513                      | 0.136±0.005   | 0.02516 | 0.147±0.005   | 0.02521 | 0.155±0.005   |
| 0.04027                      | 0.166±0.006   | 0.04033 | 0.179±0.004   | 0.04040 | 0.193±0.005   |
| 0.05546                      | 0.187±0.006   | 0.05553 | 0.206±0.006   | 0.05563 | 0.223±0.006   |
| 0.07070                      | 0.207±0.007   | 0.07079 | 0.231±0.007   | 0.07091 | 0.256±0.007   |
| 0.08598                      | 0.227±0.008   | 0.08609 | 0.256±0.008   | 0.08623 | 0.278±0.008   |

\*Standard uncertainties values of  $u$  are:  $u(T) = \pm 0.01\text{K}$ , \*molality has been expressed per kg of (IL + water) solvent mixture. Standard error in  $(\eta)$  and  $u(\eta/\eta^{\circ}-1)/\sqrt{m}$  is given in the parenthesis. (0.68 level of confidence). #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{ mol kg}^{-1}$  \*Standard uncertainty in pressure  $u(P) = \pm 0.01 \text{ MPa}$

**Table S8.** Refractive index ( $n_D$ ) and molar refraction ( $R_M$ ) of (L-ARGININE+TBMS+H<sub>2</sub>O) in aqueous IL (TBMS) solutions of different concentrations (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K and 308.15 K and at pressure 0.1MPa.

| Molality( $m$ )<br>/ mol.kg <sup>-1</sup> | ( $n_D$ ) | Molality( $m$ )<br>/ mol.kg <sup>-1</sup> | ( $n_D$ ) | Molality( $m$ )<br>/ mol.kg <sup>-1</sup> | ( $n_D$ ) |
|---|-----------|---|-----------|---|-----------|
|   | 298.15K   |   | 303.15K   |   | 308.15K   |
| (L-ARGININE+TBMS+H <sub>2</sub> O)        |           |   |           |   |           |
| 0.001mL/mol.kg <sup>-1</sup>              |           |   |           |   |           |
| 0.01004                                   | 1.3319    | 0.01005                                   | 1.3317    | 0.01007                                   | 1.3316    |
| 0.02515                                   | 1.3324    | 0.02518                                   | 1.3322    | 0.02523                                   | 1.332     |
| 0.04032                                   | 1.3328    | 0.04037                                   | 1.3326    | 0.04044                                   | 1.3324    |
| 0.05554                                   | 1.3332    | 0.05562                                   | 1.333     | 0.05572                                   | 1.3328    |
| 0.07082                                   | 1.3336    | 0.07092                                   | 1.3334    | 0.07105                                   | 1.3332    |
| 0.08616                                   | 1.3340    | 0.08628                                   | 1.3338    | 0.08644                                   | 1.3336    |
| 0.003mL/mol.kg <sup>-1</sup>              |           |   |           |   |           |
| 0.01004                                   | 1.3321    | 0.01005                                   | 1.3319    | 0.01007                                   | 1.3318    |
| 0.02515                                   | 1.3326    | 0.02518                                   | 1.3324    | 0.02523                                   | 1.3323    |
| 0.04031                                   | 1.333     | 0.04037                                   | 1.3328    | 0.04044                                   | 1.3327    |
| 0.05554                                   | 1.3334    | 0.05562                                   | 1.3332    | 0.05572                                   | 1.3331    |
| 0.07082                                   | 1.3338    | 0.07092                                   | 1.3336    | 0.07104                                   | 1.3335    |
| 0.08615                                   | 1.3342    | 0.08628                                   | 1.334     | 0.08643                                   | 1.3339    |

| 0.005mL/mol.kg <sup>-1</sup> |                               |         |                               |         |                               |
|------------------------------|-------------------------------|---------|-------------------------------|---------|-------------------------------|
| 0.01004                      | 1.3325                        | 0.01005 | 1.3323                        | 0.01007 | 1.3322                        |
| 0.02515                      | 1.333                         | 0.02518 | 1.3328                        | 0.02522 | 1.3326                        |
| 0.04031                      | 1.3334                        | 0.04037 | 1.3332                        | 0.04044 | 1.333                         |
| 0.05554                      | 1.3338                        | 0.05561 | 1.3336                        | 0.05571 | 1.3334                        |
| 0.07082                      | 1.3342                        | 0.07091 | 1.334                         | 0.07104 | 1.3338                        |
| 0.08615                      | 1.3346                        | 0.08627 | 1.3344                        | 0.08642 | 1.3342                        |
|                              | ( <sup>R</sup> <sub>M</sub> ) |         | ( <sup>R</sup> <sub>M</sub> ) |         | ( <sup>R</sup> <sub>M</sub> ) |
| 0.001mL/mol.kg <sup>-1</sup> |                               |         |                               |         |                               |
| 0.01004                      | 35.863±0.022                  | 0.01005 | 35.882±0.022                  | 0.01007 | 35.926±0.022                  |
| 0.02515                      | 35.865±0.022                  | 0.02518 | 35.886±0.022                  | 0.02523 | 35.930±0.022                  |
| 0.04032                      | 35.868±0.022                  | 0.04037 | 35.888±0.022                  | 0.04044 | 35.933±0.022                  |
| 0.05554                      | 35.870±0.022                  | 0.05562 | 35.890±0.022                  | 0.05572 | 35.935±0.022                  |
| 0.07082                      | 35.872±0.022                  | 0.07092 | 35.892±0.022                  | 0.07105 | 35.937±0.022                  |
| 0.08616                      | 35.874±0.022                  | 0.08628 | 35.893±0.022                  | 0.08644 | 35.939±0.022                  |
|                              |                               |         |                               |         |                               |
| 0.003mL/mol.kg <sup>-1</sup> |                               |         |                               |         |                               |
| 0.01004                      | 35.890±0.022                  | 0.01005 | 35.909±0.022                  | 0.01007 | 35.953±0.022                  |
| 0.02515                      | 35.894±0.022                  | 0.02518 | 35.914±0.022                  | 0.02523 | 35.957±0.022                  |
| 0.04031                      | 35.896±0.022                  | 0.04037 | 35.917±0.022                  | 0.04044 | 35.960±0.022                  |
| 0.05554                      | 35.898±0.022                  | 0.05562 | 35.918±0.022                  | 0.05572 | 35.963±0.022                  |
| 0.07082                      | 35.900±0.022                  | 0.07092 | 35.920±0.022                  | 0.07104 | 35.964±0.022                  |
| 0.08615                      | 35.902±0.022                  | 0.08628 | 35.922±0.022                  | 0.08643 | 35.966±0.022                  |
|                              |                               |         |                               |         |                               |
| 0.005mL/mol.kg <sup>-1</sup> |                               |         |                               |         |                               |
| 0.01004                      | 35.908±0.022                  | 0.01005 | 35.936±0.022                  | 0.01007 | 35.978±0.022                  |
| 0.02515                      | 35.912±0.022                  | 0.02518 | 35.940±0.022                  | 0.02522 | 35.983±0.022                  |
| 0.04031                      | 35.914±0.022                  | 0.04037 | 35.944±0.022                  | 0.04044 | 35.986±0.022                  |
| 0.05554                      | 35.916±0.022                  | 0.05561 | 35.946±0.022                  | 0.05571 | 35.988±0.022                  |
| 0.07082                      | 35.918±0.022                  | 0.07091 | 35.948±0.022                  | 0.07104 | 35.990±0.022                  |
| 0.08615                      | 35.920±0.022                  | 0.08627 | 35.950±0.022                  | 0.08642 | 35.991±0.022                  |

\*Standard uncertainties  $u$  are:  $u(n_D) = \pm 0.0002$ , Standard error in  $u$  ( $^R_M$ ) is given in parenthesis. and  $u(T) = \pm 0.01K$  (0.68 is the level of confidence). #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{ mol kg}^{-1}$  \*Standard uncertainty in pressure  $u(p) = \pm 0.01 \text{ MPa}$ .

**Table S9.** Refractive index ( $n_D$ ) and molar refraction ( $^R_M$ ) of (L-HISTIDINE+TBMS+H<sub>2</sub>O) in aqueous IL (TBMS) solutions of different concentrations (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K and 308.15 K and at pressure 0.1MPa.

| Molality(m)<br>/ mol.kg-1           | ( $n_D$ ) | Molality(m)<br>/ mol.kg-1 | ( $n_D$ ) | Molality(m)<br>/ mol.kg-1 | ( $n_D$ ) |
|-------------------------------------|-----------|---------------------------|-----------|---------------------------|-----------|
|                                     | 298.15K   |                           | 303.15K   |                           | 308.15K   |
| (L-HISTIDINE+TBMS+H <sub>2</sub> O) |           |                           |           |                           |           |
| 0.001mL/mol.kg <sup>-1</sup>        |           |                           |           |                           |           |
| 0.01003                             | 1.3324    | 0.01005                   | 1.3321    | 0.01007                   | 1.3319    |
| 0.02513                             | 1.3327    | 0.02517                   | 1.3324    | 0.02518                   | 1.3322    |
| 0.04028                             | 1.333     | 0.04033                   | 1.3327    | 0.04041                   | 1.3325    |
| 0.05547                             | 1.3333    | 0.05549                   | 1.333     | 0.05564                   | 1.3328    |
| 0.07070                             | 1.3336    | 0.07080                   | 1.3333    | 0.07093                   | 1.3331    |
| 0.08598                             | 1.3339    | 0.08610                   | 1.3336    | 0.08626                   | 1.3334    |
|                                     |           |                           |           |                           |           |
| 0.003mL/mol.kg <sup>-1</sup>        |           |                           |           |                           |           |
| 0.01003                             | 1.3327    | 0.01005                   | 1.3324    | 0.01007                   | 1.3322    |
| 0.02513                             | 1.333     | 0.02517                   | 1.3327    | 0.02521                   | 1.3325    |
| 0.04028                             | 1.3333    | 0.04033                   | 1.333     | 0.04040                   | 1.3328    |
| 0.05554                             | 1.3336    | 0.05540                   | 1.3333    | 0.05564                   | 1.3331    |

|                              |                               |         |                               |         |                               |
|------------------------------|-------------------------------|---------|-------------------------------|---------|-------------------------------|
| 0.07070                      | 1.3339                        | 0.07080 | 1.3336                        | 0.07093 | 1.3334                        |
| 0.08598                      | 1.3342                        | 0.08610 | 1.3339                        | 0.08626 | 1.3337                        |
| 0.005mL/mol.kg <sup>-1</sup> |                               |         |                               |         |                               |
| 0.01003                      | 1.3329                        | 0.01005 | 1.3327                        | 0.01006 | 1.3325                        |
| 0.02513                      | 1.3332                        | 0.02516 | 1.333                         | 0.02521 | 1.3328                        |
| 0.04027                      | 1.3335                        | 0.04033 | 1.3333                        | 0.04040 | 1.3331                        |
| 0.05546                      | 1.3338                        | 0.05553 | 1.3336                        | 0.05563 | 1.3334                        |
| 0.07070                      | 1.3341                        | 0.07079 | 1.3339                        | 0.07091 | 1.3337                        |
| 0.08598                      | 1.3344                        | 0.08609 | 1.3342                        | 0.08623 | 1.3340                        |
|                              | ( <sup>R</sup> <sub>M</sub> ) |         | ( <sup>R</sup> <sub>M</sub> ) |         | ( <sup>R</sup> <sub>M</sub> ) |
| 0.001mL/mol.kg <sup>-1</sup> |                               |         |                               |         |                               |
| 0.01003                      | 31.895±0.019                  | 0.01005 | 31.922±0.019                  | 0.01007 | 31.969±0.019                  |
| 0.02513                      | 31.913±0.019                  | 0.02517 | 31.940±0.019                  | 0.02518 | 31.979±0.019                  |
| 0.04028                      | 31.922±0.019                  | 0.04033 | 31.949±0.019                  | 0.04041 | 31.988±0.019                  |
| 0.05547                      | 31.931±0.019                  | 0.05549 | 31.957±0.019                  | 0.05564 | 31.997±0.019                  |
| 0.07070                      | 31.939±0.019                  | 0.07080 | 31.966±0.019                  | 0.07093 | 32.005±0.019                  |
| 0.08598                      | 31.947±0.019                  | 0.08610 | 31.973±0.019                  | 0.08626 | 32.014±0.019                  |
| 0.003mL/mol.kg <sup>-1</sup> |                               |         |                               |         |                               |
| 0.01003                      | 31.911±0.019                  | 0.01005 | 31.937±0.019                  | 0.01007 | 31.983±0.019                  |
| 0.02513                      | 31.929±0.019                  | 0.02517 | 31.956±0.019                  | 0.02521 | 32.003±0.019                  |
| 0.04028                      | 31.938±0.019                  | 0.04033 | 31.965±0.019                  | 0.04040 | 32.012±0.019                  |
| 0.05554                      | 31.947±0.019                  | 0.05540 | 31.974±0.019                  | 0.05564 | 32.021±0.019                  |
| 0.07070                      | 31.956±0.019                  | 0.07080 | 31.982±0.019                  | 0.07093 | 32.030±0.019                  |
| 0.08598                      | 31.964±0.019                  | 0.08610 | 31.990±0.019                  | 0.08626 | 32.038±0.019                  |
| 0.005mL/mol.kg <sup>-1</sup> |                               |         |                               |         |                               |
| 0.01003                      | 31.944±0.019                  | 0.01005 | 31.968±0.019                  | 0.01006 | 32.015±0.019                  |
| 0.02513                      | 31.963±0.019                  | 0.02516 | 31.987±0.019                  | 0.02521 | 32.025±0.019                  |
| 0.04027                      | 31.972±0.019                  | 0.04033 | 31.996±0.019                  | 0.04040 | 32.034±0.019                  |
| 0.05546                      | 31.972±0.019                  | 0.05553 | 32.004±0.019                  | 0.05563 | 32.042±0.019                  |
| 0.07070                      | 31.990±0.019                  | 0.07079 | 32.012±0.019                  | 0.07091 | 32.049±0.019                  |
| 0.08598                      | 31.998±0.019                  | 0.08609 | 32.019±0.019                  | 0.08623 | 32.056±0.019                  |

\*Standard uncertainties  $u$  are:  $u(n_D) = \pm 0.0002$ , Standard uncertainty in  $u$  (<sup>R</sup><sub>M</sub>) is given in parenthesis.  $u(T) = \pm 0.01\text{K}$  (0.68 level of confidence), #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{ mol kg}^{-1}$ \*Standard uncertainty in pressure  $u(p) = \pm 0.01 \text{ MPa}$ .

**Table S10.** Specific conductance ( $\kappa$ ) of (L-ARGININE+TBMS+H<sub>2</sub>O) and (L-HISTIDINE+TBMS+H<sub>2</sub>O) Systems in aqueous TBMS solutions of different concentrations (0.001, 0.003, 0.005) m at 298.15 K, 303.15 K, 308.15 K at atmospheric pressure 0.1MPa.

| Molality( <i>m</i> ) / mol.kg-1    | $\kappa$ (mS/cm) | Molality( <i>m</i> ) / mol.kg-1 | $\kappa$ (mS/cm) | Molality( <i>m</i> ) / mol.kg-1 | $\kappa$ (mS/cm) |
|------------------------------------|------------------|---------------------------------|------------------|---------------------------------|------------------|
|                                    | 298.15K          |                                 | 303.15K          |                                 | 308.15K          |
| (L-ARGININE+TBMS+H <sub>2</sub> O) |                  |                                 |                  |                                 |                  |
| 0.001mL/mol.kg <sup>-1</sup>       |                  |                                 |                  |                                 |                  |
| 0.01004                            | 0.185±0.008      | 0.01005                         | 0.206±0.010      | 0.01007                         | 0.221±0.010      |
| 0.02515                            | 0.215±0.010      | 0.02518                         | 0.235±0.010      | 0.02523                         | 0.249±0.005      |
| 0.04032                            | 0.243±0.003      | 0.04037                         | 0.265±0.003      | 0.04044                         | 0.281±0.010      |
| 0.05554                            | 0.261±0.003      | 0.05562                         | 0.285±0.010      | 0.05572                         | 0.303±0.010      |
| 0.07082                            | 0.282±0.005      | 0.07092                         | 0.299±0.004      | 0.07105                         | 0.329±0.010      |
| 0.08616                            | 0.303±0.010      | 0.08628                         | 0.339±0.010      | 0.08644                         | 0.361±0.010      |
| 0.003mL/mol.kg <sup>-1</sup>       |                  |                                 |                  |                                 |                  |
| 0.01004                            | 0.270±0.008      | 0.01005                         | 0.309±0.010      | 0.01007                         | 0.340±0.005      |
| 0.02515                            | 0.290±0.010      | 0.02518                         | 0.340±0.010      | 0.02523                         | 0.369±0.010      |

|                                     |             |         |             |         |             |
|-------------------------------------|-------------|---------|-------------|---------|-------------|
| 0.04031                             | 0.340±0.003 | 0.04037 | 0.370±0.010 | 0.04044 | 0.401±0.004 |
| 0.05554                             | 0.355±0.010 | 0.05562 | 0.382±0.010 | 0.05572 | 0.418±0.010 |
| 0.07082                             | 0.386±0.004 | 0.07092 | 0.417±0.005 | 0.07104 | 0.448±0.010 |
| 0.08615                             | 0.423±0.005 | 0.08628 | 0.460±0.010 | 0.08643 | 0.493±0.010 |
| 0.005mL/mol.kg <sup>-1</sup>        |             |         |             |         |             |
| 0.01004                             | 0.386±0.005 | 0.01005 | 0.420±0.004 | 0.01007 | 0.478±0.004 |
| 0.02515                             | 0.412±0.010 | 0.02518 | 0.473±0.010 | 0.02522 | 0.517±0.010 |
| 0.04031                             | 0.439±0.004 | 0.04037 | 0.484±0.003 | 0.04044 | 0.529±0.003 |
| 0.05554                             | 0.465±0.005 | 0.05561 | 0.512±0.010 | 0.05571 | 0.559±0.010 |
| 0.07082                             | 0.485±0.006 | 0.07091 | 0.545±0.010 | 0.07104 | 0.585±0.008 |
| 0.08615                             | 0.526±0.010 | 0.08627 | 0.585±0.010 | 0.08642 | 0.626±0.010 |
| (L-HISTIDINE+TBMS+H <sub>2</sub> O) |             |         |             |         |             |
| 0.001mL/mol.kg <sup>-1</sup>        |             |         |             |         |             |
| 0.01003                             | 0.228±0.006 | 0.01005 | 0.251±0.004 | 0.01007 | 0.268±0.005 |
| 0.02513                             | 0.29±0.004  | 0.02517 | 0.268±0.010 | 0.02518 | 0.288±0.002 |
| 0.04028                             | 0.273±0.010 | 0.04033 | 0.297±0.005 | 0.04041 | 0.312±0.010 |
| 0.05547                             | 0.283±0.005 | 0.05549 | 0.313±0.010 | 0.05564 | 0.332±0.010 |
| 0.07070                             | 0.324±0.010 | 0.07080 | 0.342±0.003 | 0.07093 | 0.359±0.010 |
| 0.08598                             | 0.351±0.006 | 0.08610 | 0.389±0.010 | 0.08626 | 0.400±0.008 |
| 0.003mL/mol.kg <sup>-1</sup>        |             |         |             |         |             |
| 0.01003                             | 0.325±0.004 | 0.01005 | 0.358±0.005 | 0.01007 | 0.389±0.009 |
| 0.02513                             | 0.343±0.010 | 0.02517 | 0.378±0.010 | 0.02521 | 0.414±0.010 |
| 0.04028                             | 0.368±0.010 | 0.04033 | 0.399±0.010 | 0.04040 | 0.440±0.010 |
| 0.05554                             | 0.392±0.008 | 0.05540 | 0.427±0.010 | 0.05564 | 0.459±0.007 |
| 0.07070                             | 0.426±0.010 | 0.07080 | 0.469±0.009 | 0.07093 | 0.498±0.010 |
| 0.08598                             | 0.465±0.007 | 0.08610 | 0.507±0.010 | 0.08626 | 0.549±0.009 |
| 0.005mL/mol.kg <sup>-1</sup>        |             |         |             |         |             |
| 0.01003                             | 0.436±0.002 | 0.01005 | 0.464±0.005 | 0.01006 | 0.511±0.010 |
| 0.02513                             | 0.469±0.010 | 0.02516 | 0.494±0.010 | 0.02521 | 0.536±0.004 |
| 0.04027                             | 0.498±0.010 | 0.04033 | 0.529±0.003 | 0.04040 | 0.566±0.010 |
| 0.05546                             | 0.519±0.005 | 0.05553 | 0.565±0.010 | 0.05563 | 0.613±0.003 |
| 0.07070                             | 0.568±0.010 | 0.07079 | 0.597±0.002 | 0.07091 | 0.638±0.002 |
| 0.08598                             | 0.596±0.007 | 0.08609 | 0.626±0.010 | 0.08623 | 0.669±0.006 |

\*Standard errors in specific conductance/ms.cm<sup>-1</sup> is given in their parenthesis. #Combined standard uncertainties in molality according to stated purity u (m) =±0.0092 mol kg<sup>-1</sup> u (T) =±0.01K (0.68 level of confidence), \*Standard uncertainty in pressure u (p)= ±0.01 MPa.

**Table S11.** Specific conductance ( $\kappa$ ) of (L-ARGININE+TBMS+H<sub>2</sub>O) system in aqueous IL (TBMS) solutions of concentration 0.001m at 298.15 K, 303.15 K and 308.15 K and at atmospheric pressure 0.1MPa.

| Specific conductivity/ $\mu\text{S cm}^{-1}$<br>0.001mL/mol.kg <sup>-1</sup> |                         |                                     |                                     |         |         |         |
|--|-------------------------|-------------------------------------|-------------------------------------|---------|---------|---------|
| Added IL/mL  | Total volume (IL+AA)/mL | Conc. of AA at each titration point | Conc. of IL at each titration point | 298.15K | 303.15K | 308.15K |
| 0  | 20                      | 0.01                                | 0.00000                             | 167     | 176     | 192     |
| 1  | 21                      | 0.0095                              | 0.00047                             | 165     | 173     | 188     |
| 2  | 22                      | 0.0090                              | 0.00044                             | 164     | 171     | 185     |
| 3  | 23                      | 0.0086                              | 0.00043                             | 162     | 170     | 182     |
| 4  | 24                      | 0.0083                              | 0.00041                             | 161     | 169     | 180     |
| 5  | 25                      | 0.0080                              | 0.00040                             | 160     | 168     | 178     |
| 6  | 26                      | 0.0076                              | 0.00038                             | 159     | 166     | 175     |
| 7  | 27                      | 0.0074                              | 0.00037                             | 158     | 165     | 174     |
| 8  | 28                      | 0.0071                              | 0.00035                             | 157     | 164     | 172     |
| 9  | 29                      | 0.0068                              | 0.00034                             | 156     | 163     | 170     |

|    |    |        |         |     |     |     |
|----|----|--------|---------|-----|-----|-----|
| 10 | 30 | 0.0066 | 0.00033 | 155 | 162 | 169 |
| 11 | 31 | 0.0064 | 0.00032 | 154 | 161 | 168 |
| 12 | 32 | 0.0062 | 0.00031 | 153 | 160 | 166 |
| 13 | 33 | 0.0060 | 0.00030 | 152 | 158 | 165 |
| 14 | 34 | 0.0058 | 0.00029 | 151 | 157 | 164 |
| 15 | 35 | 0.0057 | 0.00028 | 150 | 156 | 163 |
| 16 | 36 | 0.0055 | 0.00027 | 149 | 155 | 162 |
| 17 | 37 | 0.0054 | 0.00027 | 147 | 155 | 161 |
| 18 | 38 | 0.0052 | 0.00026 | 146 | 154 | 160 |
| 19 | 39 | 0.0051 | 0.00025 | 145 | 154 | 159 |
| 20 | 40 | 0.0050 | 0.00025 | 145 | 154 | 158 |

\*Standard uncertainties  $u(\kappa) = \pm 0.010 (\text{ms} \cdot \text{cm}^{-1})$ ,  $u(T) = \pm 0.01 \text{K}$  (0.68 level of confidence),

\*Standard uncertainty in pressure  $u(p) = \pm 0.01 \text{MPa}$ . #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{mol kg}^{-1}$ . Initial concentration of Amino acid in the cell was 0.01 mole/kg. Initial added concentration of IL in the cell in term of molality was  $0.001 \text{mol/kg}^{-1}$ .

**Table S12.** Specific conductance ( $\kappa$ ) of (L-ARGININE+TBMS+H<sub>2</sub>O) system in aqueous IL (TBMS) solutions of concentration 0.003m at 298.15K, 303.15K and 308.15 K and at atmospheric pressure 0.1MPa.

| Specific conductivity/ $\mu\text{S cm}^{-1}$<br>0.003mIL/mol.kg <sup>-1</sup> |                         |                                     |                                     |         |         |         |
|---|-------------------------|-------------------------------------|-------------------------------------|---------|---------|---------|
| Added IL/mL   | Total volume (IL+AA)/mL | Conc. of AA at each titration point | Conc. of IL at each titration point | 298.15K | 303.15K | 308.15K |
| 0   | 20                      | 0.01                                | 0.00000                             | 310     | 330     | 355     |
| 1   | 21                      | 0.0095                              | 0.00014                             | 308     | 327     | 351     |
| 2   | 22                      | 0.0090                              | 0.00013                             | 306     | 325     | 348     |
| 3   | 23                      | 0.0086                              | 0.00013                             | 303     | 323     | 345     |
| 4   | 24                      | 0.0083                              | 0.00012                             | 300     | 320     | 342     |
| 5   | 25                      | 0.0080                              | 0.00011                             | 298     | 317     | 339     |
| 6   | 26                      | 0.0076                              | 0.00011                             | 296     | 316     | 337     |
| 7   | 27                      | 0.0074                              | 0.00010                             | 294     | 314     | 335     |
| 8   | 28                      | 0.0071                              | 0.00010                             | 292     | 311     | 332     |
| 9   | 29                      | 0.0068                              | 0.00010                             | 291     | 309     | 330     |
| 10  | 30                      | 0.0066                              | 0.00009                             | 289     | 307     | 328     |
| 11  | 31                      | 0.0064                              | 0.00009                             | 287     | 304     | 326     |
| 12  | 32                      | 0.0062                              | 0.00009                             | 284     | 303     | 323     |
| 13  | 33                      | 0.0060                              | 0.00008                             | 283     | 302     | 322     |
| 14  | 34                      | 0.0058                              | 0.00008                             | 282     | 301     | 321     |
| 15  | 35                      | 0.0057                              | 0.00008                             | 281     | 300     | 320     |
| 16  | 36                      | 0.0055                              | 0.00007                             | 280     | 299     | 319     |
| 17  | 37                      | 0.0054                              | 0.00007                             | 279     | 298     | 317     |
| 18  | 38                      | 0.0052                              | 0.00007                             | 278     | 298     | 316     |
| 19  | 39                      | 0.0051                              | 0.00007                             | 277     | 298     | 315     |
| 20  | 40                      | 0.0050                              | 0.00006                             | 277     | 298     | 315     |

\*Standard uncertainties  $u(\kappa) = \pm 0.010 (\text{ms} \cdot \text{cm}^{-1})$ , #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{mol kg}^{-1}$   $u(T) = \pm 0.01 \text{K}$  (0.68 level of confidence),

\*Standard uncertainty in pressure  $u(p) = \pm 0.01 \text{MPa}$ . Initial concentration of Amino acid in the cell was 0.01 mole/kg. Initial added concentration of IL in the cell in term of molality was  $0.003 \text{mol.kg}^{-1}$ .

**Table S13.** Specific conductance ( $\kappa$ ) of (L-ARGININE+TBMS+H<sub>2</sub>O) system in aqueous IL (TBMS) solutions of concentration 0.005m at 298.1 K, 303.15 K and 308.15 K and at atmospheric pressure 0.1MPa.

| Specific conductivity/ $\mu\text{S cm}^{-1}$<br>0.005mL/mol.kg <sup>-1</sup> |                         |                                     |                                     |         |         |         |
|--|-------------------------|-------------------------------------|-------------------------------------|---------|---------|---------|
| Added IL/mL  | Total volume (IL+AA)/mL | Conc. of AA at each titration point | Conc. of IL at each titration point | 298.15K | 303.15K | 308.15K |
| 0  | 20                      | 0.01                                | 0.00000                             | 438     | 470     | 503     |
| 1  | 21                      | 0.0095                              | 0.00023                             | 436     | 466     | 498     |
| 2  | 22                      | 0.0090                              | 0.00022                             | 434     | 463     | 494     |
| 3  | 23                      | 0.0086                              | 0.00021                             | 432     | 461     | 490     |
| 4  | 24                      | 0.0083                              | 0.00020                             | 430     | 459     | 487     |
| 5  | 25                      | 0.0080                              | 0.00019                             | 428     | 457     | 484     |
| 6  | 26                      | 0.0076                              | 0.00018                             | 426     | 454     | 480     |
| 7  | 27                      | 0.0074                              | 0.00017                             | 424     | 452     | 474     |
| 8  | 28                      | 0.0071                              | 0.00017                             | 423     | 450     | 472     |
| 9  | 29                      | 0.0068                              | 0.00016                             | 421     | 448     | 470     |
| 10   | 30                      | 0.0066                              | 0.00016                             | 419     | 446     | 468     |
| 11   | 31                      | 0.0064                              | 0.00015                             | 418     | 444     | 464     |
| 12   | 32                      | 0.0062                              | 0.00015                             | 417     | 443     | 464     |
| 13   | 33                      | 0.0060                              | 0.00014                             | 416     | 442     | 462     |
| 14   | 34                      | 0.0058                              | 0.00014                             | 415     | 441     | 460     |
| 15   | 35                      | 0.0057                              | 0.00013                             | 414     | 440     | 458     |
| 16   | 36                      | 0.0055                              | 0.00013                             | 413     | 439     | 456     |
| 17   | 37                      | 0.0054                              | 0.00013                             | 411     | 438     | 454     |
| 18   | 38                      | 0.0052                              | 0.00012                             | 410     | 437     | 453     |
| 19   | 39                      | 0.0051                              | 0.00012                             | 409     | 435     | 451     |
| 20   | 40                      | 0.0050                              | 0.00011                             | 408     | 434     | 450     |

\*Standard uncertainties  $u(\kappa)=\pm 0.010(\text{ms.cm}^{-1})$ , #Combined standard uncertainties in molality according to stated purity  $u(m)=\pm 0.0092 \text{ mol kg}^{-1}$   $u(T)=\pm 0.01\text{K}$ (0.68 level of confidence), \*Standard uncertainty in pressure  $u(p)=\pm 0.01 \text{ MPa}$ . Initial concentration of Amino acid in the cell was 0.01mole/kg. Initial added concentration of IL in the cell in term of molality was 0.005mol.kg<sup>-1</sup>.

**Table S14.** Specific conductance ( $\kappa$ ) of (L-HISTIDINE +TBMS+H<sub>2</sub>O) system in aqueous IL (TBMS) solutions of concentration 0.001m at 298.15 K, 303.15 K and 308.15 K and at atmospheric pressure 0.1MPa.

| Specific conductivity/ $\mu\text{S cm}^{-1}$<br>0.001mL/mol.kg <sup>-1</sup> |                         |                                     |                                     |         |         |         |
|--|-------------------------|-------------------------------------|-------------------------------------|---------|---------|---------|
| Added IL/mL  | Total volume (IL+AA)/mL | Conc. of AA at each titration point | Conc. of IL at each titration point | 298.15K | 303.15K | 308.15K |
| 0  | 20                      | 0.01                                | 0.00000                             | 210     | 239     | 261     |
| 1  | 21                      | 0.0095                              | 0.00047                             | 208     | 236     | 258     |
| 2  | 22                      | 0.0090                              | 0.00044                             | 206     | 234     | 256     |
| 3  | 23                      | 0.0086                              | 0.00043                             | 205     | 231     | 254     |
| 4  | 24                      | 0.0083                              | 0.00041                             | 204     | 229     | 251     |
| 5  | 25                      | 0.0080                              | 0.00040                             | 203     | 226     | 249     |
| 6  | 26                      | 0.0076                              | 0.00038                             | 202     | 223     | 247     |
| 7  | 27                      | 0.0074                              | 0.00037                             | 201     | 221     | 245     |
| 8  | 28                      | 0.0071                              | 0.00035                             | 200     | 219     | 244     |
| 9  | 29                      | 0.0068                              | 0.00034                             | 198     | 217     | 242     |

|    |    |        |         |     |     |     |
|----|----|--------|---------|-----|-----|-----|
| 10 | 30 | 0.0066 | 0.00033 | 197 | 215 | 239 |
| 11 | 31 | 0.0064 | 0.00032 | 196 | 213 | 236 |
| 12 | 32 | 0.0062 | 0.00031 | 194 | 210 | 235 |
| 13 | 33 | 0.0060 | 0.00030 | 193 | 209 | 233 |
| 14 | 34 | 0.0058 | 0.00029 | 192 | 207 | 232 |
| 15 | 35 | 0.0057 | 0.00028 | 191 | 205 | 230 |
| 16 | 36 | 0.0055 | 0.00027 | 190 | 204 | 229 |
| 17 | 37 | 0.0054 | 0.00027 | 188 | 203 | 228 |
| 18 | 38 | 0.0052 | 0.00026 | 187 | 202 | 227 |
| 19 | 39 | 0.0051 | 0.00025 | 186 | 201 | 228 |
| 20 | 40 | 0.0050 | 0.00025 | 186 | 201 | 225 |

\*Standard uncertainties  $u(\kappa)=\pm 0.010(\text{ms.cm}^{-1})$ , #Combined standard uncertainties in molality according to stated purity  $u(m)=\pm 0.0092 \text{ mol kg}^{-1}$   $u(T)=\pm 0.01\text{K}$ (0.68 level of confidence), \*Standard uncertainty in pressure  $u(p)=\pm 0.01 \text{ MPa}$ . Initial concentration of Amino acid in the cell was 0.01mole/kg. Initial added concentration of IL in the cell in term of molality was 0.001mol.kg<sup>-1</sup>.

**Table S15.** Specific conductance ( $\kappa$ ) of (L-HISTIDINE +TBMS+H<sub>2</sub>O) system in aqueous IL (TBMS) solutions of concentration 0.003m at 298.15K, 303.15K and 308.15 K and at atmospheric pressure 0.1MPa.

| Specific conductivity/ $\mu\text{S cm}^{-1}$<br>0.003mL/mol.kg <sup>-1</sup> |                         |                                     |                                     |         |         |         |
|--|-------------------------|-------------------------------------|-------------------------------------|---------|---------|---------|
| Added IL/mL  | Total volume (IL+AA)/mL | Conc. of AA at each titration point | Conc. of IL at each titration point | 298.15K | 303.15K | 308.15K |
| 0  | 20                      | 0.01                                | 0.00000                             | 361     | 421     | 472     |
| 1  | 21                      | 0.0095                              | 0.00047                             | 356     | 419     | 469     |
| 2  | 22                      | 0.0090                              | 0.00044                             | 354     | 417     | 467     |
| 3  | 23                      | 0.0086                              | 0.00043                             | 352     | 415     | 464     |
| 4  | 24                      | 0.0083                              | 0.00041                             | 350     | 413     | 461     |
| 5  | 25                      | 0.0080                              | 0.00040                             | 348     | 411     | 457     |
| 6  | 26                      | 0.0076                              | 0.00038                             | 346     | 409     | 455     |
| 7  | 27                      | 0.0074                              | 0.00037                             | 344     | 407     | 452     |
| 8  | 28                      | 0.0071                              | 0.00035                             | 342     | 405     | 450     |
| 9  | 29                      | 0.0068                              | 0.00034                             | 340     | 403     | 448     |
| 10   | 30                      | 0.0066                              | 0.00033                             | 338     | 401     | 446     |
| 11   | 31                      | 0.0064                              | 0.00032                             | 335     | 399     | 444     |
| 12   | 32                      | 0.0062                              | 0.00031                             | 333     | 397     | 442     |
| 13   | 33                      | 0.0060                              | 0.00030                             | 330     | 394     | 440     |
| 14   | 34                      | 0.0058                              | 0.00029                             | 327     | 393     | 437     |
| 15   | 35                      | 0.0057                              | 0.00028                             | 326     | 392     | 435     |
| 16   | 36                      | 0.0055                              | 0.00027                             | 325     | 391     | 433     |
| 17   | 37                      | 0.0054                              | 0.00027                             | 324     | 390     | 432     |
| 18   | 38                      | 0.0052                              | 0.00026                             | 323     | 389     | 431     |
| 19   | 39                      | 0.0051                              | 0.00025                             | 323     | 388     | 430     |
| 20   | 40                      | 0.0050                              | 0.00025                             | 323     | 387     | 429     |

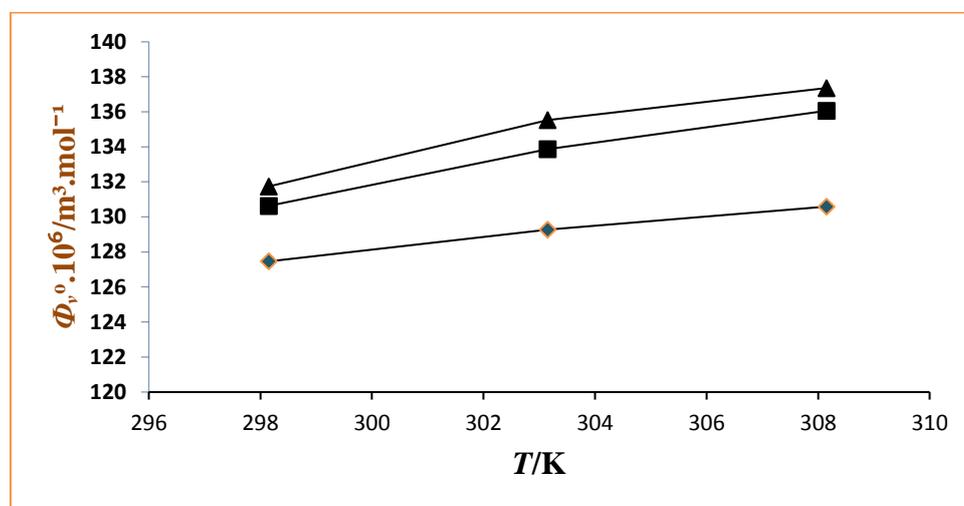
\*Standard uncertainties  $u(\kappa)=\pm 0.010(\text{ms.cm}^{-1})$ , #Combined standard uncertainties in molality according to stated purity  $u(m)=\pm 0.0092 \text{ mol kg}^{-1}$   $u(T)=\pm 0.01\text{K}$ (0.68 level of confidence), \*Standard uncertainty in pressure  $u(p)=\pm 0.01 \text{ MPa}$ . Initial concentration of Amino acid in the cell was 0.01mole/kg. Initial added concentration of IL in the cell in term of molality was 0.003mol.kg<sup>-1</sup>.

**Table S16.** Specific conductance ( $\kappa$ ) of (L-HISTIDINE +TBMS+H<sub>2</sub>O) system in aqueous IL (TBMS) solutions of concentration 0.005m at 298.15K, 303.15 K and 308.15 K and at atmospheric pressure 0.1MPa

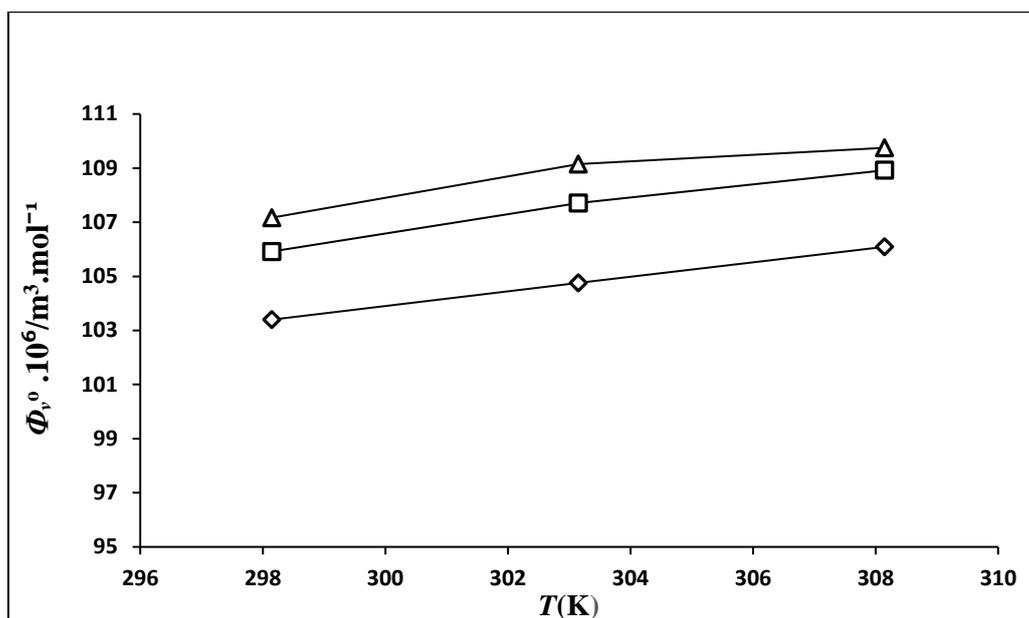
| Specific conductivity/ $\mu\text{S cm}^{-1}$<br>0.005mL/mol.kg <sup>-1</sup> |                         |                                     |                                     |         |         |         |
|--|-------------------------|-------------------------------------|-------------------------------------|---------|---------|---------|
| Added IL/mL  | Total volume (IL+AA)/mL | Conc. of AA at each titration point | Conc. of IL at each titration point | 298.15K | 303.15K | 308.15K |
| 0  | 20                      | 0.01                                | 0.00000                             | 520     | 578     | 702     |
| 1  | 21                      | 0.0095                              | 0.00047                             | 518     | 575     | 698     |
| 2  | 22                      | 0.0090                              | 0.00044                             | 516     | 572     | 695     |
| 3  | 23                      | 0.0086                              | 0.00043                             | 514     | 570     | 692     |
| 4  | 24                      | 0.0083                              | 0.00041                             | 512     | 568     | 689     |
| 5  | 25                      | 0.0080                              | 0.00040                             | 510     | 566     | 686     |
| 6  | 26                      | 0.0076                              | 0.00038                             | 507     | 564     | 683     |
| 7  | 27                      | 0.0074                              | 0.00037                             | 505     | 562     | 680     |
| 8  | 28                      | 0.0071                              | 0.00035                             | 503     | 560     | 677     |
| 9  | 29                      | 0.0068                              | 0.00034                             | 501     | 558     | 675     |
| 10   | 30                      | 0.0066                              | 0.00033                             | 499     | 556     | 673     |
| 11   | 31                      | 0.0064                              | 0.00032                             | 498     | 554     | 672     |
| 12   | 32                      | 0.0062                              | 0.00031                             | 497     | 553     | 671     |
| 13   | 33                      | 0.0060                              | 0.00030                             | 496     | 550     | 670     |
| 14   | 34                      | 0.0058                              | 0.00029                             | 495     | 549     | 669     |
| 15   | 35                      | 0.0057                              | 0.00028                             | 494     | 548     | 668     |
| 16   | 36                      | 0.0055                              | 0.00027                             | 493     | 547     | 667     |
| 17   | 37                      | 0.0054                              | 0.00027                             | 492     | 546     | 666     |
| 18   | 38                      | 0.0052                              | 0.00026                             | 491     | 545     | 665     |
| 19   | 39                      | 0.0051                              | 0.00025                             | 490     | 544     | 664     |
| 20   | 40                      | 0.0050                              | 0.00025                             | 489     | 543     | 663     |

\*Standard uncertainties  $u(\kappa) = \pm 0.010 (\text{ms.cm}^{-1})$ , #Combined standard uncertainties in molality according to stated purity  $u(m) = \pm 0.0092 \text{ mol kg}^{-1}$   $u(T) = \pm 0.01\text{K}$  (0.68 level of confidence), \*Standard uncertainty in pressure  $u(p) = \pm 0.01 \text{ MPa}$ . Initial concentration of Amino acid in the cell was 0.01mole/kg. Initial added concentration of IL in the cell in term of molality was 0.005mol.kg<sup>-1</sup>.

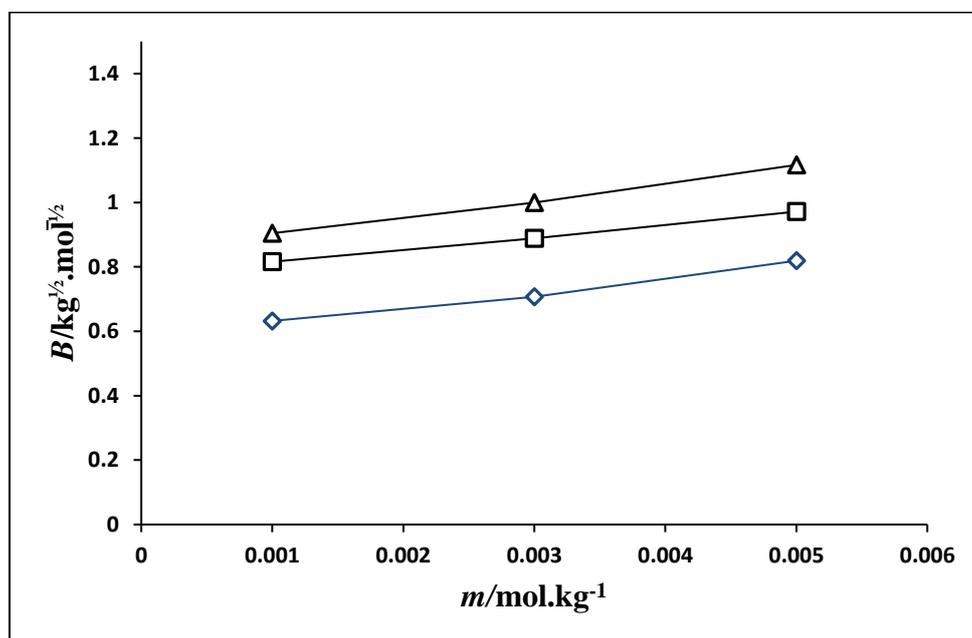
## Figures



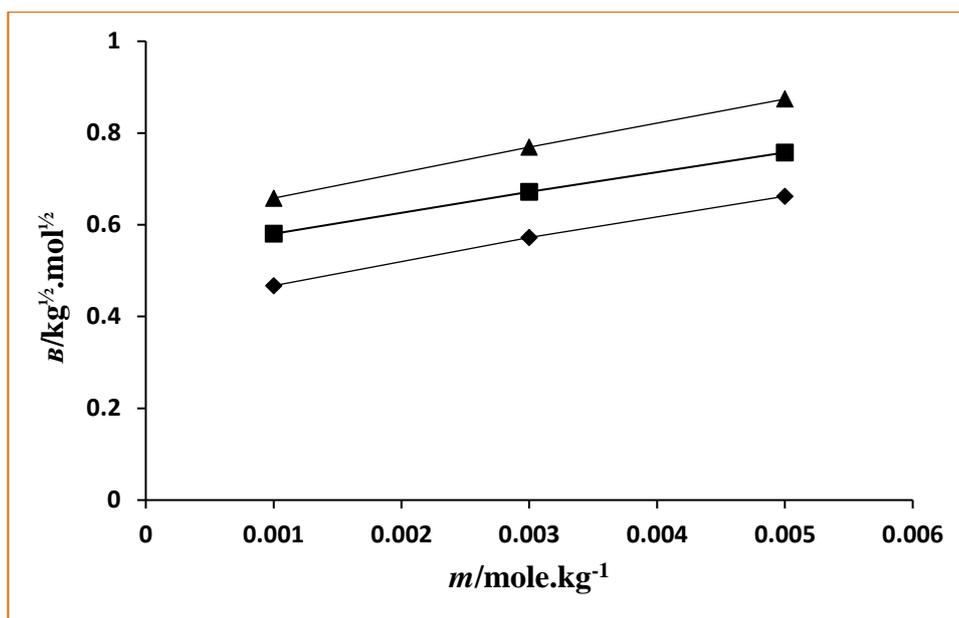
**Figure 1.** Variation of limiting apparent molar volumes ( $\Phi_v^0$ ) of L-Arginine as a function of temperature /K in aqueous TBMS solutions of different concentrations (-▲- 0.001m/mol.kg<sup>-1</sup>; -■- 0.003m/mol.kg<sup>-1</sup>; -◆- 0.005m/mol.kg<sup>-1</sup>).



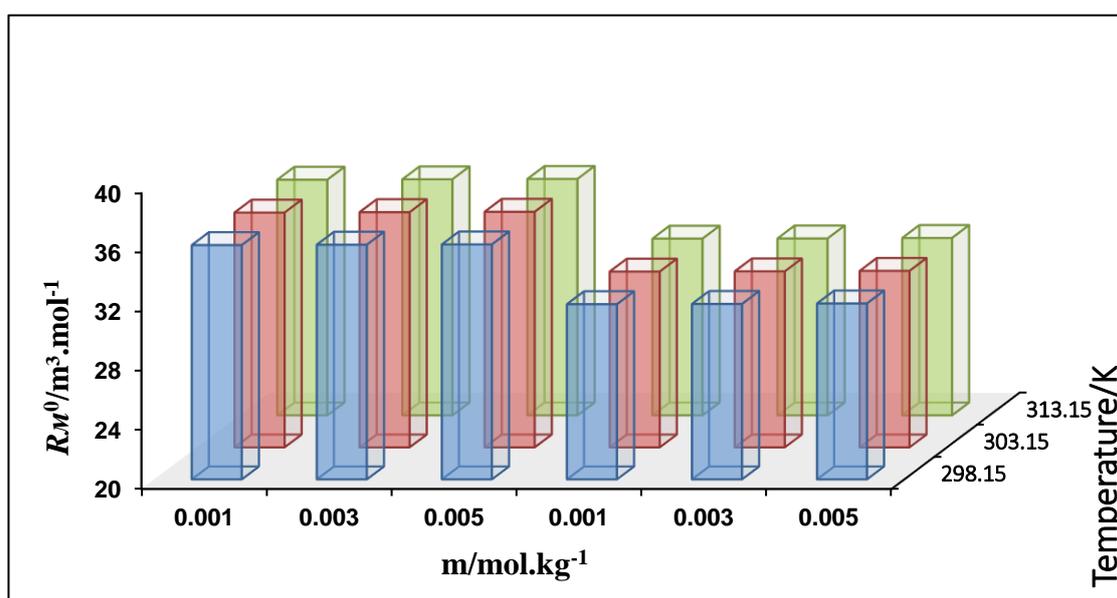
**Figure 2.** Variation of limiting apparent molar volumes ( $\Phi_v^0$ ) of L-Histidine as a function of temperature /K in aqueous TBMS solutions of different concentrations (- $\Delta$ - 0.001m/mol.kg<sup>-1</sup>; - $\square$ - 0.003m/mol.kg<sup>-1</sup>; - $\diamond$ - 0.005m/mol.kg<sup>-1</sup>).



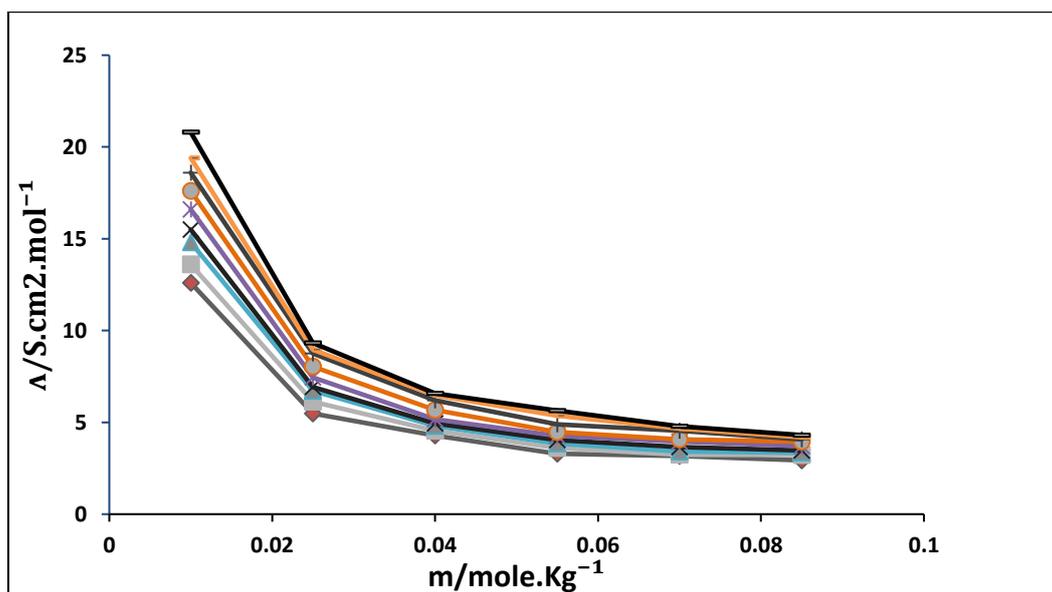
**Figure 3.** Variation of viscosity  $B$ -coefficient of L-Arginine as a function of different concentrations of aqueous TBMS (IL) solutions at (- $\diamond$ - 298.15K; - $\square$ - 303.15K; - $\Delta$ - 308.15K).



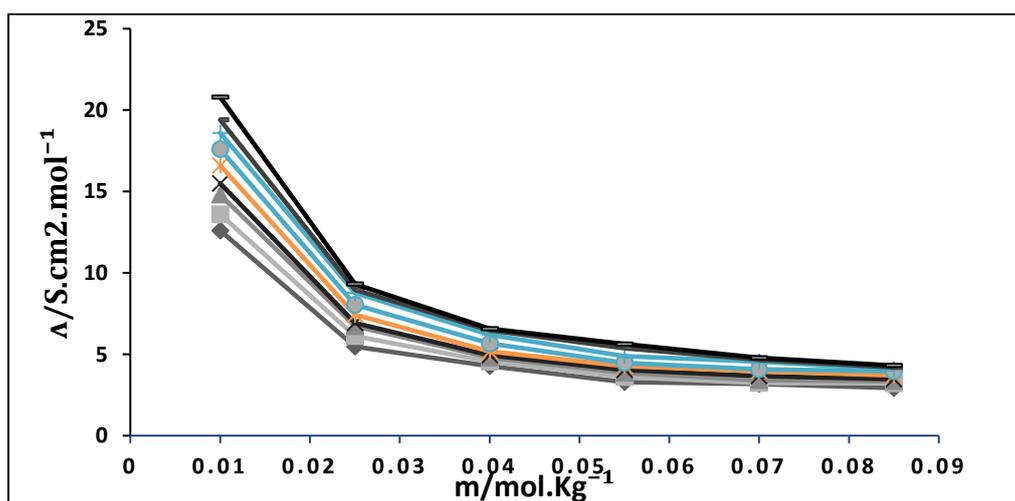
**Figure 4.** Variation of viscosity  $B$ -coefficient of L-Histidine as a function of different concentrations of aqueous TBMS (IL) solutions at (-♦- 298.15K; -■- 303.15K; -▲- 308.15K).



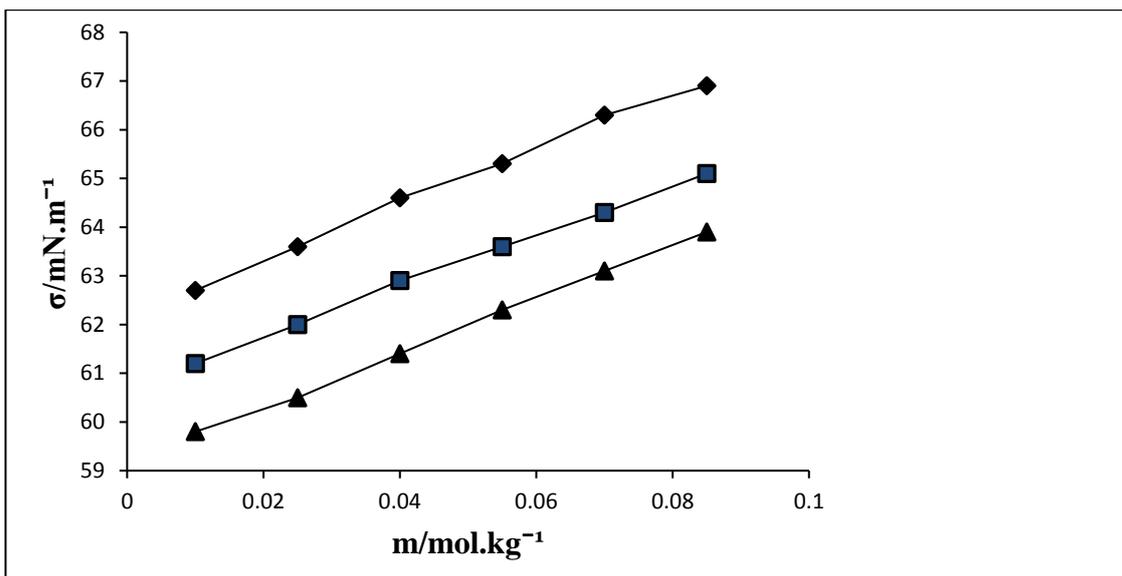
**Figure 5.** Variation of limiting molar refraction ( $R_M^0$ ) plot of L-Arginine (big size figure) and L-Histidine (small size figure) as a function of different concentrations of aqueous TBMS solutions and as a function of temperature ( $T/K$ ).



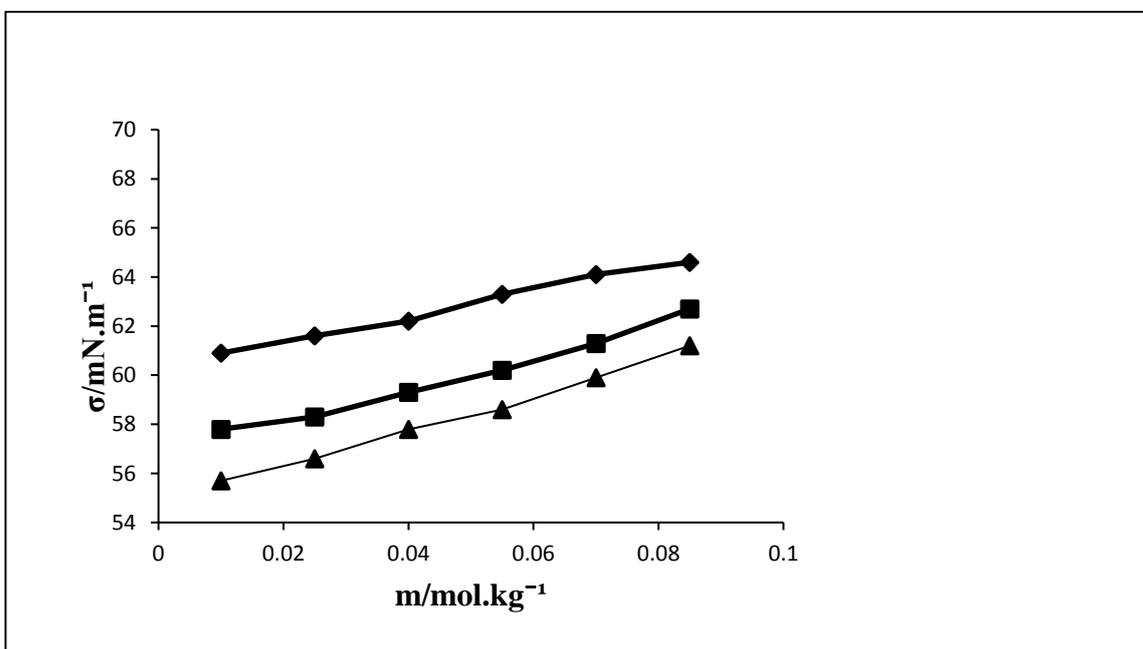
**Figure 6.** Variation of molar conductance ( $\Lambda$ ) plot as a function of the concentration of L-Arginine (amino acid) in different concentrations aqueous TBMS solutions at different temperatures ( $T/K$ ) ( $\diamond$ - concentration(IL)0.001m/mol.kg<sup>-1</sup> at 298.15K;  $\square$ -concentration(IL) 0.001m/mol.kg<sup>-1</sup> at 303.15K;  $\Delta$ -concentration(IL)0.001m/mol.kg<sup>-1</sup> at 308.15K,  $\times$ -concentration (IL) 0.003m/mol.kg<sup>-1</sup> at 298.15K;  $*$ - concentration (IL) 0.003m/mol.kg<sup>-1</sup> at 303.15K;  $\bullet$ - concentration (IL) 0.003m/mol.kg<sup>-1</sup> at 308.15K;  $\text{---}$  concentration (IL) 0.005 at 298.15K;  $\text{---}$  concentration (IL) 0.005m/mol.kg<sup>-1</sup> at 303.15K and  $\text{---}$  concentration (IL) 0.005m/mol.kg<sup>-1</sup> at 308.15K.



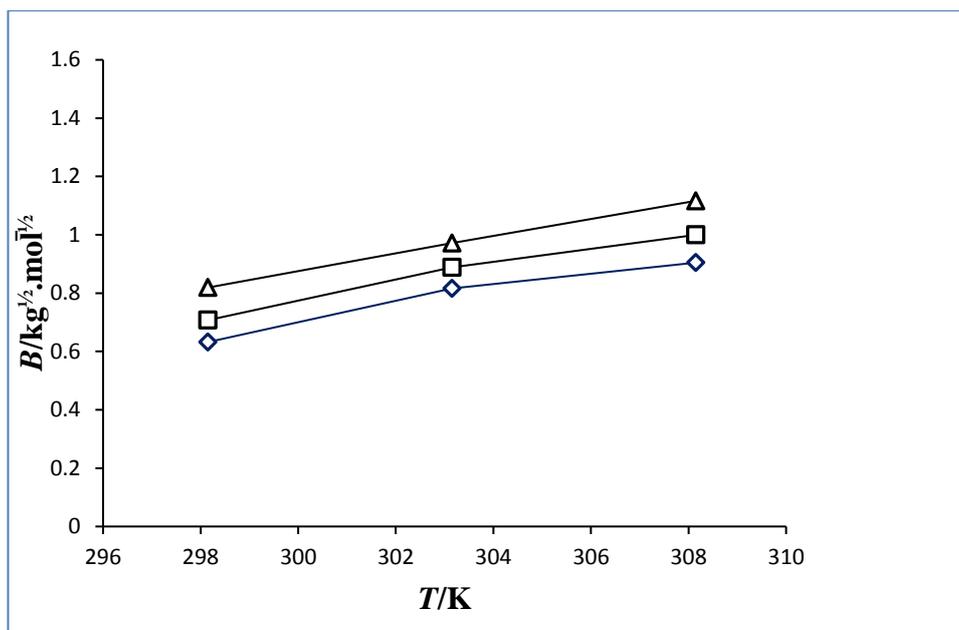
**Figure 7.** Variation of molar conductance ( $\Lambda$ ) plot as a function of the concentration of L-Histidine (Amino acid) in different concentrations aqueous TBMS solutions at different temperatures ( $T/K$ ) ( $\diamond$ - concentration(IL)0.001m/mol.kg<sup>-1</sup> at 298.15K;  $\square$ -concentration(IL)0.001m/mol.kg<sup>-1</sup> at 303.15K;  $\Delta$ -concentration(IL)0.001m/mol.kg<sup>-1</sup> at 308.15K,  $\times$ - concentration (IL) 0.003m/mol.kg<sup>-1</sup> 0.003 at 298.15K;  $*$ - concentration (IL) 0.003m/mol.kg<sup>-1</sup> at 303.15K;  $\bullet$ - concentration (IL) 0.003m/mol.kg<sup>-1</sup> at 308.15K;  $\text{---}$  concentration (IL) 0.005m/mol.kg<sup>-1</sup> at 298.15K;  $\text{---}$  concentration (IL) 0.005m/mol.kg<sup>-1</sup> at 303.15K and  $\text{---}$  concentration (IL) 0.005m/mol.kg<sup>-1</sup> at 308.15K.



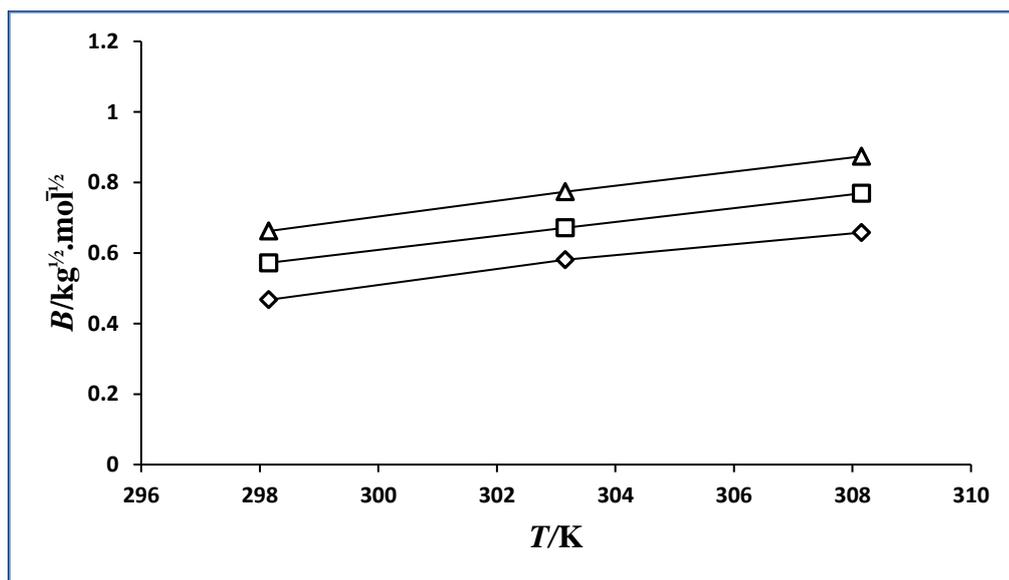
**Figure 8.** Variation of surface tension ( $\sigma$ ) plot of L-Arginine as a function of different concentrations (-▲- 0.001 $\text{m}/\text{mol}\cdot\text{kg}^{-1}$ ; -■- 0.003 $\text{m}/\text{mol}\cdot\text{kg}^{-1}$ ; -◆- 0.005 $\text{m}/\text{mol}\cdot\text{kg}^{-1}$ ) of aqueous TBMS solutions at 298.15 K.



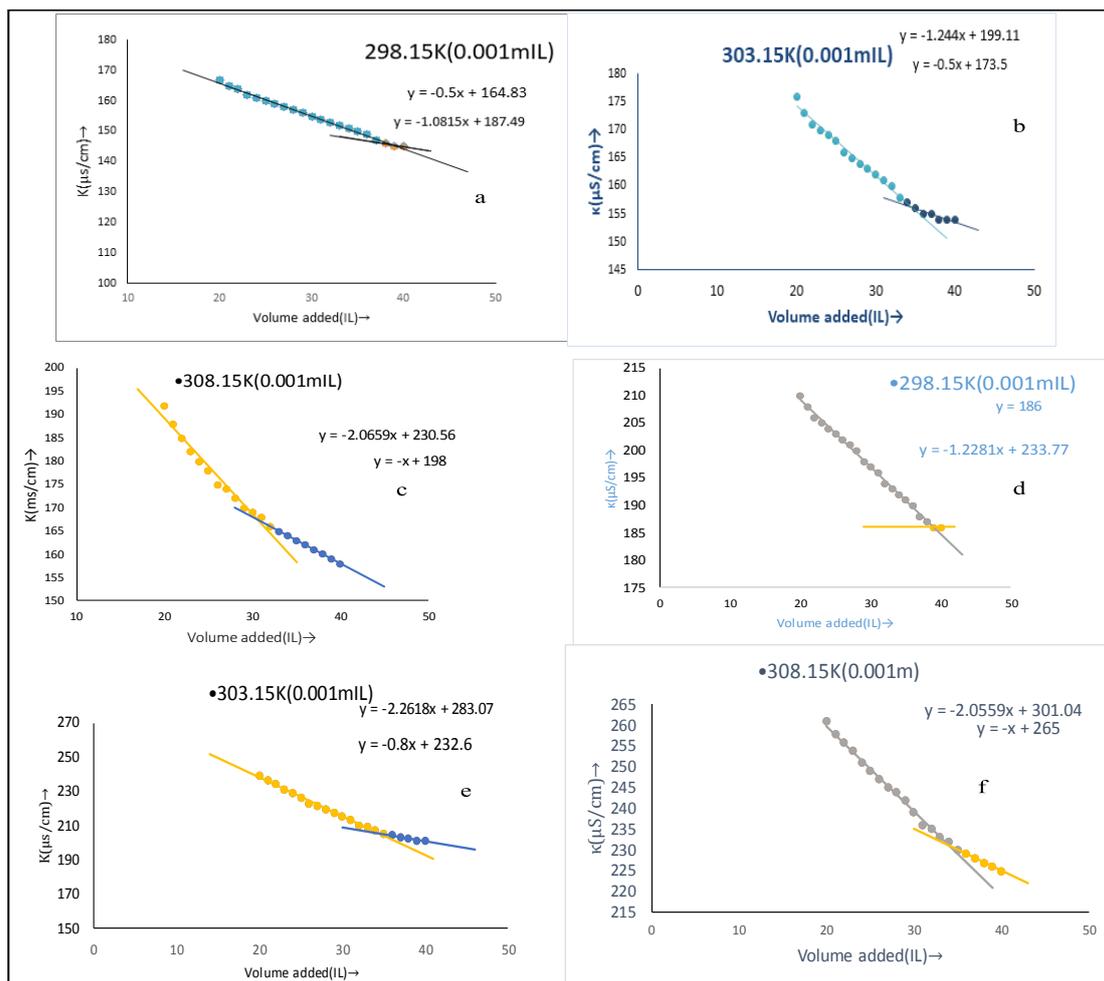
**Figure 9.** Variation of surface tension ( $\sigma$ ) plot of L-Histidine as a function of different concentrations (-▲- 0.001 $\text{m}/\text{mol}\cdot\text{kg}^{-1}$ ; -■- 0.003 $\text{m}/\text{mol}\cdot\text{kg}^{-1}$ ; -◆- 0.005 $\text{m}/\text{mol}\cdot\text{kg}^{-1}$ ) of aqueous TBMS solutions at 298.15 K.

**Supporting figures**

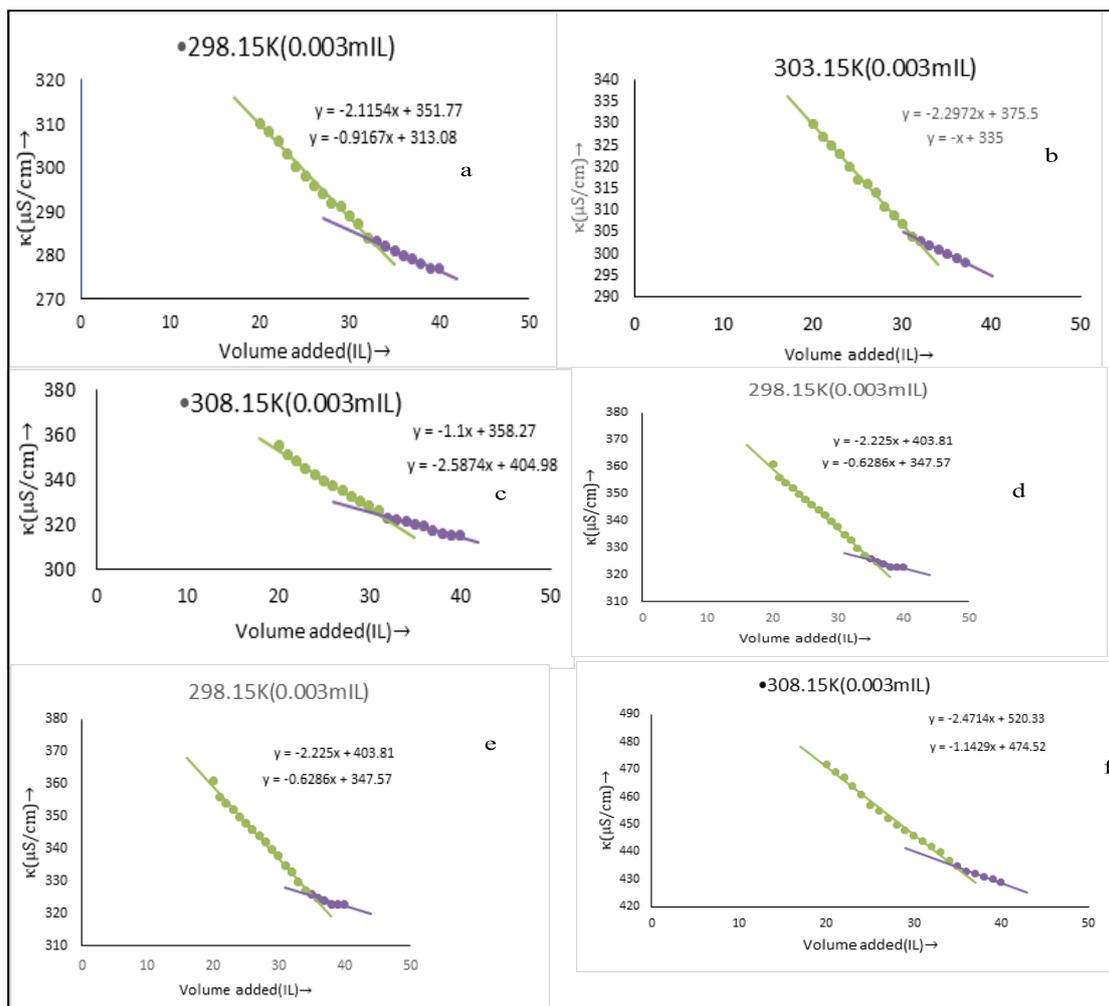
**Figure S1.** Variation of viscosity  $B$ -coefficient of L-Arginine against temperature in different concentrations ( $\diamond$ - 0.001m/mol.kg<sup>-1</sup>;  $\square$ - 0.003m/mol.kg<sup>-1</sup>;  $\Delta$ - 0.005m/mol.kg<sup>-1</sup>) of aqueous IL Solution.



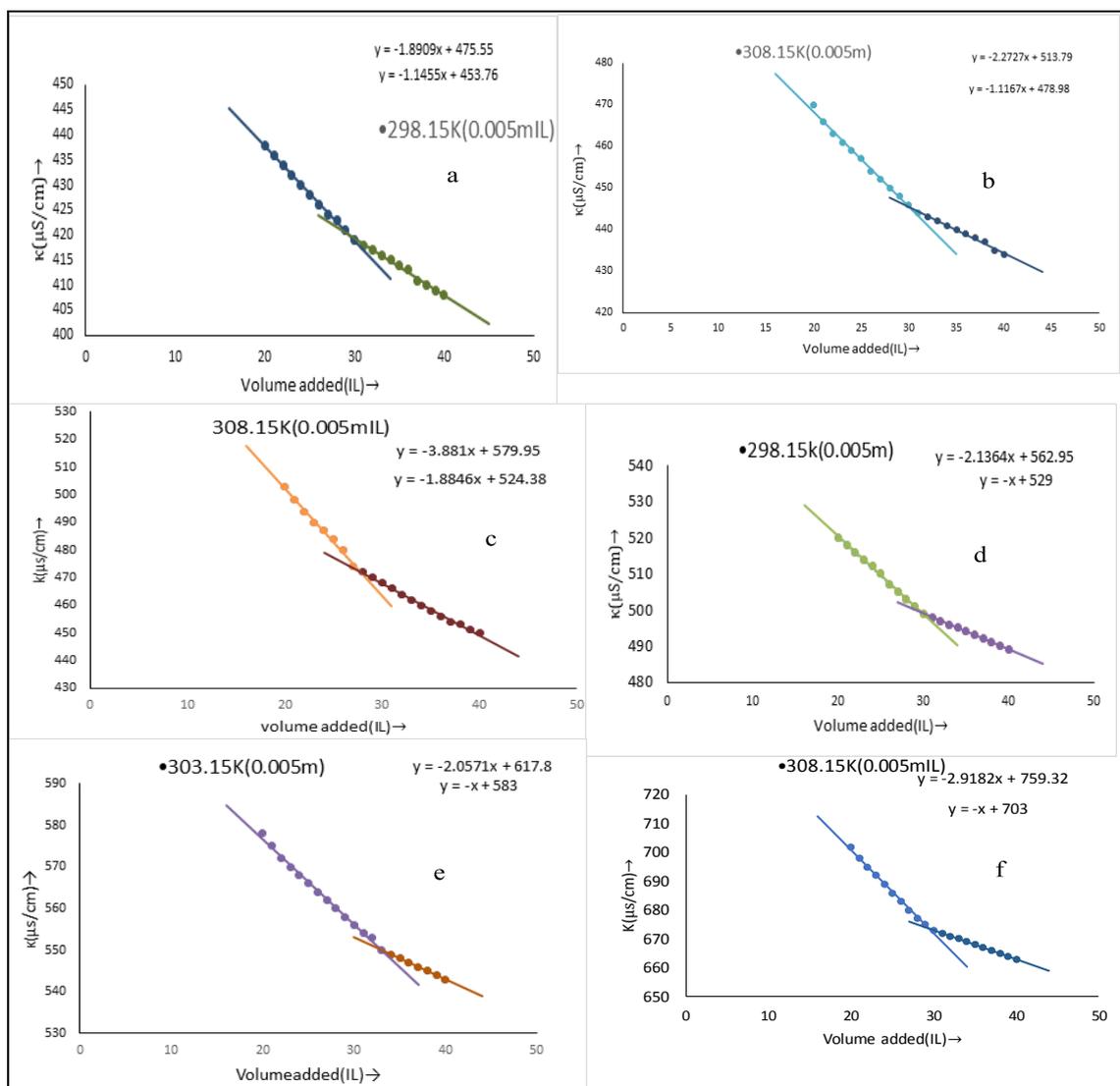
**Figure S2.** Variation of viscosity  $B$ -coefficient of L-Histidine solution against temperature in different concentrations ( $\diamond$ - 0.001m/mol.kg<sup>-1</sup>;  $\square$ - 0.003m/mol.kg<sup>-1</sup>;  $\Delta$ - 0.005m/mol.kg<sup>-1</sup>) of aqueous solutions of IL.



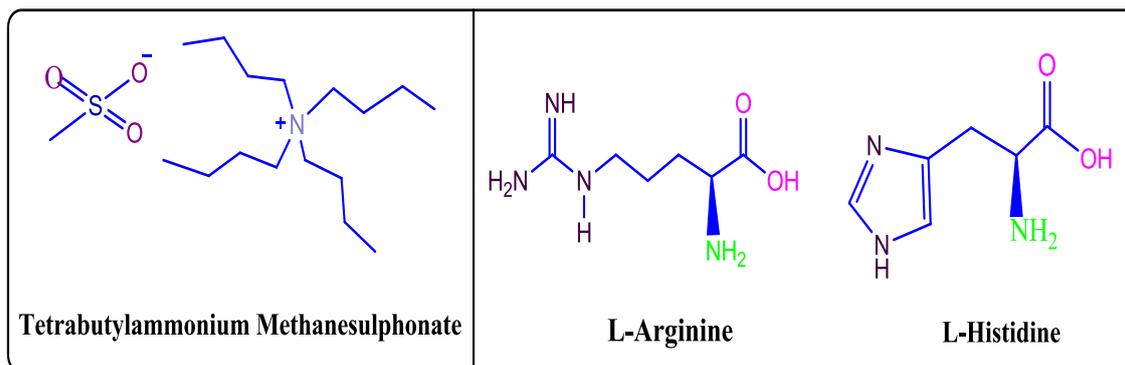
**Figure S3.** CMC plot of conductance of L-Arginine (a, b, c) and L-Histidine (d, e, f) with addition of 0.001 m aqueous solution of TBMS IL.



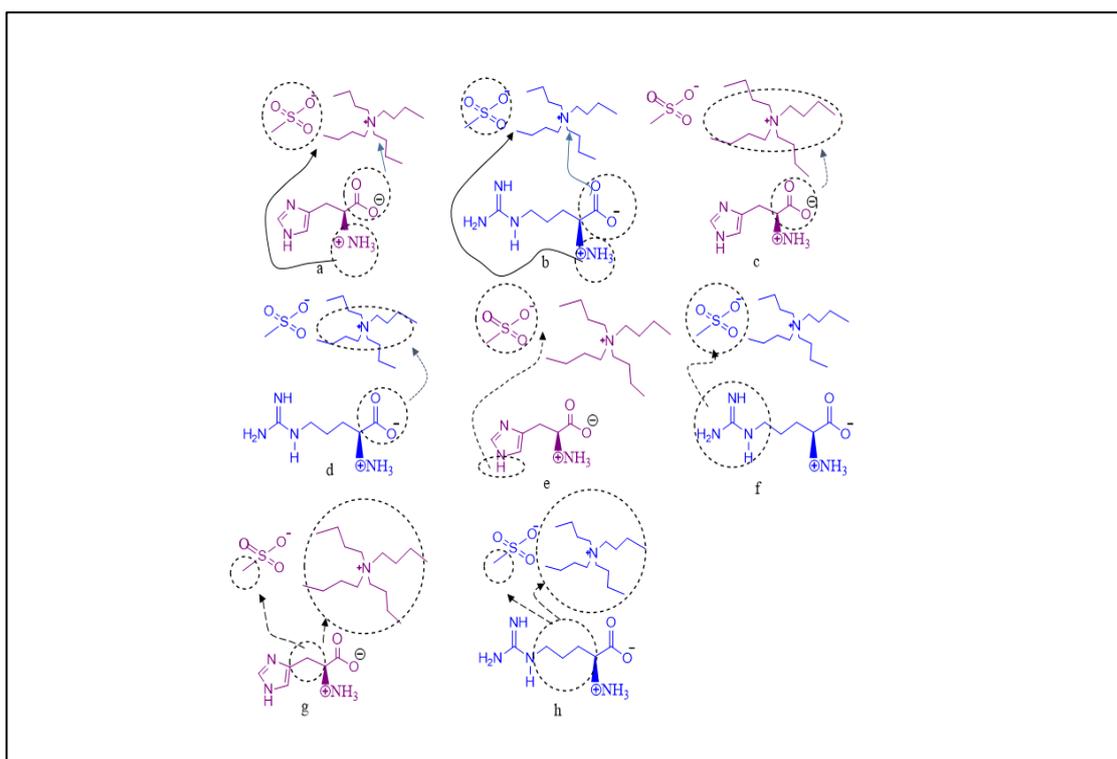
**Figure S4.** CMC plot of conductance of L-Arginine (a, b, c) and L-Histidine (d, e, f) with addition of aqueous solutions of IL (0.003 m) at different temperatures.



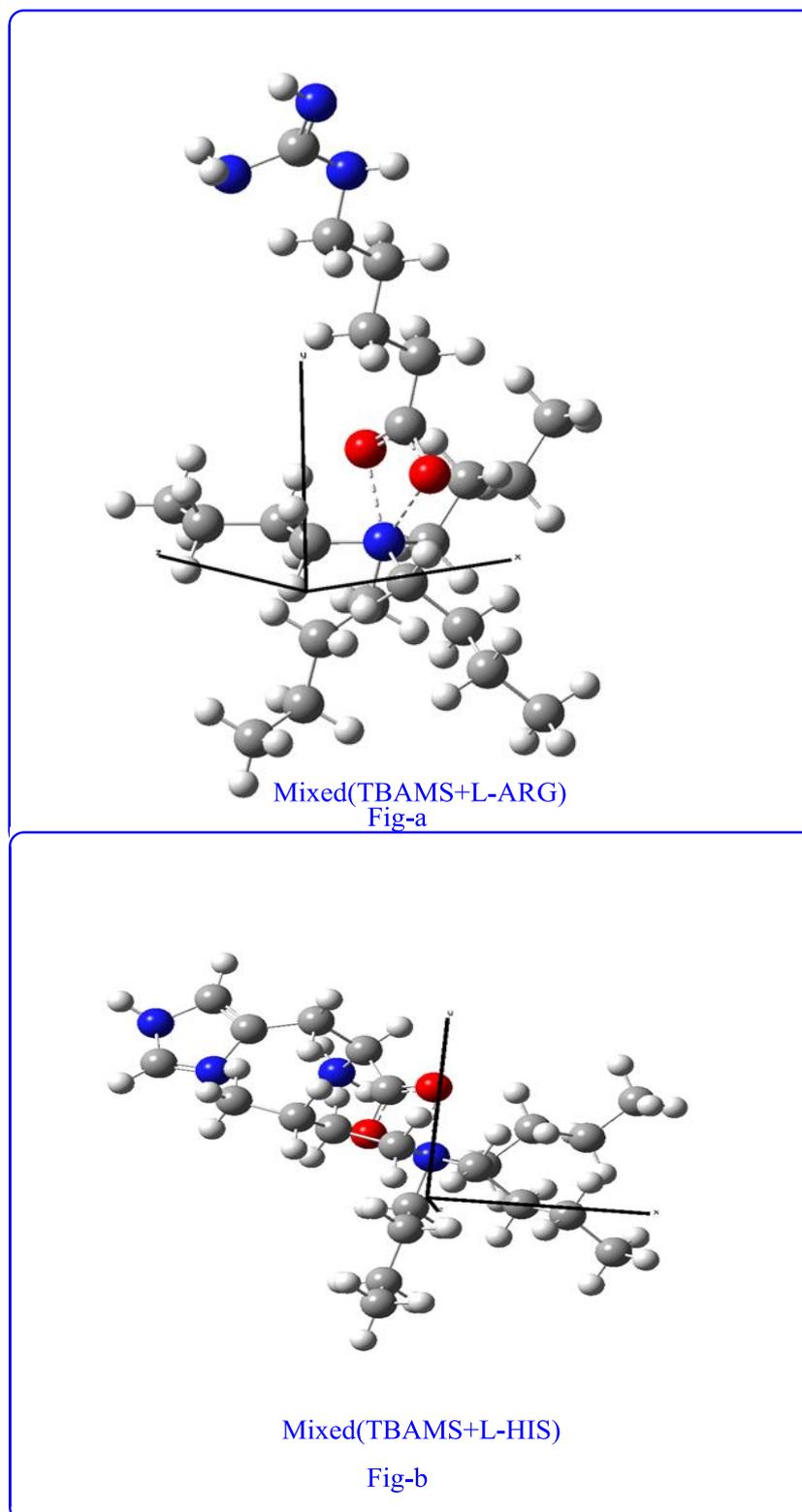
**Figure S5.** CMC plot of conductance of L-Arginine (a, b, c) and L-Histidine (d, e, f) with addition 0.005 m aqueous solution of IL (TBMS).

**Schemes**

**Scheme 1.** Molecular Structure of Tetrabutylammonium Methanesulphonate and L-Arginine and L-Histidine.



**Scheme 3.** Schematic representation of plausible molecular interactions between amino acid and ionic liquid, a & b ion-ion interactions (→); c & d ion-hydrophobic interactions (⇌); e & f hydrogen bonding interactions (⇌); g & h hydrophobic-hydrophobic interactions (→).

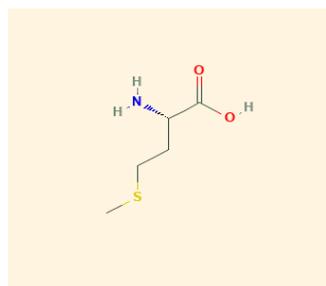


**Scheme 2 (a, b)** Optimized geometry of (a) (TBMS+ L-ARG) and(b) TBMS+ L-HIS Systems.

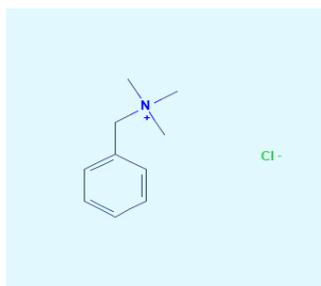
## CHAPTER-VIII

### **EXPLORATION OF DIVERSE INTERACTIONS OF L-METHIONINE IN AQUEOUS SIGNIFICANT MIXED IONIC LIQUID SOLUTIONS OPTIMIZED BY COMPUTATIONAL THEORY**

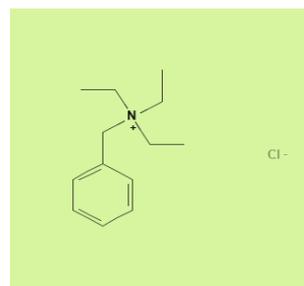
**ABSTRACT:** Solution behaviour prevailing in L-methionine in two aqueous ionic liquid solutions (Benzyl tri-methyl ammonium chloride and Benzyl tri-ethyl ammonium chloride) have been studied by investigation of some physico-chemical parameters namely density, viscosity, refractive index, conductance and surface tension. The nature of interactions occurring in the solution have been elucidated on the basis of apparent molar volume, viscosity A and B-coefficient, molar refraction at different temperatures and concentrations from density, viscosity, refractive index, surface tension measurements, respectively. Molecular interactions has also been explained based on Molar conductance ( $\Lambda$ ) measurement. The experimental slopes and the limiting apparent molar volumes obtained from Masson equation, viscosity parameters, A and B coefficients obtained from Jones-Doles equation, Molar refraction from the Lorentz-Lorenz equation and specific conductance obtained, so, describe the nature of solute-solute and solute-solvent interactions in the solution. Spectroscopic techniques such as FTIR,  $^1\text{H-NMR}$ , UV-Vis also gives the supportive information for the interactions associated among two ionic liquid with L-methionine in aqueous medium.. Furthermore, density functional theory has been employed to evaluate adsorption energies and type of interactions which is concordant with the experimental observations.



L-Methionine



Benzyl tri-methyl ammonium chloride



Benzyl tri-ethyl ammonium chloride

**Keywords:** L-Methionine; Benzyl tri-methyl ammonium chloride; Benzyl tri-ethyl ammonium chloride; solute-solvent interaction; solute-solute interaction; Amino acids; Ionic liquid, structure-breaker solutes.

#### **1. INTRODUCTION**

The thermodynamic data of aqueous solutions of small amino acids chain are important for pharmaceuticals and food industries to improve the design and operation of the unit operations, as surface tension and volumetric properties are vital for understanding the multiplied phase transport processes.<sup>1</sup> Thermodynamic properties of amino acids in aqueous electrolyte solutions can provide valuable information regarding the conformation stability of proteins in these solutions, their solubility, denaturation, dissociation into subunits, the activity of enzymes,

separation and purification, solute–solvent and solute–solute interactions.<sup>2-5 6-9</sup> Consequently, the study of the volumetric properties of amino acids in aqueous ionic liquid solutions will be very useful for obtaining information about various kinds of interactions occurring in these solutions, which are mostly hydrophobic and electrostatic. Studying these interactions can provide important insight into the conformational stability and unfolding behaviour of globular proteins.

Thermodynamic properties of amino acids in aqueous solutions containing salts can provide valuable information about solute–solute and solute–solvent interactions. The conformational properties of amino acids containing salts affect in aqueous solutions and cause denaturation of proteins which is an important biological phenomenon. Therefore, keeping the importance and applicability in view, the systematic thermodynamic investigation of mixtures containing IL and amino acids is undertaken to understand the solvation behaviour of these biomolecules.<sup>10</sup> Study of transport properties of electrolytes in aqueous media is extremely very useful to obtain information regarding the solvation and association behaviour of ions in solutions. The electrical conductivity of electrolytes in solvents mainly depends on the concentration of the electrolyte and also the viscosity of the solvent. From the study of ionic solvation the application of salt is well understood.

The physicochemical and as well as the thermodynamic both properties of amino acids are of considerable interest, as these bio molecules are the building blocks of all living organisms, and are found to provide valuable information that leads to a better understanding of proteins. Therefore, one useful approach is to investigate interactions of the model compounds of proteins, e.g., amino acids, in aqueous solutions. It has also been recognized that in the absence of experimental thermodynamic data of proteins, amino acids can serve as useful models in estimating their properties. The choice of water for preparing mixed solvent stems from its important and unique role in determining the structure and stability of protein since its presence give rise to hydrophobic forces, which are of prime importance in stabilizing native globular structure of protein.<sup>11</sup>

An ionic liquid, IL<sup>12</sup> is a salt in the liquid state of melting point below some arbitrary temperature such as 373 K. They have specific intrinsic properties, such as negligible vapour pressure, high thermal stability, large liquid range, ability of dissolving a variety of chemicals, large electrochemical window. Ionic liquids are used as “designer solvents” and “green” substitutes for volatile organic solvents used in reactions involving inorganic and biocatalytic reactions, etc. For processing biomass, ionic liquids are also utilized as heat transfer fluids. It can also utilized as electrically conductive liquids in electrochemistry (batteries and solar cells). They are used in analytical equipment. They make up electrolytes in lithium-ion batteries, super capacitors and metal plating baths.<sup>13-19</sup>

The chemicals used in this investigation find wide industrial usage. Benzyl tri-methyl ammonium chloride or BTMAC is soluble in water and has lyophilic and hydrophilic group. BTMAC can also be used as a corrosion inhibitor in oilfield. L-Methionine or L-Met is an essential amino acid in humans because it takes a critical role in the case of metabolism and health of many species. It is found in meat, fish and dairy products and is involved in many cell functions. It is also applied for increasing the acidity level of urine, treating as liver disorders and improving wound healing. Methionine can be synthesized from all plants and some forms of bacteria. Cobalamine enzyme is used to synthesize mammalian tissues and many bacteria whereas all the plants and some bacteria synthesize it from homocysteine. Cerebrospinal fluid levels of Methionine, cystathionine and homocysteine were very carefully investigated in patients with psychotic disorders.<sup>20</sup>

In the modern technology, the application of the salt is well known from the study of ionic solvation or ion association. Ionic association of electrolytes in solution depends on the mode of solvation of its ions that in turn depends on the nature of the solvent/solvent mixtures.<sup>21-24</sup> The association and solvation behaviour of ions in solution is obtained from the conductance measurement. Moreover, viscosity and the relative permittivity as solvent properties help in determining the degree of ion association and the solvent-solvent interactions. The volumetric, viscometric, refractometric, conductometric and surface tension parameters of solutes has been found to be very useful in elucidating the various interactions occurring in solutions.

In continuation of our investigation, the present work deals with the transport and thermodynamic properties of L-Methionine in aqueous Benzyl tri-methyl ammonium chloride and Benzyl tri-ethyl ammonium chloride at 298.15K, 303.15K and 308.15K supported spectroscopically.

## 2. EXPERIMENTAL DETAILS

**2.1. Materials.** The studied ILs, Benzyl tri-methyl ammonium chloride,  $C_{10}H_{16}ClN$  (M.W. 185.69 g/mole), Benzyl tri-ethyl ammonium chloride,  $C_{13}H_{22}ClN$  (M.W. 227.77 g/mole) and amino acid, L-Methionine,  $C_5H_{11}NO_2S$  (M.W. 149.21 g/mole) of puriss grade were purchased from Sigma Aldrich India, Germany and Japan, respectively and was used as purchased. The purity of mass of taken salts was nearly 0.97 to 0.99 in mass fraction. The ionic liquids and amino acid were taken for experiment without further purification. The Specification of the chemical samples are given in **Table 1**. The chemicals were dried in vacuum over blue silica gel for at least 72 h at room temperature before use.

**2.2. Experimental Procedures.** The vibrating-tube Anton Paar Density-Meter (DMA 4500M) was used to measure the density ( $\rho$ ) with a precision of  $0.00001 \times 10^{-3} \text{ (kg}\cdot\text{m}^{-3}\text{)}$ . The double-distilled water and dry air was used to calibrate the density meter.<sup>25</sup> The temperature was kept constant within range  $\pm 0.01 \text{ K}$  with the help of an automatic built-in Peltier device.

The viscosity was measured with the help of suspended Ubbelohde viscometer which was calibrated at room temperature (298.15K) using doubly distilled water. It was purified with methanol and using viscosity, density data from literature.<sup>26, 27</sup> The viscometer was dried and cleaned perfectly through hot thermostat and then filled with experimental solution, vertically placed in a glass-walled thermostat (Bose–Panda instruments Pvt.Ltd.) This instrument was maintained to 0.01K. At thermal equilibrium the flow-time were recorded with the help of a stop watch with an accuracy of  $\pm 0.01 \text{ s}$ . The uncertainty for the measurement of viscosity was  $\pm 0.2 \times 10^{-3} \text{ mPa}\cdot\text{s}$ .

Measurement of refractive index has been done with the help of a Digital Refractometer Mettler Toledo instrument. The accuracy for the refractive index measurement was  $\pm 0.0002$  units approximately. The refractometer was calibrated twice using distilled water for measurement of the refractive indices of experimental solutions. The calibration of instrument was made after few seconds of each measurement.<sup>25</sup> The light source was light-emitting diode,  $\lambda = 589.3 \text{ nm}$ . The temperature of the solution was maintained during the experiment in a Brookfield Digital TC-500 Thermostatic water bath.

The conductivity measurement was done by Mettler Toledo Instrument (In Lab730 probe cell). The specification of the cell has measurement of conductivity range (0.01-1000 mS/cm). The cell type 4 graphite having a cell constant  $0.56 \text{ cm}^{-1}$ . The calibration of the cell has been done with 0.01N (NaCl solution). The accuracy of the conductance measurement was  $\pm 0.5\%$ . The specific conductance of the experimental solution having concentration (0.0010, 0.0025, 0.0040, 0.0055, 0.0070, 0.0085) m was reported at 298.15 K, 303.15K, 308.15 K (Where the symbol “m” represents molality of the solution of amino acid & ionic liquid mixture and unit was given by  $\text{kg}\cdot\text{mol}^{-1}$ ) and was converted into molar conductance by the following equation,  $\Lambda = 1000 \kappa / c$  (where  $c$  is the molar concentration of the amino acid solutions in the ionic liquids.  $\kappa$  is the specific conductance of the specified solutions.<sup>28, 29</sup>

Surface Tension measurements of the solutions were carried out by a digital K9 Tensiometer (Kruss, Germany) using the platinum ring detachment technique at 298K. The temperature of this device was maintained by circulating auto-thermostatic water through the solution in a double-wall glass vessel with an accuracy of  $\pm 0.1 \text{ mNm}^{-1}$ . The calibration of the digital K9 Tensiometer (Kruss, Germany) was carried out with doubly distilled water.

FTIR (Fourier Transformation Infrared) spectra were taken by using a PerkinElmer spectrometer with resolution of  $4 \text{ cm}^{-1}$  by disk method at room temperature.

Solution-state Nuclear Magnetic Resonance (NMR) measurements were performed in  $\text{D}_2\text{O}$  solvent using Bruker AVANCE DRX 400 NMR spectrometer operating at 400MHz for obtaining the  $^1\text{H}$  NMR spectra at 298K. Signals were symolised as  $\delta$  values in ppm using residual protonated solvent signals as internal standard ( $\text{D}_2\text{O}$ : 4.79 ppm). The differences in chemical shifts were recorded to analyze the interaction between the amino acid and ILs molecules. The chemical shift values of protons are reported as  $\delta$  units (ppm). The chemical shift values of peaks of interest were get by using peak pick facility. The uncertainty of  $\delta$  units was estimated to be better than 0.0005 ppm.<sup>14</sup>

JASCO V-530 UV–Vis spectrophotometer was used to record the UV-visible spectra of experimental solutions of different concentration. The accuracy of wavelength of this spectrophotometer was  $\pm 0.5 \text{ nm}$ . During the experiment the cell temperature was maintained from 298.15K to 308.15K with a digital thermostat.

Adequate precautions of measurements were taken to minimize evaporation losses during the actual measurements. Mass measurements for stock solutions were done on a Mettler AG-285 electronic balance with a precision of  $\pm 0.0003 \times 10^{-3} \text{ kg}$ . The combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095 \text{ mol. kg}^{-1}$ .

The conversion of molarity into molality was accomplished using experimental density values using the following formula:<sup>30</sup>

$$m = \frac{1}{\left\{ \left( \frac{\rho}{c} \right) - \left( \frac{M}{1000} \right) \right\}} \quad (1)$$

**2.3 Computational Details.** All the density functional theory (DFT) calculations were performed utilizing the Gaussian 16 program.<sup>31</sup> Ground state geometry optimization of the L-methionine, ionic liquids, and the composites were done at B3LYP/6-31+G(d) level of theory. In the course of ground state optimization, solvent effects (water) were introduced employing the Polarizable Continuum Model (PCM) using the integral equation formalism variant by Gaussian 16 package. To check whether the energy minimized geometries correspond to the true ground state geometries, vibration frequency analysis were performed at the same level of theory. No imaginary frequency confirms that the geometries are minima on the potential energy surfaces. Meanwhile the different kinds of weak forces like Van der Waals interactions, H-bonding, steric interactions were investigated by Non-Covalent Interaction (NCI) index plots of the reduced

density gradient (RDG)<sup>32</sup> using the Multiwfn 3.7suite.<sup>33</sup> Furthermore, molecular electrostatic potential (MESP) maps were visualized at the ground state geometries to understand the type and the moieties involved in the interactions. Finally, by the utilizing the formula, adsorption energies ( $\Delta E_{ads}$ ) for all the composite systems were analysed:

$$\Delta E_{ads} = E_{IL-L-methionine} - E_{IL} - E_{L-methionine}$$

Where  $E_{IL-L-methionine}$ ,  $E_{IL}$ ,  $E_{L-methionine}$  are the total energy of the geometry optimized complexes, free IL and the L-methionine molecules, respectively.

### 3. RESULTS AND DISCUSSION

Experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of different molality ( $m$ ) of aqueous ionic liquids (BTMAC and BTEAC) solutions at 298.15 K, 303.15 K and 308.15 K and at pressure at 1.013bar are shown in **Table S1** and **Table S2** whereas **Table S3** and **Table S4** gives the experimental values of refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of different molality ( $m$ ) of the aqueous ionic liquids (BTMAC and BTEAC) solutions at 298.15K, 303.15K and 308.15K. Also the density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of L-Methionine solutions in different molality of aqueous ionic liquids solutions at different temperature at pressure 1.013bar are shown in **Table S5** and **S6**.

#### 3.1. Density

The limiting apparent molar volumes ( $\Phi_v^0$ ), limiting molar refraction ( $R_M^0$ ), experimental slopes ( $S_v^*$ ), viscosity A, B-coefficients of L-Methionine solution in ILs (BTMAC and BTEAC) at different temperatures and pressure at 1.013bar are presented in **Table 2** and **Table 3**, respectively. The apparent molar volumes ( $\Phi_v$ ) were determined from the solution densities using the following equation<sup>34</sup> the result are provided in **Table S7** and **S8**.

$$\Phi_v = M / \rho_0 - (\rho - \rho_0) / m \rho_0 \quad (2)$$

where,  $M$  is the molar mass of the solute,  $m$  is the molality of the solution,  $\rho$  and  $\rho_0$  are the densities of the solution and solvent, respectively. For the analysis of the interactions occurring here, the knowledge of the limiting apparent molar volumes are important. The limiting apparent molar volumes ( $\Phi_v^0$ ) were calculated using a least-squares treatment to the plots of ( $\Phi_v$ ) versus  $\sqrt{m}$  using the following Masson equation:<sup>35</sup>

$$\Phi_v = \Phi_v^0 + S_v^* \sqrt{m} \quad (3)$$

where,  $\Phi_v^0$  is the limiting apparent molar volume at infinite dilution and  $S_v^*$  is the experimental slope. Here, we observe the variation of  $\Phi_v^0$  values of L-Methionine solutions at 0.001m, 0.003m and 0.005m concentration of the ILs at 298.15K, 303.15K and 308.15K. The  $\Phi_v^0$  values are positive and seem to increase with the increase in concentration of the solutions

which were in good agreement with the previous literature values<sup>88</sup> and also with the increase in temperature whereas BTEAC has higher values than BTMAC. But  $S_V^*$  values are negative and decreases with the increase in concentration of the solutions and also with the rise in temperature. Also it is observed that BTEAC have lower  $S_V^*$  values than BTMAC.

$\Phi_V^0$  values indicate the extent of solute-solvent interaction. A perusal of **Table 2** and **Table 3** along with **Figure 1** and **Figure 2** reveals that the  $\Phi_V^0$  values are positive and is maximum for L-Met in 0.005m BTEAC at 308.15K indicating highest solute-solvent interaction here and minimum for L-Met in 0.001m BTMAC at 298.15K, indicating that the solute-solvent interaction is the least here. This is probably due to the release of a number of the solvent molecules from loose solvation layers during the solute-solvent interactions.<sup>36</sup> Also the higher  $\Phi_V^0$  values of L-Met in BTEAC indicates that the interaction is more with BTEAC than in BTMAC under any conditions. On the contrary, the  $S_V^*$  indicates the extent of solute-solute interaction. The values of  $S_V^*$  show that the extent of solute-solute interaction is highest in L-Met 0.001m BTMAC solution at 298.15K and minimum in 0.005m BTEAC solution at 308.15K. Here again the higher values of  $S_V^*$  in BTMAC indicates that it exhibits better interaction among itself than BTEAC molecules under any conditions.

Possible reasons for this behaviour could be the structural orientation of the larger alkyl group of BTEAC than BTMAC as depicted by their molecular structures in **Scheme 1**. A quantitative comparison of the magnitude of  $\Phi_V^0$  values shows that it is much greater in magnitude than  $S_V^*$  values for the solutions. This suggests that strong solute-solvent interactions dominate over the weak solute-solute interactions in all the solutions.<sup>37, 38</sup> There is hydrophobic hydration, or the caging effect of water molecules<sup>39</sup> which reflects hydrophobic interactions in the amino acids that cause volume contractions in solutions. Similar linear correlations have been observed earlier for homologous series of amino acids in aqueous electrolytes.<sup>40</sup>

Temperature dependency of the limiting apparent molar volume ( $\Phi_V^0$ ) were studied between the temperature range 298.15K to 308.15K and the results obtained were found to follow the following polynomial equation:<sup>41</sup>

$$\Phi_V^0 = a_0 + a_1T + a_2T^2 \quad (4)$$

where,  $a_0$ ,  $a_1$  and  $a_2$  are the empirical coefficients depending on the nature of solute and mass fraction (W) of co-solvent whereas T is the temperature in Kelvin scale. **Table 4** shows the empirical coefficient values ( $a_0$ ,  $a_1$  and  $a_2$ ) of L-Met in different concentration of the ILs, BTMAC and BTEAC at 298.15K, 303.15K, 308.15K and pressure at 1.013bar. First derivative of Equation(4) gives the values of limiting apparent molar expansibilities ( $\Phi_E^0$ ) which have been calculated for various temperatures and listed in **Table 5** and **Table 6** for L-Met in BTMAC and BTEAC solutions, respectively at pressure 1.013bar.

$$\Phi_E^0 = (\delta\Phi_v^0 / \delta T)_P = a_1 + 2a_2T \quad (5)$$

Limiting apparent molar expansibilities ( $\Phi_E^0$ ) for all the systems are found positive except for 0.005m IL at 308.15K in BTMAC. It signifies the absence of caging or packing effect in the other solutions except this one. The solute–solvent interaction studied so far is now at a state that, it may be structure-breaker or synergistic structure-maker interaction. In this connection, Hepler developed a way to examine the nature of the solute–solvent interaction taking place in the solution phase.<sup>42</sup> According to Hepler, values of  $(\delta\Phi_E^0/\delta T)_P$  in the expression given below, determines whether, it is structure-breaker or structure-maker interaction:<sup>43</sup>

$$(\delta\Phi_E^0 / \delta T)_P = (\delta^2\Phi_v^0 / \delta T^2)_P = 2a_2 \quad (6)$$

On the basis of this expression, it has been deduced that structure-making solutes should have positive value, whereas structure-breaking solutes should have negative values. Here, the negative values listed in **Table 7** and **Table 8** respectively for L-Met in BTMAC and BTEAC solutions at different temperatures confirms the mode of solute–solvent interaction is structure-breaking and the structure-breaking effect is strongest in 0.001m aqueous BTMAC solution with highest packing or caging effect.

### 3.2. Viscosity

In aqueous electrolytic solutions the extent of ionic hydration and structural interactions<sup>44-46</sup> within the ionic hydration co-spheres<sup>47</sup> can be explored easily by studying viscosity coefficient with varying concentration and temperature of the aqueous solution. The results in **Table S1** and **Table S2** show that the viscosity of the solutions increases with increasing molality of the ILs. The number of collisions among the molecules also increases upon increasing the molality of the ionic liquid, resulting in a loss of kinetic energy. Consequently, the molecules tend to stick together with increasing viscosity.

Viscosity data so obtained were analysed with the help of Jones-Dole equation:<sup>48</sup>

$$\eta_r = \eta / \eta^0 = 1 + A \sqrt{c} + Bc \quad (7)$$

where,  $\eta$  and  $\eta^0$  are viscosities of solution and solvent respectively,  $c$  is the concentration of solution in molarity. This is possibly due to stronger hydrophobic–hydrophobic interactions for longer alkyl chains of BTEAC.

Rearrangement of the above Equation (7) gives following:

$$(\eta_r - 1) / \sqrt{c} = A + B\sqrt{c} \quad (8)$$

Here, viscosity A-coefficient is a constant, also known as Falkenhagen coefficient,<sup>34</sup> stands for long-range coulombic forces, so represents the solute-solute interaction in solution, while B-coefficient is an adjustable parameter, which is the measure of the effective hydrodynamic volume that reflects the solute-solvent interaction. The value of viscosity B-coefficient which depends on the shape, size and partial molar entropies of the ions involving in solutions. According to the Jones-Dole equation from the plots of  $(\eta_r - 1) / \sqrt{c}$  vs  $\sqrt{c}$ , the viscosity A, B-coefficients obtained by linear least-square analysis, are reported in **Table 2** and **Table 3** for L-Met solutions in BTMAC and BTEAC at (298.15, 303.15 and 308.15)K and pressure at 1.013bar, respectively. **Figure 3** shows the variation of B values of L-Methionine in BTMAC and BTEAC respectively, against 0.001m IL, 0.003m IL and 0.005m IL solutions at different temperatures which were in good agreement with the previous literature values.<sup>88</sup>

The viscosity B-coefficient is an empirical constant which depends on size and shape effects as well as structural effects induced by (solute+solvent) interactions.<sup>8</sup> In all cases the viscosity B-coefficients are larger compared to A-coefficients in the aqueous ionic liquid solutions which indicates promotion of the liquid structure in the presence of an ionic liquid, thus supporting the conclusions obtained from volumetric properties. It is observed From **Table 2** and **Table 3**, that the values of the B-coefficient are positive, thereby suggesting the presence of strong solute-solvent interactions in solution, that strengthened with an increase in the solvent viscosity value, in accordance with the results obtained from  $\Phi_v^0$  values explained earlier. The values of the A-coefficient are found to very small as compared to B-coefficients. The above obtained results of A-coefficient indicate the presence of very weak solute-solute interactions. These results are in outstanding agreement with those obtained from  $S_v^*$  values. The extent of solute-solvent interaction obtained from the B-coefficient occurs into the local vicinity of the solute molecules in the solutions. The higher B-coefficient values for higher viscosity values is due to the solvated solute molecules associated by the solvent molecules all around because of the formation of associated molecule by solute-solvent interactions.<sup>49</sup>

Furthermore, these types of interactions are strengthened with rise in temperatures. It shows that the solute-solvent interaction increases with increase in temperature and the concentration of the IL solutions with more interaction between L-Met and aqueous BTEAC solutions. There placement of water molecules by more co-solvent molecules from the solvation sphere brings solute and co-solvent closer thereby increasing viscosity B-coefficients and accounts for the higher solute-solvent interaction. The overall viscometric studies show that, viscosity B-coefficients are positive and greater than viscosity A-coefficient, suggesting solute-solvent interaction is predominant over the solute-solute interaction.

Extensively study of the viscosity B-coefficient such that, its first derivative over temperature is an upgradation of viscosity B-coefficient in predicting the nature of solute–solvent interaction as structure-maker or structure-breaker. The value of dB/dT is a measure of activation energy required for the viscous flow in solution. This is the reason, why the measure of dB/dT is indicative towards the structure making or structure breaking ability than sign or magnitude of the B-coefficient.<sup>50-52</sup> Viscosity B-coefficients of L-Met solutions along with dB/dT values in different concentrations of the ILs, BTMAC and BTEAC at (298.15, 303.15 and 308.15) K and pressure at 1.013bar are given in **Table 7** and **Table 8**, respectively. The negative value of dB/dT indicates as a structure-making (kosmotropic) properties of the system whereas the positive value signifies it as structure-breaking (chaotropic) properties of the system. Here the positive dB/dT values indicate the amino acid, L-Met to behave as structure-breaker in the aqueous ionic liquid solutions, BTMAC and BTEAC.

According to theory of Eyring and co-workers,<sup>53</sup>  $\Delta\mu_1^{0\#}$ , the free energy of activation per mole of the solvent of viscous flow can be obtained by using the following equation:

$$\eta_0 = \frac{hN}{V_1^0} \exp\left(-\frac{\Delta\mu_1^{0\#}}{RT}\right) \quad (9)$$

where h signify as Planck constant, N denotes Avogadro's number and  $V_1^0$  indicates the solvent's partial molar volume. Rearranging the above equation, we get the following form:

$$\Delta\mu_1^{0\#} = RT \ln (\eta_0 V_1^0 / hN) \quad (10)$$

Feakins et al. have suggested the following expression based on the transition state treatment of the relative viscosity of electrolyte solution.<sup>54, 55</sup>

$$B = (V_1^0 - V_2^0) / 1000 + V_1^0 (\Delta\mu_1^{0\#} - \Delta\mu_2^{0\#}) / 1000RT \quad (11)$$

Following equation can be obtained from the above equation(11):

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + \frac{RT}{V_1^0} [B - (V_1^0 - V_2^0)] \quad (12)$$

According to the theory of transition state, solvent molecules passes to the transition state by the viscous flow. The  $\Delta\mu_2^{0\#}$  is the involvement of free energy transfer of ionic liquid from ground state to transition state. It was observed from **Table 9** that the values of  $\Delta\mu_2^{0\#}$  are all positive and which are much higher than that of  $\Delta\mu_1^{0\#}$  representing in the ground state, which designates that the interaction between the amino acid (L-Met) with two aqueous ionic liquids, BTMAC and BTEAC mixture is stronger in the ground state than that in the transition state which were in good agreement with the previous literature values.<sup>88</sup> In the ground state the solute and solvent molecules are held together strongly than that in the transition state. Later on, in the transition state distortion and breaking of intermolecular bond take place frequently. Besides the

value of  $\Delta\mu_1^{0\#}$  increase with increasing the molality of the ionic liquids in the presence of amino acid (L-Met) which indicate that with increasing the molality, ionic liquids in the ground state become more structured. The following equation has been used for determination of entropy for activation,  $\Delta S_2^{0\#}$  in the experimental mixture of solutions:<sup>56</sup>

$$d(\Delta\mu_2^{0\#})/dT = -\Delta S_2^{0\#} \quad (13)$$

From the plot of  $\Delta\mu_2^{0\#}$  versus T, using the least-squares method, the value of  $\Delta S_2^{0\#}$  has been attained from the negative slope of the plot.

Enthalpy of activation ( $\Delta H_2^{0\#}$ ) has been calculated from the following relation:<sup>56</sup>

$$\Delta H_2^{0\#} = \Delta\mu_2^{0\#} + T \Delta S_2^{0\#} \quad (14)$$

The value of  $\Delta H_2^{0\#}$ ,  $\Delta S_2^{0\#}$  are shown in **Table 9**. The value of  $\Delta\mu_2^{0\#}$  depend on both viscosity B-coefficient and limiting molar volume ( $\bar{v}_1^0 - \bar{v}_2^0$ ) of the solution in the presence of ionic liquid.

In view of Feakins et al.,<sup>54</sup> for positive viscosity B-coefficient,  $\Delta\mu_2^{0\#} > \Delta\mu_1^{0\#}$  that indicates greater solute–solvent interactions resulting in the formation of the transition state followed by breaking and altering the intermolecular forces prevailing in the solvent structure of the medium.<sup>57, 58</sup> For positive values of  $\Delta S_2^{0\#}$  and  $\Delta H_2^{0\#}$  recommend that the formation of transition state is related with bond-breaking and rising accordingly. However, any specific mechanism in this context is quite difficult to develop though the disordered state of the slip-plane may be proposed.<sup>58</sup> Finally, according to Feakins et al. model, as  $\Delta\mu_2^{0\#} > \Delta\mu_1^{0\#}$ , the amino acid (L-Met) performs as structure breakers that again supports the dB/dT characteristics in an aqueous BTMAC and BTEAC mixture.

### 3.3. Refractive Index

Optical data of refractive index of the studied systems has provided interesting information allied to molecular interactions, structure of solutions in these assay. The refractive index of mixing can be interrelated by the application of a composition dependent polynomial equation and molar refraction,  $R_M$  in solution. The refractive index of amino acid (L-Methionine) solutions in both ionic liquid are provided in **Table S9**, **Table S10** and **Table S11**.

The molar refraction  $R_M$  can be evaluated from the Lorentz–Lorenz relation:<sup>58</sup>

$$R_M = \{(n_D^2 - 1) / (n_D^2 + 2)\} (M/\rho) \quad (15)$$

where  $R_M$ ,  $n_D$ , M and  $\rho$  are the molar refraction, the refractive index, the molar mass and the density of the solution, respectively. The refractive index of a substance is

well-defined as the ratio of the speed of light in vacuum to that in the medium. Stated the definition of refractive index more simply, the refractive index of a compound describes its ability to refract light as it moves from one medium to another medium and thus, the higher the refractive index of a compound, the more the light is refracted.<sup>59</sup> As stated by Deetlefs et al. the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser.<sup>60</sup> Generally, refractive index of a system is the capability to refract light and hence it can simultaneously measure the compactness of that system.

Hence, it is observed that the refractive index ( $n_D$ ) **Table (S3-S4) and Table (S9-S11)** decrease but the molar refraction ( $R_M$ ) (**Table S1 and Table S2**) increases with increase in temperature. However, both the parameters show an increase with increase in concentration of the amino acid and IL solutions. Again L-Met in BTEAC have higher values than in BTMAC solutions. This is in good agreement with the volumetric and viscometric results attained here. The higher refractive index shows that the molecules are more tightly packed in the solution.

The limiting molar refraction, ( $R_M^0$ ) listed in **Table 1 and Table 2** can be calculated using the following equation:

$$R_M = R_M^0 + R_S \sqrt{m} \quad (16)$$

where, 'm' is the molality of solution and  $R_M^0$  is the limiting molar refraction that signifies solute-solvent interaction. So, this measurement of molar refraction operates as an expensive tool for studying the molecular interaction in solution. Gradual increase in the values of  $R_M^0$  as shown in **Figure 4 and Figure 5** with rise in mass fraction of co-solvent and temperature also signifies that solute-solvent interaction predominant over solute-solute interactions.

### 3.4. Electrical Conductance

The specific conductance of L-Methionine in two ionic liquid solutions at different concentration are shown in the **Table (S9-S11). Table 10** shows Molar conductance ( $\Lambda$ ) of L-Methionine solutions in aqueous BTMAC & BTEAC ionic liquid solution in (0.001m, 0.003m, 0.005m) at 298.15K, 303.15K and 308.15K and pressure at 1.013bar. **Figure 6 and Figure 7** shows the variation of molar conductance ( $\Lambda$ ) of L-methionine in aqueous IL(BTMAC) and IL (BTEAC) solutions, respectively at 298.15K(0.001m), 303.15K(0.003m), 308.15K(0.005m). The molar conductance ( $\Lambda$ ) values increase with increase in temperature and increase in concentration of aqueous IL solution but decrease with the increase in concentration of amino acid solutions. However, the values are lesser in L-Met BTEAC solutions under all conditions. The molar conductance ( $\Lambda$ ) has been obtained from the specific conductance ( $\kappa$ ) value using the following equation:<sup>61</sup>

$$\Lambda = (1000 \kappa) / c \quad (17)$$

Linear conductivity curves ( $\Lambda$  vs.  $\sqrt{c}$ ) were obtained for the amino acid in ILs solutions and extrapolation of  $\sqrt{c} = 0$  was used to evaluate the limiting molar conductance for the ILs. ILs has benzyl trimethyl ammonium cation, benzyl triethyl ammonium cation and chloride anion. The terminal  $-\text{COO}^-$  functional group of the amino acid interact with the  $\text{N}^+$  centre of benzyl trimethyl and triethyl ammonium ring through ion–dipole interaction (**Scheme 1**).

Another contributing factor in the amino acids is the carboxylic ( $-\text{O}-$ ) atom. The lone pair donating tendency of carboxylic oxygen increases with the increase in  $+I$  effect of alkyl group of the studied ionic liquids. Thus  $+I$  effect in BTEAC is greater than in BTMAC. Hence, the interaction is more prominent in L-Met BTEAC solution due to the presence of more lone pair availability of oxygen atom, making the interaction strong with IL. So the free ions are more available in L-Met BTMAC solution giving higher conductance values than L-Met BTEAC solution.

### 3.5. Surface Tension

Surface Tension ( $\gamma$ ) values of L-Methionine solutions in IL (BTMAC) and L-Methionine solutions in IL(BTEAC) at different concentration (0.001m,0.003m,0.005m) at room temperature and pressure at 1.013bar\* are given in **Table 11**. A liquid is always in contact with its vapour in a closed vessel. A molecule in the bulk of the liquid is subjected to forces of attraction from all directions by the surrounding molecules and is practically in a uniform field of force. But for a molecule at the surface, the net attraction towards the bulk of the liquid is much greater than that towards the vapour where the attracting molecules are more widely dispersed. This means that the molecules at the surface are pulled inwards. The result is liquid surfaces in absence of other forces tend to contract to minimum areas. The surface layer seems to behave as a stretched membrane and this pseudo-membrane tends to contract. Now, since the surface is in a state of tension, an attempt to make a penetration along any line in the surface will require an application of force to hold the separate portions of the surface together.<sup>62</sup>

**Figure S5** and **Figure S6** shows the variation of the surface tension with different concentration of L-Met in BTMAC and BTEAC, respectively at room temperature. The values increase with increase in concentration of the amino acid in both the ILs. However, surface tension decreases then increases with increase in concentration of the ionic liquids. Further, it was observed that surface tension is more for molecules in L-Met BTEAC solution compared to L-Met BTMAC solution.

The lower surface tension values is attributed to the hydrophobicity of the amino acids. The increase in surface tension values shows a significant amount of molecular association is present between adjacent molecules as the concentration shows an increasing trend, producing a robust surface film.<sup>63</sup>

The hydrophobic and hydrophilic nature of solute with respect to the concentration depend upon the sign and magnitude of slopes ( $\partial\sigma/\partial m$ ) of surface tension as it reflects the type of interactions that predominate on the surface of solute.<sup>64, 65</sup> The limiting slope obtained from surface tension data were determined in very dilute region and area that are shown in the listed **Table 12** .

It was found that the values of ( $\partial\sigma/\partial m$ ) are positive for L-methionine solutions in both aqueous solution of ionic liquid (BTMAC&BTEAC) are typical for electrolyte and very hydrophilic compounds<sup>66</sup> and this can be determined from the result of favorable interaction between the Zwitterionic group of amino acid (L-methionine) and an ionic group of two ionic liquid (BTMAC and BTEAC). Since L-Methionine contain hydrophobic part as a result it readily migrates to the liquid–air interface where it can be absorbed.

The cosphere overlap model<sup>60</sup> can explain the above effect. According to this model four types of possible interactions can exist in the ternary systems containing amino acid, ionic liquid and water (a) hydrophilic-ionic interactions between ions of IL and hydrophilic group ( $\text{NH}_3^+$ ,  $\text{COO}^-$ ) of amino acid; (b) hydrophobic-ionic interactions between hydrophobic part of amino acid and ions of IL; (c) hydrophobic–hydrophobic interactions between the hydrophobic groups of amino acid and alkyl groups of IL; (d) hydrophilic–hydrophobic interactions between hydrophilic groups of amino acid and the hydrophobic parts of ILs.<sup>50, 67</sup>

### 3.6. FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) spectra have been used to study the hydrogen bond formation through molecular interactions between the amino acid, L-Methionine (L-Met) and the two ionic liquids, Benzyl tri-methyl ammonium chloride (BTMAC) and Benzyl tri-ethyl ammonium chloride (BTEAC) aqueous solutions. Every pure substance has its own characteristic infrared spectrum different from that of any other substance. The spectral picture thus helps in confirming and identifying the sample of pure variety.

The FTIR spectra of pure ILs and pure Amino acid (**Figure A1**) show some common absorption peaks at frequencies such as  $3431.6\text{ cm}^{-1}$ ,  $3403.5\text{ cm}^{-1}$  and  $3428.2\text{ cm}^{-1}$ , respectively for aliphatic C-H groups present in these molecules. Besides this the presence of water in a sample is detected by these characteristic absorption bands in this region along with additional peaks at  $1609.2\text{ cm}^{-1}$ ,  $1614.6\text{ cm}^{-1}$  and  $1610.7\text{ cm}^{-1}$  for BTMAC, BTEAC and L-Met, respectively.

The bands observed at  $520\text{ cm}^{-1}$ ,  $452\text{ cm}^{-1}$  for BTMAC,  $529.7\text{ cm}^{-1}$ ,  $471.8\text{ cm}^{-1}$  for BTEAC and  $543.2\text{ cm}^{-1}$ ,  $449.6\text{ cm}^{-1}$  for L-Met confirms the presence of water as lattice water with these molecules.<sup>68</sup>

When L-Met and BTMAC are mixed in the ratio 1:3, 2:2 and 3:1, the absorption peaks obtained for the mixtures are shown in the FTIR spectra, **Figure A2**. When L-Met and BTEAC are mixed in the ratio 1:3, 2:2 and 3:1, the absorption peaks obtained for the mixtures are shown in the FTIR spectra, **Figure A3**. The spectra show that the common bands for the amino acid and ILs are retained in the figures.

Above  $2500\text{ cm}^{-1}$  nearly all fundamental vibrations involve a hydrogen stretching mode. Hydrogen bonding O-H lowers the frequency and broadens the band. The N-H stretch occurs in the  $3300\text{-}3400\text{ cm}^{-1}$  region. These bands often overlap the hydrogen bonded O-H bands but the N-H peaks are usually sharper. The N-H stretch in ammonium and alkylammonium ions occurs at lower frequencies,  $2900\text{-}3200\text{ cm}^{-1}$ . The C-H stretch occurs in the region  $2850\text{-}3000\text{ cm}^{-1}$  for the aliphatic compound, L-Met and in the region  $3000\text{-}3100\text{ cm}^{-1}$  for the aromatic compounds, BTMAC and BTEAC. Absorptions corresponding to S-H occur at  $2500\text{ cm}^{-1}$ . The  $2000\text{-}1600\text{ cm}^{-1}$  region contains stretching vibrations for doubly-bonded molecules and bending vibrations for the O-H, C-H and N-H groups.

The region below  $1600\text{ cm}^{-1}$  is referred to as the fingerprint region for these organic compounds studied here. This is the single bond region and it is very common to get coupling of individual single bonds which have similar force constants and connect similar masses, like C-O, C-C and C-N stretches often couple. The absorption bands in this region for a given functional group occur at different frequencies depending upon the skeleton of the molecule, because each vibration often involves oscillation of a considerable number of atoms of the molecular skeleton.

**Table A: The characteristic frequencies of some of the groups:**<sup>57</sup>

| GROUPs | BAND FREQUENCIES, $\bar{\nu}\text{ cm}^{-1}$ |
|--------|--|
| C-H    | 2880-3030                                    |
| =C-H   | 3000-3120                                    |
| C=O    | 1660-1870                                    |
| C=C    | 1600-1680                                    |
| O-H    | 3500-3700                                    |
| N-H    | 3300-3500                                    |
| C-C    | 750-1300                                     |
| C-N    | 700-1400                                     |
| C-O    | 950-1300                                     |
| S-H    | 2500-2600                                    |

The regular recurrence of some absorption bands when certain groups are present in the molecule points to the fact that these bands are characteristic of those groups. All compounds having a C-H bond exhibit bands in the region 3200-3500  $\text{cm}^{-1}$ . The exact position of the band is somewhat influenced by the rest of the molecule. In the ionic liquids and amino acid aqueous solution mixtures, the C-H band is observed around 3250  $\text{cm}^{-1}$ , N-H bonds have bands at 2900-3000  $\text{cm}^{-1}$  and O-H at 2700-2800  $\text{cm}^{-1}$ . This is very useful as it confirms the presence of a group in a molecule. In a mixture, the positions and intensities of the bands for a particular substance are not affected by the presence of other components. So, in a mixture of closely related compounds, the identification as well as the quantitative estimation of a particular component can be spectroscopically ascertained.

The broad peaks around 3427.5  $\text{cm}^{-1}$  in 1:3 L-Met and BTMAC aqueous mixture is likely to be due to the overlap of O-H and N-H stretching vibrations, indicating the presence of both surface free hydroxyl groups and chemisorbed water. The peaks around 2929.7  $\text{cm}^{-1}$  in 3:1 L-Met and BTMAC solution and 1386.6  $\text{cm}^{-1}$  in 2:2 L-Met and BTEAC solution correspond to the C-H symmetric stretch of the methylene groups ( $-\text{CH}_2$ ) and deformation vibration of methyl groups ( $-\text{CH}_3$ ). The peak at 1252.7  $\text{cm}^{-1}$  in 3:1 L-Met and BTMAC solution can be attributed to C=O stretching vibration of carboxylate ( $-\text{COO}^-$ ) groups. Some shifts in wave numbers result from change in bonding energy in the corresponding functional groups.<sup>69</sup>

The peak at 1609.4  $\text{cm}^{-1}$  and 1597.9  $\text{cm}^{-1}$  in 2:2 and 3:1 L-Met and BTEAC solution is indicative of an asymmetric  $-\text{COO}^-$  stretching bond (carboxylate) and the peak at 1413.1  $\text{cm}^{-1}$  and 1406.9  $\text{cm}^{-1}$  in 2:2 L-Met and BTMAC solution indicates a symmetric  $-\text{COO}^-$  stretching bond.<sup>70</sup> In addition, there was a new peak at 3231.2  $\text{cm}^{-1}$  in 1:3 L-Met and BTEAC aqueous solution due to N-H stretch after absorption.<sup>71</sup>

Absorption bands are clearly observed at 600–700  $\text{cm}^{-1}$  in 2:2 and 3:1 L-Met and BTMAC solution due to OH out-of-plane bending. Therein, peculiar stretching of C-O and C-C bonds, rocking of  $\text{CH}_2$  and other skeletal modes, not easily encountered in other organic molecules, give their unique IR signatures. The peaks at 1272.5  $\text{cm}^{-1}$  and 1319.1  $\text{cm}^{-1}$  in L-Met are related to stretching, bending, and rocking of  $-\text{CH}_2$  groups. As expected, the most prominent features are due to the IR absorption from the carboxyl group around 1600  $\text{cm}^{-1}$  in the L-Met and BTEAC solutions.<sup>72-74</sup>

So from the above observations and nature of the spectra it may be concluded that the aqueous mixture of L-Methionine and Benzyl tri-ethyl ammonium chloride when mixed in the ratio 3:1 (**Figure A3**) indicates highest interactions and that in the ratio 1:3 of L-Methionine and Benzyl tri-methyl ammonium chloride exhibits the lowest interactions (**Figure A2**). Thus, the

FTIR spectroscopy has been found to be one of the most convenient method for investigating the molecular interactions in solutions.<sup>75</sup>

### 3.7. <sup>1</sup>H NMR studies

We thus see that Nuclear Magnetic Resonance studies<sup>76-79</sup> reveal the presence of particular functional groups, relative number of nuclei present in the group and the relative positions of these groups from the multiplicities of the lines. Hence, NMR provides means for the investigation of intimate details of the internal structure of molecules not available through other methods. The NMR phenomenon has significance to the chemist because the energy of the resonance is dependent upon the electronic environment about the nucleus.

The chemical shift,  $\delta$  gives the difference in the shielding constants of the sample and reference. The chemical shift of a solute molecule in a solvent will be not only influenced by shielding of electrons but also by the volume diamagnetic susceptibility of the solvent. The diamagnetic contributions to the shielding of the solute would depend upon the average number of solute and solvent molecules, i.e., the number of solvent and solute neighbours. Consequently, the chemical shift will be concentration dependent. There is more intermolecular interactions associate with concentrated solutions than in dilute solutions. The effect of this interaction is to reduce the screening of the proton, causing a shift to lower field.<sup>80</sup>

As the nucleus is being examined, the static component of another nucleus causes a slight variation in the effective field at this nucleus. The contribution to the effective magnetic field

A variation in the environments of nuclei undergoing the NMR transition exists because of the random arrangements of neighbouring molecules. Thus<sup>81, 82</sup> Nuclear magnetic resonance (NMR) is an effective tool to study the changes of the electronic environment around the different protons of IL in presence amino acids. The chemical shifts of the amino acids and the IL studied depends on the electron density present in their surrounding area.

Here, <sup>1</sup>H NMR spectroscopy of pure BTMAC, BTEAC, L-Met and also in the mixture of amino acid with ILs has been done. The chemical shift value of various protons ( $\delta_1$  to  $\delta_3$ ) of BTMAC and ( $\delta_1$  to  $\delta_4$ ) BTEAC in D<sub>2</sub>O solvent are shown in **Figure B1 & Figure B2**, respectively. The results obtained from <sup>1</sup>H NMR spectrum of [BTMA]<sup>+</sup> ion has three characteristic peaks corresponding to the terminal -CH<sub>3</sub> ( $\delta_1$ ) protons of the alkyl chain at 3.022 ppm, benzyl-CH<sub>2</sub> ( $\delta_2$ ) protons at 4.401 ppm, and -C<sub>6</sub>H<sub>5</sub> protons ( $\delta_3$ ) at 7.497 ppm. In addition, the [BTEA]<sup>+</sup> ion has four characteristic peaks corresponding to terminal-CH<sub>3</sub> ( $\delta_1$ ) protons at 1.320 ppm of ethyl chain, -CH<sub>2</sub> ( $\delta_2$ ) protons at 3.149 ppm of ethyl chain, benzyl-CH<sub>2</sub> ( $\delta_3$ ) protons at 4.329 ppm, and -C<sub>6</sub>H<sub>5</sub> protons ( $\delta_4$ ) at 7.527 ppm. The chemical shift of different protons of L-Met in D<sub>2</sub>O solvent is shown in **Figure B3**. In the <sup>1</sup>H NMR spectrum of L-Methionine there are

four characteristic peaks observed corresponding to terminal  $-\text{CH}_3$  ( $\delta 1$ ) protons at 2.054 ppm,  $\text{CH}_2$  ( $\delta 2$ ) protons at 2.552 ppm,  $\text{CH}_2$  ( $\delta 3$ ) protons at 2.096 ppm, Methane( $-\text{CH}$ ) proton ( $\delta 4$ ) directly attached to  $-\text{NH}_2$  group resonates at 3.753 ppm.

The chemical shift ( $\delta$ ) values of protons of any compound are greatly influenced by the nature of moieties present in their close vicinity. The change in chemical shift values of (L-Met + BTMAC) and (L-Met + BTEAC) system in the ratio 4:1 in  $\text{D}_2\text{O}$  are shown in **Figure B4** and **Figure B5**, respectively. It is well-known fact that the  $\delta$  values shift upfield (lower frequency) or downfield (higher frequency) depending upon the shielding and deshielding effects of the surrounding groups. In our present study, the results point out that the chemical shifts of BTMAC protons move to lower frequency when it interacts upon addition of amino acids. It has also been found that there are upfield chemical shift ( $\delta$ ) values of protons for the amino acid (L-Met). An upfield shift is indicative of an increase in electron density around the protons of BTMAC, BTEAC and the amino acid, which may be owing to the intermolecular interactions.

**Figure B4** and **Figure B5** shows the change in chemical shifts of each proton of BTMAC, BTEAC and L-Met in the presence of each other (AA: IL = 4:1) by comparing with their corresponding pure BTMAC, BTEAC and pure amino acid. It has been found that the terminal  $-\text{CH}_3$  ( $\delta 1$ ) protons (moved from 3.022 ppm to 3.010 ppm), benzyl- $\text{CH}_2$  ( $\delta 2$ ) protons (moved from 4.401 ppm to 4.405 ppm), and the phenyl ring ( $\delta 3$ ) protons (moved from 7.497 ppm to 7.494 ppm) of BTMAC and it has also been found that the terminal  $-\text{CH}_3$  ( $\delta 1$ ) protons (moved from 1.320 ppm to 1.214 ppm),  $-\text{CH}_2$  ( $\delta 2$ ) protons (moved from 3.149 ppm to 3.130 ppm), benzyl- $\text{CH}_2$  ( $\delta 3$ ) protons (moved from 4.329 ppm to 4.310 ppm), and the phenyl ring ( $\delta 4$ ) protons (moved from 7.527 ppm to 7.464 ppm) of BTEAC. But it has been noticed that an upfield shift with much higher magnitude of BTEAC is shown compared with BTMAC in presence of L-Me. On the other hand, the chemical shifts of protons of terminal  $-\text{CH}_3$  ( $\delta 1$ ) (moved from 3.022 ppm to 3.010 ppm), benzyl- $\text{CH}_2$  ( $\delta 2$ ) protons (shifted from 4.401 ppm to 4.405 ppm) of BTMAC and also the chemical shift of protons of terminal  $-\text{CH}_3$  ( $\delta 1$ ) (moved from 1.320 ppm to 1.214 ppm), ethyl chain- $\text{CH}_2$  ( $\delta 2$ ) (moved from 3.149 ppm to 3.130 ppm), benzyl- $\text{CH}_2$  ( $\delta 4$ ) protons (shifted from 4.329 ppm to 4.310 ppm) of BTEAC give the smallest changes and the significant change in chemical shifts of terminal  $-\text{CH}_3$  ( $\delta 1$ ) protons attached with S atom (shifted from 2.054 ppm to 1.993 ppm),  $-\text{CH}_2$  ( $\delta 2$ ) protons attached with S atom (shifted from 2.552 ppm to 2.548 ppm) and  $-\text{CH}_2$  ( $\delta 3$ ) protons (shifted from 2.096 ppm to 1.301 ppm) and  $-\text{CH}$  ( $\delta 3$ ) protons directly attached with  $-\text{NH}_2$  group (shifted from 3.753 ppm to 3.759 ppm) of L-Met is observed in case of (L-Met + BTMAC) system and also the significant chemical change is observed of nearer S- $\text{CH}_3$  ( $\delta 1$ ) protons (shifted from 2.054 ppm to 2.062 ppm),  $-\text{CH}_2$  ( $\delta 2$ ) protons (shifted from 2.552 ppm to 2.541 ppm) and  $-\text{CH}_2$  ( $\delta 3$ ) protons shifted from 2.096 ppm to 1.336 ppm,  $-\text{CH}_2$  ( $\delta 4$ ) directly attached with  $-\text{NH}_2$  group (shifted from 3.753 ppm to 3.766 ppm). However, if we compare the

change of chemical shift between two system (L-Met + BTMAC) and (L-Met + BTEAC), higher chemical shift of protons has been found in case of L-Met + BTEAC system.

The above results suggest that the hydrophobic interactions may primarily be between the hydrophobic part of alkyl chains and phenyl group of ILs, BTMAC and BTEAC and hydrophobic portion (-CH<sub>3</sub> group attached with sulphur atom, -CH<sub>2</sub> group attached with sulphur atom, one -CH<sub>2</sub> group and one -CH group of L-Met attached with -NH<sub>2</sub> group.<sup>52, 82, 83</sup> It can be also found that the hydrophobic interaction is more stronger in (BTEAC + L-Met) system (as more up field shifts of terminal -CH<sub>3</sub> (δ1), -CH<sub>2</sub> (δ2), phenyl ring (δ3), phenyl ring (δ4), protons of BTEAC and -CH<sub>3</sub>(δ1), attached with S atom-CH<sub>2</sub> (δ2) attached with S atom, -CH(δ3) protons of L-Met compared to (BTMAC + L-Met) system .

The nature of the spectra, number, intensity and broadness of the peaks obtained by proton NMR spectroscopy of the systems mixed in the ratio of (4:1)(AA:IL) shows that the aqueous mixture of L-Methionine and Benzyl tri-ethyl ammonium chloride (**Figure B5**) exhibits more interactions compared to the aqueous mixture of L-Methionine and Benzyl tri-methyl ammonium chloride (**Figure B5**)

Thus, the NMR data provide a conclusion about the plausible contributing factors such as ion-dipole, ion-ion interactions between amino acid and ILs as well as the hydrophobic interactions.<sup>43,50</sup> All the possible type of interactions between ionic liquids (ILs) and amino acid (AA) are presented in **Scheme 1**. The conclusion from NMR measurements is in good agreement with the results obtained by FTIR studies of the Ionic liquids and the Amino acid studied here.

### 3.8. UV-Visible Spectra Measurement

The binding affinity and stability of the molecular association between the amino acid, AA (L-Met) with two ionic liquids, ILs (BTMAC & BTEAC) exhibited in the solution mixture due to manifestation of solute-solvent interaction were measured by the association or stability constant (K<sub>a</sub>) with the help of UV-Vis spectroscopic technique.<sup>84</sup> The data obtained in the solution mixture from the above mentioned technique helps to determine the stability constant or association constant. The association constant (K<sub>a</sub>) can be determined by observing the changes in absorbance (ΔA) of BTMAC and BTEAC at λ<sub>max</sub> = 208 nm (**Figure C1** and **Figure C2**, respectively) with increasing the concentration of L-Methionine at 298.15 K.

The Benesi-Hildebrand method which represents one of the popular and most renowned technique to measure the association constant (K<sub>a</sub>), the double reciprocal plots were obtained using the following equation<sup>85</sup> and the plots were found to be linear in nature (**Figure C3** and **Figure C4**) that usually states about the solute:solvent ratio in solution.<sup>86</sup>

$$1/\Delta A = 1/\Delta \epsilon [\text{IL}] \cdot 1/[\text{AA}] + 1/\Delta \epsilon [\text{IL}] \quad (18)$$

where  $\Delta A$  denotes the difference in absorbance of ILs in absence or presence of AA. [IL] denotes the concentration of BTMAC and BTEAC. [AA] denotes the concentration of L-Methionine. The value of association constant of the system (BTMAC+L-Met) and (BTEAC+L-Met) were obtained from the slope/intercept of the plots using the equation of Benesi–Hildebrand and the result of the  $K_a$  value are listed in **Table 12** and **Table 13**.<sup>87</sup>

The change of free energy for the molecular assemble taking place between amino acid with ionic liquid can be obtained by the following association constant-free energy relationship:

$$\Delta G = -RT \ln K_a \quad (19)$$

where,  $\Delta G$  is the change in free energy,  $K_a$  denotes the association constant,  $R$  refer to the universal gas constant,  $T$  stands for temperature in Kelvin scale.

### 3.9. Theoretical study of solute-solvent (amino acid and IL) interaction

Optimized geometries of L-Met-BTMAC and L-Met-BTEAC composites are illustrated in the **Figure C5 (a-b)**. In both the composites, L-Met and ionic liquids strongly interacted by H bonds within a range of 2.28-3.34 Angstrom. L-Met-BTMAC composite experiences higher adsorption energy ( $E_{ads} = -13.61$ kJ/mole) than the corresponding L-Met-BTEAC composite ( $E_{ads} = -7.39$ kJ/mole). This data clearly indicates that H bonding is more prominent in L-Met-BTMAC than L-Met-BTEAC which is confirmed from the shorter H bonding distance for the former than the later.

To gain insight on the hydrophobic and electrostatic interactions between L-Met and ionic liquids, we have plotted molecular electrostatic maps (ESP), as illustrated in **Figure C6**. From the ESP maps it is clear that interaction is purely electrostatic (red region) and offer by the interactions between the carboxylic groups and the hydrogen of the methyl group attached to the nitrogen atom of the ionic liquids.

The presence of hydrogen bonding in the composites has also been confirmed by the scattered area of the negative region of the RDG plot (0.01-0.02 region) for both the composite systems **Figure C7**.

## 4. CONCLUSIONS

Density, viscosity, refractive index, conductance and surface tension measurements of aqueous solution of amino acid, L-Methionine in the ionic liquids, Benzyl tri-methyl ammonium chloride and Benzyl tri-ethyl ammonium chloride supported by FTIR,  $^1\text{H-NMR}$  and UV-Vis spectroscopy provided the information that strong solute-solvent interactions dominate over the weak solute-solute interactions in the studied compounds. Further, L-Met in 0.005m BTEAC at 308.15K indicates highest solute-solvent interaction whereas, L-Met in 0.001m BTMAC at

298.15K shows the lowest. Again, mode of solute–solvent interaction is structure-breaking and the structure-breaking effect of L-Met is strongest in 0.001m aqueous BTMAC solution with highest packing or caging effect. The free energy of activation of viscous flow indicated greater solute–solvent interactions resulting in the formation of the transition state followed by breaking and altering the intermolecular forces prevailing in the solvent structure of the medium. Due to larger alkyl group, +I effect in BTEAC is greater than in BTMAC making the interaction more prominent in L-Met BTEAC solution as there is presence of more lone pair availability of oxygen atom, making the interaction strong with the Ionic liquid.

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**Declaration of competing Interest:** The authors declare that they have no known competing for any financial interests or personal relationships among the groups that could have appeared to affect the work in this manuscript.

### Tables

**Table 1.** Specification of chemical samples

| SL. No. | Name of Chemicals   | CAS NO. | Abbreviation | Supplier                | Purity (mass fraction) | Molar mass(g/mole) |
|---------|---|---------|--------------|-------------------------|------------------------|--------------------|
| 1       | Benzyl tri-methyl ammonium chloride (C <sub>10</sub> H <sub>16</sub> ClN) | 56-37-1 | BTMAC        | SigmaAldrich (India)    | ≥ 0.99                 | 185.69             |
| 2       | Benzyl tri-ethyl ammonium chloride (C <sub>13</sub> H <sub>22</sub> ClN)  | 56-93-9 | BTEAC        | Sigma Aldrich (Germany) | ≥ 0.97                 | 227.77             |
| 3       | L-Methionine (C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub> S)           | 63-68-3 | L-Met        | Sigma Aldrich (Japan)   | ≥ 0.98                 | 149.21             |

**Table 2. Limiting apparent molar volumes ( $\Phi_V^0$ ), Limiting molar refraction ( $R_M^0$ ), experimental slopes ( $S_V^*$ ), viscosity A, B-coefficients of L-Methionine solution in IL (BTMAC) at different temperatures and pressure at 1.013bar\***

| Temperature (K) | $\Phi_V^0 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $R_M^0$ | $S_V^* \times 10^6$ (m <sup>3</sup> .mol <sup>-3/2</sup> .kg <sup>1/2</sup> ) | B (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | A (kg.mol <sup>-1</sup> ) |
|-----------------|---|---------|---|---|---------------------------|
| 0.001m IL       |   |         |   |   |                           |
| 298.15          | 112.80±0.02   | 30.5990 | -125.26±0.01  | 4.456±0.034                                 | 0.109±0.001               |
| 303.15          | 115.24±0.04   | 30.5690 | -150.91±0.05  | 5.220±0.016                                 | 0.090±0.003               |
| 308.15          | 117.02±0.03   | 30.5840 | -176.65±0.07  | 6.474±0.013                                 | 0.052±0.004               |
| 0.003m IL       |   |         |   |   |                           |
| 298.15          | 128.14±0.02   | 30.5750 | -288.55±0.01  | 4.658±0.033                                 | 0.071±0.002               |
| 303.15          | 130.10±0.02   | 30.5790 | -298.40±0.06  | 5.632±0.027                                 | 0.049±0.004               |
| 308.15          | 130.87±0.03   | 30.6000 | -301.94±0.09  | 6.825±0.040                                 | 0.016±0.003               |
| 0.005m IL       |   |         |   |   |                           |
| 298.15          | 137.84±0.02   | 30.5840 | -398.45±0.08  | 4.975±0.064                                 | 0.029±0.003               |
| 303.15          | 140.70±0.04   | 30.5930 | -405.47±0.04  | 5.927±0.053                                 | 0.017±0.004               |
| 308.15          | 141.68±0.03   | 30.6090 | -445.11±0.03  | 7.037±0.035                                 | 0.013±0.003               |

\*Standard uncertainties values of  $u$  are:  $u(T) = 0.01\text{K}$ ,  $u(R_M^0) = \pm 0.0002$  (0.68 level of confidence)

#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol. kg<sup>-1</sup>\*molality has been expressed per kg of (IL + water) solvent mixture.

**Table 3. Limiting apparent molar volumes ( $\Phi_V^0$ ), Limiting molar refraction ( $R_M^0$ ), experimental slopes ( $S_V^*$ ), viscosity A, B-coefficients of L-Methionine solution in IL (BTEAC) at different temperatures and pressure at 1.013bar\***

| Temperature (K) | $\Phi_V^0 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $R_M^0$ | $S_V^* \times 10^6$ (m <sup>3</sup> .mol <sup>-3/2</sup> .kg <sup>1/2</sup> ) | B (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | A (kg.mol <sup>-1</sup> ) |
|-----------------|---|---------|---|---|---------------------------|
| 0.001m IL       |   |         |   |   |                           |
| 298.15          | 113.42±0.02   | 30.5690 | -137.64±0.03  | 4.630±0.039                                 | 0.085±0.004               |
| 303.15          | 115.83±0.05   | 30.6070 | -153.49±0.03  | 5.530±0.067                                 | 0.055±0.005               |
| 308.15          | 117.30±0.05   | 30.6440 | -184.96±0.01  | 6.751±0.020                                 | 0.019±0.007               |
| 0.003m IL       |   |         |   |   |                           |
| 298.15          | 128.76±0.05   | 30.5830 | -300.93±0.05  | 4.789±0.052                                 | 0.049±0.005               |
| 303.15          | 130.79±0.04   | 30.6230 | -307.04±0.03  | 5.760±0.038                                 | 0.028±0.007               |

|           |             |         |              |             |             |
|-----------|-------------|---------|--------------|-------------|-------------|
| 308.15    | 131.56±0.05 | 30.6720 | -310.61±0.04 | 7.079±0.034 | 0.012±0.004 |
| 0.005m IL |             |         |              |             |             |
| 298.15    | 140.20±0.05 | 30.6120 | -400.22±0.01 | 5.113±0.059 | 0.011±0.005 |
| 303.15    | 143.87±0.04 | 30.6510 | -455.31±0.00 | 6.018±0.054 | 0.001±0.006 |
| 308.15    | 145.45±0.05 | 30.6950 | -463.77±0.02 | 7.213±0.071 | 0.009±0.002 |

\*Standard uncertainties values of  $u_{\rho}$ :  $u(T) = 0.01\text{K}$   $u(R_M) = \pm 0.0002$  (0.68 level of confidence)

#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol.  $\text{kg}^{-1}$ \*molality has been expressed per kg of (IL + water) solvent mixture.

**Table 4. The empirical coefficient values ( $a_0$ ,  $a_1$  and  $a_2$ ) of L-Methionine solution in different concentration of the ILs (BTMAC) & (BTEAC) (0.001m,0.003m,0.005m) at 298.15K, 303.15K and 308.15K and pressure at 1.013bar\***

| Conc. of aq. ILs (BTMAC) & (BTEAC) solns. in molality (mol.kg <sup>-1</sup> ) | $a_0 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $a_1 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-1</sup> ) | $a_2 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-2</sup> ) | $a_0 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $a_1 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-1</sup> ) | $a_2 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-2</sup> ) |
|---|--|---|---|--|---|---|
|   | L-Methionine in BTMAC                                  |   |   | L-Methionine in BTEAC                                  |   |   |
|   | 298.15K  | 303.15K   | 308.15K   | 298.15K  | 303.15K   | 308.15K   |
| 0.001   | -1224.5  | 8.4212  | -0.0132   | -1727.7  | 11.781  | -0.0188   |
| 0.003   | -2137.7  | 14.696  | -0.0238   | -2267.6  | 15.551  | -0.0252   |
| 0.005   | -3427.7  | 23.170  | -0.0376   | -3852.8  | 25.856  | -0.0418   |

\*standard uncertainty in density  $u(\rho) = \pm 0.0066$  g.cm<sup>-1</sup>, \*Standard uncertainties values of  $u_{\rho}$ :  $u(T) = 0.01\text{K}$  (0.68 level of confidence) #

#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol.  $\text{kg}^{-1}$ \*molality has been expressed per kg of (IL + water) solvent mixture.

**Table 5. Values of limiting molar expansibilities ( $\Phi_E^0$ ) for L-Methionine solutions in IL (BTMAC) at different temperatures and pressure at 1.013bar\***

| Conc. of aq. IL soln. in molality (mol.kg <sup>-1</sup> ) | $\Phi_E^0 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-1</sup> ) |         |          | $(\delta\Phi_E^0/\delta T)_P \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-2</sup> ) |
|---|--|---------|----------|---|
|   | 298.15K  | 303.15K | 308.15K  |   |
| 0.001   | 0.55004  | 0.41804 | 0.28604  | -0.0264   |
| 0.003   | 0.50406  | 0.26606 | 0.02806  | -0.0476   |
| 0.005   | 0.74912  | 0.37312 | -0.00288 | -0.0752   |

\*standard uncertainty in density  $u(\rho) = \pm 0.0066$  g.cm<sup>-1</sup>, \*Standard uncertainties values of  $u_{\rho}$ :  $u(T) = 0.01\text{K}$  (0.68 level of confidence) #

#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol.  $\text{kg}^{-1}$ \*molality has been expressed per kg of (IL + water) solvent mixture.

**Table 6.** Values of limiting molar expansibilities ( $\Phi_E^0$ ) for L-Methionine solution in IL (BTEAC) at different temperatures and pressure at 1.013bar\*

| Conc. of aq. IL soln. in molality (mol.kg <sup>-1</sup> ) | $\Phi_E^0 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-1</sup> ) |         |         | $(\delta\Phi_E^0/\delta T)_P \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-2</sup> ) |
|---|--|---------|---------|---|
|   | 298.15K  | 303.15K | 308.15K |   |
| 0.001   | 0.57056  | 0.38256 | 0.19456 | -0.0376   |
| 0.003   | 0.52424  | 0.27224 | 0.02024 | -0.0504   |
| 0.005   | 0.93066  | 0.51266 | 0.09466 | -0.0836   |

\*standard uncertainty in density  $u(\rho) = \pm 0.0066$  g.cm<sup>-1</sup>, \*Standard uncertainties values of  $u_{are}:u(T) = 0.01$ K(0.68 level of confidence) #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol. kg<sup>-1</sup>\*molality has been expressed per kg of (IL + water) solvent mixture.

**Table 7.** Viscosity B-coefficients of L-Methionine solution along with dB/dT values in different concentrations of IL (BTMAC) at (298.15, 303.15 and 308.15) K and pressure at 1.013bar\*

| Temperature (K) | 0.001m IL |  | 0.003m IL |  | 0.005m IL |  | dB/dT |
|-----------------|-----------|--|-----------|--|-----------|--|-------|
|                 | B         |  | B         |  | B         |  |       |
| 298.15          | 4.456     |  | 5.220     |  | 6.474     |  | 0.052 |
| 303.15          | 4.658     |  | 5.632     |  | 6.825     |  | 0.071 |
| 308.15          | 4.975     |  | 5.927     |  | 7.037     |  | 0.056 |

\*Standard uncertainties values of  $u_{are}:u(T) = 0.01$ K(0.68 level of confidence) #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol. kg<sup>-1</sup>,\*molality has been expressed per kg of (IL + water) solvent mixture

**Table 8.** Viscosity B-coefficients of L-Methionine solution along with dB/dT values in different concentrations of IL (BTEAC) at (298.15, 303.15 and 308.15) K and pressure at 1.013bar\*

| Temperature (K) | 0.001m IL |  | 0.003m IL |  | 0.005m IL |  | dB/dT |
|-----------------|-----------|--|-----------|--|-----------|--|-------|
|                 | B         |  | B         |  | B         |  |       |
| 298.15          | 4.630     |  | 5.530     |  | 6.751     |  | 0.048 |
| 303.15          | 4.789     |  | 5.760     |  | 7.079     |  | 0.049 |
| 308.15          | 5.113     |  | 6.018     |  | 7.213     |  | 0.046 |

\*Standard uncertainties values of  $u_{are}:u(T) = 0.01$ K(0.68 level of confidence) #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol. kg<sup>-1</sup>\*molality has been expressed per kg of (IL + water) solvent mixture

**Table 9. Values of  $(\bar{V}_1^0 - \bar{V}_2^0)$ ,  $\Delta\mu_1^{0\#}$ ,  $\Delta\mu_2^{0\#}$ ,  $T\Delta S_2^{0\#}$ ,  $\Delta H_2^{0\#}$  for L-Methionine in different molality(m) of aqueous solution of IL(BTMAC&BTEAC) mixture at different temperatures and atmospheric pressure 0.1MPa**

| parameters  | 0.001m    |          |          | 0.003m    |          |          | 0.005m   |          |          |
|---|-----------|----------|----------|-----------|----------|----------|----------|----------|----------|
|   | T=298.15K | 303.15K  | 308.15K  | T=298.15K | 303.15K  | 308.15K  | 298.15K  | 303.15K  | 308.15K  |
| <b>L-Met + BTMAC</b>  |           |          |          |           |          |          |          |          |          |
| $(\bar{V}_1^0 - \bar{V}_2^0)$<br>/m <sup>3</sup> .mol <sup>-1</sup> | -94.79    | -97.82   | -97.29   | -110.13   | -112.09  | -112.86  | -119.82  | -122.68  | -123.66  |
| $\Delta\mu_1^{0\#}$ /KJ.mol <sup>-1</sup>                           | 8.91      | 9.03     | 9.07     | 8.95      | 9.06     | 9.17     | 9.01     | 9.14     | 9.17     |
| $\Delta\mu_2^{0\#}$ /KJ.mol <sup>-1</sup>                           | 634.10    | 758.47   | 944.49   | 665.33    | 817.07   | 996.17   | 710.11   | 861.49   | 1027.66  |
| $T\Delta S_2^{0\#}$ /KJ.mol <sup>-1</sup>                           | 9254.57   | 9409.74  | 9564.97  | 9863.99   | 10029.41 | 10194.83 | 9467.75  | 9626.52  | 9785.30  |
| $\Delta H_2^{0\#}$ /KJ.mol <sup>-1</sup>                            | 9888.67   | 10168.21 | 10509.46 | 10529.32  | 10846.48 | 11191.00 | 10177.86 | 10488.01 | 10812.96 |
| <b>L-Met + BTEAC</b>  |           |          |          |           |          |          |          |          |          |
| $(\bar{V}_1^0 - \bar{V}_2^0)$<br>/m <sup>3</sup> .mol <sup>-1</sup> | -95.41    | -97.83   | -99.29   | -110.75   | -112.78  | -113.55  | -122.18  | -125.85  | -127.43  |
| $\Delta\mu_1^{0\#}$ /KJ.mol <sup>-1</sup>                           | 8.94      | 9.07     | 9.10     | 8.98      | 9.12     | 9.16     | 9.01     | 9.14     | 9.17     |
| $\Delta\mu_2^{0\#}$ /KJ.mol <sup>-1</sup>                           | 659.65    | 802.21   | 988.98   | 683.55    | 836.57   | 1031.31  | 729.43   | 874.52   | 1053.32  |
| $T\Delta S_2^{0\#}$ /KJ.mol <sup>-1</sup>                           | 9664.83   | 9826.91  | 9988.99  | 10368.46  | 10542.34 | 10716.22 | 9653.50  | 9815.39  | 9977.28  |
| $\Delta H_2^{0\#}$ /KJ.mol <sup>-1</sup>                            | 10324.48  | 10629.11 | 10977.97 | 11052.01  | 11378.91 | 11747.53 | 10382.93 | 10689.91 | 11030.60 |

\*Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol. kg<sup>-1</sup>. Standard uncertainty in temperature  $u(T) = \pm 0.01$  K

Standard uncertainty in pressure  $u(P) = \pm 0.01$  MPa\* molality has been expressed per kg of (IL + water) solvent mixture.

**Table 10. Molar conductance ( $\Lambda$ ) of L-Methionine solutions in aqueous BTMAC & BTEAC ionic liquid solution in (0.001m, 0.003m, 0.005m) at 298.15K, 303.15K and 313.15K and pressure at 1.013bar\***

| Concentration of amino acid<br>solutions in molality,<br>m(mole/kg) | Molar Conductance of L-Methionine in<br>BTMAC solutions<br>$\Lambda \times 10^{-4}(\text{S.m}^2.\text{mol}^{-1})$ |         |         | Molar conductance of L- Methionine<br>in BTEAC solutions<br>$\Lambda \times 10^{-4}(\text{S.m}^2.\text{mol}^{-1})$ |         |         |
|---|---|---------|---------|--|---------|---------|
|   | 298.15K   | 303.15K | 308.15K | 298.15K  | 303.15K | 308.15K |
| 0.001mIL  |   |         |         |  |         |         |
| 0.0010  | 125.1   | 170.0   | 190.2   | 110.3  | 38.2    | 41.0    |
| 0.0025  | 52.0  | 73.0    | 79.0    | 18.1   | 19.4    | 20.9    |
| 0.0040  | 35.5  | 49.5    | 54.8    | 13.9   | 14.6    | 15.4    |
| 0.0055  | 27.3  | 37.2    | 45.2    | 11.6   | 12.6    | 12.9    |
| 0.0070  | 22.7  | 30.6    | 36.1    | 10.8   | 11.3    | 11.7    |
| 0.0085  | 19.9  | 26.3    | 31.1    | 9.9  | 10.5    | 10.6    |
| 0.003m IL   |   |         |         |  |         |         |
| 0.0010  | 300.0   | 330.3   | 380.3   | 44.1   | 46.3    | 49.6    |
| 0.0025  | 135.0   | 140.0   | 158.0   | 21.7   | 22.8    | 23.9    |
| 0.0040  | 87.5  | 91.5    | 99.2    | 17.1   | 17.6    | 18.1    |
| 0.0055  | 64.5  | 68.0    | 75.1    | 14.3   | 14.9    | 14.9    |
| 0.0070  | 51.9  | 55.1    | 62.3    | 12.9   | 13.2    | 13.5    |
| 0.0085  | 44.0  | 47.7    | 53.6    | 11.5   | 12.1    | 12.4    |
| 0.005mIL  |   |         |         |  |         |         |
| 0.0010  | 480.5   | 550.3   | 600.0   | 54.2   | 58.2    | 61.2    |
| 0.0025  | 196.0   | 225.4   | 245.1   | 25.6   | 26.8    | 27.6    |
| 0.0040  | 125.5   | 143.3   | 155.5   | 19.2   | 19.4    | 19.9    |
| 0.0055  | 93.5  | 107.0   | 115.3   | 15.8   | 15.9    | 16.5    |
| 0.0070  | 74.1  | 85.6    | 92.3    | 14.0   | 14.1    | 14.4    |
| 0.0085  | 62.6  | 72.1    | 77.8    | 12.5   | 12.7    | 12.8    |

\*Standard uncertainties  $u(\Lambda) = 0.5 \text{ Sm}^2 \text{ mol}^{-1}$ ,  $u(T) = 0.01\text{K}$  (0.68 level of confidence)#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol. kg<sup>-1</sup>\*molality has been expressed per kg of (IL + water) solvent mixture

**Table 11. Surface Tension ( $\gamma$ ) values of L-Methionine solutions in IL (BTMAC) and L-Methionine solutions in IL (BTEAC) at different concentration(0.001m,0.003m,0.005m) at room temperature and pressure at 1.013bar\***

| Concentration of amino acid solutions in molality(mole/kg) | Surface Tension of L- Methionine solutions in IL (BTMAC) $\gamma$ (mN/m) | Surface Tension of L- Methionine solutions in IL (BTEAC) $\gamma$ (mN/m) |
|--|--|--|
| 0.001mIL   |  |  |
| 0.0010   | 59.3   | 59.8   |
| 0.0025   | 60.3   | 60.6   |
| 0.0040   | 61.9   | 61.3   |
| 0.0055   | 62.3   | 62.5   |
| 0.0070   | 62.6   | 63.4   |
| 0.0085   | 64.3   | 64.8   |
| 0.003mIL   |  |  |
| 0.0010   | 56.3   | 56.6   |
| 0.0025   | 57.8   | 60.2   |
| 0.0040   | 60.1   | 64.2   |
| 0.0055   | 60.3   | 66.4   |
| 0.0070   | 62.3   | 67.8   |
| 0.0085   | 63.2   | 69.2   |
| 0.005mIL   |  |  |
| 0.0010   | 58.0   | 58.9   |
| 0.0025   | 58.6   | 61.2   |
| 0.0040   | 59.0   | 63.5   |
| 0.0055   | 59.6   | 64.9   |
| 0.0070   | 60.1   | 66.1   |
| 0.0085   | 60.8   | 69.5   |

\*Standard uncertainties  $u(Y)=\pm 0.1(mN/m)$  (0.68 level of confidence)#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095 \text{ mol. kg}^{-1}$ \*molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence).

**Table 12. Limiting Slopes ( $\partial\sigma/\partial m$ ) of the Surface Tension of the Aqueous Solutions of  $\alpha$ -Amino acid**

| Aqueous Mixture | IL | $(\partial\sigma/\partial m) / \text{mN m}^{-1} \cdot \text{Kg. mol}^{-1}$ |                       |
|-----------------|----|--|-----------------------|
|                 |    | L-Methionine+Aq.BTMAC  | L-Methionine+Aq.BTEAC |
| 0.001           |    | 61.90  | 68.76                 |
| 0.003           |    | 76.57  | 106.67                |
| 0.005           |    | 88.57  | 117.14                |

\*Standard uncertainties  $u(Y)=\pm 0.1(mN/m)$  (0.68 level of confidence)#Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095 \text{ mol. kg}^{-1}$ \*molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence).

**Table 13. UV-Vis Spectroscopic data for the Benesi-Hildebrand double reciprocal plot of BTMAC+L-Met system at 298.15K**

| BTMAC+L-Met |                      |                        |         |         |            |                               |              |           |        |                                    |                              |
|-------------|----------------------|------------------------|---------|---------|------------|-------------------------------|--------------|-----------|--------|------------------------------------|------------------------------|
| Temp/K      | IL/<br>$\mu\text{M}$ | [AA]<br>$/\mu\text{M}$ | $A_0$   | A       | $\Delta A$ | $1/[\text{AA}]/\text{M}^{-1}$ | $1/\Delta A$ | Intercept | Slope  | $K_a/\text{M}^{-1} \times 10^{-3}$ | $\Delta G/\text{KJmol}^{-1}$ |
| 298.15      | 300                  | 20                     | 0.56530 | 0.59036 | 0.02505    | 0.0500                        | 39.1117      | 2.0918    | 759.25 | 2.75                               | -19.6                        |
|             | 300                  | 40                     | 0.56530 | 0.61686 | 0.04736    | 0.0250                        | 21.1107      |           |        |                                    |                              |
|             | 300                  | 60                     | 0.56530 | 0.63080 | 0.06617    | 0.0166                        | 15.1107      |           |        |                                    |                              |
|             | 300                  | 80                     | 0.56530 | 0.64903 | 0.08427    | 0.0125                        | 11.8657      |           |        |                                    |                              |
|             | 300                  | 100                    | 0.56530 | 0.66593 | 0.10090    | 0.0100                        | 9.9108       |           |        |                                    |                              |
|             | 300                  | 120                    | 0.56530 | 0.68707 | 0.12203    | 0.0088                        | 8.1948       |           |        |                                    |                              |
|             | 300                  | 140                    | 0.56530 | 0.70875 | 0.14375    | 0.0062                        | 6.9589       |           |        |                                    |                              |

**Table 14. UV-Vis Spectroscopic data for the Benesi-Hildebrand double reciprocal plot of BTEAC+L-Met system at 298.15K**

| BTEAC+L-Met |                      |                        |         |         |            |                               |              |           |        |                                    |                               |
|-------------|----------------------|------------------------|---------|---------|------------|-------------------------------|--------------|-----------|--------|------------------------------------|-------------------------------|
| Temp/K      | IL/<br>$\mu\text{M}$ | [AA]<br>$/\mu\text{M}$ | $A_0$   | A       | $\Delta A$ | $1/[\text{AA}]/\text{M}^{-1}$ | $1/\Delta A$ | Intercept | Slope  | $K_a/\text{M}^{-1} \times 10^{-3}$ | $\Delta G/\text{KJ mol}^{-1}$ |
| 298.15      | 300                  | 20                     | 0.79716 | 0.82339 | 0.02623    | 0.0500                        | 38.1242      | 2.8794    | 711.05 | 3.85                               | -20.4                         |
|             | 300                  | 40                     | 0.79716 | 0.84560 | 0.04844    | 0.0250                        | 20.6406      |           |        |                                    |                               |
|             | 300                  | 60                     | 0.79716 | 0.85986 | 0.06270    | 0.0166                        | 15.9489      |           |        |                                    |                               |
|             | 300                  | 80                     | 0.79716 | 0.87791 | 0.08070    | 0.0125                        | 12.3915      |           |        |                                    |                               |
|             | 300                  | 100                    | 0.79716 | 0.90063 | 0.10345    | 0.0100                        | 9.6602       |           |        |                                    |                               |
|             | 300                  | 120                    | 0.79716 | 0.91899 | 0.12093    | 0.0088                        | 8.2695       |           |        |                                    |                               |
|             | 300                  | 140                    | 0.79716 | 0.93426 | 0.13717    | 0.0062                        | 7.2932       |           |        |                                    |                               |

## Tables

**Table S1.** Experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of different molality (m) of aqueous IL (BTMAC) solution at 298.15K, 303.15K and 308.15K and pressure at 1.013bar\*

| Conc. of Aq.<br>IL(BTMAC)<br>soln. in<br>molality, m<br>(mol.kg <sup>-1</sup> ) | $\rho \times 10^{-3} (\text{kg.m}^{-3})$ |         |         | $\eta (\text{mPa.s})$ |         |         | $R_M$   |         |         |
|---|--|---------|---------|-----------------------|---------|---------|---------|---------|---------|
|   | 298.15K                                  | 303.15K | 308.15K | 298.15K               | 303.15K | 308.15K | 298.15K | 303.15K | 308.15K |
|   |  |         |         | 308.15K               |         |         |         |         |         |
| 0.001   | .99713                                   | .99574  | .99413  | 0.810                 | 0.781   | 0.765   | 30.5618 | 30.5711 | 30.5866 |
| 0.003   | .99717                                   | .99577  | .99416  | 0.821                 | 0.791   | 0.779   | 30.5777 | 30.5783 | 30.5950 |
| 0.005   | .99720                                   | .99581  | .99421  | 0.831                 | 0.803   | 0.785   | 30.6017 | 30.6108 | 30.6179 |

\*standard uncertainty in density  $u(\rho) = \pm 0.0066 \text{ g.cm}^{-3}$ , \*molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence). \* Standard uncertainty in refractive index  $u(n_D) = \pm 0.01528$  and  $u(T) = 0.01\text{K}$ , (0.68 level of confidence). #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095 \text{ mol.kg}^{-1}$ . \*Standard uncertainty in viscosity (u)  $\eta = \pm 0.0152 \text{ mPa.s}$ .

**Table S2.** Experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of different molality ( $m$ ) of aqueous IL (BTEAC) solution at 298.15K, 303.15K and 308.15K. and pressure at 1.013bar\*

| Conc. of Aq. IL(BTEAC) soln. in molality, $m$ (mol.kg <sup>-1</sup> ) | $\rho \times 10^{-3}$ (kg.m <sup>-3</sup> ) |        |        | $\eta$ (mPa.s)         |       |       | $R_M$                  |         |         |
|---|---|--------|--------|------------------------|-------|-------|------------------------|---------|---------|
|   | <u>298.15K 303.15K</u>                      |        |        | <u>298.15K 303.15K</u> |       |       | <u>298.15K 303.15K</u> |         |         |
|   | <u>308.15K</u>                              |        |        | <u>308.15K</u>         |       |       | <u>308.15K</u>         |         |         |
|   |   |        |        |                        |       |       |                        |         |         |
| 0.001   | .99711                                      | .99572 | .99410 | 0.819                  | 0.793 | 0.774 | 30.5709                | 30.5883 | 30.6213 |
| 0.003   | .99715                                      | .99575 | .99414 | 0.830                  | 0.807 | 0.792 | 30.5864                | 30.6042 | 30.6366 |
| 0.005   | .99720                                      | .99579 | .99420 | 0.840                  | 0.816 | 0.795 | 30.6101                | 30.6198 | 30.6435 |

\*standard uncertainty in density  $u(\rho) = \pm 0.0066 \text{ g.cm}^{-1}$ , \*molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence). \* Standard uncertainty in refractive index  $u(n_D) = \pm 0.01528$  and  $u(T) = 0.01\text{K}$ , (0.68 level of confidence).# Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095 \text{ mol.kg}^{-1}$ . \*Standard uncertainty in viscosity ( $u$ )  $\eta = \pm 0.0152 \text{ mPa.s}$ .

**Table S3.** Experimental values of refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of different molality ( $m$ ) of aqueous IL (BTMAC) solution at 298.15 K, 303.15 K and 308.15 K and pressure at 1.013bar\*

| Conc. of Aq. IL (BTMAC) soln. in molality, $m$ (mol.kg <sup>-1</sup> ) | $n_D$          |                |                | $\kappa$ (mS/cm) |                |                |
|--|----------------|----------------|----------------|------------------|----------------|----------------|
|  | <u>298.15K</u> | <u>303.15K</u> | <u>308.15K</u> | <u>298.15K</u>   | <u>303.15K</u> | <u>313.15K</u> |
|  |                |                |                |                  |                |                |
| 0.001  | 1.3304         | 1.3300         | 1.3296         | 0.107            | 0.160          | 0.175          |
| 0.003  | 1.3306         | 1.3301         | 1.3297         | 0.280            | 0.310          | 0.368          |
| 0.005  | 1.3309         | 1.3305         | 1.3302         | 0.469            | 0.520          | 0.580          |

\*Standard Uncertainties of refractive index ( $u$ ) are:  $u(n_D) = \pm 0.01528$ , \*molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence).  $u(\sigma) = \pm 0.01 \text{ (mS cm}^{-1})$   
<sup>1)</sup>  $u(Y) = \pm 0.1 \text{ (mN/m)}$  #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095 \text{ mol.kg}^{-1}$

**Table S4.** Experimental values of refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of different molality (m) of aqueous IL (BTEAC) solution at 298.15 K, 303.15 K and 308.15 K. and pressure at 1.013bar\*

| Conc. of Aq. IL (BTEAC) soln. in molality, m (mol.kg <sup>-1</sup> ) | $n_D$   |         |         | $\kappa$ (mS/cm) |         |         |
|--|---------|---------|---------|------------------|---------|---------|
|  | 298.15K | 303.15K | 308.15K | 298.15K          | 303.15K | 308.15K |
| 0.001  | 1.3305  | 1.3302  | 1.3300  | 0.100            | 0.112   | 0.131   |
| 0.003  | 1.3307  | 1.3304  | 1.3302  | 0.278            | 0.300   | 0.310   |
| 0.005  | 1.3310  | 1.3306  | 1.3303  | 0.459            | 0.500   | 0.529   |

\*Standard Uncertainties in refractive index (u) are:  $u(n_D) = \pm 0.01528$  \*molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence).  $u(\sigma) = \pm 0.01$  (mScm<sup>-1</sup>)  $u(Y) = \pm 0.1$  (mN/m) #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol. kg<sup>-1</sup>

**Table S5.** Density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of L-Methionine in aqueous (BTMAC) ionic liquid solutions at 298.15K, 303.15K and 308.15K and pressure at 1.013bar\*

| Conc. of L-Methionine soln. in molality, m(mol.kg <sup>-1</sup> ) | $\rho \times 10^{-3}$ (kg.m <sup>-3</sup> ) |         |         | $\eta$ (mPa.s) |         |         | $R_M$   |         |          |
|---|---|---------|---------|----------------|---------|---------|---------|---------|----------|
|   | 298.15K                                     | 303.15K | 308.15K | 298.15K        | 303.15K | 308.15K | 298.15K | 303.15K | 308.15K  |
| 0.001m IL   |   |         |         |                |         |         |         |         |          |
| 0.0010  | 0.99717                                     | 0.99578 | 0.99417 | 0.919          | 0.882   | 0.845   | 30.5774 | 30.5949 | 30.6022  |
| 0.0025  | 0.99724                                     | 0.99584 | 0.99423 | 0.925          | 0.888   | 0.851   | 30.5921 | 30.6098 | 30.6173  |
| 0.0040  | 0.99731                                     | 0.99592 | 0.99431 | 0.931          | 0.894   | 0.857   | 30.5983 | 30.6158 | 30.6235  |
| 0.0055  | 0.99738                                     | 0.99599 | 0.99438 | 0.936          | 0.899   | 0.863   | 30.6046 | 30.6305 | 30.6295  |
| 0.0070  | 0.99747                                     | 0.99606 | 0.99446 | 0.941          | 0.905   | 0.869   | 30.6105 | 30.6367 | 30.6358  |
| 0.0085  | 0.99754                                     | 0.99615 | 0.99455 | 0.946          | 0.910   | 0.875   | 30.6165 | 30.6424 | 30.6411  |
| 0.003mIL  |   |         |         |                |         |         |         |         |          |
| 0.0010  | 0.99720                                     | 0.99580 | 0.99419 | 0.926          | 0.885   | 0.851   | 30.5933 | 30.6027 | 30.6185  |
| 0.0025  | 0.99726                                     | 0.99585 | 0.99424 | 0.932          | 0.892   | 0.858   | 30.6083 | 30.6176 | 30.6338  |
| 0.0040  | 0.99733                                     | 0.99593 | 0.99431 | 0.938          | 0.898   | 0.864   | 30.6145 | 30.6323 | 30.6401  |
| 0.0055  | 0.99741                                     | 0.99601 | 0.99440 | 0.943          | 0.904   | 0.870   | 30.6205 | 30.6386 | 30.6460  |
| 0.0070  | 0.99749                                     | 0.99608 | 0.99447 | 0.948          | 0.909   | 0.877   | 30.6264 | 30.6445 | 30.6520  |
| 0.0085  | 0.99757                                     | 0.99617 | 0.99456 | 0.954          | 0.915   | 0.883   | 30.6323 | 30.6502 | 30.6577  |
| 0.005mIL  |   |         |         |                |         |         |         |         |          |
| 0.0010  | 0.99722                                     | 0.99583 | 0.99423 | 0.935          | 0.897   | 0.856   | 30.6095 | 30.6186 | 30.6341  |
| 0.0025  | 0.99729                                     | 0.99589 | 0.99429 | 0.941          | 0.903   | 0.862   | 30.6241 | 30.6335 | 30.6491  |
| 0.0040  | 0.99736                                     | 0.99595 | 0.99435 | 0.947          | 0.909   | 0.868   | 30.6304 | 30.6395 | 30.65.54 |
| 0.0055  | 0.99743                                     | 0.99602 | 0.99445 | 0.952          | 0.915   | 0.874   | 30.6450 | 30.6542 | 30.6695  |
| 0.0070  | 0.99750                                     | 0.99611 | 0.99452 | 0.958          | 0.921   | 0.880   | 30.6513 | 30.6601 | 30.6757  |
| 0.0085  | 0.99760                                     | 0.99620 | 0.99461 | 0.964          | 0.927   | 0.887   | 30.6566 | 30.6661 | 30.6814  |

\*standard uncertainty in density  $u(\rho) = \pm 0.0066$  g.cm<sup>-1</sup>,  $u(T) = 0.01$ K, \*molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence). #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol. kg<sup>-1</sup> \*Standard uncertainty in viscosity (u)  $\eta = \pm 0.0152$  mPa. S.

**Table S6.** Density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of L-Methionine in aqueous (BTEAC) ionic liquid solutions at 298.15K, 303.15K and 308.15K. and pressure at 1.013bar\*

| Conc. of<br>L-<br>Methionine<br>soln.in<br>molality<br>(mol.kg <sup>-1</sup> ) | $\rho \times 10^{-3}(\text{kg.m}^{-3})$ |         |         | $\eta(\text{mPa.s})$ |         |         | $R_M$   |         |         |
|--|---|---------|---------|----------------------|---------|---------|---------|---------|---------|
|  | 298.15K                                 | 303.15K | 308.15K | 298.15K              | 303.15K | 308.15K | 298.15K | 303.15K | 308.15K |
| 0.001m IL  |   |         |         |                      |         |         |         |         |         |
| 0.0010   | 0.99715                                 | 0.99576 | 0.99414 | 0.921                | 0.884   | 0.849   | 30.6116 | 30.6375 | 30.6790 |
| 0.0025   | 0.99722                                 | 0.99582 | 0.99420 | 0.930                | 0.893   | 0.858   | 30.6263 | 30.6525 | 30.7025 |
| 0.0040   | 0.99728                                 | 0.99589 | 0.99427 | 0.939                | 0.902   | 0.867   | 30.6412 | 30.6672 | 30.7172 |
| 0.0055   | 0.99736                                 | 0.99597 | 0.99436 | 0.948                | 0.912   | 0.877   | 30.6556 | 30.6731 | 30.7231 |
| 0.0070   | 0.99744                                 | 0.99604 | 0.99443 | 0.956                | 0.921   | 0.887   | 30.6699 | 30.6878 | 30.7378 |
| 0.0085   | 0.99753                                 | 0.99613 | 0.99453 | 0.965                | 0.929   | 0.897   | 30.6842 | 30.6934 | 30.7515 |
| 0.003mIL   |   |         |         |                      |         |         |         |         |         |
| 0.0010   | 0.99718                                 | 0.99578 | 0.99418 | 0.929                | 0.888   | 0.853   | 30.6191 | 30.6538 | 30.6862 |
| 0.0025   | 0.99724                                 | 0.99583 | 0.99423 | 0.938                | 0.896   | 0.863   | 30.6425 | 30.6690 | 30.7015 |
| 0.0040   | 0.99730                                 | 0.99590 | 0.99429 | 0.947                | 0.906   | 0.872   | 30.6574 | 30.6837 | 30.7250 |
| 0.0055   | 0.99739                                 | 0.99599 | 0.99439 | 0.957                | 0.917   | 0.882   | 30.6711 | 30.6977 | 30.7387 |
| 0.0070   | 0.99747                                 | 0.99606 | 0.99446 | 0.967                | 0.926   | 0.894   | 30.6774 | 30.7037 | 30.7447 |
| 0.0085   | 0.99756                                 | 0.99615 | 0.99455 | 0.977                | 0.936   | 0.904   | 30.6914 | 30.7096 | 30.7506 |
| 0.005m IL  |   |         |         |                      |         |         |         |         |         |
| 0.0010   | 0.99722                                 | 0.99581 | 0.99422 | 0.939                | 0.899   | 0.859   | 30.6431 | 30.6697 | 30.7019 |
| 0.0025   | 0.99728                                 | 0.99586 | 0.99427 | 0.949                | 0.909   | 0.869   | 30.6664 | 30.6849 | 30.7172 |
| 0.0040   | 0.99735                                 | 0.99593 | 0.99433 | 0.960                | 0.919   | 0.880   | 30.6811 | 30.6909 | 30.7321 |
| 0.0055   | 0.99743                                 | 0.99602 | 0.99440 | 0.970                | 0.929   | 0.891   | 30.6870 | 30.6974 | 30.7381 |
| 0.0070   | 0.99749                                 | 0.99609 | 0.99451 | 0.980                | 0.939   | 0.901   | 30.7016 | 30.7028 | 30.7518 |
| 0.0085   | 0.99759                                 | 0.99619 | 0.99461 | 0.990                | 0.950   | 0.912   | 30.7073 | 30.7090 | 30.7581 |

\*standard uncertainty in density  $u(\rho) = \pm 0.0066 \text{ g.cm}^{-1}$ , \*  $u(T) = \pm 0.01\text{K}$ , \*molality has been expressed per kg of (IL + water) solvent mixture (0.68 level of confidence). #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095 \text{ mol.kg}^{-1}$  \*Standard uncertainty in viscosity ( $u$ )  $\eta = \pm 0.0152 \text{ mPa. S}$ .

**Table S7.** Apparent molar volume, ( $\Phi_v$ ) and  $(\eta/\eta^0 - 1)/\sqrt{m}$  of L-Methionine solution in 0.001m, 0.003m and 0.005m aqueous BTMAC solution at different temperatures 298.15K, 303.15K, 308.15K and pressure at 1.013bar\*

| Conc. of L-Methionine soln. in molality, m (mol.kg <sup>-1</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) |
|--|---|--|---|--|---|--|
| 0.001mIL   | <b>298.15K</b>  |  | <b>303.15K</b>  |  | <b>308.15K</b>  |  |
| 0.0010   | 109.52±0.03   | 0.243±0.003  | 109.62±0.03   | 0.270±0.004  | 109.73±0.03   | 0.285±0.005  |
| 0.0025   | 105.51±0.03   | 0.334±0.003  | 109.62±0.03   | 0.340±0.004  | 109.73±0.03   | 0.347±0.005  |
| 0.0040   | 104.50±0.03   | 0.403±0.003  | 104.59±0.03   | 0.412±0.004  | 107.21±0.03   | 0.448±0.005  |
| 0.0055   | 104.05±0.03   | 0.434±0.004  | 104.13±0.03   | 0.446±0.004  | 104.23±0.03   | 0.527±0.005  |
| 0.0070   | 102.36±0.03   | 0.486±0.005  | 102.43±0.03   | 0.541±0.005  | 102.52±0.03   | 0.609±0.006  |
| 0.0085   | 101.26±0.03   | 0.512±0.005  | 101.33±0.03   | 0.578±0.005  | 100.23±0.03   | 0.659±0.007  |
| 0.003mIL   | <b>298.15K</b>  |  | <b>303.15K</b>  |  | <b>308.15K</b>  |  |
| 0.0010   | 119.54±0.03   | 0.218±0.004  | 119.67±0.03   | 0.241±0.005  | 119.81±0.03   | 0.248±0.007  |
| 0.0025   | 113.53±0.03   | 0.307±0.004  | 117.66±0.03   | 0.318±0.005  | 117.80±0.03   | 0.340±0.006  |
| 0.0040   | 109.52±0.03   | 0.361±0.005  | 109.61±0.03   | 0.403±0.005  | 112.25±0.03   | 0.440±0.006  |
| 0.0055   | 105.87±0.03   | 0.424±0.005  | 107.78±0.03   | 0.458±0.006  | 109.89±0.03   | 0.513±0.007  |
| 0.0070   | 103.79±0.03   | 0.463±0.005  | 105.30±0.03   | 0.534±0.007  | 105.40±0.03   | 0.600±0.008  |
| 0.0085   | 102.44±0.03   | 0.499±0.007  | 102.52±0.03   | 0.572±0.007  | 102.60±0.03   | 0.651±0.009  |
| 0.005mIL   | <b>298.15K</b>  |  | <b>303.15K</b>  |  | <b>308.15K</b>  |  |
| 0.0010   | 129.57±0.03   | 0.200±0.006  | 129.72±0.03   | 0.220±0.007  | 129.90±0.03   | 0.219±0.008  |
| 0.0025   | 113.52±0.03   | 0.261±0.006  | 117.65±0.03   | 0.302±0.007  | 117.79±0.03   | 0.295±0.009  |
| 0.0040   | 109.51±0.03   | 0.335±0.006  | 114.64±0.03   | 0.375±0.007  | 112.24±0.03   | 0.413±0.009  |
| 0.0055   | 107.69±0.03   | 0.411±0.006  | 111.44±0.03   | 0.452±0.007  | 106.05±0.03   | 0.487±0.010  |
| 0.0070   | 106.65±0.03   | 0.446±0.008  | 106.74±0.03   | 0.531±0.008  | 105.40±0.03   | 0.554±0.010  |
| 0.0085   | 102.44±0.03   | 0.491±0.010  | 103.70±0.03   | 0.566±0.010  | 102.60±0.03   | 0.643±0.010  |

\*standard uncertainty in density  $u(\rho) = \pm 0.0066$  g.cm<sup>-1</sup>, \*Standard uncertainties  $u$  are:  $u(T) = 0.01$ K, \*molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence). #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol. kg<sup>-1</sup> \*Standard uncertainty in viscosity ( $u$ )  $\eta = \pm 0.0152$  mPa. S.

**Table S8.** Apparent molar volume, ( $\Phi_v$ ) and  $(\eta/\eta^0 - 1)/\sqrt{m}$  of L-Methionine solutions in 0.001m, 0.003m and 0.005m in aqueous (BTEAC) solution at different temperatures 298.15K, 303.15K, 308.15K and pressure at 1.013bar\*

| Conc. of L-Methionine soln. in molality (mol.kg <sup>-1</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) |
|---|---|--|---|--|---|--|
| 0.001m IL   | <b>298.15K</b>  |  | <b>303.15K</b>  |  | <b>308.15K</b>  |  |
| 0.0010  | 109.52±0.05   | 0.230±0.005  | 109.62±0.05   | 0.251±0.006  | 109.73±0.05   | 0.259±0.007  |
| 0.0025  | 105.51±0.05   | 0.317±0.005  | 109.62±0.05   | 0.302±0.006  | 109.73±0.05   | 0.337±0.007  |
| 0.0040  | 104.51±0.05   | 0.387±0.005  | 107.10±0.05   | 0.410±0.006  | 107.21±0.05   | 0.424±0.007  |
| 0.0055  | 104.05±0.05   | 0.424±0.006  | 104.13±0.05   | 0.458±0.007  | 102.39±0.05   | 0.515±0.008  |
| 0.0070  | 102.36±0.05   | 0.475±0.006  | 102.43±0.05   | 0.521±0.008  | 102.52±0.05   | 0.596±0.009  |

|           |                |             |                |             |                |             |
|-----------|----------------|-------------|----------------|-------------|----------------|-------------|
| 0.0085    | 100.08±0.05    | 0.511±0.008 | 101.34±0.05    | 0.576±0.009 | 99.05±0.05     | 0.656±0.009 |
| 0.003mIL  | <b>298.15K</b> |             | <b>303.15K</b> |             | <b>308.15K</b> |             |
| 0.0010    | 119.55±0.05    | 0.207±0.007 | 119.67±0.05    | 0.228±0.008 | 119.82±0.05    | 0.225±0.009 |
| 0.0025    | 113.53±0.05    | 0.292±0.007 | 117.66±0.05    | 0.303±0.008 | 117.80±0.05    | 0.303±0.010 |
| 0.0040    | 109.52±0.05    | 0.340±0.007 | 112.13±0.05    | 0.376±0.009 | 114.77±0.05    | 0.396±0.010 |
| 0.0055    | 105.87±0.05    | 0.401±0.008 | 105.96±0.05    | 0.455±0.010 | 106.06±0.05    | 0.489±0.010 |
| 0.0070    | 103.79±0.05    | 0.453±0.009 | 105.30±0.05    | 0.519±0.010 | 105.40±0.05    | 0.577±0.011 |
| 0.0085    | 101.26±0.05    | 0.500±0.010 | 102.52±0.05    | 0.568±0.010 | 102.61±0.05    | 0.642±0.011 |
| 0.005m IL | <b>298.15K</b> |             | <b>303.15K</b> |             | <b>308.15K</b> |             |
| 0.0010    | 129.57±0.05    | 0.191±0.008 | 129.72±0.05    | 0.207±0.009 | 129.90±0.05    | 0.198±0.010 |
| 0.0025    | 117.54±0.05    | 0.242±0.008 | 121.68±0.05    | 0.290±0.008 | 121.83±0.05    | 0.293±0.011 |
| 0.0040    | 114.53±0.05    | 0.326±0.009 | 114.64±0.05    | 0.368±0.009 | 117.29±0.05    | 0.355±0.011 |
| 0.0055    | 109.51±0.05    | 0.401±0.010 | 107.78±0.05    | 0.446±0.010 | 113.39±0.05    | 0.475±0.012 |
| 0.0070    | 108.08±0.05    | 0.445±0.011 | 106.74±0.05    | 0.515±0.011 | 105.40±0.05    | 0.561±0.012 |
| 0.0085    | 103.62±0.05    | 0.483±0.012 | 102.51±0.05    | 0.562±0.012 | 101.42±0.05    | 0.625±0.014 |

\*Standard uncertainties  $u$  are:  $u(T) = 0.01K$ , \*standard uncertainty in viscosity  $u(\eta) = \pm 0.0152 \text{ mPa} \cdot \text{s}$ , \*molality has been expressed per kg of (IL + water) solvent mixture. (0.68 level of confidence), #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095 \text{ mol} \cdot \text{kg}^{-1}$

**Table S9.** Refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of L-Methionine in aqueous IL (BTMAC) solution at 298.15K, 303.15K and 308.15K and pressure at 1.013bar\*

| Conc. of L-Methionine soln. in molality, $m$ ( $\text{mol} \cdot \text{kg}^{-1}$ ) | $n_D$   |         |         | $\kappa$ (mS/cm) |         |         |
|--|---------|---------|---------|------------------|---------|---------|
|  | 298.15K | 303.15K | 313.15K | 298.15K          | 303.15K | 313.15K |
| 0.001Mil   |         |         |         |                  |         |         |
| 0.0010   | 1.3306  | 1.3303  | 1.3298  | 0.1251           | 0.170   | 0.190   |
| 0.0025   | 1.3308  | 1.3305  | 1.3300  | 0.130            | 0.182   | 0.197   |
| 0.0040   | 1.3309  | 1.3306  | 1.3301  | 0.142            | 0.198   | 0.219   |
| 0.0055   | 1.3310  | 1.3308  | 1.3302  | 0.149            | 0.204   | 0.248   |
| 0.0070   | 1.3311  | 1.3309  | 1.3303  | 0.158            | 0.213   | 0.252   |
| 0.0085   | 1.3312  | 1.3310  | 1.3304  | 0.169            | 0.223   | 0.264   |
| 0.003mIL   |         |         |         |                  |         |         |
| 0.0010   | 1.3308  | 1.3304  | 1.3300  | 0.300            | 0.330   | 0.380   |
| 0.0025   | 1.3310  | 1.3306  | 1.3302  | 0.337            | 0.350   | 0.392   |
| 0.0040   | 1.3311  | 1.3308  | 1.3303  | 0.350            | 0.366   | 0.396   |
| 0.0055   | 1.3312  | 1.3309  | 1.3304  | 0.354            | 0.374   | 0.412   |
| 0.0070   | 1.3313  | 1.3310  | 1.3305  | 0.362            | 0.386   | 0.435   |
| 0.0085   | 1.3314  | 1.3311  | 1.3306  | 0.374            | 0.405   | 0.455   |
| 0.005mIL   |         |         |         |                  |         |         |
| 0.0010   | 1.3310  | 1.3306  | 1.3302  | 0.481            | 0.550   | 0.600   |
| 0.0025   | 1.3312  | 1.3308  | 1.3304  | 0.490            | 0.563   | 0.612   |
| 0.0040   | 1.3313  | 1.3309  | 1.3305  | 0.502            | 0.573   | 0.622   |
| 0.0055   | 1.3314  | 1.3311  | 1.3307  | 0.513            | 0.588   | 0.633   |
| 0.0070   | 1.3316  | 1.3312  | 1.3308  | 0.518            | 0.598   | 0.645   |
| 0.0085   | 1.3317  | 1.3313  | 1.3309  | 0.532            | 0.612   | 0.660   |

\*Standard uncertainties values of  $u$  are:  $u(T) = 0.01K$  (0.68 level of confidence) #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095 \text{ mol} \cdot \text{kg}^{-1}$  \*molality has been expressed per kg of (IL + water) solvent mixture).

**Table S10.** Refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of L-Methionine in aqueous IL (BTMAC) solution at 298.15K, 303.15K and 308.15K and pressure at 1.013bar\*

| Conc. of L-Methionine soln. in molality, m (mol.kg <sup>-1</sup> ) | $n_D$   |         |         | $\kappa$ (mS/cm) |         |         |
|--|---------|---------|---------|------------------|---------|---------|
|  | 298.15K | 303.15K | 313.15K | 298.15K          | 303.15K | 313.15K |
| 0.001Mil   |         |         |         |                  |         |         |
| 0.0010   | 1.3306  | 1.3303  | 1.3298  | 0.125            | 0.170   | 0.190   |
| 0.0025   | 1.3308  | 1.3305  | 1.3300  | 0.130            | 0.182   | 0.197   |
| 0.0040   | 1.3309  | 1.3306  | 1.3301  | 0.142            | 0.198   | 0.219   |
| 0.0055   | 1.3310  | 1.3308  | 1.3302  | 0.149            | 0.204   | 0.248   |
| 0.0070   | 1.3311  | 1.3309  | 1.3303  | 0.158            | 0.213   | 0.252   |
| 0.0085   | 1.3312  | 1.3310  | 1.3304  | 0.169            | 0.223   | 0.264   |
| 0.003Mil   |         |         |         |                  |         |         |
| 0.0010   | 1.3308  | 1.3304  | 1.3300  | 0.300            | 0.330   | 0.380   |
| 0.0025   | 1.3310  | 1.3306  | 1.3302  | 0.337            | 0.350   | 0.392   |
| 0.0040   | 1.3311  | 1.3308  | 1.3303  | 0.350            | 0.366   | 0.396   |
| 0.0055   | 1.3312  | 1.3309  | 1.3304  | 0.354            | 0.374   | 0.412   |
| 0.0070   | 1.3313  | 1.3310  | 1.3305  | 0.362            | 0.386   | 0.435   |
| 0.0085   | 1.3314  | 1.3311  | 1.3306  | 0.374            | 0.405   | 0.455   |
| 0.005mIL   |         |         |         |                  |         |         |
| 0.0010   | 1.3311  | 1.3305  | 1.3302  | 0.481            | 0.550   | 0.600   |
| 0.0025   | 1.3312  | 1.3307  | 1.3304  | 0.490            | 0.563   | 0.612   |
| 0.0040   | 1.3313  | 1.3308  | 1.3305  | 0.502            | 0.573   | 0.622   |
| 0.0055   | 1.3314  | 1.3309  | 1.3307  | 0.513            | 0.588   | 0.633   |
| 0.0070   | 1.3315  | 1.3311  | 1.3308  | 0.518            | 0.598   | 0.645   |
| 0.0085   | 1.3317  | 1.3312  | 1.3309  | 0.532            | 0.612   | 0.660   |

\*Standard uncertainties values of  $u$  are:  $u(T) = 0.01K$  (0.68 level of confidence), #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095$  mol. kg<sup>-1</sup>\*molality has been expressed per kg of (IL + water) solvent mixture

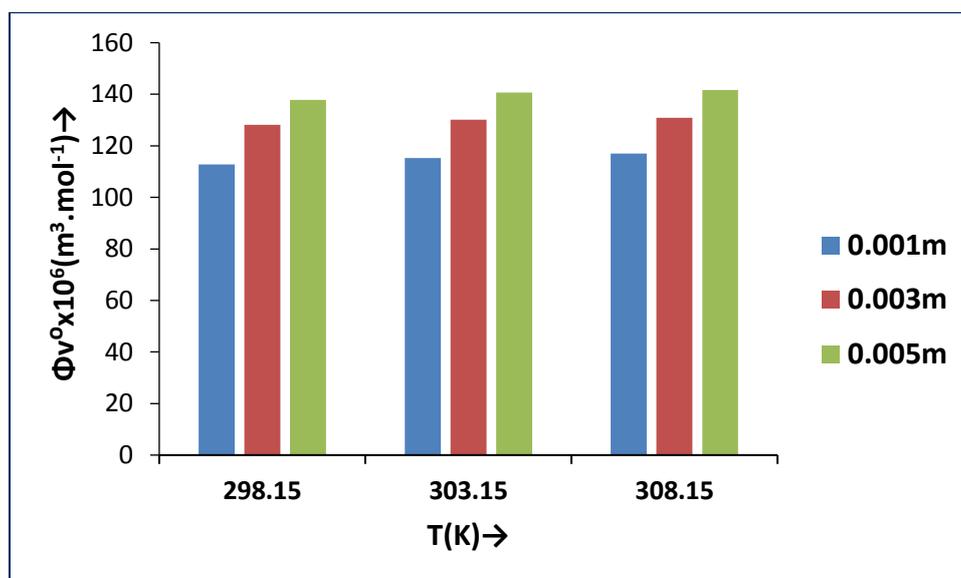
**Table S11.** Refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of L-Methionine in aqueous IL (BTEAC) solution at 298.15K, 303.15K and 308.15K and pressure at 1.013bar\*

| Conc. of L-Methionine soln. in molality, m (mol.kg <sup>-1</sup> ) | $n_D$   |         |         | $\kappa$ (mS/cm) |         |         |
|--|---------|---------|---------|------------------|---------|---------|
|  | 298.15K | 303.15K | 308.15K | 298.15K          | 303.15K | 308.15K |
| 0.001Mil   |         |         |         |                  |         |         |
| 0.0010   | 1.3310  | 1.3308  | 1.3307  | 0.110            | 0.120   | 0.140   |
| 0.0025   | 1.3312  | 1.3310  | 1.3310  | 0.120            | 0.133   | 0.152   |
| 0.0040   | 1.3314  | 1.3312  | 1.3312  | 0.129            | 0.146   | 0.168   |
| 0.0055   | 1.3316  | 1.3313  | 1.3313  | 0.141            | 0.156   | 0.176   |
| 0.0070   | 1.3318  | 1.3315  | 1.3315  | 0.144            | 0.168   | 0.190   |
| 0.0085   | 1.3320  | 1.3316  | 1.3317  | 0.150            | 0.179   | 0.206   |
| 0.003Mil   |         |         |         |                  |         |         |
| 0.0010   | 1.3311  | 1.3310  | 1.3308  | 0.290            | 0.310   | 0.330   |
| 0.0025   | 1.3314  | 1.3312  | 1.3310  | 0.300            | 0.322   | 0.345   |
| 0.0040   | 1.3316  | 1.3314  | 1.3313  | 0.310            | 0.330   | 0.354   |
| 0.0055   | 1.3318  | 1.3316  | 1.3315  | 0.317            | 0.345   | 0.363   |
| 0.0070   | 1.3319  | 1.3317  | 1.3316  | 0.324            | 0.352   | 0.371   |
| 0.0085   | 1.3321  | 1.3318  | 1.3317  | 0.334            | 0.360   | 0.389   |

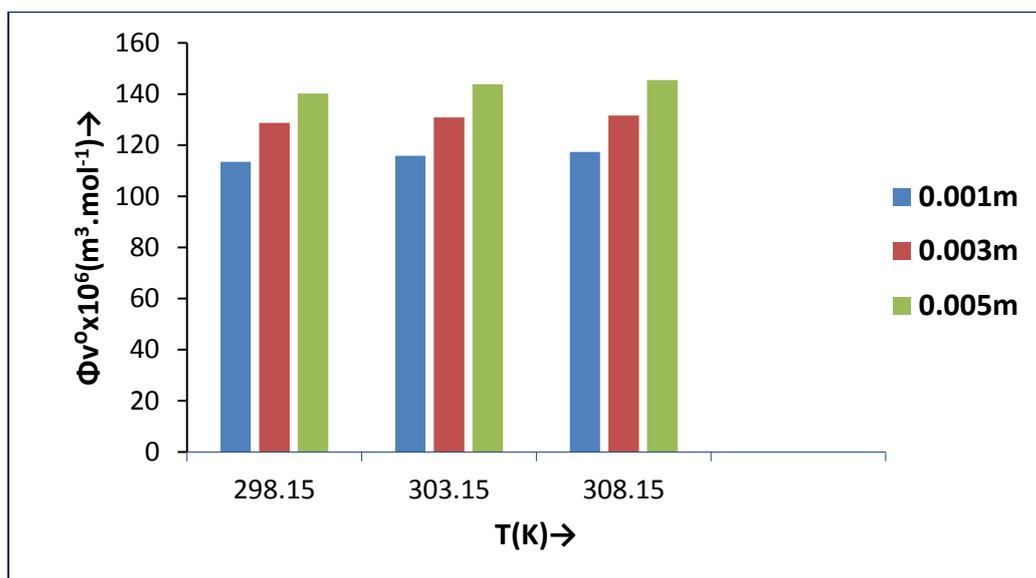
|          |        |        |        |       |       |       |
|----------|--------|--------|--------|-------|-------|-------|
| 0.005mIL |        |        |        |       |       |       |
| 0.0010   | 1.3314 | 1.3312 | 1.3310 | 0.470 | 0.520 | 0.540 |
| 0.0025   | 1.3317 | 1.3314 | 1.3312 | 0.480 | 0.533 | 0.552 |
| 0.0040   | 1.3319 | 1.3315 | 1.3314 | 0.492 | 0.540 | 0.562 |
| 0.0055   | 1.3320 | 1.3316 | 1.3315 | 0.498 | 0.553 | 0.574 |
| 0.0070   | 1.3322 | 1.3317 | 1.3317 | 0.511 | 0.565 | 0.583 |
| 0.0085   | 1.3323 | 1.3318 | 1.3318 | 0.527 | 0.576 | 0.604 |

\*Standard uncertainties values of  $u$  are:  $u(T) = 0.01\text{K}$  (0.68 level of confidence), #Combined standard uncertainty in molality according to mass purity of the samples is estimated to be  $\pm 0.0095 \text{ mol. kg}^{-1}$  \*molality has been expressed per kg of (IL + water) solvent mixture.

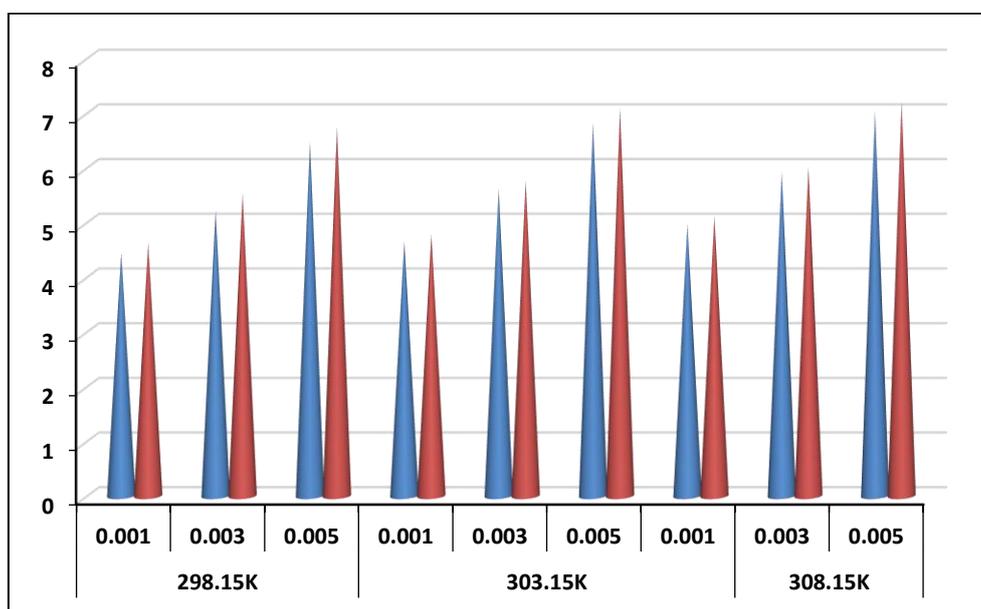
## Figures



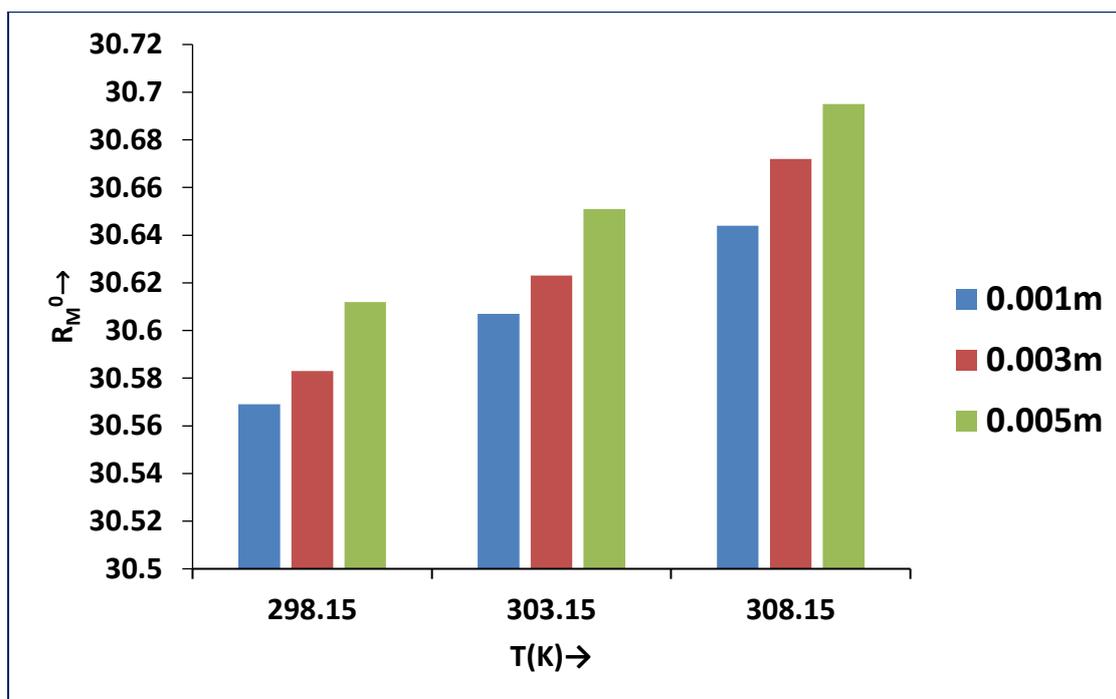
**Figure 1** .Variation of limiting apparent molar volume ( $\Phi_v^0$ ) of L-methionine as a function of temperature ( $T/\text{K}$ ) and different concentrations of(0.001,0.003,0.005)m aqueous BTMAC solutions



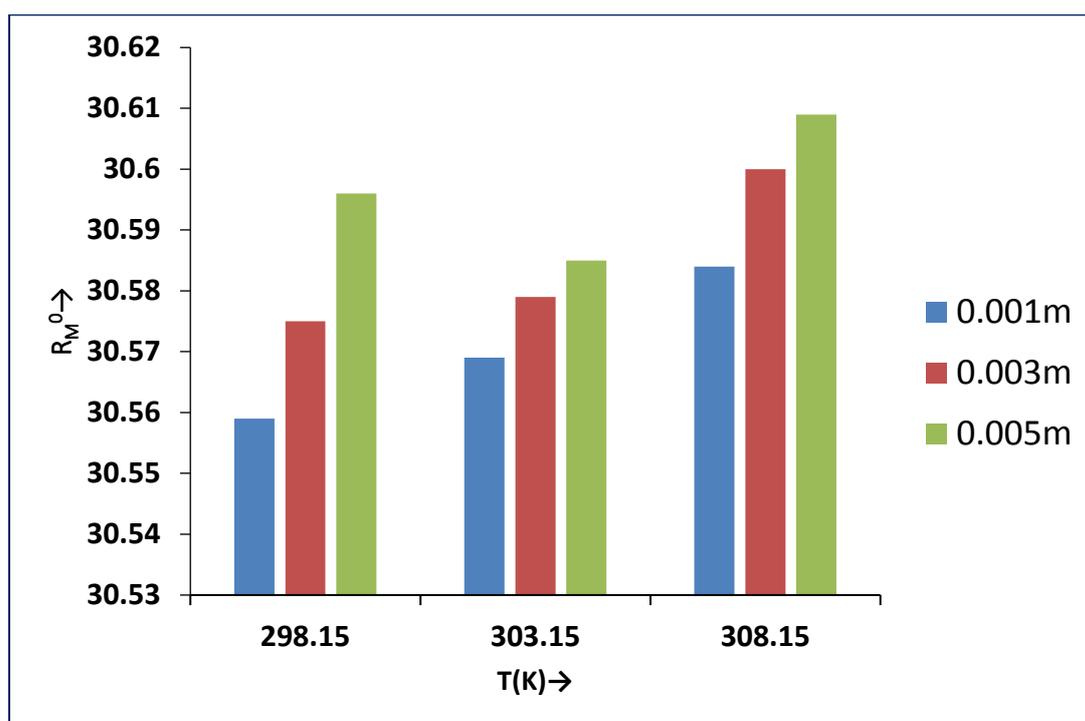
**Figure 2** .Variation of limiting apparent molar volume ( $\Phi_v^0$ ) of L-methionine as a function of temperature ( $T/\text{K}$ ) and different concentrations of(0.001,0.003,0.005)m aqueous BTEAC solutions



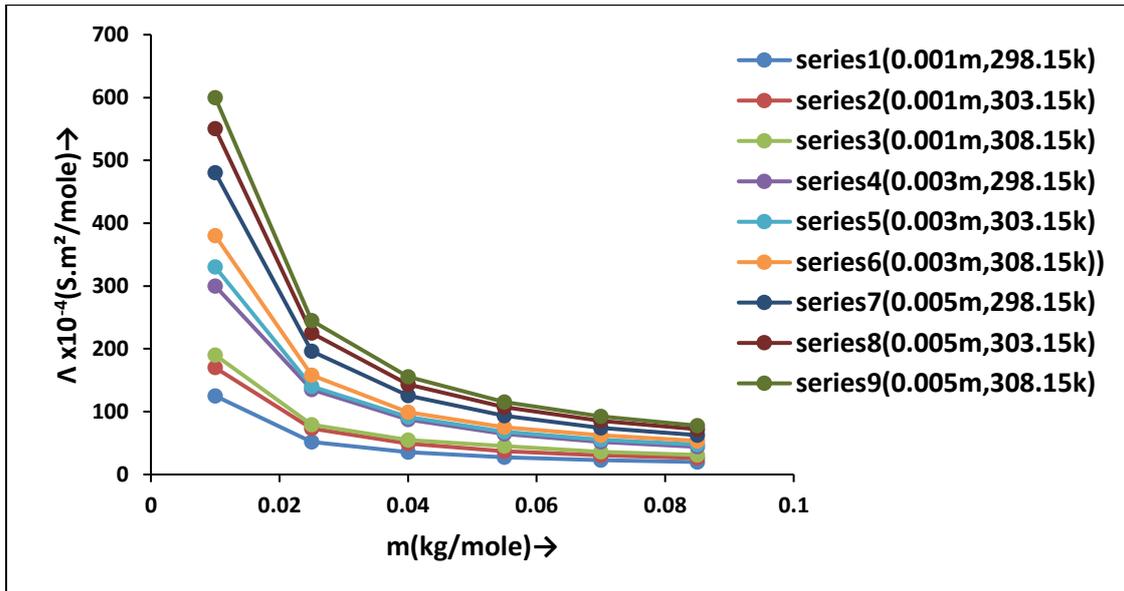
**Figure 3.**Variation of viscosity B-coefficient of L-methionine as a function of different temperature( $T/\text{K}$ ) and different concentrations of aqueous BTEAC (IL) and BTMAC (IL) solutions



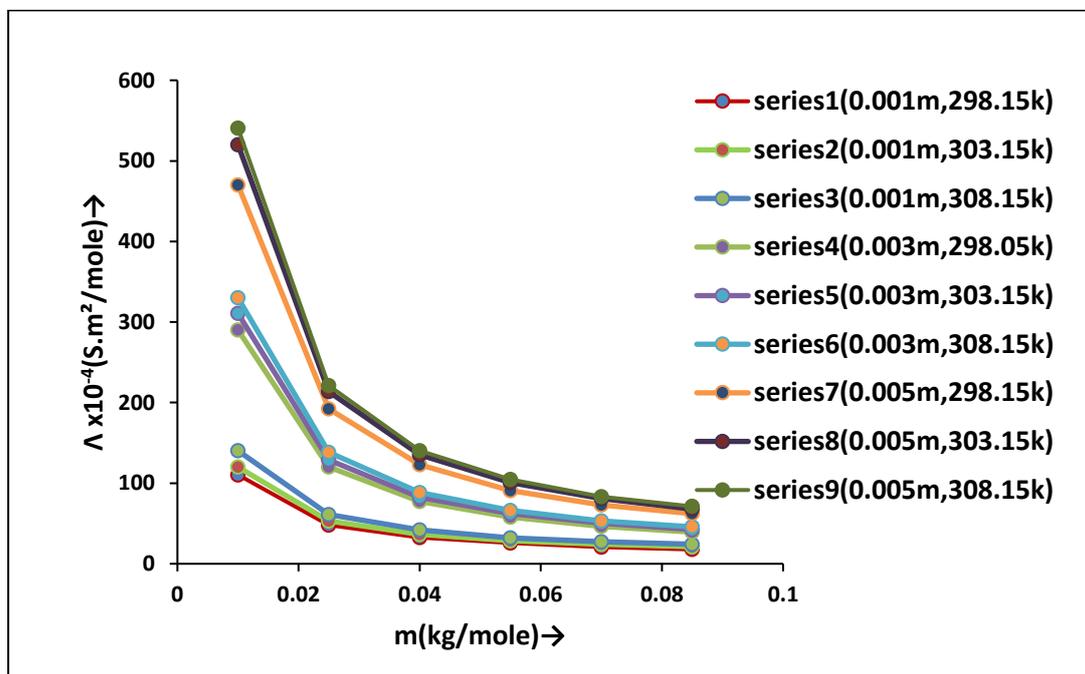
**Figure 4.** Variation of Limiting Molar refraction ( $R_M^0$ ) of L-methionine as a function of temperature ( $T/K$ ) and different concentrations of (0.001,0.003,0.005)m aqueous BTMAC solutions



**Figure 5.** Variation of Limiting Molar refraction ( $R_M^0$ ) of L-methionine methionine as a function of temperature ( $T/K$ ) and different concentrations of (0.001,0.003,0.005)m aqueous BTEAC solutions



**Figure 6.** Variation of molar conductance ( $\Lambda$ ) plot as a function of the concentration of L-Methionine (amino acid) in different concentrations of aqueous BTMAC solutions at different temperatures ( $T/K$ )



**Figure 7.** Variation of molar conductance ( $\Lambda$ ) plot as a function of the concentration of L-Methionine (amino acid) in different concentrations of aqueous BTEAC solutions at different temperatures ( $T/K$ )

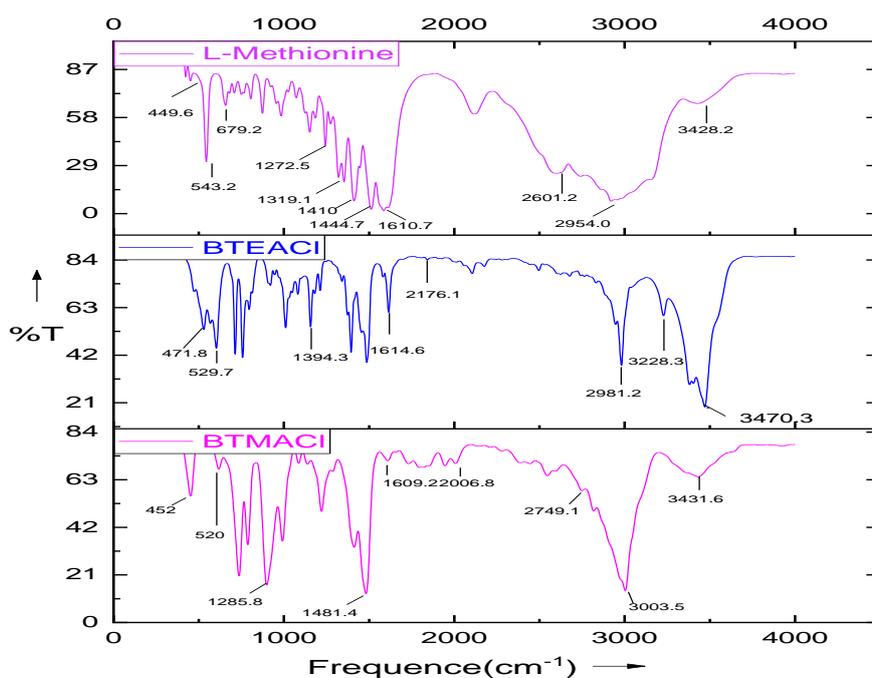


Figure A1. FTIR Spectrum of pure ILs (BTMAC & BTEAC) and AA (L-Met)

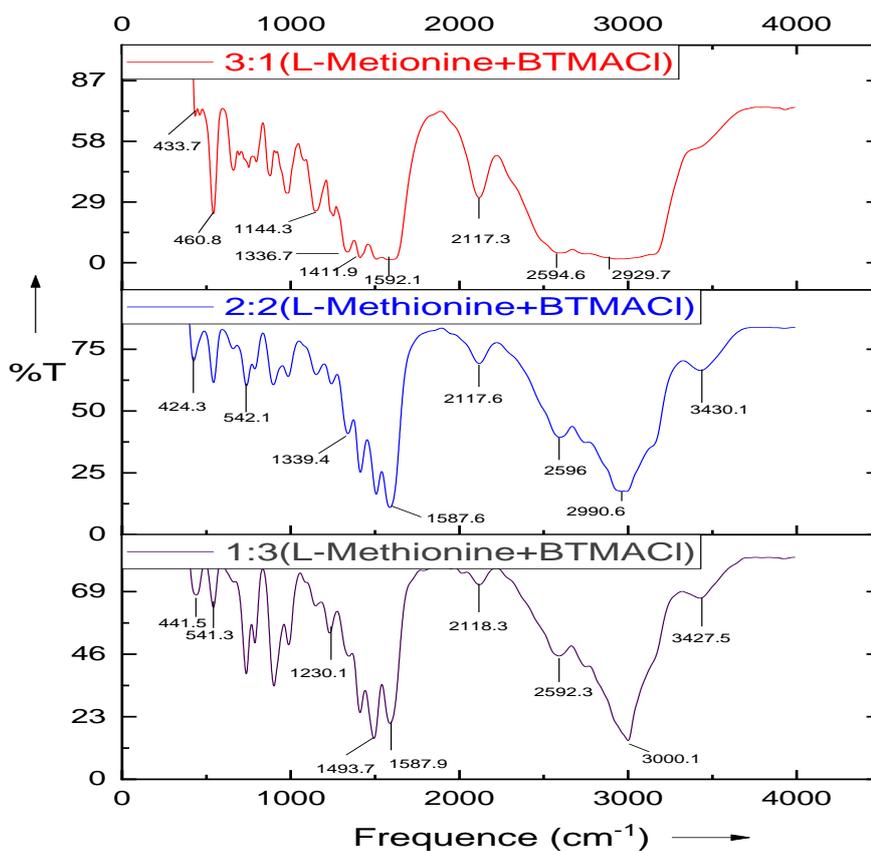


Figure A2. FTIR Spectrum of L-Met + BTMAC Mixture (AA:IL=1:3,2:2,3:1)

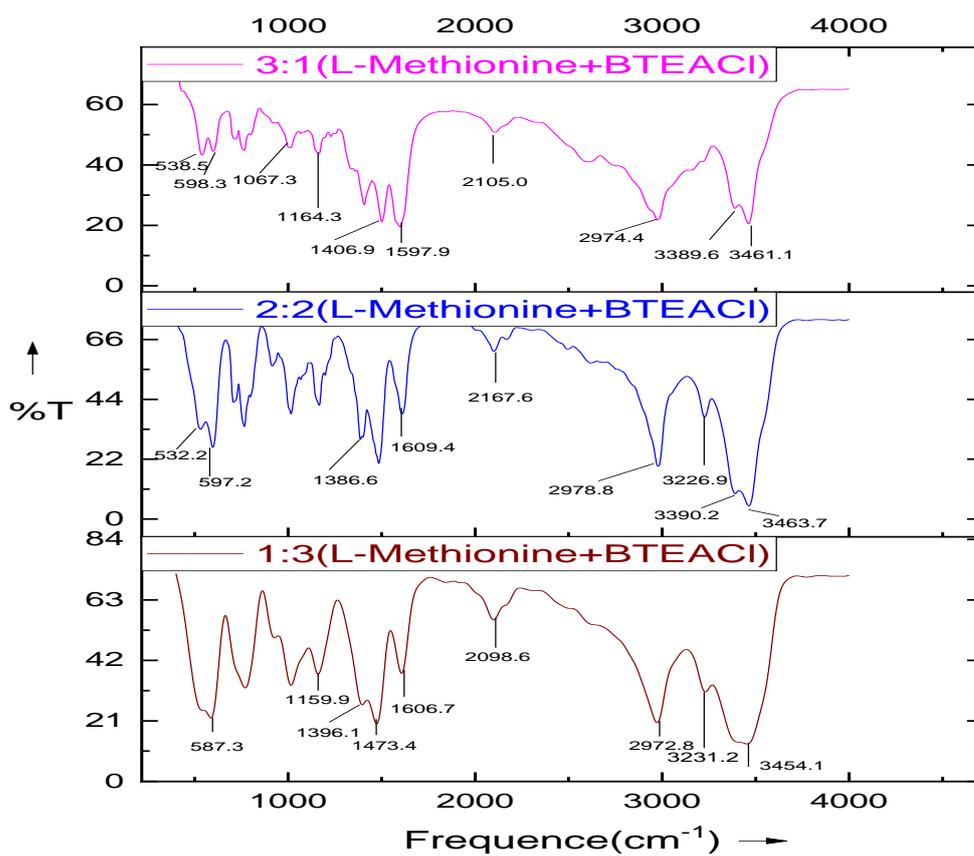


Figure A3. FTIR Spectrum of L-Met + BTEAC Mixture (AA:IL=1:3, 2:2, 3:1)

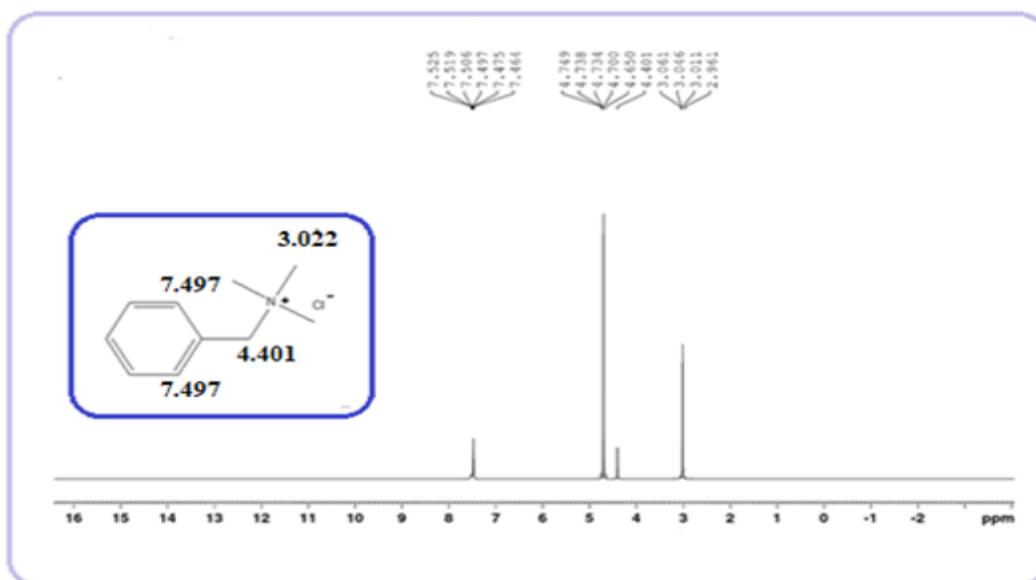


Figure B1.  $^1\text{H-NMR}$  Spectrum of pure BTMAC in  $\text{D}_2\text{O}$

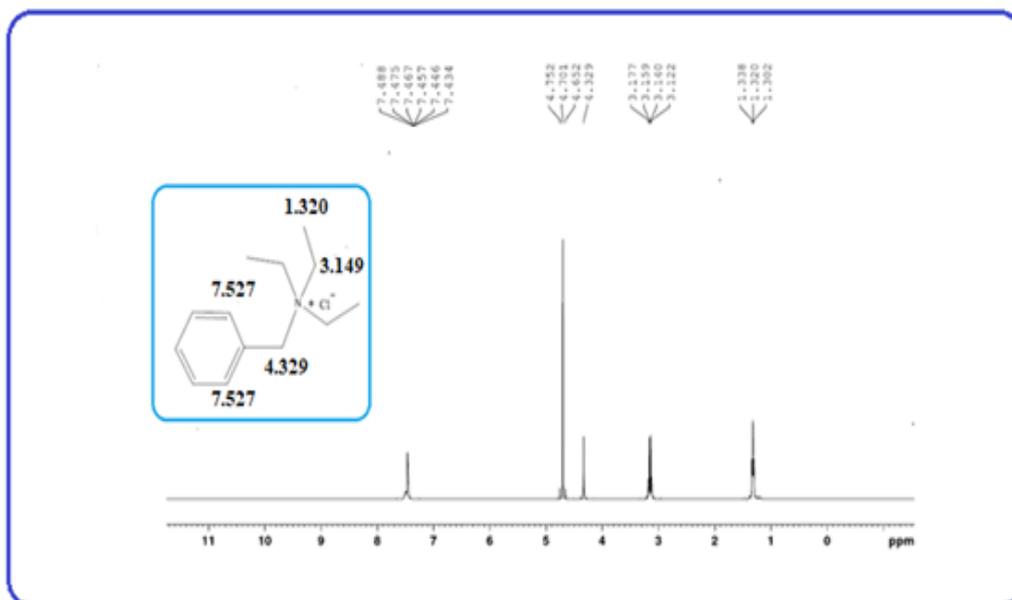


Figure B2. <sup>1</sup>H-NMR Spectrum of pure BTEAC in D<sub>2</sub>O

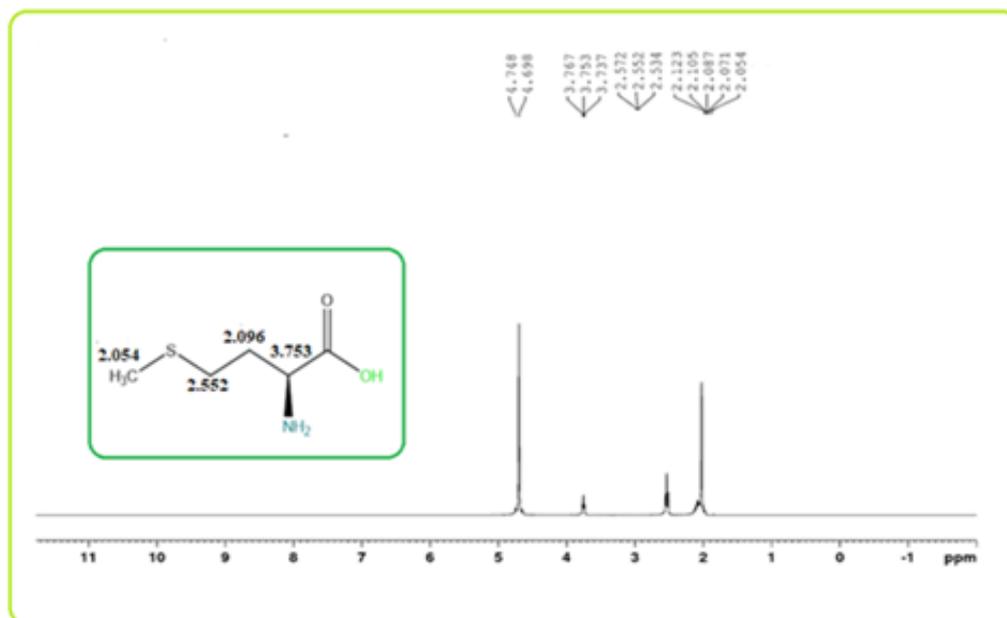
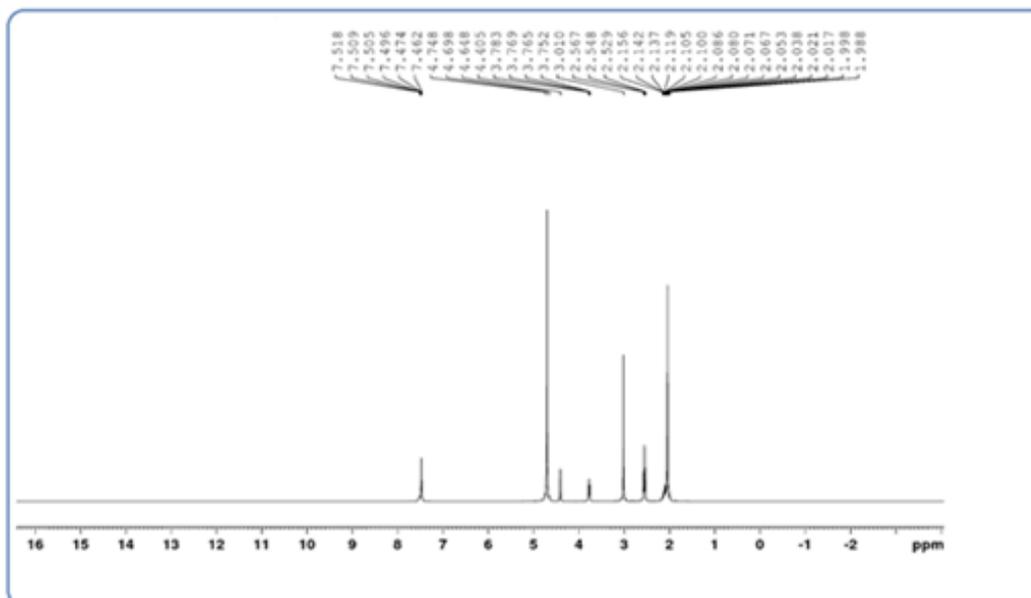
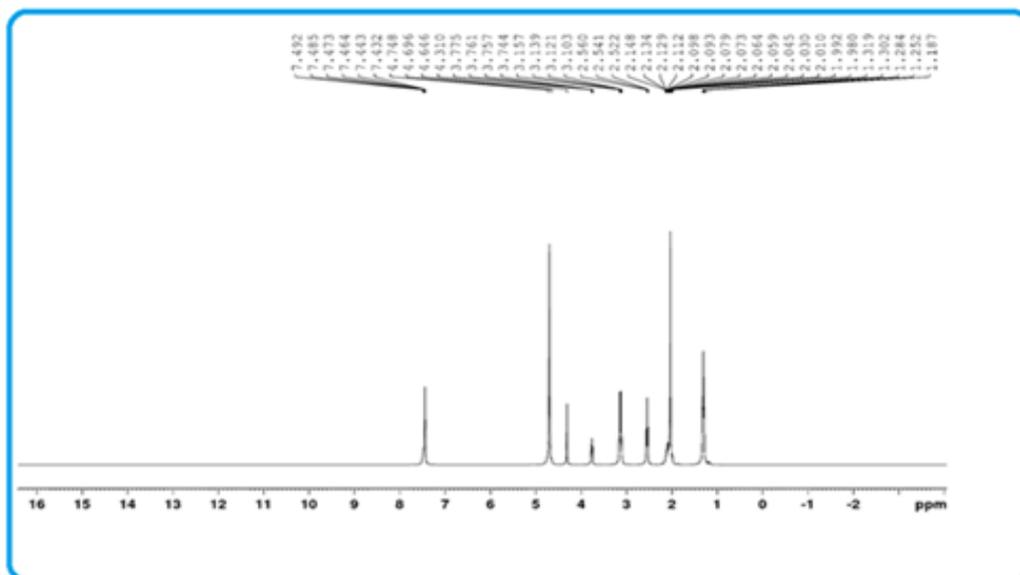


Figure B3. <sup>1</sup>H-NMR Spectrum of pure L-Methionine in D<sub>2</sub>O



**Figure B4.**  $^1\text{H-NMR}$  Spectrum of L-Met + BTMAC(AA:IL=4:1) in  $\text{D}_2\text{O}$



**Figure B5.**  $^1\text{H-NMR}$  Spectrum of L-Met + BTEAC (AA:IL=4:1) in  $\text{D}_2\text{O}$

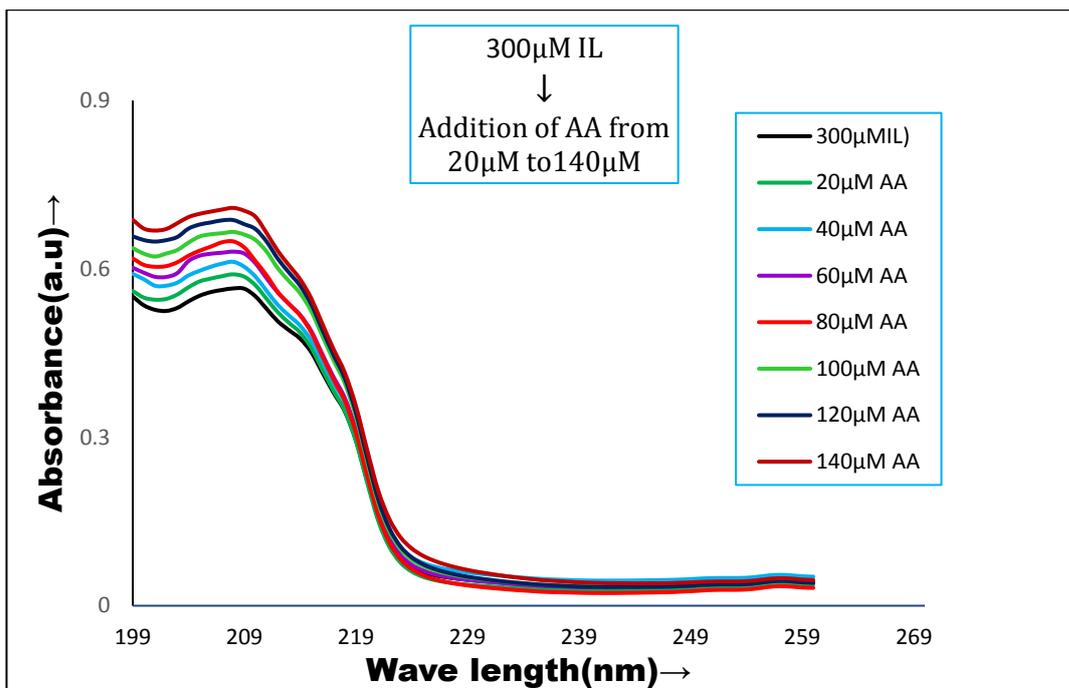


Figure C1. UV-Vis spectra of (BTMAC+L-Met) system

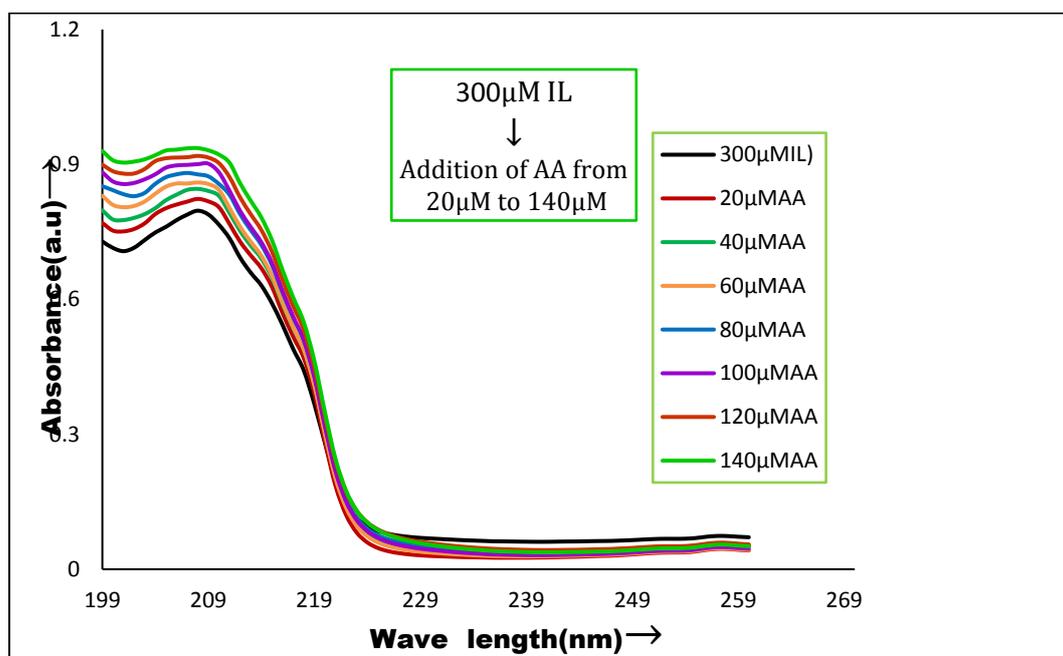


Figure C2. UV-Vis spectra of (BTEAC+L-Met) system

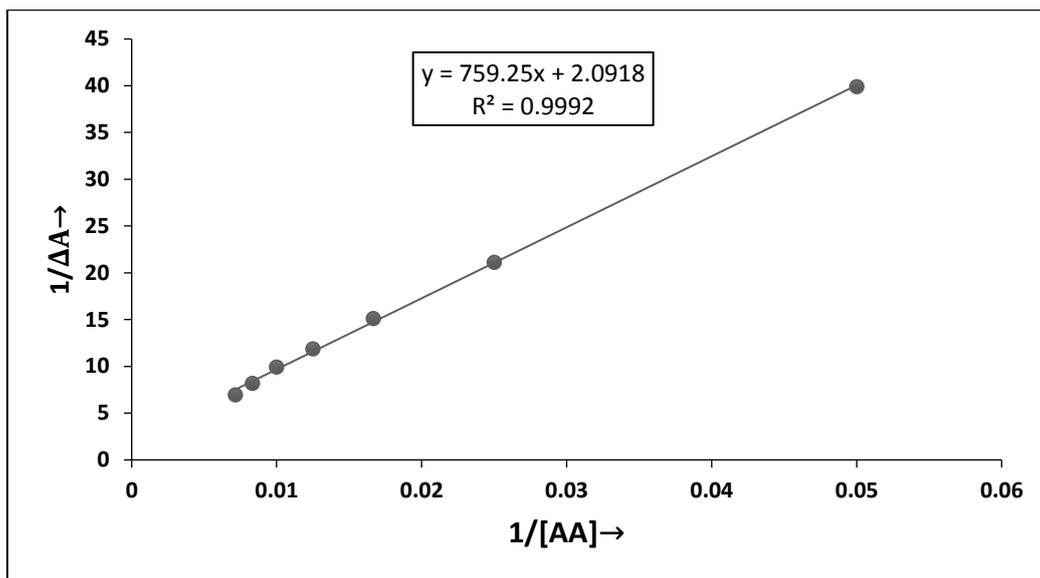


Figure C3. Benesi double reciprocal plot of BTMAC+L-Met system

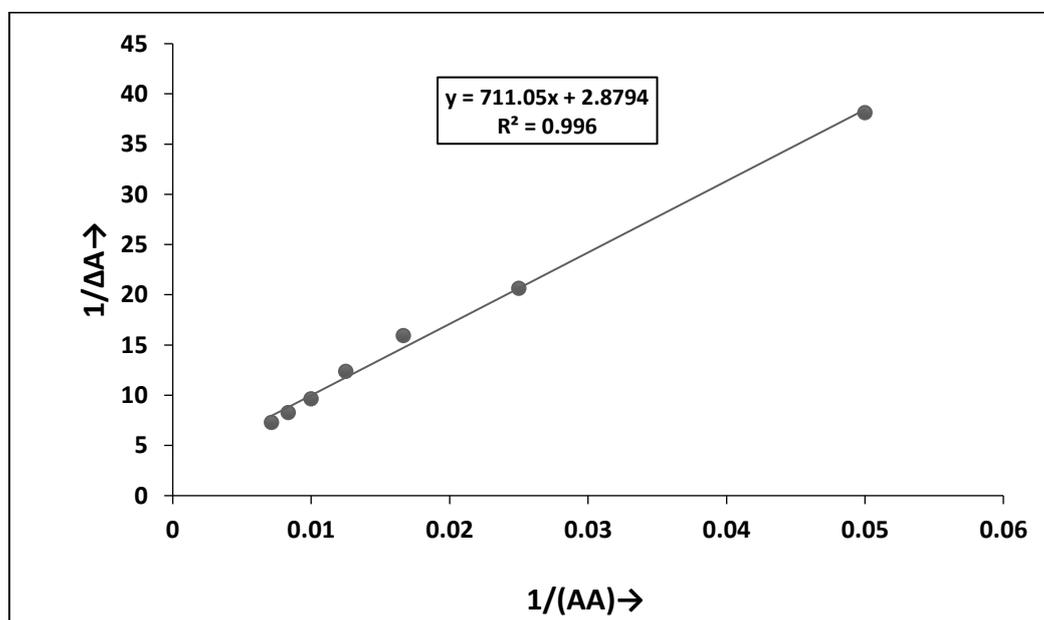
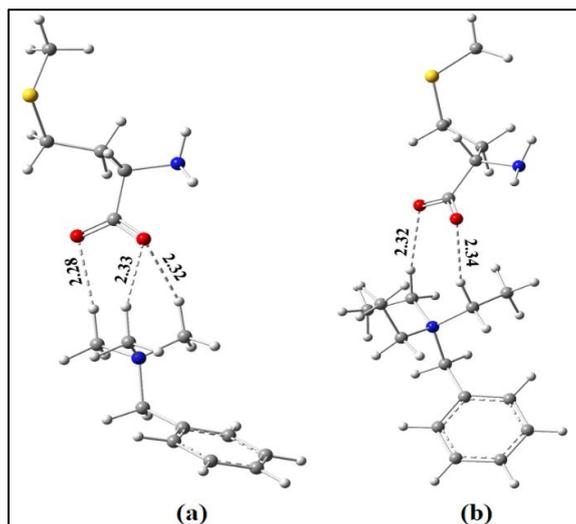
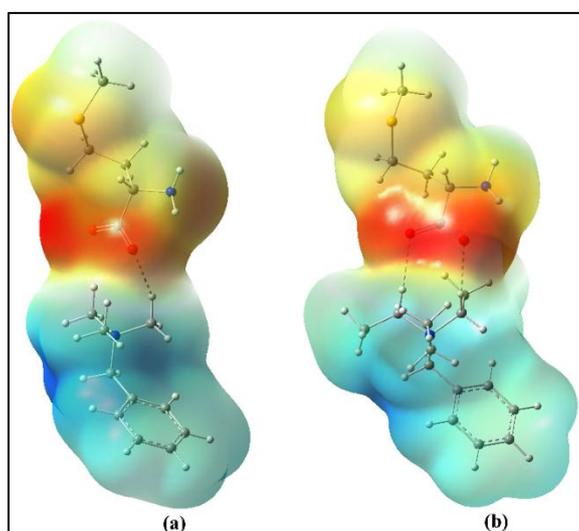


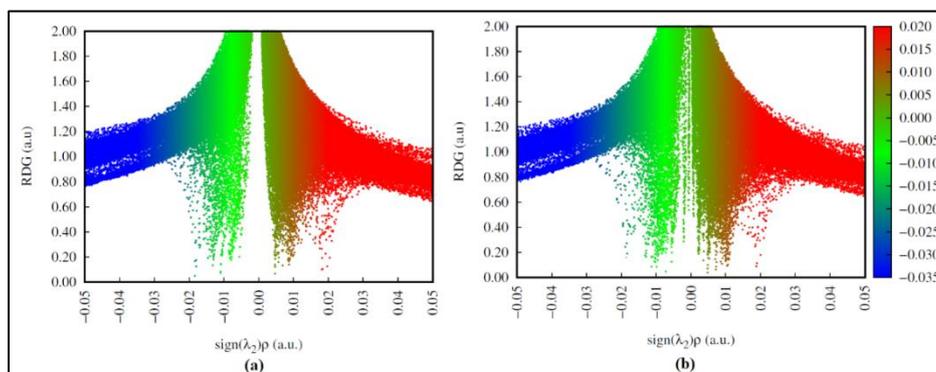
Figure C4. Benesi double reciprocal plot of BTEAC+L-Met system



**Figure C5:** Optimized geometries of the (a) L-Met-BTMAC (b) L-Met-BTEAC in aqueous solution

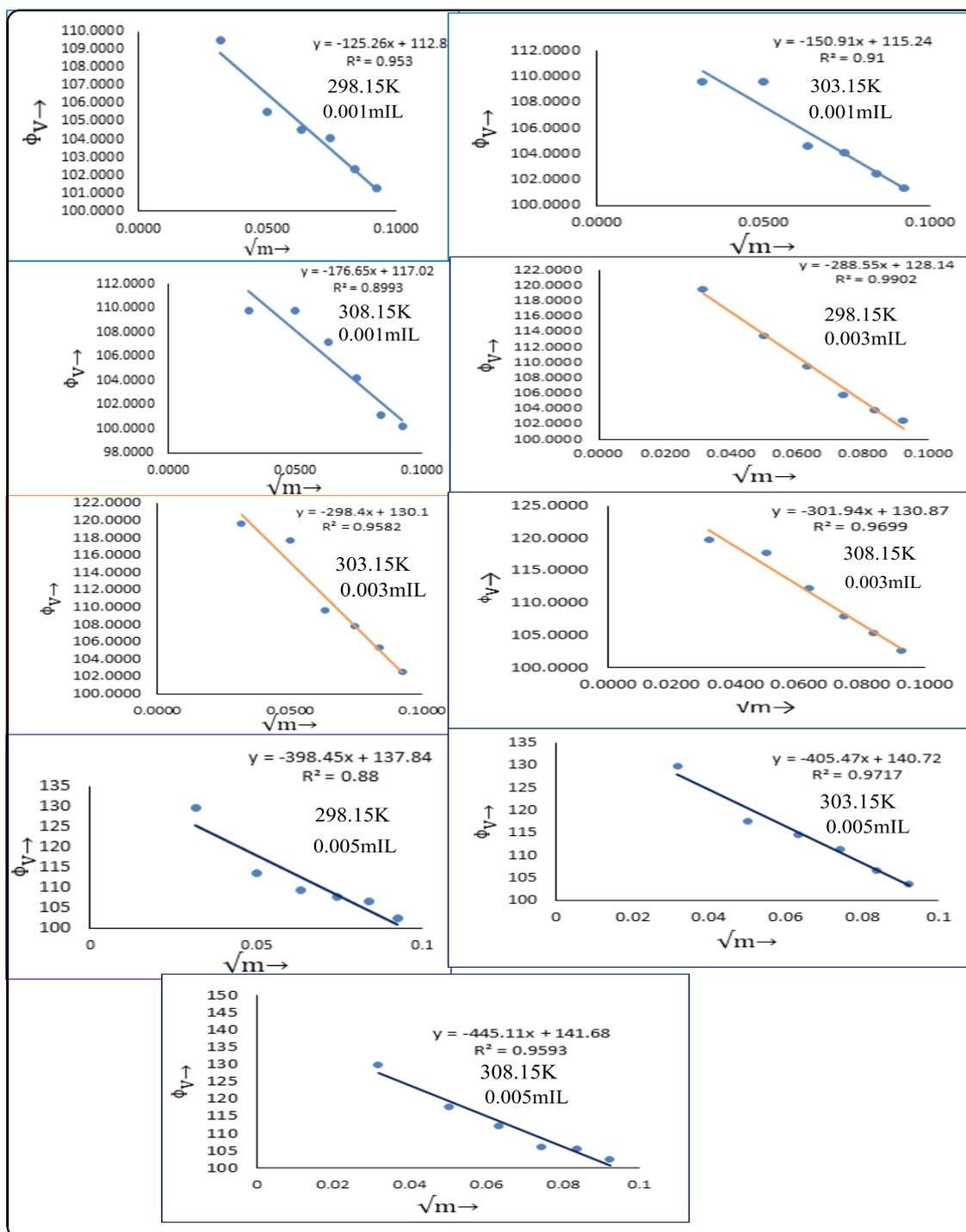


**Figure C6:** Electrostatic potential maps for (a) L-Met-BTMAC (b) L-Met-BTEAC in aqueous medium

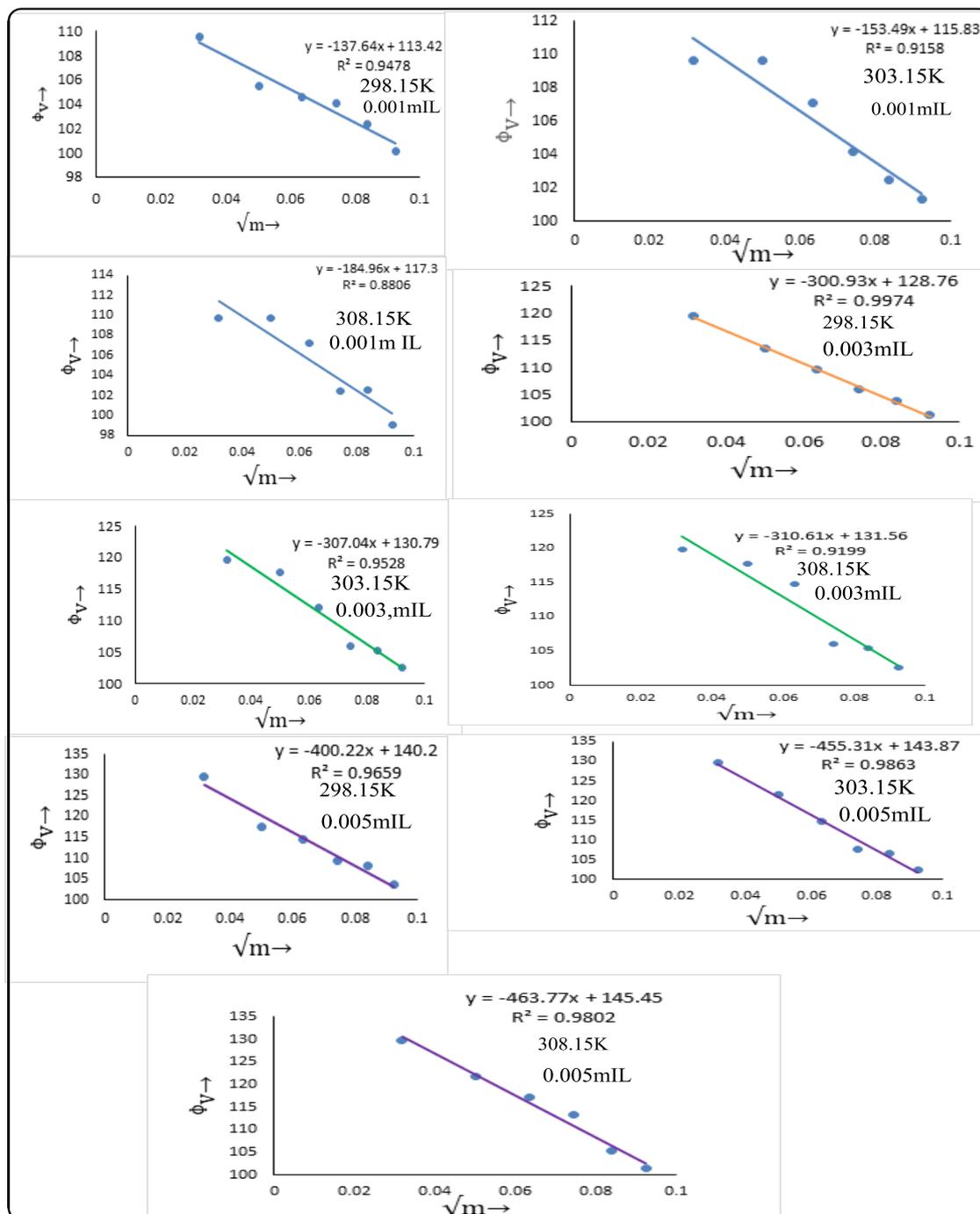


**Figure C7:** Plots of reduced density gradient (RDG) for (a) L-Met-BTMAC (b) L-Met-BTEAC composites

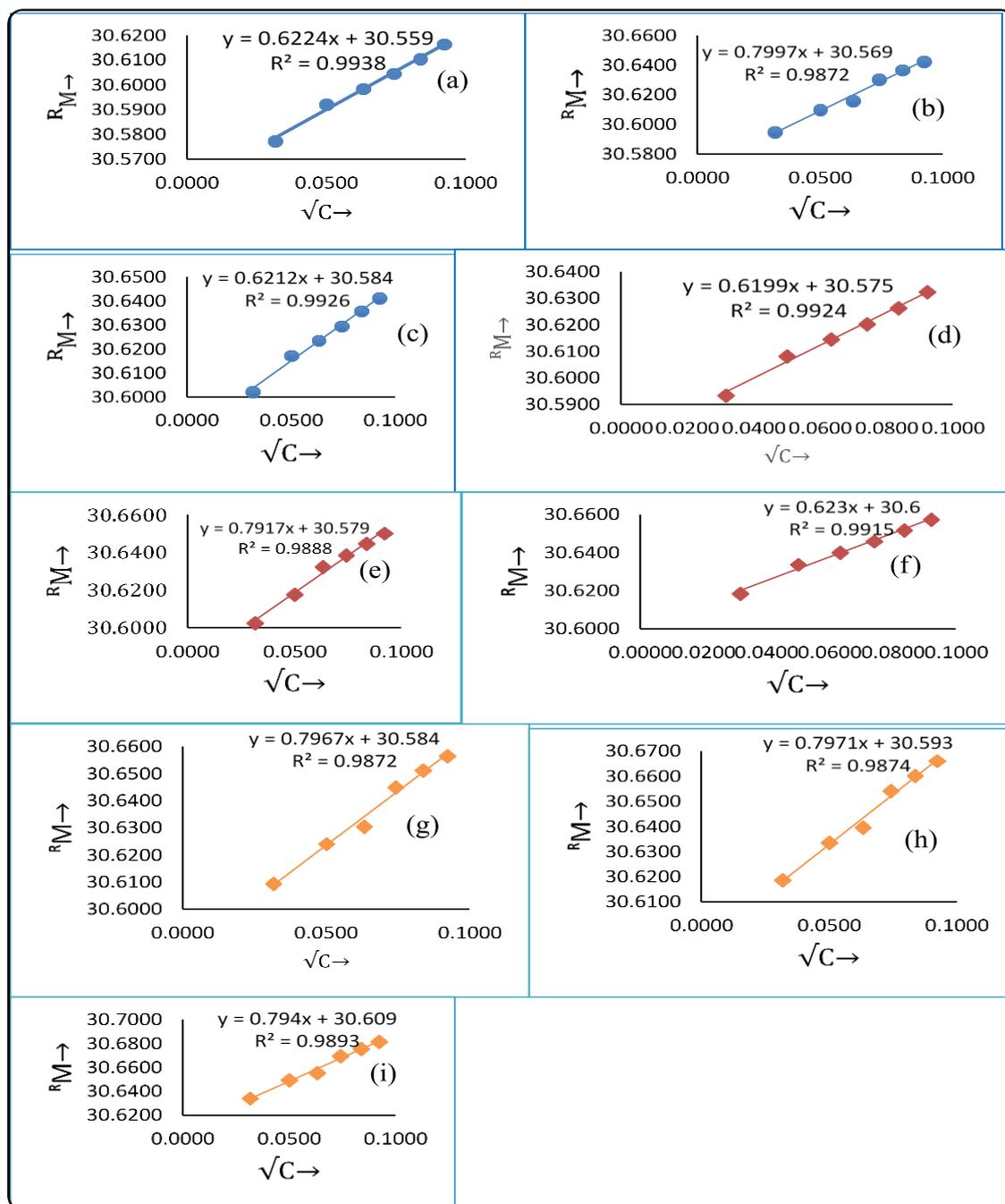
## Supporting figures



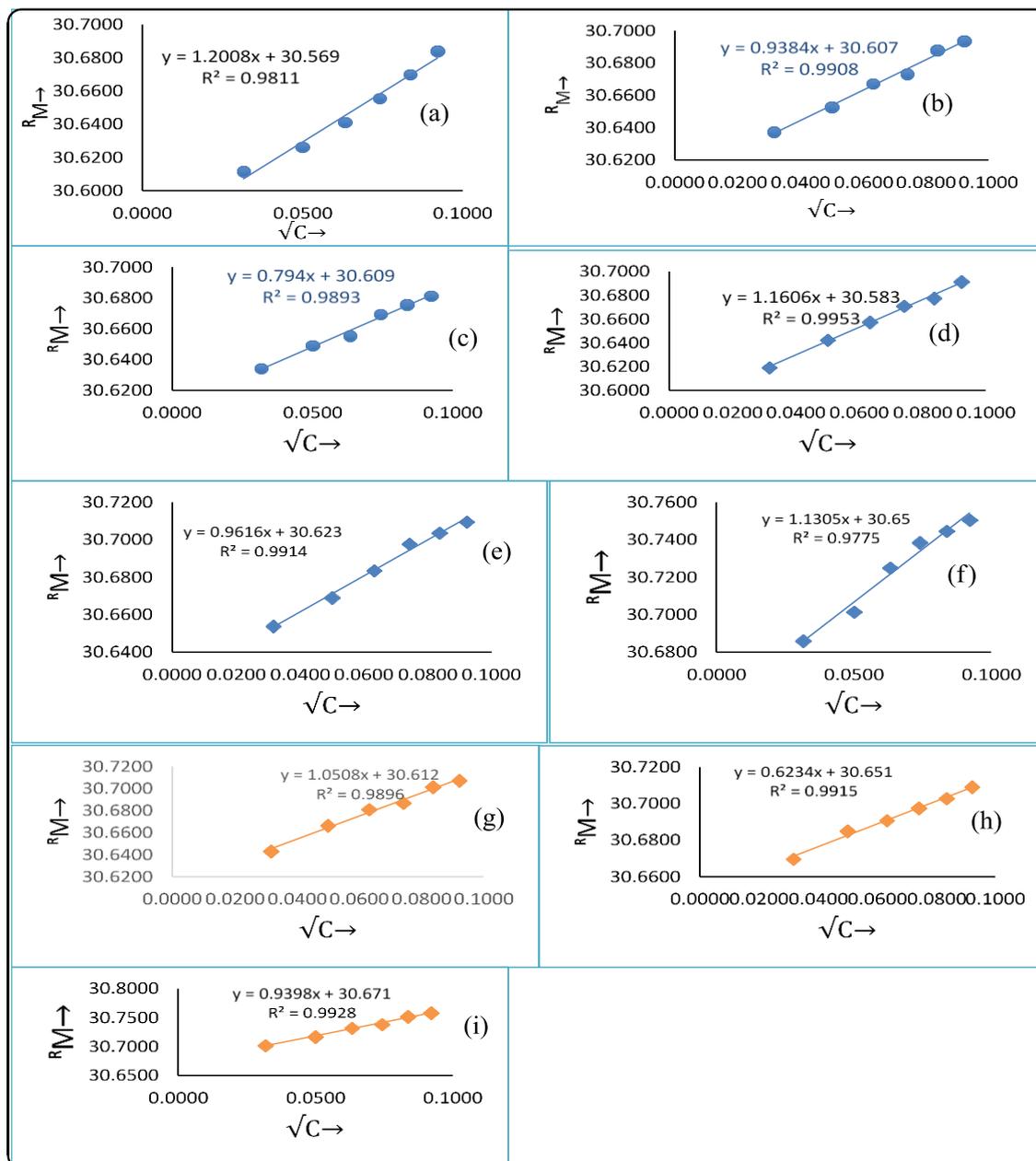
**Figure S1.** Variation of Apparent molar volume,  $\Phi_v$  of L-methionine solutions with concentration,  $\sqrt{m}$  against different temperature in 0.001m, 0.003m, 0.005m aqueous IL (BTMAC) solutions



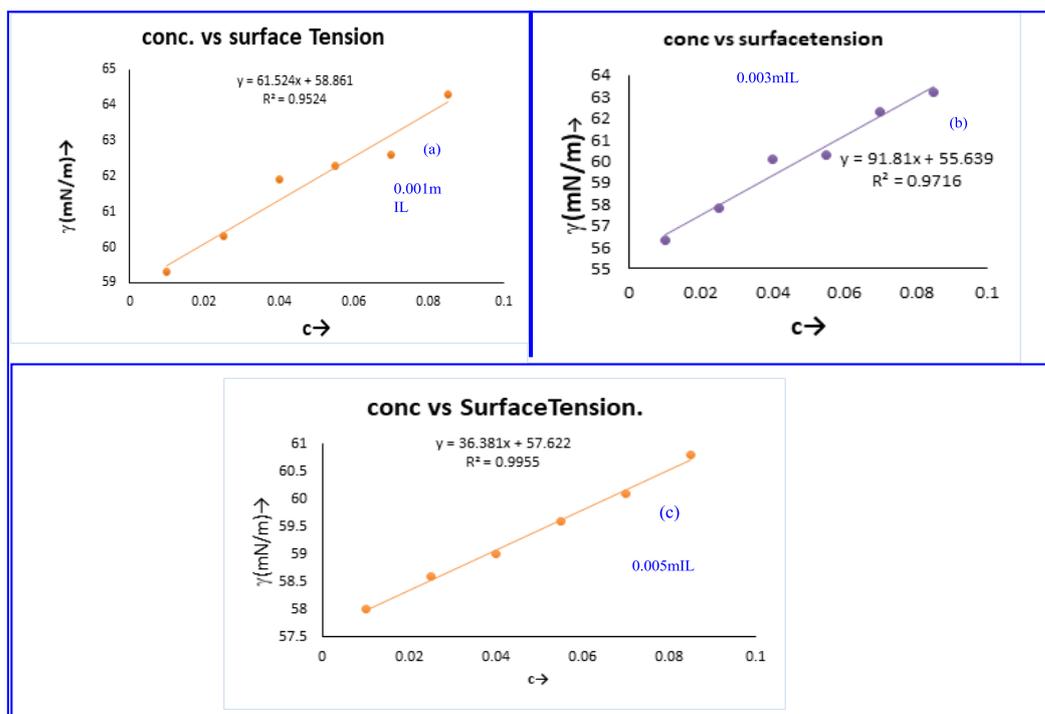
**Figure S2.** Variation of Apparent molar volume,  $\Phi_v$  of L-methionine solutions with concentration,  $\sqrt{m}$  against different temperature in 0.001m, 0.003m, 0.005m aqueous IL (BTEAC) solutions



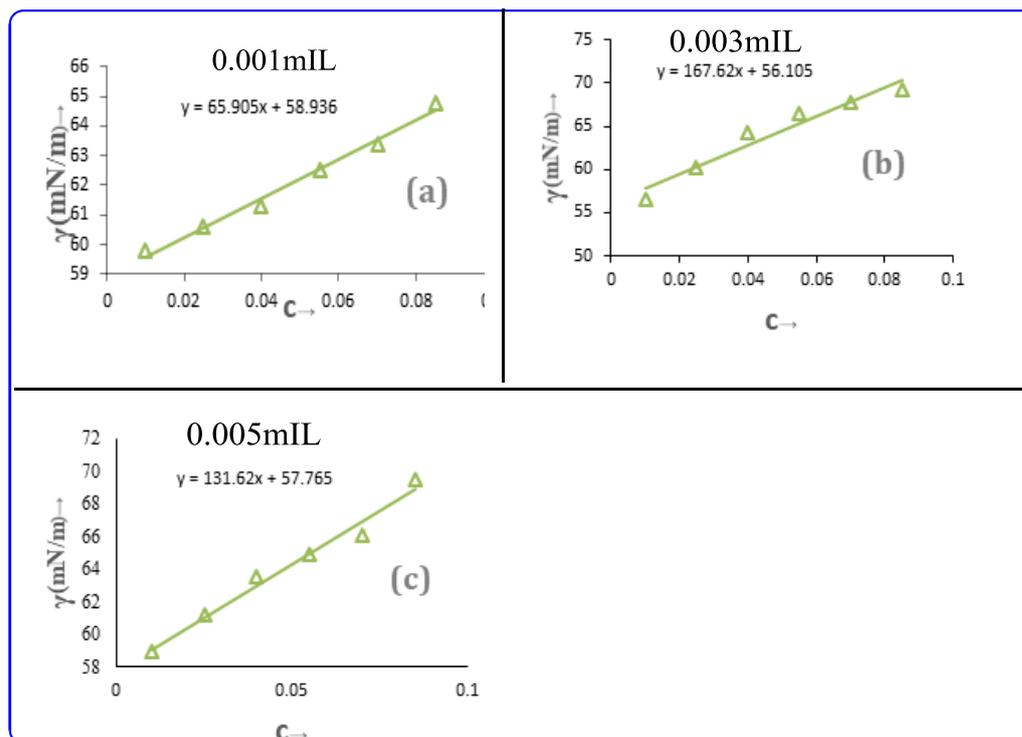
**Figure S3.** Variation of Molar refraction,  $R_M$  plot (a,b,c,d,e,f,g,h,i) of L-methionine against concentration,  $\sqrt{C}$  at different temperature in 0.001m, 0.003m, 0.005m aqueous solutions of IL(BTMAC)



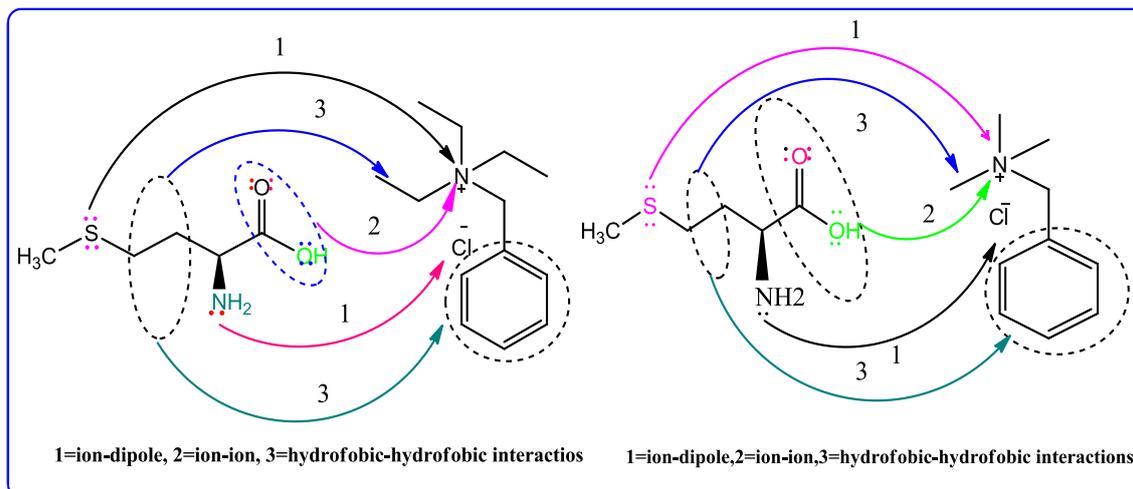
**Figure S4.** Variation of Molar refraction,  $R_M$  plot (a,b,c,d,e,f,g,h,i) of L-methionine against concentration,  $\sqrt{C}$  at different temperature in 0.001m, 0.003m, 0.005m aqueous solutions of IL (BTEAC)



**Figure S5.** Variation of surface tension plot ( $\gamma$ ) (a ,b , c ) with different conc. of L-methionine at room temperature in 0.001m, 0.003m, 0.005m aqueous solutions of ionic liquid (BTMAC)



**Figure S6.** Variation of surface tension ( $\gamma$ ) plot (a ,b , c ) with different conc. of L-methionine at room temperature in 0.001m, 0.003m, 0.005m aqueous solutions of ionic Liquid(BTEAC)

**Schemes**

**Scheme 1.** Plausible molecular interactions between the ionic liquids, BTMAC and BTEAC with the amino acid, L-Methionine

## CHAPTER-IX

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# SOLVATION BEHAVIOUR OF L-ASPARAGINE AND L-GLUTAMINE PREVAILING IN AQUEOUS IONIC LIQUID SOLUTION BY PHYSICOCHEMICAL AND COMPUTATIONAL INVESTIGATIONS

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**Abstract:** Physicochemical properties (Density, viscosity, refractive index, conductivity and surface tension) of L-Asparagine and L-Glutamine in aqueous solution of an ionic liquid, benzyltributylammonium chloride, have been measured at 0.001m, 0.003m, 0.005m concentrations and at 298.15K, 303.15K and 308.15K temperatures. <sup>1</sup>H-NMR Spectroscopy also applied to ascertain the molecular interaction in solute-solvent systems. There are some important physicochemical parameters that have been derived from the above physicochemical experiments namely as limiting apparent molar volume ( $\phi_V^0$ ) and viscosity *B*-coefficients using extended Masson equation and Jones-Dole equation respectively. The limiting molar refraction and molar refractive index ( $R_M$ ) values obtained of the solutions by using the very popular equation( Lorentz-Lorenz equation). Specific Conductivity measurement of the experimental solution which applied to ascertain ionic nature of the system. Optimization energy calculation by the computational technique leads to the consequence of stability of ternary system (solute-solvent system) in molecular level.

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**Keywords:** Solute-cosolute interactions, apparent molar volume, viscosity B-coefficient, molar refraction, conductivity, NMR spectroscopy, Computational study.

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### 1. Introduction

Ionic liquids (ILs) are greener organic solvents that are large chemical window and liquids at or near room temperature in their pure form. They have been extensively used in a number of fields in both academia and industry and exhibit many useful advantages such as a low melting point (<373 K), are liquid over a wide temperature

range, and have suitable viscosity, thermal stability, and the ability to dissolve a diversity of chemicals, and most importantly, insignificant vapor pressure [1,2]. Ionic liquids have been proposed as green and benign replacements for traditional volatile organic solvents, and a rising number of applications in the fields of catalysis, chemical reactions, separations, electrochemistry, nanoscience and bioscience so far considered [3,4]. So the cationic ionic liquid Benzyltributylammonium chloride (BTBAC) having hydrophobic and hydrophilic part, attracted immense interest in the development of methods for separation, purification, extraction of DNA; and also been tested for gene delivery and gene transfection that involve in recent clinical trials based on gene therapy [5].

**L-Glutamine** is an amino acid commonly found as a component in total parenteral nutrition. L-Glutamine is the most plentiful free amino acid in the body. L-Glutamine is produced in the muscles and is distributed by the blood to the organs that need it. Glutamine might help intuitive function, the immune system, and other crucial processes in the body, especially in times of stress. L-asparaginase has been used extensively for the treatment of acute lymphoblastic leukemia on the supposition that the circulating L-asparagine is vital for leukemic cells which appear to lack the ability of creating L-asparagine. However, the use of L-asparaginase and L-glutamine involves several problems, such as hypersensitivity, antibody formation, rebound phenomenon due to the rapid induction of liver L-asparagine synthetase [6].

To overcome these biological problems, the enzyme was immobilized in solid drug carriers, such as microspheres and liposomes, giving a higher stability against denaturation and reduced immunogenicity. Also, it was reported that L-glutaminase used together with L-asparaginase reduced the rebound phenomenon. Here, we perform the physicochemical, computational and spectroscopic investigation of L-glutamine and L-asparagine with the cationic ionic liquid.

Measurements of density, viscosity and refractive index, conductivity, surface tension of aqueous IL solution with amino acids have not been made over significant temperature and concentration ranges. These measurements are important for elucidation of ion-solvent, ion-ion and solvent-solvent interactions in aqueous ternary ( $H_2O + IL +$  amino acid) systems [6-9].

Therefore, in present study we have endeavoured to make ascertain nature of interaction of solute itself (amino acid) and with co-solute IL in  $w_I=0.001, 0.003$  and

0.005 mass fraction of aqueous medium at different temperatures (298.15K, 303.15K and 313.15K) to explain various noncovalent interactions foremost in the ternary systems under investigation.

## 2. Experimental section

### 2.1 Source and purity of materials

Benzyltributylammonium chloride and L-Asparagine and L-Glutamine were purchased from Sigma-Aldrich, Germany. The mass fractions purity of these three chemicals were  $\geq 0.98$ ,  $\geq 0.99$  and  $\geq 0.99$  respectively. All the reagents were always stored in the desiccators over  $P_2O_5$  to keep them in dry environment. These chemicals were then subsequently applied as received without further purification.

### 2.2 Apparatus and procedure

Aqueous (deionised, doubly distilled) solubility of the benzyltributylammonium chloride (IL) and L-Asparagine and L-Glutamine has been checked prior to start of the experimental work and perceived that all the reagent are freely soluble in all proportion of aqueous solution. The stock solution of 0.001m, 0.003m and 0.005m concentration of IL were prepared by mass (Mettler Toledo AG-285 with uncertainty 0.0003g) in doubly distilled water. L-Asparagine and L-Glutamine solutions were made by mass and then the working solutions (six sets) were prepared by mass dilution. The conversion of molarity into molality [10] has been done using experimental density values of respective solutions.

The densities ( $\rho$ ) of the experimental solutions were measured by the vibrating u-tube Anton Paar digital density meter (DMA 4500M) having a precision of  $\pm 0.00005$  g.cm<sup>-3</sup> with maintained at  $\pm 0.01$  K of the anticipated temperature. Apparatus was calibrated by passing deionised, triply distilled water and then dry air [11].

The viscosities ( $\eta$ ) of the studied solution were measured using a Brookfield DV-III Ultra Programmable Rheometer with fitted spindle size-42. The detail description of the instrument has already been described earlier [12].

Refractive indices ( $n_D$ ) were measured from the Digital Refractometer Mettler Toledo. The light source was LED,  $\lambda=589.3$ nm. The refractometer was calibrated twice using distilled water and then calibration was checked after every few measurements [13]. The uncertainty of refractive indices measurement was  $\pm 0.0002$  units.

Specific conductivity of the solutions was measured through Systronics- 308 conductivity meter of working frequency 1 kHz with an accuracy of  $\pm 1\%$ . The calibration of conductivity cell was done and determination of cell constant that proposed by the technique as suggested by Lind et al.[14]. The cell constant was carried out using freshly prepared 0.01 M aqueous KCl solution and it was maintained within the range 0.09–1.00  $\text{cm}^{-1}$  during the experiment. All the solutions were placed in a dip-type immersion conductivity (CD-10) cell with a cell constant of about  $(0.1 \pm 0.001) \text{cm}^{-1}$ . The cell was attached to a temperature-controlled water bath to sustain the investigational temperature.

K9 digital Tensiometer (Kruss GmbH, Hamburg, Germany) instrument was used to determine the surface tension of different concentrations of mixed and pure experimental solutions. The accuracy of the instrument was  $\pm 0.1(\text{mN/m})$ . For the determination of surface tension( $\sigma$ ) the platinum ring detachment technique was used. The calibration of the K9 digital Tensiometer was carried out with doubly distilled water and the calibration value of surface tension( $\sigma$ ) was found to be 71.8 mN/m which is in good agreement with the literature values of surface tension 71.57 mN/m[15]. This tensiometer is a very good precision instrument that contains a solid and vibration-free base. This instrument puts on such a place that same demand on its neighbour as a laboratory balance with a resolution of 0.1 mg. In addition, a clean and dust-free atmosphere is needed for the measurements of surface tension.  $^1\text{H}$  NMR study, spectra were recorded at 600 MHz Bruker advance at  $T = 298.15 \text{ K}$  in  $\text{D}_2\text{O}$  for obtaining the  $^1\text{H}$  NMR spectra as well as chemical shifts for various protons.

### 3. Result and Discussion

The physical parameters of binary mixtures in different mass fractions ( $w_1=0.001, 0.003, 0.005$ ) of aqueous ionic liquid(IL) solutions at three different temperatures ( 298.15K,303.15K,308.15K) and at 1.013 bar have been stated in table 1&2. The experimental measured values of density and viscosity of L-Asparagine and L-Glutamine as a function of concentration (molality), in different mass fractions of aqueous ionic liquid (IL) mixture at above mentioned temperatures have been given in **Table 3&4.**

### 3.1 Apparent molar volume

Calculation of apparent molar volume ( $\varphi_V$ ) and the limiting apparent molar volume ( $\varphi_V^0$ ) of solutions both were consider as a substantial tools for understanding of interactions taking place in ternary solution systems. Therefore, the apparent molar volumes ( $\varphi_V$ ) determined from the solutions densities using the suitable equation [16] and the values are given in **Table 5&6**.

$$\varphi_V = \frac{M}{\rho} - (\rho - \rho_0) / m\rho\rho_0 \quad (1)$$

where M stands for the molar mass of the solute, m signifies the molality of the solution,  $\rho$  and  $\rho_0$  imply the densities of the solution and solvent respectively. The  $\Phi_V$  values are positive and get decrease with the intensification of the concentration (molality) of (L-Glutamine + BTEAC + H<sub>2</sub>O) and (L-Asparagine + BTEAC + H<sub>2</sub>O) solutions. Conversely,  $\Phi_V$  values increase with the increase in temperature at all the concentrations of L-Glutamine and L-Histidine as well. The experimental values of  $\Phi_V$  also increase with an increase in mass fraction of the aqueous TBMS solution accordingly. It was further observed that L-Gluamine have  $\Phi_V$  values higher than that of L-Asparagine.

The limiting apparent molar volumes ( $\Phi_V^0$ ), i.e. apparent molar volume at infinite dilution were determined using a least-squares fitting linear method as the plots of  $\Phi_V$  versus square root of the molar concentration,  $\sqrt{m}$  using the Masson equation as follows [17] to analyse the different interactions taking place in the solutions:

$$\Phi_V = \Phi_V^0 + S_V^* \sqrt{m} \quad (2)$$

$\varphi_V^0$  denotes as the apparent molar volume at infinite dilution,  $S_V^*$  is signify as the experimental slope. At infinite dilution solute molecule is enclosed only by the solvent molecules and remains infinite distant from each other. Consequently, that  $\varphi_V^0$  is unaffected by itself interaction of L-Asparagine and L-Glutamine molecules and it is a measure only of the solute-cosolute interaction. limiting molar volume, values represented in **Table 7(a)&7(b)**

An inspection of **Table 7(a)&7(b)** shows that  $\varphi_V^0$  are large and positive for L-Glutamine compared to L-Asparagine at all the studied temperatures, suggesting the occurrence of strong solute-cosolute interaction in L-Glutamine than that of L-Asparagine (**scheme 1**). Comparing  $\varphi_V^0$  with  $S_V^*$  values show that the magnitude of  $\varphi_V^0$  is greater than  $S_V^*$ , suggesting that solute-cosolute interactions predominates over itself

interaction of solute molecules in all solutions at all studied temperatures. Moreover,  $S_V^*$  values are negative at all studied temperatures indicates force of itself interaction of L-Asparagine and L-Glutamine molecules is very poor.

Dependency of temperature of the limiting apparent molar volume ( $\Phi_V^0$ ), the temperature range 298.15K to 308.15K and the results obtained were found to follow the following polynomial equation:[18]

$$\Phi_V^0 = a_0 + a_1T + a_2T^2 \quad (3)$$

where,  $a_0$ ,  $a_1$  and  $a_2$  are the empirical coefficients depending on the nature of solute and mass fraction (W) of co-solvent whereas T is the temperature in Kelvin scale. **Table 8** shows the empirical coefficient values ( $a_0$ ,  $a_1$  and  $a_2$ ) of L-Asparagine and L-Glutamine in different concentration of the ILs BTBAC at 298.15K, 303.15K, 308.15K and pressure at 1.013bar. First derivative of Equation(4) gives the values of limiting apparent molar expansibilities ( $\Phi_E^0$ ) which have been calculated for various temperatures and listed in **Table 9(a)** and **Table 9 (b)** for L-Asparagine and L-Glutamine in BTBAC solution respectively at pressure 1.013bar.

$$\Phi_E^0 = (\delta\Phi_V^0 / \delta T)_P = a_1 + 2a_2T \quad (4)$$

Limiting apparent molar expansibilities ( $\Phi_E^0$ ) for all the systems are found positive except for 0.005m IL at 308.15K in BTMAC. It signifies the absence of caging or packing effect in the other solutions except this one. The solute–solvent interaction studied so far is now at a state that, it may be structure-breaker or synergistic structure-maker interaction. In this connection, Hepler developed a way to examine the nature of the solute–solvent interaction taking place in the solution phase.[19] According to Hepler, values of  $(\delta\Phi_E^0/\delta T)_P$  in the expression given below, determines whether, it is structure-breaker or structure-maker interaction:[20]

$$(\delta\Phi_E^0 / \delta T)_P = (\delta^2\Phi_V^0 / \delta T^2)_P = 2a_2 \quad (5)$$

On the basis of this expression, it has been deduced that structure-making solutes should have positive value, whereas structure-breaking solutes should have negative values. Here, the negative values listed in **Table 9(a)** and **Table 9(b)** respectively for L-Asparagine and L-Glutamine in BTBAC solution at different temperatures confirms the mode of solute–solvent interaction is structure-breaking and the structure-breaking effect is strongest in 0.001m aqueous BTEAC solution with highest packing or caging effect.

### 3.2 Viscosity

In aqueous electrolytic solutions the extent of ionic hydration and structural interactions[21-23] within the ionic hydration co-spheres [24] can be explored easily by

studying viscosity coefficient with varying concentration and temperature of the aqueous solution. The results in **Table 3** and **Table 4** show that the viscosity of the solutions increases with increasing molality of the ILs. The number of collisions among the molecules also increases upon increasing the molality of the ionic liquid (BTBAC), resulting in a loss of kinetic energy. Consequently, the molecules tend to stick together with increasing viscosity.

Viscosity data so obtained were analysed with the help of Jones-Dole equation:[25]

$$\eta_r = \eta / \eta^0 = 1 + A \sqrt{c} + Bc \quad (6)$$

where,  $\eta$  and  $\eta^0$  are viscosities of solution and solvent respectively,  $c$  is the concentration of solution in molarity. This is possibly due to stronger hydrophobic–hydrophobic interactions for longer alkyl chains of BTBAC.

Rearrangement of the above Equation (7) gives following:

$$(\eta_r - 1) / \sqrt{c} = A + B\sqrt{c} \quad (7)$$

Here, viscosity A-coefficient is a constant, also known as Falkenhagen coefficient,[26] stands for long-range coulombic forces, so represents the solute-solute interaction in solution, while B-coefficient is an adjustable parameter, which is the measure of the effective hydrodynamic volume that reflects the solute-solvent interaction. The value of viscosity B-coefficient which depends on the shape, size and partial molar entropies of the ions involving in solutions. According to the Jones-Dole equation from the plots of  $(\eta_r - 1) / \sqrt{c}$  vs  $\sqrt{c}$ , the viscosity A, B-coefficients obtained by linear least-square analysis, are reported in **Table 7(a)** and **Table 7 (b)** for L-Glutamine and L-Asparagine solutions in BTBAC at (298.15, 303.15 and 308.15)K and pressure at 1.013bar, respectively. **Figure 1** shows the variation of B values of L-Glutamine and L-Asparagine in aqueous solution of BTBAC respectively, against 0.001m IL, 0.003m IL and 0.005m IL solutions at different temperatures .

The viscosity B-coefficient is an empirical constant which depends on size and shape effects as well as structural effects induced by (solute+solvent) interactions.[27] In all cases the viscosity B-coefficients are larger compared to A-coefficients in the aqueous ionic liquid solutions which indicates promotion of the liquid structure in the presence of an ionic liquid, thus supporting the conclusions obtained from volumetric properties. It is observed From **Table 8(a)** and **Table 8 (b)**, that the values of the B-coefficient are positive, thereby suggesting the presence of strong solute-solvent interactions in solution, that strengthened with an increase in the solvent viscosity value, in accordance with the results obtained from  $\Phi_v^0$  values explained earlier. The values of the A-coefficient are found to very small as compared to B-coefficients. The above obtained results of A-coefficient indicate the presence of very weak solute–solute interactions.

These results are in outstanding agreement with those obtained from  $S_v^*$  values. The extent of solute–solvent interaction obtained from the B-coefficient occurs into the local vicinity of the solute molecules in the solutions. The higher B-coefficient values for higher viscosity values is due to the solvated solute molecules associated by the solvent molecules all around because of the formation of associated molecule by solute-solvent interactions.[24]

Furthermore, these types of interactions are strengthened with rise in temperatures. It shows that the solute-solvent interaction increases with increase in temperature and the concentration of the IL solutions with more interaction between L-Glutamine and L-Asparagine in aqueous BTBAC solutions. There placement of water molecules by more co-solvent molecules from the solvation sphere brings solute and co-solvent closer thereby increasing viscosity B-coefficients and accounts for the higher solute-solvent interaction. The overall viscometric studies show that, viscosity B-coefficients are positive and greater than viscosity A-coefficient, suggesting solute–solvent interaction is predominant over the solute-solute interaction.

Extensively study of the viscosity B-coefficient such that, its first derivative over temperature is an upgradation of viscosity B-coefficient in predicting the nature of solute–solvent interaction as structure-maker or structure-breaker. The value of  $dB/dT$  is a measure of activation energy required for the viscous flow in solution. This is the reason, why the measure of  $dB/dT$  is indicative towards the structure making or structure breaking ability than sign or magnitude of the B-coefficient.[28-30] Viscosity B-coefficients of L-Arginine and L-Glutamine solutions along with  $dB/dT$  values in different concentrations of the IL, BTBAC at (298.15, 303.15 and 308.15) K and pressure at 1.013bar are given in **Table 10(a)** and **Table 10(b)**, respectively. The negative value of  $dB/dT$  indicates as a structure-making (kosmotropic) properties of the system whereas the positive value signifies it as structure-breaking (chaotropic) properties of the system. Here the positive  $dB/dT$  values indicate the amino acid, L-Glutamine and L-Asparagine both behave as structure-breaker in the aqueous ionic liquid solutions BTBAC.

According to Eyring and co-workers [31], that the  $\Delta\mu_1^{0\ddagger}$ , the free energy of activation per mole of the solvent of viscous flow can be get from the given following equation

$$\eta_0 = \frac{hN}{V_1^0} \exp\left(\frac{\Delta\mu_1^{0\ddagger}}{RT}\right) \quad (8)$$

Where  $h$  denotes as Planck constant,  $N_A$  indicates Avogadro's number and  $V_1^0$  signify as the solvent's partial molar volume. The above equation reframe to get in the following form

$$\Delta\mu_1^{0\ddagger} = RT \ln (\eta_0 V_1^0 / hN_A) \quad (9)$$

Applying two Equations. (7) As well as (9) [32, 33] then the following equation can be attained

$$B = (V_1^0 - V_2^0) / 1000 + V_1^0 (\Delta\mu_1^{0\ddagger} - \Delta\mu_2^{0\ddagger}) / 1000 RT \quad (10)$$

Where  $V_2^0$  express as a limiting partial molar volume ( $\Phi_r^0$ ) of the solute present in the solution mixture, at infinite dilution,  $\Delta\mu_2^{0\ddagger}$  denotes ionic activation energy per mole of solute. Using the above equation (10) the following equation can be get

$$\Delta\mu_2^{0\ddagger} = \Delta\mu_1^{0\ddagger} + \frac{RT}{V_1^0} [B - (V_1^0 - V_2^0)] \quad (11)$$

According to transition state theory, solvent molecules also passes to the transition state by the viscous flow. The  $\Delta\mu_2^{0\ddagger}$  is the contribution of free energy transfer of ionic liquid from ground state to transition state. It was found from the **Table11** that the  $\Delta\mu_2^{0\ddagger}$  values are all positive and much higher than that of  $\Delta\mu_1^{0\ddagger}$  representing in the ground state, which indicates that the interaction between the two amino acid and the aqueous BTBAC mixture is stronger in the ground state than that in the transition state. The solute and solvent molecules are held together strongly in the ground state than that of in the transition state thereafter in the transition state distortion and breaking of intermolecular bond take place frequently (34). Moreover the value of  $\Delta\mu_1^{0\ddagger}$  increase with increasing the molality of the ionic liquid in the presence of amino acid which signify that with increasing the molality of ionic liquid in the ground state become more structured. To determination of entropy for activation,  $\Delta S_2^{0\ddagger}$  [34] in the experimental mixture of solutions, the following equation has been used

$$d(\Delta\mu_2^{0\ddagger}) / dt = - \Delta S_2^{0\ddagger} \quad (12)$$

From the plot of  $\Delta\mu_2^{0\ddagger}$  versus T, Using the least-squares method, the value of  $\Delta S_2^{0\ddagger}$  has been obtained from the negative slope.

Enthalpy of activation ( $\Delta H_2^{0\ddagger}$ ) has been calculated from the following relation (34)

$$\Delta H_2^{0\ddagger} = \Delta\mu_2^{0\ddagger} + T \Delta S_2^{0\ddagger} \quad (13)$$

The value of  $\Delta H_2^{0\ddagger}$ ,  $\Delta S_2^{0\ddagger}$  which show in the table the value of  $\Delta\mu_2^{0\ddagger}$  depend on both viscosity B-coefficient and limiting molar volume ( $\bar{V}_1^0 - \bar{V}_2^0$ ) of the solution in the presence of ionic liquid.

In view of Eakins et al. [32], for positive viscosity B-coefficient  $\Delta\mu_2^{0\ddagger} > \Delta\mu_1^0$  that indicates greater solute–solvent interactions resulting in the formation of the transition state followed by breaking and altering the intermolecular forces prevailing in the solvent structure of the medium [32,33]. For positive values of  $\Delta S_2^{0\ddagger}$  and  $\Delta H_2^{0\ddagger}$  suggest that the formation of transition state is associated with bond breaking and rising accordingly. However, any specific mechanism in this context is quite difficult to develop though the disordered state of the slip-plane may be proposed [34]. Finally, according to Feakins et al. model, as  $\Delta\mu_2^{0\ddagger} > \Delta\mu_1^{0\ddagger}$  the both the amino acid (L-Asparagine & L-glutamine) performs as structure breakers that again supports the  $dB/dT$  characteristics in an aqueous BTBAC mixture.

The ratio of  $(B/\Phi_r^0)$  which has a high value [35] indicates that the primary solvation shell is formed.

According to a **Table 12**, B-coefficients for both the amino acids increase with temperature (positive  $dB/dT$ ) and also the high value of the ratio  $(B/\Phi_r^0)$  signifying the construction of a primary solvation shell as structure-disruptor.

The ratio of  $(B/\Phi_r^0)$  which has a high value [35] indicates that the primary solvation shell is formed. according to a **Table 12**, ratio  $(B/\Phi_r^0)$  for both the amino acids(L-Asparagine and L-Glutamine) increase with increasing temperature and also the high value of the ratio  $(B/\Phi_r^0)$  suggesting the construction of a primary solvation shell as structure-disruptor.

### 3.3 Refractive Index

Optical data of refractive index of the studied systems has provided interesting information allied to molecular interactions, structure of solutions in these assay. The refractive index of mixing can be interrelated by the application of a composition dependent polynomial equation and molar refraction,  $R_M$  in solution. The refractive index of amino acids (L-Glutamine and L-Asparagine) solutions in ionic liquid(IL) are provided in **Table 13(a)** , **Table 13(b)** .

The molar refraction  $R_M$  can be evaluated from the Lorentz–Lorenz relation:[36]

$$R_M = \{(n_D^2 - 1) / (n_D^2 + 2)\} (M/\rho) \quad (14)$$

where  $R_M$ ,  $n_D$ ,  $M$  and  $\rho$  are the molar refraction, the refractive index, the molar mass and the density of the solution, respectively. The refractive index of a substance is

well-defined as the ratio of the speed of light in vacuum to that in the medium. Stated the definition of refractive index more simply, the refractive index of a compound describes its ability to refract light as it moves from one medium to another medium and thus, the higher the refractive index of a compound, the more the light is refracted.[37] As stated by Deetlefs et al. the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser.[38] Generally, refractive index of a system is the capability to refract light and hence it can simultaneously measure the compactness of that system.

Hence, it is observed that the refractive index ( $n_D$ ) **Table 13(a)** , **Table 13(b)** decrease but the molar refraction ( $R_M$ ) **Table 3** and **Table 4** increases with increase in temperature. However, both the parameters show an increase with increase in concentration of the amino acid and IL solutions. Again L-Glutamine in BTBAC have higher values than that of L-Asparagine in BTBAC solutions. This is in good agreement with the volumetric and viscometric results attained here. The higher refractive index shows that the molecules are more tightly packed in the solution.

The limiting molar refraction, ( $R_M^0$ ) listed in **Table 7 (a)**and **Table 7(b)** can be calculated using the following equation:

$$R_M = R_M^0 + R_S \sqrt{m} \quad (15)$$

where, 'm' is the molality of solution and  $R_M^0$  is the limiting molar refraction that signifies solute–solvent interaction. So, this measurement of molar refraction operates as an expensive tool for studying the molecular interaction in solution. Gradual increase in the values of  $R_M^0$  as shown in **Figure 2** and **Figure 3** with rise in mass fraction of co-solvent and temperature also signifies that solute–solvent interaction predominant over solute-solute interactions

### 3.4 Conductivity Study

The conductivity study of the L-Asparagine and L-Glutamine a for the interaction (solute – cosolute) in the aqueous solution of IL has been done at three different temperatures. Transport phenomena, molecular and ionic interaction in the ternary system gives some valuable information [39]. The specific conductivities ( $k$ ) of aqueous IL solution has been monitored with increasing the concentration of L-Asp and L-Glu acid at three different temperatures and Tabulated in Table 14. Consequently, it has been observed that molal conductivity( $\Lambda$ ) values increases with increase in temperatures and gradual addition of L-Asp and L-Glu acid to the IL solution causes a continuous decrease in molal conductivity of the solution. The mobility of the ionic species in solution playing

the important role, in spite of growing number of ionic species with added L-ascorbic acid solution, as a result the molal conductivity decreases [39,40]. It may be due to the growing of solute-solvent interaction governed by the dipole-dipole, ion-dipole and hydrophobic – hydrophobic interaction in solution mixtures between the solute and solvent molecules.

### 3.5 Surface Tension

Surface tension ( $\gamma$ ) measurement gives notable indication about solute-solvent interaction in the ternary systems. Solute amino acids molecules have surface active property as described in earlier literature [41]. Studied solvent systems contain IL with positively charged hydrophilic head group and a hydrophobic tail group acts as prominent surface-active agents. Thus, this study has attracted immense interest in the strengthening of Surface phenomena. value of surface tension of L-Asparagine and L-Glutamine is tabulated in Table 15.

The surface tension values vary linearly with an increase concentration of amino acids. The linear raising surface tension data demonstrates that with increase in concentrations amino acid molecules interact with the IL and moves from surface to the bulk of the solutions. This definitely due to the solute-solvent interaction which subsequently lower the surface activity of the amino acids and IL in this solution system.

### 3.6 NMR Study

The <sup>1</sup>H NMR spectroscopy [42] is used to elucidate the changes in the electronic location of various protons of amino acids in the presence of IL. The chemical shift of all detectable protons of IL and amino acids in D<sub>2</sub>O are shown in Fig. 4 (Pic. 1,2,3). The chemical shift of various protons of L-Asparagine+IL and L-Glutamine+IL in D<sub>2</sub>O are also shown in Fig. 5 (Pic. 4 and Pic. 5). The nature of moieties present in the vicinity of protons affects their chemical change ( $\delta$ ) values. The change in chemical shifts ( $\delta$ ) values of amino acid in presence of IL are shown in Fig. 5. The deshielding and shielding effects of the surrounding groups are known to cause downfield (higher frequency) or upfield (lower frequency) shifts in  $\delta$  values. The downfield chemical shifts of aromatic protons and upfield shifts of most of the aliphatic protons of amino acids are observed in presence of both amino acids. The various types of protons of both the amino acids show upfield shifts in <sup>1</sup>H NMR in presence of BTBAC. An upfield shift is revealing an increase in electron density around the amino acids due to hydrophobic-hydrophobic interaction between amino acids and BTBAC[43,44–46]. The pi-electron cloud of the quinoline group of BTBAC interacts with the protons of amino acids, increasing the electron density around the protons of amino acids (shielding effect). However the upfield shift is maximum in the case

of l-glutamine+BTBAC is maximum compared to l-asparagine+BTBAC indicates greater interaction in L-glutamine+ BTBAC system.

### 3.7 Computational Study

#### Gaussian 09 Quantum Chemical calculation: Theoretical basis of the interaction

Theoretically, this is very interest field. There is no obey the exact sequence of the structure of molecules. The basic idea is to evaluate the empirical formula that repeats the physical forces and chemical contacts. Using the method of UB3LYP for numerical calculation, diffused basis function has been used to evaluate the weak molecular interaction associate with atoms in molecule. For this purpose, we apply the 6-31G (d) as a basis set for an accurate explanation of weak molecular interactions which represented by the transition states of the structure.

The Quantum chemical calculation reveals that the  $O \cdots N \cdots O, C=O \cdots H-O, H \cdots O-H$ , weak H-bond interactions in L-Glu/L-Asp cluster surrounded by the solvent sphere in aqueous IL (47) . There is formation of weak H-bond interaction, cohesive force of interaction.(47,48) . Under proper conditions the hydrogen atom is attracted strong force between two atoms rather than one atom. The aforementioned statement was good thought out in our present work. We have depicted the L-Glu $\cdots$ ILs and L-Asp $\cdots$ ILs Complex of cluster through quantum chemical contrivance. So hereby, we compared the calculated values with experimental values in order to verify the correct sequence of interactions associated with atoms in molecule theoretically.

Several approximate properties of different systems of aqueous L-Glu-IL and L-Asp-IL Cluster are summarized in the table 16. The extent of stabilization energy (E) that can be obtained from the values of optimization energy of pure as well as mixed of molecular assembly. optimization energy signifies the solute-solvent interaction. The higher the value of solute – solvent interaction, lower is the optimization energy. It was observed that the stabilization is more prominent in case of (BTBAC+L-GLU+H<sub>2</sub>O) System among all the systems which also signify that the geometry gets optimum in case of (BTBAC+L-GLU+H<sub>2</sub>O) system. The weak non covalent bond between IL with L-Glu and IL with L-ASP can be explained from the idea of solution thermodynamic.

### 4. Conclusion

In the overview of this study, that there is a strong interaction between L-glutamine and BTBAC and it becomes stronger with rise in temperature and increase in mass fraction of BTBAC. All of these above physicochemical and spectroscopic along

with computational works confirms the amino acids and IL (BTBAC) have engaged each other, solute-cosolute interaction is much greater than the solute-solute and solvent-solvent interactions in the ternary system.

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**Table 1.** Experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of different molality ( $m$ ) of aqueous IL (BTBAC) solution at 298.15K, 303.15K and 308.15K

| Conc. of Aq. IL (BTBAC) $m$ /mol.kg <sup>-1</sup> | $\rho \times 10^{-3} (\text{kg.m}^{-3})$ |         |                | $\eta (\text{mPa.s})$ |       |                | $R_M$          |         |                |
|---|--|---------|----------------|-----------------------|-------|----------------|----------------|---------|----------------|
|   | <u>298.15K</u>                           |         | <u>303.15K</u> | <u>298.15K</u>        |       | <u>303.15K</u> | <u>298.15K</u> |         | <u>303.15K</u> |
|   | <u>308.15K</u>                           |         |                | <u>308.15K</u>        |       |                | <u>308.15K</u> |         |                |
| 0.001   | 0.99709                                  | 0.99574 | 0.99410        | 0.913                 | 0.876 | 0.839          | 26.8978        | 26.8908 | 26.8764        |
| 0.003   | 0.99715                                  | 0.99580 | 0.99415        | 0.921                 | 0.880 | 0.846          | 26.9125        | 26.9055 | 26.8985        |
| 0.005   | 0.99719                                  | 0.99589 | 0.99419        | 0.930                 | 0.893 | 0.853          | 26.9272        | 26.9202 | 26.9058        |

**Table 2.** Experimental values of refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of different molality ( $m$ ) of aqueous IL (BTBAC) solution at 298.15 K, 303.15 K and 308.15 K

| Conc. of Aq. IL (BTAC) soln. in molality, $m$ (mol.kg <sup>-1</sup> ) | $n_D$          |                |                | $\kappa (\text{mS/cm})$ |                |                |
|---|----------------|----------------|----------------|-------------------------|----------------|----------------|
|   | <u>298.15K</u> | <u>303.15K</u> | <u>308.15K</u> | <u>298.15K</u>          | <u>303.15K</u> | <u>313.15K</u> |
|   | 0.001          | 1.3320         | 1.3319         | 1.3317                  | 0.105          | 0.171          |
| 0.003   | 1.3322         | 1.3321         | 1.3320         | 0.203                   | 0.243          | 0.288          |
| 0.005   | 1.3324         | 1.3323         | 1.3321         | 0.255                   | 0.327          | 0.349          |

**Table 3.** Density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of L-Asparagine in aqueous (BTBAC) ionic liquid solutions at 298.15K, 303.15K and 308.15K

| Conc. of L-Asparagine soln.in molality, m(mol.kg <sup>-1</sup> ) | $\rho \times 10^{-3}$ (kg.m <sup>-3</sup> ) |                |                | $\eta$ (mPa.s) |                |                | $R_M$          |                |                |
|--|---|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|  | <u>298.15K</u>                              | <u>303.15K</u> | <u>308.15K</u> | <u>293.15K</u> | <u>303.15K</u> | <u>308.15K</u> | <u>293.15K</u> | <u>303.15K</u> | <u>308.15K</u> |
| <b>0.001m IL</b>   |   |                |                |                |                |                |                |                |                |
| 0.010  | 0.99761                                     | 0.99624        | 0.99459        | 0.919          | 0.882          | 0.845          | 27.1822        | 27.2121        | 27.2424        |
| 0.025  | 0.99843                                     | 0.99702        | 0.99535        | 0.925          | 0.888          | 0.851          | 27.1747        | 27.1983        | 27.2364        |
| 0.040  | 0.99926                                     | 0.99782        | 0.99615        | 0.931          | 0.894          | 0.857          | 27.1670        | 27.1913        | 27.2295        |
| 0.055  | 1.00008                                     | 0.99862        | 0.99697        | 0.936          | 0.899          | 0.863          | 27.1595        | 27.1844        | 27.2219        |
| 0.070  | 1.00089                                     | 0.99945        | 0.99782        | 0.941          | 0.905          | 0.869          | 27.1523        | 27.1766        | 27.2136        |
| 0.085  | 1.00177                                     | 1.00029        | 0.99868        | 0.946          | 0.910          | 0.875          | 27.1507        | 27.1760        | 27.2124        |
| <b>0.003m IL</b>   |   |                |                |                |                |                |                |                |                |
| 0.010  | 0.99767                                     | 0.99629        | 0.99462        | 0.926          | 0.885          | 0.851          | 27.1954        | 27.2256        | 27.2564        |
| 0.025  | 0.99848                                     | 0.99705        | 0.99538        | 0.932          | 0.892          | 0.858          | 27.1882        | 27.2123        | 27.2431        |
| 0.040  | 0.99931                                     | 0.99785        | 0.99615        | 0.938          | 0.898          | 0.864          | 27.1804        | 27.2053        | 27.2369        |
| 0.055  | 1.00018                                     | 0.99869        | 0.99695        | 0.943          | 0.904          | 0.870          | 27.1716        | 27.1973        | 27.2299        |
| 0.070  | 1.00105                                     | 0.99952        | 0.99784        | 0.948          | 0.909          | 0.877          | 27.1628        | 27.1895        | 27.2279        |
| 0.085  | 1.00196                                     | 1.00038        | 0.99872        | 0.954          | 0.915          | 0.883          | 27.1603        | 27.1884        | 27.2187        |
| <b>0.005m IL</b>   |   |                |                |                |                |                |                |                |                |
| 0.010  | 0.99773                                     | 0.99638        | 0.99464        | 0.935          | 0.897          | 0.856          | 27.2086        | 27.2380        | 27.2633        |
| 0.025  | 0.99855                                     | 0.99711        | 0.99544        | 0.941          | 0.903          | 0.862          | 27.1937        | 27.2253        | 27.2489        |
| 0.040  | 0.99942                                     | 0.99792        | 0.99627        | 0.947          | 0.909          | 0.868          | 27.1848        | 27.2183        | 27.2411        |
| 0.055  | 1.00032                                     | 0.99874        | 0.99712        | 0.952          | 0.915          | 0.874          | 27.1752        | 27.2108        | 27.2327        |
| 0.070  | 1.00126                                     | 0.99962        | 0.99797        | 0.958          | 0.921          | 0.880          | 27.1645        | 27.2016        | 27.2243        |
| 0.085  | 1.00223                                     | 1.00059        | 0.99892        | 0.964          | 0.927          | 0.887          | 27.1604        | 27.1975        | 27.2207        |

**Table 4.** Density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of L-Glutamine in aqueous (BTBAC) ionic liquid solutions at 298.15K, 303.15K and 308.15K

| Conc. of L-Glutamine soln.in molality (mol.kg <sup>-1</sup> ) | $\rho \times 10^{-3}$ (kg.m <sup>-3</sup> ) |                |                | $\eta$ (mPa.s) |                |                | $R_M$          |                |                |
|---|---|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|   | <u>298.15K</u>                              | <u>303.15K</u> | <u>308.15K</u> | <u>298.15K</u> | <u>303.15K</u> | <u>308.15K</u> | <u>298.15K</u> | <u>303.15K</u> | <u>308.15K</u> |
| <b>0.001m IL</b>  |   |                |                |                |                |                |                |                |                |
| 0.010   | 0.99764                                     | 0.99628        | 0.99462        | 0.921          | 0.884          | 0.849          | 30.0657        | 30.0903        | 30.1240        |
| 0.025   | 0.99849                                     | 0.99709        | 0.99542        | 0.930          | 0.893          | 0.858          | 30.0483        | 30.0741        | 30.1081        |
| 0.040   | 0.99938                                     | 0.99795        | 0.99627        | 0.939          | 0.902          | 0.867          | 30.0.80        | 30.0646        | 30.0988        |
| 0.055   | 1.00027                                     | 0.99882        | 0.99710        | 0.948          | 0.912          | 0.877          | 30.0276        | 30.0548        | 30.0902        |
| 0.070   | 1.00117                                     | 0.99973        | 0.99747        | 0.956          | 0.921          | 0.887          | 30.0252        | 30.0439        | 30.0804        |
| 0.085   | 1.00210                                     | 1.00064        | 0.99890        | 0.965          | 0.929          | 0.897          | 30.0137        | 30.0411        | 30.0770        |
| <b>0.003m IL</b>  |   |                |                |                |                |                |                |                |                |
| 0.010   | 0.99771                                     | 0.99632        | 0.99466        | 0.929          | 0.888          | 0.853          | 30.0718        | 30.0973        | 30.1311        |
| 0.025   | 0.99853                                     | 0.99712        | 0.99544        | 0.938          | 0.896          | 0.863          | 30.0636        | 30.0814        | 30.1157        |
| 0.040   | 0.99942                                     | 0.99800        | 0.99630        | 0.947          | 0.906          | 0.872          | 30.0532        | 30.0713        | 30.1062        |
| 0.055   | 1.00031                                     | 0.99886        | 0.99716        | 0.957          | 0.917          | 0.882          | 30.0428        | 30.0610        | 30.0966        |
| 0.070   | 1.00125                                     | 0.99975        | 0.99810        | 0.967          | 0.926          | 0.894          | 30.0310        | 30.0515        | 30.0929        |
| 0.085   | 1.00219                                     | 1.00067        | 0.99900        | 0.977          | 0.936          | 0.904          | 30.0273        | 30.0402        | 30.0822        |
| <b>0.005m IL</b>  |   |                |                |                |                |                |                |                |                |
| 0.010   | 0.99776                                     | 0.99640        | 0.99469        | 0.939          | 0.899          | 0.859          | 30.0868        | 30.1196        | 30.1519        |
| 0.025   | 0.99859                                     | 0.99718        | 0.99550        | 0.949          | 0.909          | 0.869          | 30.0700        | 30.1043        | 30.1386        |
| 0.040   | 0.99950                                     | 0.99805        | 0.99640        | 0.960          | 0.919          | 0.880          | 30.0590        | 30.0944        | 30.1278        |
| 0.055   | 1.00042                                     | 0.99895        | 0.99730        | 0.970          | 0.929          | 0.891          | 30.0477        | 30.0837        | 30.1171        |
| 0.070   | 1.00136                                     | 0.99989        | 0.99832        | 0.980          | 0.939          | 0.901          | 30.0359        | 30.0718        | 30.1027        |
| 0.085   | 1.00233                                     | 1.00083        | 0.99932        | 0.990          | 0.950          | 0.912          | 30.0313        | 30.0600        | 30.0972        |

**Table 5.** Apparent molar volume, ( $\Phi_v$ ) and  $(\eta/\eta^0 - 1) / \sqrt{m}$  of L-Asparagine solution in 0.001m, 0.003m and 0.005m aqueous BTBAC solution at different temperatures (293.15K, 303.15K, 313.15K)

| Conc. of L-Asparagine soln. in molality, m (mol.kg <sup>-1</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1) / \sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1) / \sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1) / \sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) |
|--|---|--|---|--|---|--|
| <b>0.001m IL</b>   | <b>298.15K</b>  |  | <b>303.15K</b>  |  | <b>308.15K</b>  |  |
| 0.010  | 80.3507   | 0.066  | 82.4660   | 0.068  | 83.6242   | 0.071  |
| 0.025  | 79.0427   | 0.083  | 81.3108   | 0.086  | 82.6060   | 0.090  |
| 0.040  | 78.1942   | 0.098  | 80.3972   | 0.102  | 81.3261   | 0.107  |
| 0.055  | 77.6333   | 0.107  | 79.6422   | 0.111  | 80.4199   | 0.121  |
| 0.070  | 77.0868   | 0.115  | 78.9367   | 0.125  | 79.4539   | 0.134  |
| 0.085  | 76.4591   | 0.123  | 78.3389   | 0.132  | 78.7080   | 0.146  |
| <b>0.003m IL</b>   | <b>298.15K</b>  |  | <b>303.15K</b>  |  | <b>308.15K</b>  |  |
| 0.010  | 80.3664   | 0.054  | 83.4287   | 0.057  | 85.7070   | 0.059  |
| 0.025  | 79.3540   | 0.075  | 82.3121   | 0.086  | 83.7198   | 0.089  |
| 0.040  | 78.3173   | 0.092  | 81.1301   | 0.102  | 82.5750   | 0.106  |
| 0.055  | 77.2556   | 0.101  | 80.0741   | 0.116  | 81.6867   | 0.120  |
| 0.070  | 76.6260   | 0.110  | 78.8129   | 0.124  | 79.8701   | 0.138  |
| 0.085  | 75.7461   | 0.122  | 77.9808   | 0.136  | 78.8096   | 0.149  |
| <b>0.005m IL</b>   | <b>298.15K</b>  |  | <b>303.15K</b>  |  | <b>308.15K</b>  |  |
| 0.010  | 81.4171   | 0.054  | 84.9350   | 0.045  | 87.3824   | 0.035  |
| 0.025  | 79.0989   | 0.075  | 83.3595   | 0.070  | 83.7313   | 0.066  |
| 0.040  | 77.3132   | 0.091  | 81.7413   | 0.089  | 81.2187   | 0.088  |
| 0.055  | 75.9830   | 0.101  | 80.1890   | 0.105  | 79.7130   | 0.104  |
| 0.070  | 74.9495   | 0.113  | 78.6443   | 0.118  | 78.5982   | 0.119  |
| 0.085  | 73.5310   | 0.125  | 77.1799   | 0.130  | 76.9479   | 0.136  |

**Table 6.** Apparent molar volume, ( $\Phi_v$ ) and  $(\eta/\eta^0 - 1) / \sqrt{m}$  of L-Glutamine solution in 0.001m, 0.003m and 0.005m in aqueous (BTBAC) solution at different temperatures (298.15K, 303.15K, 308.15K)

| Conc. of L-Glutamine soln. in molality (mol.kg <sup>-1</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1) / \sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1) / \sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1) / \sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) |
|--|---|--|---|--|---|--|
| <b>0.001m IL</b>   | <b>298.15K</b>  |  | <b>303.15K</b>  |  | <b>308.15K</b>  |  |
| 0.010  | 91.4027   | 0.087  | 93.5098   | 0.091  | 95.5544   | 0.095  |
| 0.025  | 90.1126   | 0.117  | 92.1772   | 0.122  | 93.4547   | 0.127  |
| 0.040  | 89.1234   | 0.142  | 91.1660   | 0.148  | 92.2328   | 0.154  |
| 0.055  | 88.1717   | 0.163  | 90.0066   | 0.174  | 91.5363   | 0.182  |
| 0.070  | 87.5817   | 0.177  | 88.9201   | 0.193  | 90.7103   | 0.205  |
| 0.085  | 86.8444   | 0.194  | 88.1899   | 0.206  | 89.4326   | 0.227  |
| <b>0.003m IL</b>   | <b>298.15K</b>  |  | <b>303.15K</b>  |  | <b>308.15K</b>  |  |
| 0.010  | 92.1687   | 0.087  | 95.6445   | 0.091  | 97.1596   | 0.082  |
| 0.025  | 90.9159   | 0.116  | 93.3863   | 0.115  | 94.6480   | 0.127  |
| 0.040  | 89.6275   | 0.141  | 91.4421   | 0.147  | 92.5627   | 0.153  |
| 0.055  | 88.5420   | 0.166  | 90.3720   | 0.178  | 91.3301   | 0.180  |
| 0.070  | 87.2921   | 0.188  | 89.4958   | 0.197  | 89.5495   | 0.213  |

|                  |                |       |                |       |                |       |
|------------------|----------------|-------|----------------|-------|----------------|-------|
| 0.085            | 86.4870        | 0.207 | 88.5449        | 0.217 | 88.8343        | 0.234 |
| <b>0.005m IL</b> | <b>298.15K</b> |       | <b>303.15K</b> |       | <b>308.15K</b> |       |
| 0.010            | 93.4499        | 0.086 | 96.4599        | 0.67  | 97.5276        | 0.070 |
| 0.025            | 91.3160        | 0.112 | 94.5938        | 0.113 | 93.8561        | 0.118 |
| 0.040            | 89.3859        | 0.155 | 92.4161        | 0.145 | 90.7921        | 0.157 |
| 0.055            | 87.8234        | 0.178 | 90.3689        | 0.171 | 89.1130        | 0.189 |
| 0.070            | 86.7143        | 0.198 | 88.7711        | 0.194 | 86.9413        | 0.211 |
| 0.085            | 85.6552        | 0.216 | 87.7097        | 0.218 | 85.4925        | 0.236 |

**Table 7(a).** Limiting apparent molar volumes ( $\Phi_V^0$ ), Limiting molar refraction ( $R_M^0$ ), experimental slopes ( $S_V^*$ ), viscosity A, B-coefficients of L-Asparagine solution in IL at different temperatures

| Temp. (K)        | $\Phi_V^0 \times 10^6$ ( $m^3 \cdot mol^{-1}$ ) | $R_M^0$ | $S_V^* \times 10^6$ ( $m^3 \cdot mol^{-3/2} \cdot kg^{1/2}$ ) | B ( $kg^{1/2} \cdot mol^{-1/2}$ ) | A ( $kg \cdot mol^{-1}$ ) |
|------------------|---|---------|---|-----------------------------------|---------------------------|
| <b>0.001m IL</b> |   |         |   |                                   |                           |
| 298.15           | 82.266  | 27.201  | -19.864   | 0.3006                            | 0.0360                    |
| 303.15           | 84.704  | 27.230  | -21.702   | 0.3353                            | 0.0341                    |
| 308.15           | 86.486  | 27.261  | -26.111   | 0.3917                            | 0.0297                    |
| <b>0.003m IL</b> |   |         |   |                                   |                           |
| 298.15           | 83.005  | 27.217  | -24.226   | 0.3459                            | 0.0204                    |
| 303.15           | 86.676  | 27.245  | -29.026   | 0.3996                            | 0.0198                    |
| 308.15           | 89.406  | 27.274  | -35.091   | 0.4618                            | 0.0136                    |
| <b>0.005m IL</b> |   |         |   |                                   |                           |
| 298.15           | 85.445  | 27.235  | -40.163   | 0.3639                            | 0.0170                    |
| 303.15           | 89.546  | 27.260  | -40.881   | 0.4450                            | -0.0004                   |
| 308.15           | 92.373  | 27.285  | -52.938   | 0.5133                            | -0.0160                   |

**Table 7(b).** Limiting apparent molar volumes ( $\Phi_V^0$ ), Limiting molar refraction ( $R_M^0$ ), experimental slopes ( $S_V^*$ ), viscosity A, B-coefficients of L-Glutamine solution in IL at different temperatures

| Temperature(K)   | $\Phi_V^0 \times 10^6$ ( $m^3 \cdot mol^{-1}$ ) | $R_M^0$ | $S_V^* \times 10^6$ ( $m^3 \cdot mol^{-3/2} \cdot kg^{1/2}$ ) | B ( $kg^{1/2} \cdot mol^{-1/2}$ ) | A ( $kg \cdot mol^{-1}$ ) |
|------------------|---|---------|---|-----------------------------------|---------------------------|
| <b>0.001m IL</b> |   |         |   |                                   |                           |
| 298.15           | 93.841  | 30.091  | -23.854   | 0.5548                            | 0.0309                    |
| 303.15           | 96.586  | 30.117  | -28.424   | 0.6141                            | 0.0276                    |
| 308.15           | 98.482  | 30.148  | -30.362   | 0.6888                            | 0.0208                    |
| <b>0.003m IL</b> |   |         |   |                                   |                           |
| 298.15           | 95.554  | 30.100  | -30.603   | 0.6312                            | 0.0190                    |
| 303.15           | 99.263  | 30.128  | -37.330   | 0.6787                            | 0.0155                    |
| 308.15           | 101.68  | 30.158  | -44.776   | 0.7816                            | 0.0013                    |
| <b>0.005m IL</b> |   |         |   |                                   |                           |
| 298.15           | 97.733  | 30.117  | -41.624   | 0.6839                            | 0.0163                    |
| 303.15           | 101.73  | 30.152  | -48.014   | 0.7720                            | -0.0102                   |
| 308.15           | 103.85  | 30.187  | -63.495   | 0.8655                            | -0.0174                   |

**Table 8.** The empirical coefficient values ( $a_0$ ,  $a_1$  and  $a_2$ ) of L-Asparagine solution & L-Glutamine solution in different concentration of the IL (0.001, 0.003m, 0.005m) at 298.15K, 303.15K and 308.15K

| Conc. of aq. IL soln. in molality (mol.kg <sup>-1</sup> ) | $a_0 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> ) | $a_1 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-1</sup> ) | $a_2 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-2</sup> ) | $a_0 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> ) | $a_1 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-1</sup> ) | $a_2 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-2</sup> ) |
|---|---|---|---|---|---|---|
|   | L-Asparagine solution                                   |   |   | L-Glutamine solution                                    |   |   |
|   | 298.15K   | 303.15K   | 308.15K   | 298.15K   | 303.15K   | 308.15K   |
| 0.001   | -1249   | 8.3767  | -0.0131   | -1660.6   | 10.759  | -0.0170   |
| 0.003   | -1836.9   | 12.051  | -0.0188   | -2461.1   | 16.279  | -0.0258   |
| 0.005   | -2462.1   | 16.141  | -0.0255   | -3533.6   | 23.372  | -0.0375   |

**Table 9(a).** Values of limiting molar expansibilities ( $\Phi_E^0$ ) for L-Asparagine solution in IL(BTBAC) at different temperatures

| Conc. of aq. IL soln. in molality (mol.kg <sup>-1</sup> ) | $\Phi_E^0 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-1</sup> ) |         |         | $(\delta\Phi_E^0/\delta T)_P \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-2</sup> ) |
|---|--|---------|---------|---|
|   | 298.15K  | 303.15K | 308.15K |   |
| 0.001   | 0.56517  | 0.43417 | 0.30317 | -0.0262   |
| 0.003   | 0.84056  | 0.65266 | 0.46456 | -0.0376   |
| 0.005   | 0.93535  | 0.68035 | 0.42535 | -0.0510   |

**Table 9(b).** Values of limiting molar expansibilities ( $\Phi_E^0$ ) for L-Glutamine solution in IL(BTBAC) at different temperatures

| Conc. of aq. IL soln. in molality (mol.kg <sup>-1</sup> ) | $\Phi_E^0 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-1</sup> ) |         |         | $(\delta\Phi_E^0/\delta T)_P \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> . K <sup>-2</sup> ) |
|---|--|---------|---------|---|
|   | 298.15K  | 303.15K | 308.15K |   |
| 0.001   | 0.6219   | 0.4519  | 0.2819  | -0.0340   |
| 0.003   | 0.89446  | 0.63646 | 0.37846 | -0.0516   |
| 0.005   | 1.01075  | 0.63575 | 0.26075 | -0.0750   |

**Table 10(a).** Viscosity B-coefficients of L-Asparagine solution along with dB/dT values in different concentrations of IL at (298.15, 303.15 and 308.15) K

| Temperature (K) | 0.001m IL |  | 0.003m IL |  | 0.005m IL |  | dB/dT  |
|-----------------|-----------|--|-----------|--|-----------|--|--------|
|                 | B         |  | B         |  | B         |  |        |
| 298.15          | 0.30006   |  | 0.3459    |  | 0.3639    |  | 0.0091 |
| 303.15          | 0.3353    |  | 0.3996    |  | 0.4450    |  | 0.0116 |
| 308.15          | 0.3917    |  | 0.4618    |  | 0.5131    |  | 0.0149 |

**Table 10(b).** Viscosity B-coefficients of L-Glutamine solution along with dB/dT values in different concentrations of IL at (298.15, 303.15 and 308.15) K

| Temperature (K) | 0.001m IL |  | 0.003m IL |  | 0.005m IL |  | dB/dT  |
|-----------------|-----------|--|-----------|--|-----------|--|--------|
|                 | B         |  | B         |  | B         |  |        |
| 298.15          | 0.5548    |  | 0.6312    |  | 0.6839    |  | 0.0134 |
| 303.15          | 0.6141    |  | 0.6787    |  | 0.7720    |  | 0.0150 |
| 308.15          | 0.6888    |  | 0.7816    |  | 0.8655    |  | 0.0182 |

**Table 11.** Values of  $(\bar{V}_1^0 - \bar{V}_2^0)$ ,  $\Delta\mu_1^{0\#}$ ,  $\Delta\mu_2^{0\#}$ ,  $T\Delta S_2^{0\#}$ ,  $\Delta H_2^{0\#}$  for L-Asparagine and L-glutamine in different molality (0.001,0.003,0.005) of aqueous solution of IL(BTBAC) mixture at different temperatures and atmospheric pressure 0.1MPa

| parameters  | 0.001     |         |         | 0.003     |         |          | 0.005   |         |         |
|---|-----------|---------|---------|-----------|---------|----------|---------|---------|---------|
|   | T=298.15K | 303.15K | 308.15K | T=298.15K | 303.15K | 308.15 K | 298.15K | 303.15K | 308.15K |
| <b>L-Asparagine</b>   |           |         |         |           |         |          |         |         |         |
| $(\bar{V}_1^0 - \bar{V}_2^0)$<br>/m <sup>3</sup> .mol <sup>-1</sup> | -64.26    | -66.70  | -68.48  | -64.99    | -68.67  | -71.40   | -67.43  | -71.53  | -74.36  |
| $\Delta\mu_1^{0\#}$ /KJ.mol <sup>-1</sup>                           | 9.21      | 9.32    | 9.30    | 9.23      | 9.33    | 9.33     | 9.26    | 9.38    | 9.35    |
| $\Delta\mu_2^{0\#}$ /KJ.mol <sup>-1</sup>                           | 59.46     | 65.98   | 74.79   | 65.80     | 75.31   | 85.19    | 68.92   | 82.44   | 93.26   |
| $T\Delta S_2^{0\#}$ /KJ.mol <sup>-1</sup>                           | 297.76    | 302.75  | 307.74  | 578.14    | 587.83  | 597.53   | 725.33  | 737.50  | 749.67  |
| $\Delta H_2^{0\#}$ /KJ.mol <sup>-1</sup>                            | 357.21    | 368.73  | 382.53  | 643.98    | 663.14  | 682.72   | 749.26  | 819.94  | 842.92  |
| <b>L-Glutamine</b>  |           |         |         |           |         |          |         |         |         |
| $(\bar{V}_1^0 - \bar{V}_2^0)$<br>/m <sup>3</sup> .mol <sup>-1</sup> | -75.83    | -78.58  | -80.48  | -77.54    | -81.26  | -83.67   | -79.72  | -83.71  | -91.71  |
| $\Delta\mu_1^{0\#}$ /KJ.mol <sup>-1</sup>                           | 9.21      | 9.32    | 9.30    | 9.21      | 9.32    | 9.30     | 9.21    | 9.32    | 9.31    |
| $\Delta\mu_2^{0\#}$ /KJ.mol <sup>-1</sup>                           | 96.05     | 106.94  | 118.79  | 106.78    | 116.40  | 132.41   | 114.31  | 129.86  | 144.62  |
| $T\Delta S_2^{0\#}$ /KJ.mol <sup>-1</sup>                           | 677.69    | 689.05  | 700.49  | 871.08    | 893.52  | 922.36   | 903.93  | 919.09  | 934.24  |
| $\Delta H_2^{0\#}$ /KJ.mol <sup>-1</sup>                            | 773.74    | 795.99  | 819.28  | 764.30    | 777.12  | 789.94   | 1018.24 | 1048.95 | 1078.88 |

#Combined standard uncertainty in molality according to stated purity  $u(m) = \pm 0.0001$  mol kg<sup>-1</sup>. \*Standard uncertainty in temperature  $u(T) = \pm 0.01$  K. \*Standard uncertainty in pressure  $u(P) = \pm 0.01$  MPa

**Table 12.** Values of  $(B/\Phi_V^0)$  for L-Asparagine and L-Glutamine in different molality of aqueous TBMS (IL) solutions at different temperature and atmospheric pressure 0.1MPa

| Temperature(K) | $B / \Phi_V^0$            |                           |                           | $B / \Phi_V^0$            |                           |                           |
|----------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
|                | 0.001mol.Kg <sup>-1</sup> | 0.003mol.Kg <sup>-1</sup> | 0.005mol.Kg <sup>-1</sup> | 0.001mol.Kg <sup>-1</sup> | 0.003mol.Kg <sup>-1</sup> | 0.005mol.Kg <sup>-1</sup> |
|                | L-ASPARAGINE+ Aq. TBMS    |                           |                           | L-GLUTAMINE +Aq. TBMS     |                           |                           |
| 298.15         | 3.654                     | 4.167                     | 4.258                     | 5.912                     | 6.605                     | 6.997                     |
| 303.15         | 3.958                     | 4.612                     | 4.969                     | 6.358                     | 6.837                     | 7.588                     |
| 308.15         | 4.529                     | 5.165                     | 5.556                     | 6.994                     | 7.686                     | 8.334                     |

#Standard uncertainty in molality  $u(m) = \pm 0.0001$  mol kg<sup>-1</sup>. \*Standard uncertainty in temperature  $u(T) = \pm 0.01$  K. \*Standard uncertainty in pressure  $u(P) = \pm 0.01$ MPa

**Table-13(a).** Refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of L-Asparagine in aqueous IL (BTBAC) solution at 293.15K, 303.15K and 313.15K

| Conc. of L-Asparagine soln. in molality, m (mol.kg <sup>-1</sup> ) | $n_D$          |                |                | $\kappa$ (mS/cm) |                |                |
|--|----------------|----------------|----------------|------------------|----------------|----------------|
|  | <u>293.15K</u> | <u>303.15K</u> | <u>313.15K</u> | <u>293.15K</u>   | <u>303.15K</u> | <u>313.15K</u> |
| <b>0.001m IL</b>   |                |                |                |                  |                |                |
| 0.010  | 1.3322         | 1.3321         | 1.3319         | 0.482            | 0.503          | 0.520          |
| 0.025  | 1.3324         | 1.3322         | 1.3321         | 0.574            | 0.590          | 0.615          |
| 0.040  | 1.3326         | 1.3324         | 1.3323         | 0.653            | 0.683          | 0.709          |
| 0.055  | 1.3328         | 1.3326         | 1.3325         | 0.749            | 0.776          | 0.796          |
| 0.070  | 1.3330         | 1.3328         | 1.3327         | 0.826            | 0.859          | 0.888          |
| 0.085  | 1.3333         | 1.3331         | 1.3330         | 0.920            | 0.943          | 0.983          |
| <b>0.003m IL</b>   |                |                |                |                  |                |                |
| 0.010  | 1.3324         | 1.3323         | 1.3321         | 0.545            | 0.572          | 0.607          |
| 0.025  | 1.3326         | 1.3324         | 1.3322         | 0.634            | 0.663          | 0.714          |
| 0.040  | 1.3328         | 1.3326         | 1.3324         | 0.720            | 0.765          | 0.809          |
| 0.055  | 1.3330         | 1.3328         | 1.3326         | 0.812            | 0.854          | 0.913          |
| 0.070  | 1.3332         | 1.3330         | 1.3329         | 0.903            | 0.935          | 0.999          |
| 0.085  | 1.3335         | 1.3333         | 1.3331         | 0.997            | 1.052          | 1.080          |
| <b>0.005m IL</b>   |                |                |                |                  |                |                |
| 0.010  | 1.3326         | 1.3325         | 1.3322         | 0.660            | 0.748          | 0.813          |
| 0.025  | 1.3327         | 1.3326         | 1.3323         | 0.771            | 0.832          | 0.889          |
| 0.040  | 1.3329         | 1.3328         | 1.3325         | 0.870            | 0.917          | 0.967          |
| 0.055  | 1.3331         | 1.3330         | 1.3327         | 0.965            | 1.020          | 1.040          |
| 0.070  | 1.3333         | 1.3332         | 1.3329         | 1.053            | 1.080          | 1.123          |
| 0.085  | 1.3336         | 1.3335         | 1.3332         | 1.114            | 1.163          | 1.210          |

**Table13(b).** Refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of L-Glutamine in aqueous IL (BTBAC) solution at 298.15K, 303.15K and 308.15K

| Conc. of L-Glutamine soln. in molality, m (mol.kg <sup>-1</sup> ) | $n_D$          |                |                | $\kappa$ (mS/cm) |                |                |
|---|----------------|----------------|----------------|------------------|----------------|----------------|
|   | <u>298.15K</u> | <u>303.15K</u> | <u>308.15K</u> | <u>298.15K</u>   | <u>303.15K</u> | <u>308.15K</u> |
| <b>0.001m IL</b>  |                |                |                |                  |                |                |
| 0.010   | 1.3322         | 1.3320         | 1.3318         | 0.352            | 0.382          | 0.410          |
| 0.025   | 1.3323         | 1.3321         | 1.3319         | 0.453            | 0.486          | 0.523          |
| 0.040   | 1.3325         | 1.3323         | 1.3321         | 0.557            | 0.582          | 0.614          |
| 0.055   | 1.3327         | 1.3325         | 1.3323         | 0.640            | 0.692          | 0.710          |
| 0.070   | 1.3330         | 1.3327         | 1.3325         | 0.756            | 0.790          | 0.819          |
| 0.085   | 1.3332         | 1.3330         | 1.3328         | 0.847            | 0.896          | 0.903          |
| <b>0.003m IL</b>  |                |                |                |                  |                |                |
| 0.010   | 1.3323         | 1.3321         | 1.3319         | 0.441            | 0.463          | 0.496          |
| 0.025   | 1.3325         | 1.3322         | 1.3320         | 0.543            | 0.570          | 0.597          |
| 0.040   | 1.3327         | 1.3324         | 1.3322         | 0.683            | 0.702          | 0.724          |
| 0.055   | 1.3329         | 1.3326         | 1.3324         | 0.784            | 0.819          | 0.821          |
| 0.070   | 1.3331         | 1.3328         | 1.3326         | 0.902            | 0.923          | 0.943          |
| 0.085   | 1.3334         | 1.3330         | 1.3329         | 0.975            | 1.030          | 1.050          |
| <b>0.005m IL</b>  |                |                |                |                  |                |                |
| 0.010   | 1.3325         | 1.3324         | 1.3322         | 0.542            | 0.582          | 0.612          |
| 0.025   | 1.3326         | 1.3325         | 1.3323         | 0.641            | 0.670          | 0.690          |
| 0.040   | 1.3328         | 1.3327         | 1.3325         | 0.768            | 0.774          | 0.796          |
| 0.055   | 1.3330         | 1.3329         | 1.3327         | 0.871            | 0.876          | 0.906          |
| 0.070   | 1.3332         | 1.3331         | 1.3329         | 0.980            | 0.989          | 1.01           |
| 0.085   | 1.3335         | 1.3333         | 1.3332         | 1.06             | 1.080          | 1.09           |

**Table 14.** Molar conductance ( $\Lambda$ ) of L-Asparagine and L-Glutamine solution in (0.001m, 0.003m, 0.005m) IL at 298.15K, 303.15K and 308.15K

| Concentration of amino acid solutions in molality, m(mole/kg) | Molar Conductance of L-asparagine solution<br>$\Lambda$ (S.cm <sup>2</sup> .mol <sup>-1</sup> ) |         |          | Molar conductance of L--glutamine solution<br>$\Lambda$ (S.cm <sup>2</sup> .mol <sup>-1</sup> ) |         |         |
|---|---|---------|----------|---|---------|---------|
|   | 298.15K   | 303.15K | 308.15K  | 298.15K   | 303.15K | 308.15K |
| <b>0.001m IL</b>  |   |         |          |   |         |         |
| 0.010   | 48.20   | 50.30   | 52.00    | 35.20   | 38.20   | 41.00   |
| 0.025   | 22.96   | 23.60   | 24.60    | 18.12   | 19.44   | 20.92   |
| 0.040   | 16.325  | 17.075  | 17.725   | 13.925  | 14.55   | 15.35   |
| 0.055   | 13.6181   | 14.109  | 14.4725  | 11.6360   | 12.5818 | 12.909  |
| 0.070   | 11.800  | 12.2714 | 12.6857  | 10.80   | 11.2857 | 11.700  |
| 0.085   | 10.8235   | 11.094  | 11.5647  | 9.9647  | 10.5411 | 10.6235 |
| <b>0.003m IL</b>  |   |         |          |   |         |         |
| 0.010   | 54.50   | 57.20   | 60.7     | 44.10   | 46.30   | 49.60   |
| 0.025   | 25.36   | 26.52   | 28.56    | 21.72   | 22.80   | 23.88   |
| 0.040   | 18.00   | 19.125  | 20.225   | 17.075  | 17.55   | 18.10   |
| 0.055   | 14.7636   | 15.527  | 16.600   | 14.2545   | 14.8909 | 14.9272 |
| 0.070   | 12.900  | 13.3571 | 14.2714  | 12.8885   | 13.1857 | 13.4714 |
| 0.085   | 11.7294   | 12.3764 | 12.7058  | 11.470  | 12.117  | 12.352  |
| <b>0.005m IL</b>  |   |         |          |   |         |         |
| 0.010   | 66.00   | 74.80   | 81.30    | 54.20   | 58.20   | 61.20   |
| 0.025   | 30.84   | 33.28   | 35.56    | 25.64   | 26.80   | 27.600  |
| 0.040   | 21.75   | 22.925  | 24.175   | 19.20   | 19.35   | 19.900  |
| 0.055   | 17.5454   | 18.5454 | 18.9090  | 15.8363   | 15.9272 | 16.4727 |
| 0.070   | 15.0428   | 15.4285 | 16.04285 | 14.00   | 14.1228 | 14.4285 |
| 0.085   | 13.1058   | 13.6823 | 14.23529 | 12.47   | 12.705  | 12.8235 |

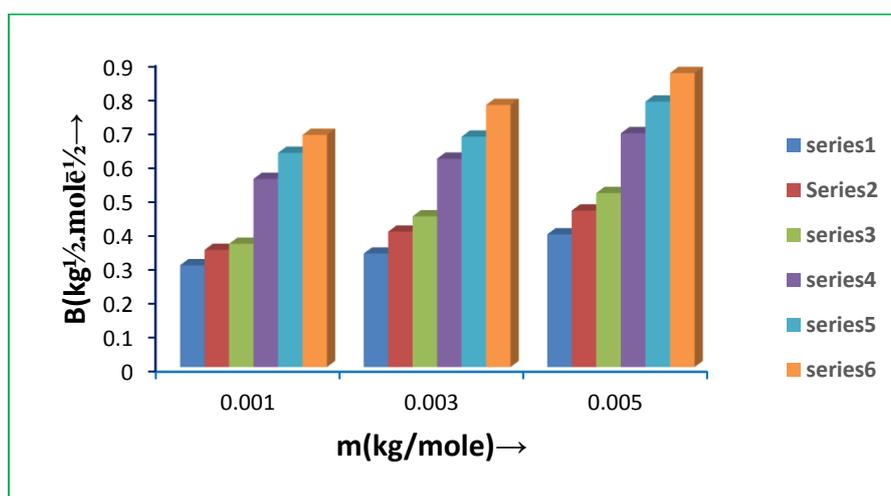
**Table15.** Surface Tension values of L-Asparagine and L-glutamine solutions in BTBAC at different concentration (0.001m, 0.003m, 0.005m) at room temperature

| Concentration of amino acid solutions in molality(mole/kg) | Surface Tension of L- Asparagine solutions (mN/m) | Surface Tension of L-Glutamine solutions (mN/m) |
|--|---|---|
| <b>0.001mIL</b>  | 60.5  | 60.5  |
| 0.010  | 62.3  | 64.2  |
| 0.025  | 63.2  | 65.5  |
| 0.040  | 63.9  | 66.6  |
| 0.055  | 64.8  | 67.5  |
| 0.070  | 65.7  | 68.6  |
| 0.085  | 66.8  | 69.8  |
| <b>0.003mIL</b>  | 57.6  | 57.6  |
| 0.010  | 63.9  | 65.9  |
| 0.025  | 64.8  | 66.8  |
| 0.040  | 65.7  | 67.7  |
| 0.055  | 66.9  | 68.7  |
| 0.070  | 68.1  | 69.4  |
| 0.085  | 69.3  | 70.3  |
| <b>0.005mIL</b>  | 54.7  | 54.7  |
| 0.010  | 64.7  | 66.5  |
| 0.025  | 65.8  | 67.2  |
| 0.040  | 66.9  | 68.3  |
| 0.055  | 67.7  | 69.1  |
| 0.070  | 68.8  | 70.2  |
| 0.085  | 69.9  | 71.1  |

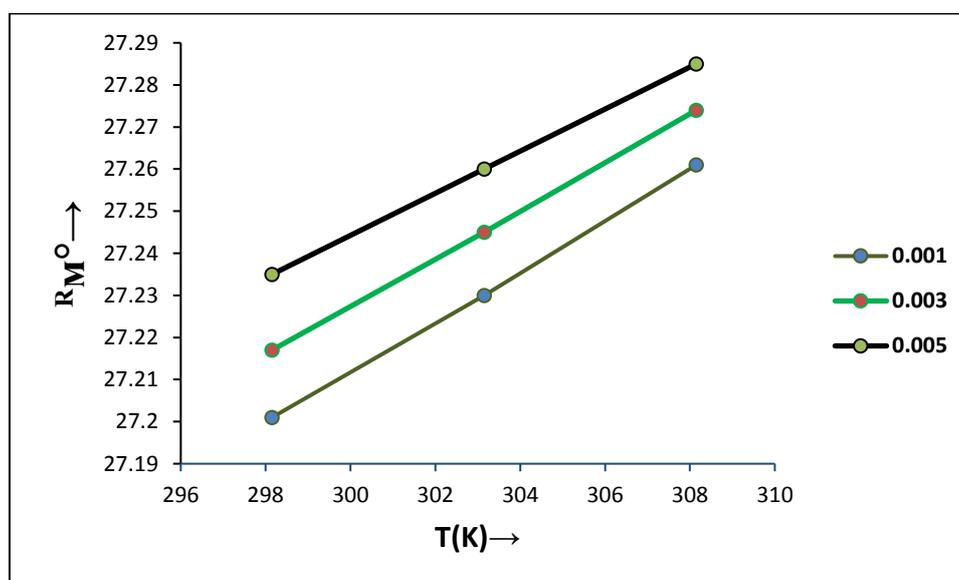
**Table16.** Optimization energies of pure BTBAC, L-Glu, L-Asp and (BTBAC + L-Glu), (BTBAC + L-Asp), systems using UB3LYP methodology and 6-31G (d) as a basis set

| System (Debye)  | Calculation Method | Basis Set | Optimization energy (a.u.) | Dipole moment |
|-----------------|--------------------|-----------|----------------------------|---------------|
| L-Glu           | UB3LYP             | 6-31G(d)  | -531.58350924              | 3.0454        |
| L-Asp           | UB3LYP             | 6-31G(d)  | -492.79440798              | 4.1309        |
| BTBAC           | UB3LYP             | 6-31G(d)  | -799.0179491               | 0.9693        |
| (BTBAC + L-Glu) | UB3LYP             | 6-31G(d)  | -1321.24634420             | 9.0790        |
| (BTBAC + L-ASP) | UB3LYP             | 6-31G(d)  | -1290.71439476             | 14.5571       |

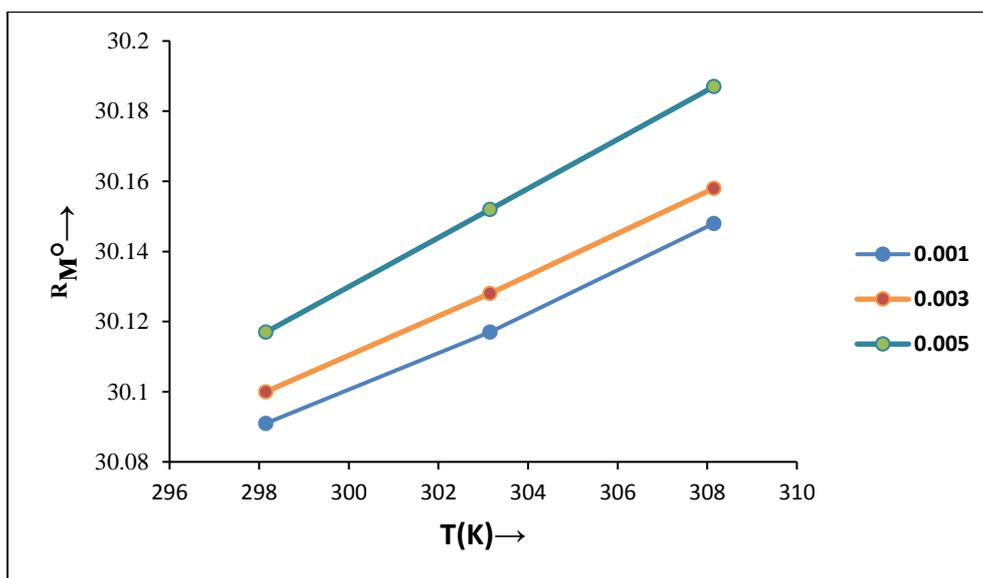
## Figures



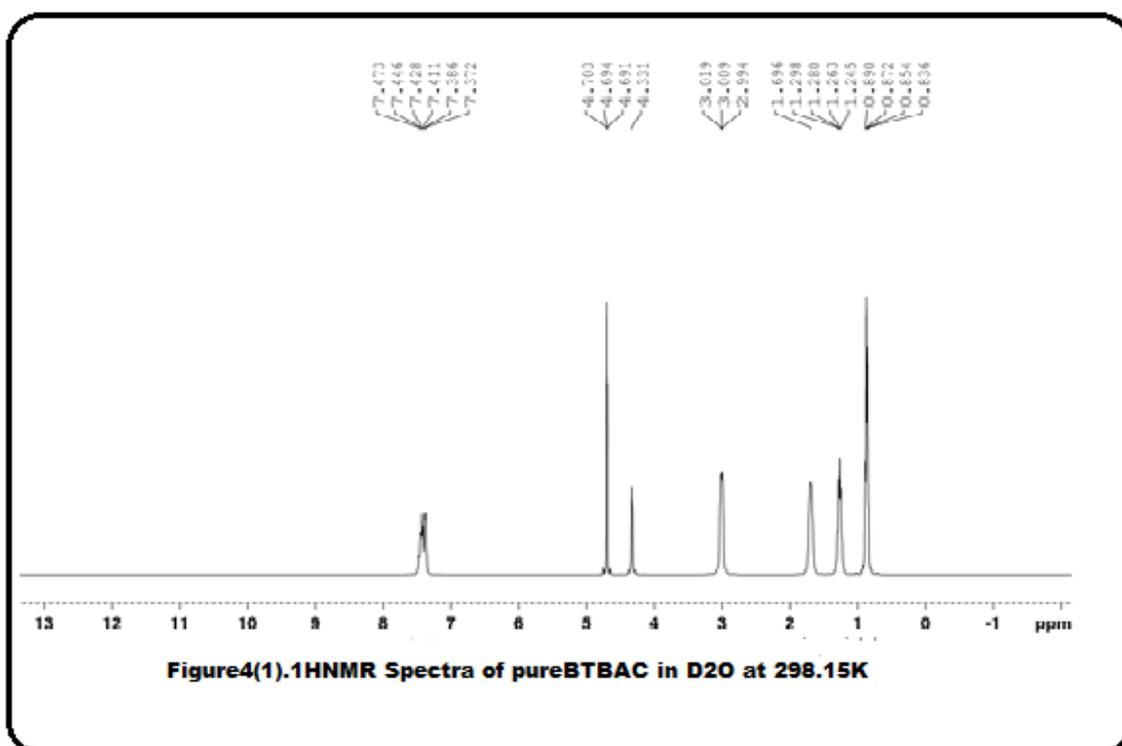
**Figure1.** Variation of B values of L-Glutamine and L-Asparagine in aqueous solution of BTBAC respectively, against 0.001m IL, 0.003m IL and 0.005m IL solutions at different temperatures

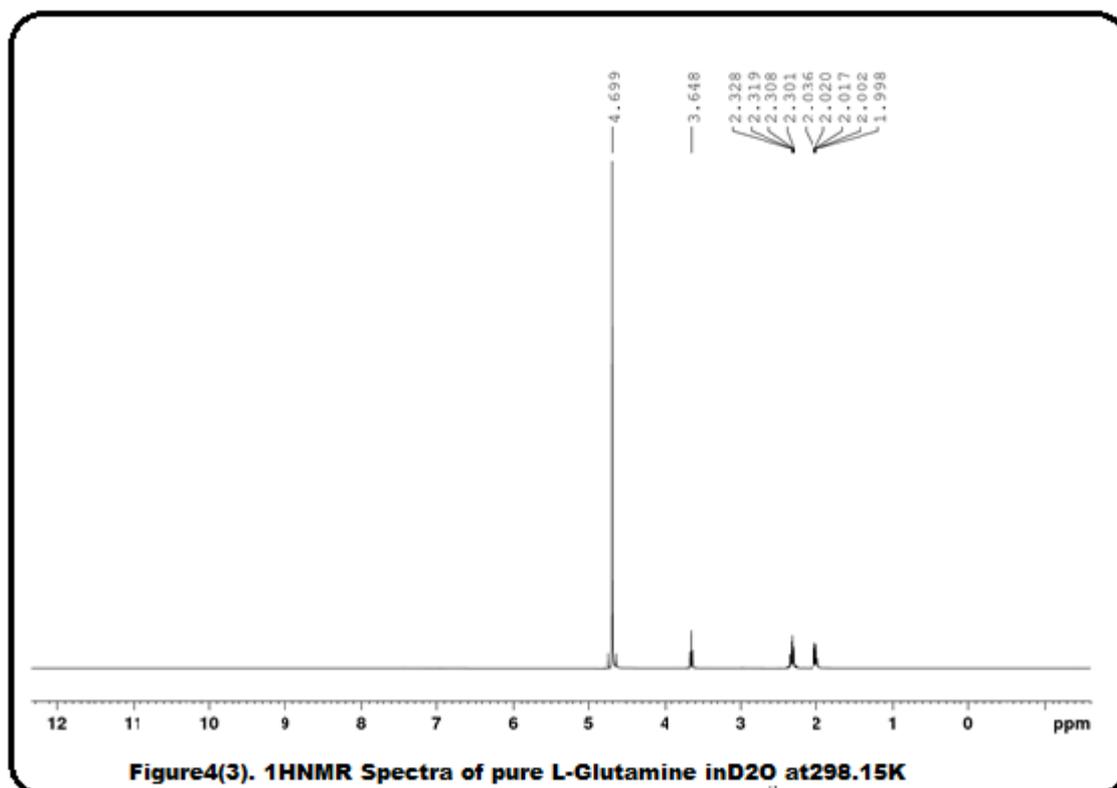
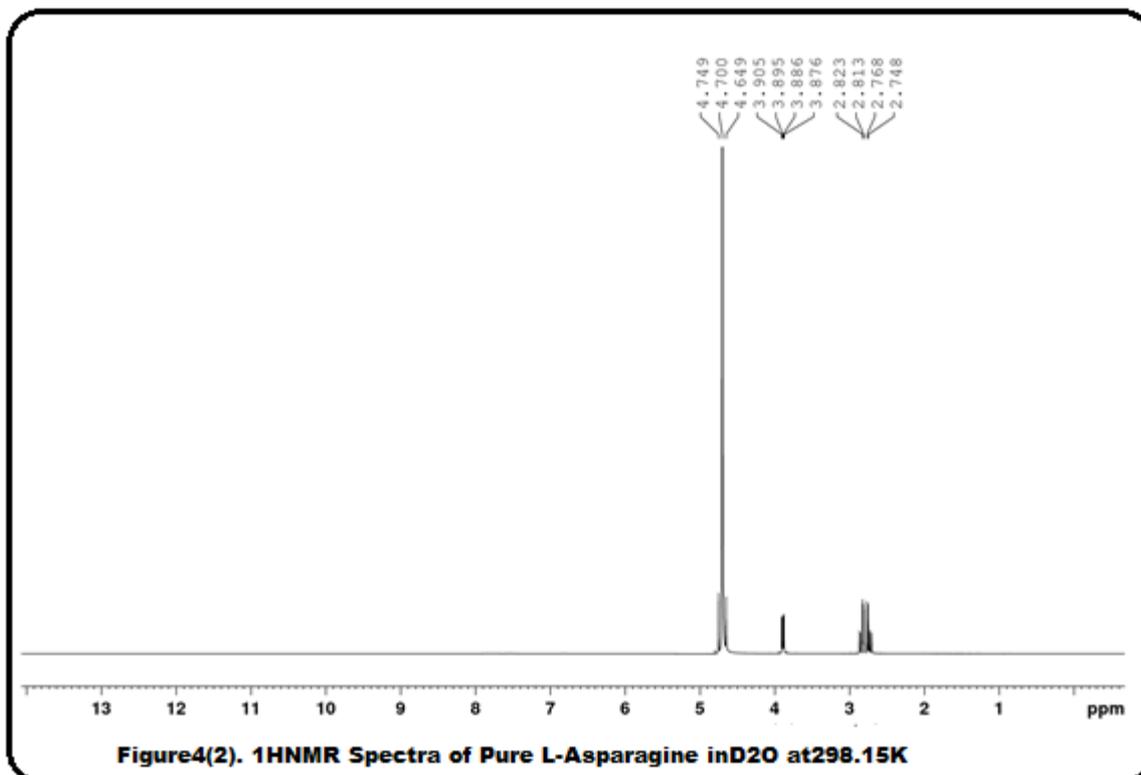


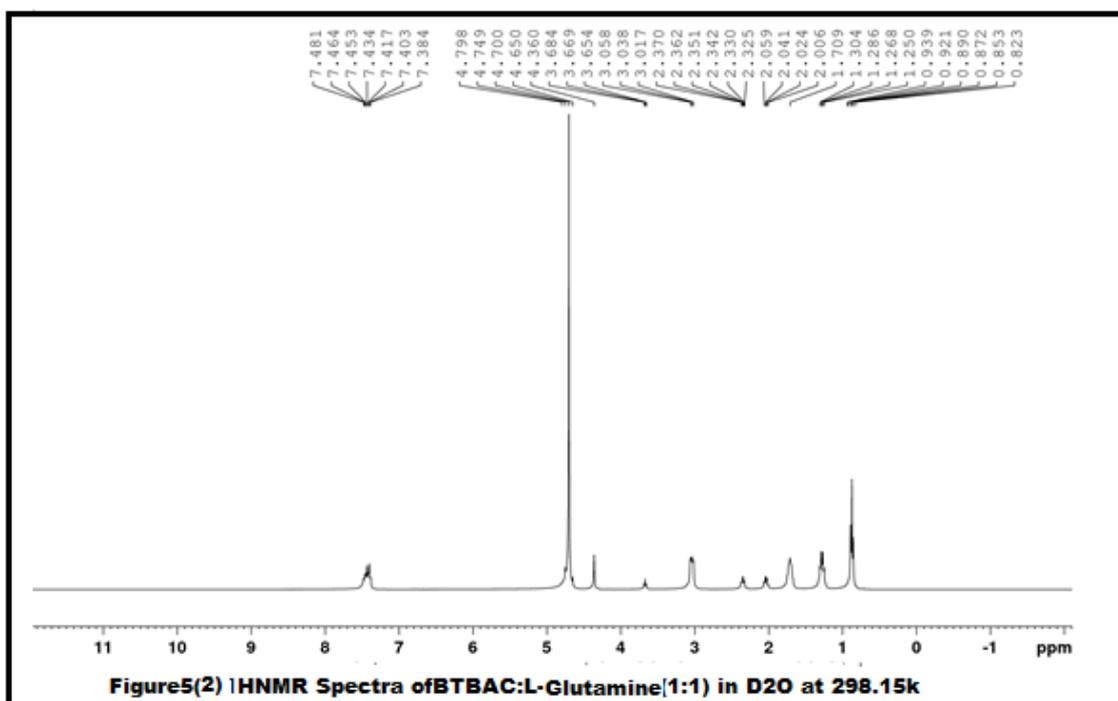
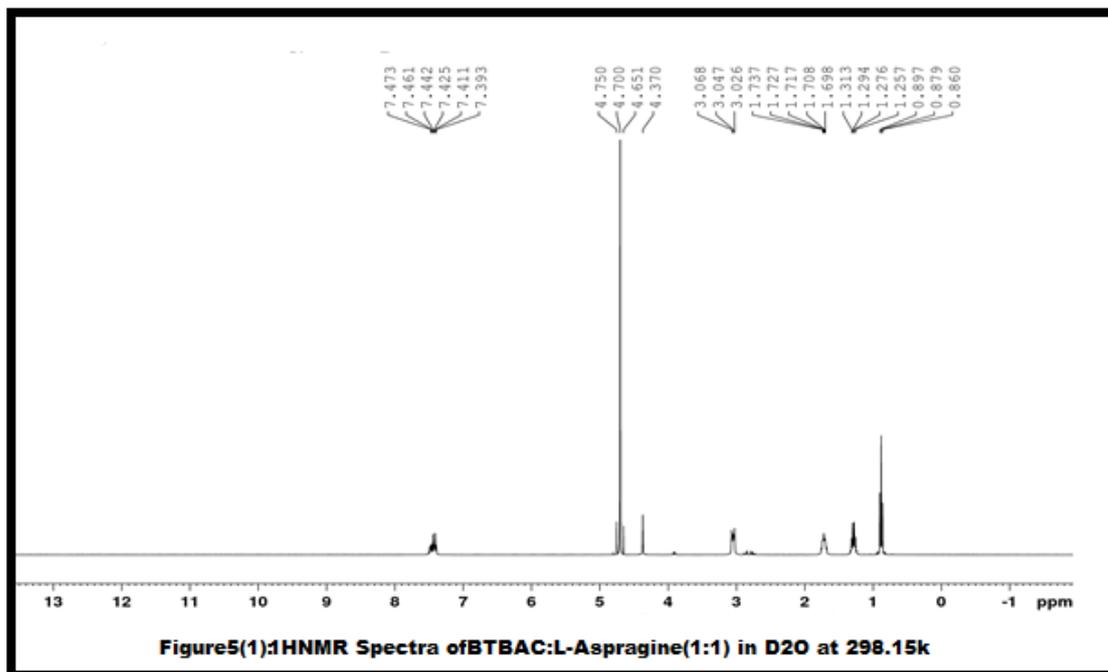
**Figure2.** variation of  $R_M^0$  values of L-asparagine solution Against(298.15k,303.15k,308.15k) in aqueous IL at 0.001m,0.003m,0.005m



**Figure3.** variation of  $R_M^O$  of L-glutamine solution Against (298.15k,303.15k,308.15k) in aqueous IL at 0.001m,0.003m,0.005m







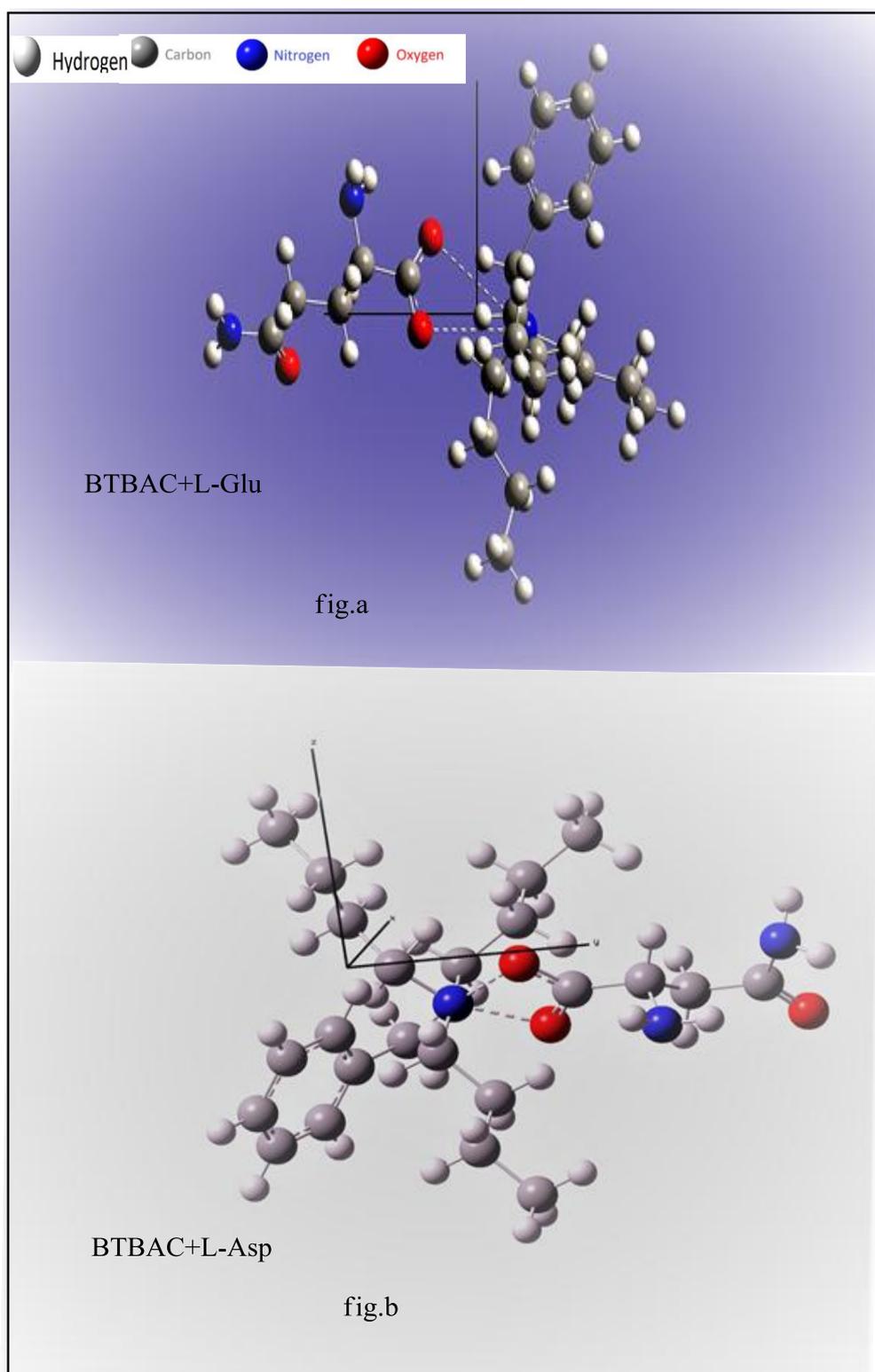


Fig. (a, b): Optimised geometry of (a) BTBAC + L-Glu and (b) BTBAC+L-Asp systems.

**Scheme-1**

# CHAPTER-X

## CONCLUDING REMARKS

The aim of the research work embodied in our thesis was to investigate the various interactions such as solute-solute, solute- solvent as well as molecular interaction associated with some ionic liquid and some biologically potent molecules(amino acids) prevailing in liquid environment. The different interactions involving ionic liquids and amino acids have been studied with the help of some physicochemical parameter, thermodynamic parameter, quantum mechanically computational study, transport phenomena, optical properties along with the help of spectroscopic investigations.

The volumetric, viscometric , conductometric, refractive index, surface tension measurement are very important properties is to used for the determination of ion-solvent interaction. Limiting apparent molar volume obtained from the density data and viscosity B – coefficients obtained from the viscosity measurements also gives the valuable information regarding the solute- solute and solute- solvent interactions.

In reality, the ion- solvent interactions is very complex in nature. There are strong electrical forces associated with the ions and ions with solvents , it is indeed not to separate them overall. However, if we noticed with carefully, valid conclusions can be obtained in many cases from apparent molar volume, viscosity, conductivity, NMR, UV-vis spectroscopy measurements relating to degree of freedom of structure and also order of the system.

In the chapter IV deals with the solute-solvent interaction behavior of studied ionic liquid and amino acids in aqueous solution have been determined by conductance measurements at three different temperatures(298.15k,303.15k,308.15k) and spectroscopic studies. The ILs and amino acids systems in aqueous solution indicate the non-covalent interactions among them and causing an increase of hydrodynamic radii of ions and a decrease of their ionic mobility, hence we have got the result a decrease in molar conductance. It has been concluded from the association constant values of the selected ILs with AAs obtained by using Uv-vis and fluorescence measurements that among the two ILs, 1-butyl-3-methylimidazolium octylsulphate [BMIM][C<sub>8</sub>SO<sub>4</sub>] interact more firmly with L-tyrosine than L-phenylalanine and in each system both IL and AA have been promoted to each due to non-covalent such as strong hydrophobic- hydrophobic, weak  $\pi \cdots \pi$ , columbic force of attraction, H-bond interactions etc. amongst themselves. The significant chemical shifts of ILs protons in presence of amino acids in

<sup>1</sup>HNMR studies also support the results obtained from other spectroscopic and conductance measurements.

Density, viscosity, refractive index and conductance measurements in the chapter V has provided the valuable information about ion-dipole interaction and show that the solute-solvent interaction between BTAC ionic liquid and biologically potent molecules, L-Aspartic acid and L-Glutamic amino acid systems is higher than the solute-solute interaction. This is resulted by hydrophobic interactions which lead to volume contraction. The physico-chemical methodologies, describes the mode of interaction in solution. Calculation of limiting apparent molar volume, limiting molar refraction, viscosity B-coefficient and molar conductance makes it possible to identify the interaction as predominant solute-solvent interaction and indicate the predominance of solute-solvent interaction than the solute-solute interaction. The values of  $(\delta\Phi_E^0/\delta T)_P$  and  $(dB/dT)$  have been calculated to provide the information that the solute-solvent interaction is structure-making. The extent of solvation is highest in L-Glutamic acid at 0.05m 313K and lowest in L-Aspartic acid at 0.01m 293K. The derived parameters obtained by analyzing various equations supplemented with experimental data sustain the same finale as discussed and explained above.

In the summary of this study obtained from chapter VI, it was found that there is a strong interaction between L-ascorbic and IL and it becomes stronger with rise in temperature. As molecules of L-ascorbic and IL have engaged each other, solute-co solute interaction is much greater than the solute-solute and solvent-solvent interactions in the ternary system.

In this chapter VII, aim of the present paper was to establish the nature of solute-solute and solute-solvent interactions in the solutions of TBMS + amino acid systems of several concentrations and temperatures (298.15K,303.15K,308.15K) for chemical and technological applications. The investigation of Physico-chemical parameters through density, viscosity, refractive index, surface tension and conductance study refers to the mode of interactions taking place in the amino acids; L-Arginine and L-Histidine in ionic liquid solutions of TBMS at different molalities (0.001,0.003,0.005) as well as different temperatures. In the present study, all the parameters were interpreted in terms of solute-solute and solute-solvent interactions occurring among the various components of the experimental solution mixtures. Analysis of apparent molar volume, limiting apparent molar volume, molar refraction, limiting molar refraction, viscosity B coefficient and surface tension signify the solute-solvent interaction is predominant over solute-solute interaction. The  $(\delta\Phi_E^0/\delta T)_P$  and  $(dB/dT)$  values have been considered to illustrate the facts that, the solute-solvent interaction is significantly structure breaking which is further established by Hepler's constant values. From the study of the investigated solutions presence of strong solute-solvent interaction was observed and also

supposed to be more effective and predominant than the solute–solute interaction occurring in experimental systems. Amino acid L-Histidine fused with the imidazole ring undergoes a lower degree of interactions in the presence of ionic liquid (TBMS) as compared to L-Arginine. Surface tension indicated the starring role of the hydrophilic and hydrophobic character of solutes in molecular interactions with TBMS in aqueous solutions. Again, conductance data also recommends the mode of interactions going on between the solute and solvent thereby the presence of mobility in the solution phase. Ultimately, strong hydrophobic-hydrophobic interactions are playing an important role too. Furthermore, electrostatic and hydrophobic interactions are more predominant for the L-Arginine-TBMS system, associating the experimental outcomes. The experiment definitely would provide for a more inclusive understanding of such systems to a large extent.

From chapter VIII, Some physicochemical parameters density, viscosity, refractive index, conductance and surface tension measurements of aqueous solution of amino acid, L-Methionine in the ionic liquids, Benzyl tri-methyl ammonium chloride and Benzyl tri-ethyl ammonium chloride. The above results supported by some spectroscopic techniques FTIR,  $^1\text{H-NMR}$  and UV-Vis spectroscopy and theoretically computational study provided the information that strong solute-solvent interactions dominate over the weak solute-solute interactions in the studied compounds. Further, L-Met in 0.005m BTEAC at 308.15K indicates highest solute-solvent interaction whereas, L-Met in 0.001m BTMAC at 298.15K shows the lowest. Again, mode of solute–solvent interaction is structure-breaking and the structure-breaking effect of L-Met is strongest in 0.001m aqueous BTMAC solution with highest packing or caging effect. The free energy of activation of viscous flow indicated greater solute–solvent interactions resulting in the formation of the transition state followed by breaking and altering the intermolecular forces prevailing in the solvent structure of the medium. Due to larger alkyl group, +I effect in BTEAC is greater than in BTMAC making the interaction more prominent in L-Met BTEAC solution, as there is presence of more lone pair availability of oxygen atom, making the interaction strong with the Ionic liquid.

From chapter IX, in the overview of this study, that there is a strong interaction between L-glutamine and BTBAC and it becomes stronger with rise in temperature and increase in mass fraction of BTBAC. All of these above physicochemical and spectroscopic along with computational works confirms the amino acids and IL (BTBAC) have engaged each other, solute-cosolute interaction is much greater than the solute-solute and solvent-solvent interactions in the ternary system.

It is very difficult to proper understanding the nature of ion-solvent interactions. However The wide range studies of the different physiochemical, thermodynamic, transport and

also spectral properties of the ionic liquid in different biologically potent molecules in liquid medium try to understanding the nature of ion- solvent interactions it is necessary to explained quantitatively the influence of the solvent and the extent of interactions associate with ions in solvents in solution chemistry.

In reality, the ion- solvent interactions is very complex in nature. There are strong electrical forces associated with the ions and ions with solvents it is indeed not to separate them overall. However, if we noticed with carefully, valid conclusions can be obtained in many cases from apparent molar volume, viscosity, conductivity, NMR, UV-vis spectroscopy measurements relating to degree of freedom of structure and also order of the system.

The ionic liquids and amino acid which used for my research work are very important in pharmaceutical industrial purpose, food industries, cosmetic and hygiene, paint industries, polymeric industry.

In the near future, we attempt to extend our research work with ionic liquids and amino acids; I hope that will certainly complement our present findings. In recent years, with the introduction of new synthetic technologies such as phase transfer catalysis, and catalysis, catalytic symmetric/asymmetric synthesis, the diversity of molecular interactions that can be studied has increased to the highest degree. I hope this thesis delivers a substantial launching point for the reader to begin their own investigation into the chemical natures of remarkable, however ionic liquids and natural amino acids. As more and more interesting and unusual ionic liquids and amino acid ionic liquids are discovered, the possibility for development of synthetic methods for these useful in different branch of science, academic, research area, industry and biologically important ionic liquids (ILS) and amino acids (AAS) grows up as well.

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## Exploring Diverse Interactions of Some Surface-Active Ionic Liquids with Amino Acids Prevalent in Aqueous Environments by Physicochemical Contrivance

Sukdev Majumder, Mitali Kundu, Raja Ghosh, Ranjoy Das, Nitish Roy, Mahendra Nath Roy\*

Department of Chemistry, University of North Bengal, Darjeeling – 734 013, West Bengal, India.

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## ABSTRACT

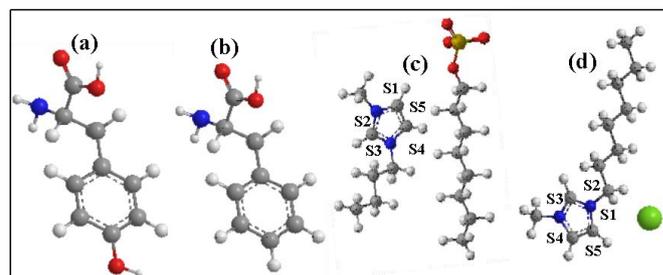
Molecular interactions of two (ILS) [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl with amino acids (AA) (AA= L-tyr, L-phe) in aqueous medium have been investigated by molar conductivities ( $\Lambda$ ) at three different temperatures. Spectroscopic studies have been performed to investigate the association behavior between the ILs and the selected amino acids and the spontaneity of this process. The <sup>1</sup>H NMR spectroscopy has also been carried out to expose the change in electronic conditions of various protons of ILs in the presence of different amino acids. All the results have been interpreted on the light of possible molecular interactions operating in the ternary system and varies in the order of ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-tyr) > ([MOIM]Cl + L-tyr) > ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-phe) > ([MOIM]Cl + L-phe) in water. The obtained experimental parameters will be extremely supportive to understand the mixing effect and other complicated biological process between amino acids and the chosen ionic liquids.

## 1. Introduction

Ionic liquids (ILs) belong to the family of those organic compounds which are nano-structured molten salts at room temperature and having cationic organic part and anionic inorganic/organic part [1]. ILs has a spacious diversity of unique physical and chemical character such as non-flammability, negligible vapor pressure, ability of dissolving large variety of compounds, high electrical conductivity etc., [2-6] which makes them a source of interest in different fields of science, industries and process such as biology, separation of amino acids electrochemistry, synthesis etc., [7-9]. Additionally, they can also be considered as green and designer solvent/electrolytes because of their uniqueness [3, 10-14]. In recent years, ILs are also used to frame the thermophysical properties of aqueous solution containing amino acid(s) (AA) and ILs which provides important information about the intermolecular interactions in solution phase [15-20]. Amino acids are used as model compounds as they are building block of proteins. Such interactions and thermodynamic properties studies helps to overcome the difficulties that arise in case of some biomolecules such as proteins due to their complexed structures and provides the information about the solute-solvent and solute-solute interactions that can be help to understand the effects of electrolytes on proteins [21-23].

It is already known that 1, 3-disubstituted imidazolium ring based ILs are important enough and widely used in solution chemistry [24-28]. The main significance about the imidazole ring is its existence in various amino acids, proteins and nucleic acids that have many biological activities. Additionally, all protons of 1, 3-disubstituted imidazolium ring are shown acidic character due to delocalization of positive charge over the ring [29].

This work is related to study the molar conductivities ( $\Lambda$ ) at different temperatures [30] (298.15 K, 305.15 K and 312.15 K) and spectroscopic methods (UV-Vis, FTIR) of two amino acids L-tyrosine (L-tyr) and L-phenylalanine (L-Phe) with 1-butyl-3-methylimidazolium octylsulphate [BMIM][C<sub>8</sub>SO<sub>4</sub>] and 1-methyl-3-octylimidazolium chloride [MOIM]Cl respectively in aqueous solution. All these data have been used to interpret the interactions (non-covalent) involved in ternary (L-tyr/L-Phe + [BMIM][C<sub>8</sub>SO<sub>4</sub>] / [BMIM][C<sub>8</sub>SO<sub>4</sub>] + water) systems. The structure of both AAs and ILs has been shown in Scheme 1. Moreover, such interactions of analogue imidazolium ILs with L-tyr and L-Phe systems are reported in theoretical background but no such works have been done to propose a model for the studied ILs and amino acids [31].



**Scheme 1** Ball and stick representation of (a) L-tyrosine, (b) L-phenylalanine, (c) 1-butyl-3-methylimidazolium octylsulphate [BMIM][C<sub>8</sub>SO<sub>4</sub>] and (d) 1-methyl-3-octylimidazolium chloride [MOIM]Cl respectively

## 2. Experimental Methods

## 2.1 Chemicals

The details of chemicals used in this work are listed in Table 1; no further purification has been performed. Triply distilled and degassed water (specific conductivity < 1  $\mu$ Scm<sup>-1</sup>) is used for preparation all solutions.

**Table 1** Brief description of the chemicals

| S.No. | Name of Chemicals                          | CAS NO.     | Abbreviation                            | supplier      | Purity |
|-------|--|-------------|---|---------------|--------|
| 1     | 1-butyl-3-methyl imidazolium octylsulphate | 445473-58-5 | [BMIM][C <sub>8</sub> SO <sub>4</sub> ] | Sigma-Aldrich | ≥ 0.95 |
| 2     | 1-methyl-3-octyl imidazolium chloride      | 64697-40-1  | [MOIM]Cl                                | Sigma-Aldrich | ≥ 0.97 |
| 3     | L-tyrosine                                 | 60-18-4     | L-tyr                                   | Sigma-Aldrich | ≥ 0.98 |
| 4     | L-phenyl alanine                           | 63-91-2     | L-phe                                   | sigma-Aldrich | ≥ 0.97 |

## 2.2 Apparatus

The mass of chemicals is measured by analytical balance METTLER TOLEDO-Model: AG-285 with an uncertainty  $\pm$  0.003 g. All the binary stock solutions are prepared carefully by mass dilution at 298.15 K ( $\pm$  0.01 K).

The conductance has been carried out in systronic-308 conductivity meter (accuracy  $\pm$ 0.01) using a dip-type immersion conductivity cell, CD-10, having a cell-constant of  $\sim$  0.1 $\pm$ 0.001 cm<sup>-1</sup>. Experiments are made in thermostatic jacket to maintain temperatures. The specific conductance

\*Corresponding Author:mahendraroy2002@yahoo.co.in(Mahendra Nath Roy)

( $\kappa$ ) of IL+ aq. amino acid solutions under investigation in three different temperatures (298.15 K, 305.15 K, 312.15 K) are measured to see the effect of temperatures on conductance for these systems. The molar conductance ( $\Lambda$ ) for the studied solutions has been calculated using following Eq.(1) and given in Figs. 1 and 2.

$$\Lambda = 1000 \kappa / c \quad (1)$$

where,  $c$  is the molar concentration of amino acids in the studied solution.

UV-visible spectra were recorded by JASCO V-530 UV/VIS Spectrophotometer. All the absorption spectra were recorded at  $25 \pm 0.1$  °C. A photon Technology International (PTI), USA, fluorescence spectrophotometer (Quantmaster-40) was used to record fluorescence spectra. NMR spectra were recorded at 600 MHz Bruker AVANCE at 298.15 K in D<sub>2</sub>O. Signals are quoted as  $\delta$  values in ppm using residual protonated solvent signals as internal standard (D<sub>2</sub>O:  $\delta$  4.700 ppm). Data are reported as chemical shift.

### 3. Results and Discussion

#### 3.1 Conductance Study

The conductance study of the interaction (solute-solvent) between the ILs ([BMIM][C<sub>8</sub>SO<sub>4</sub>]/[MOIM]Cl) with aqueous solution of L-tyr and L-phe amino acids has been performed at three different temperatures. The advantage of this study is that this measurement provides information about the interaction and transport phenomena of the (AA + ILs + water) ternary systems.

**Table 2** Conductivity values for the [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl IL with L-tyr in aqueous at three different temperatures(K<sup>a</sup>)

| Total vol.(mL) | Conc. of L-tyr (mM) | Molar conductance (Scm <sup>2</sup> mol <sup>-1</sup> ) of [BMIM][C <sub>8</sub> SO <sub>4</sub> ] |          |          | Molar conductance (Scm <sup>2</sup> mol <sup>-1</sup> ) of [MOIM]Cl |          |          |
|----------------|---------------------|--|----------|----------|---|----------|----------|
|                |                     | 298.15 K   | 305.15 K | 312.15 K | 298.15 K  | 305.15 K | 312.15 K |
| 10             | 0.0                 | 53.14  | 70.72    | 82.92    | 86.93   | 93.40    | 119.51   |
| 11             | 0.1818              | 44.28  | 59.85    | 70.66    | 71.64   | 81.53    | 90.36    |
| 12             | 0.3333              | 37.74  | 52.76    | 62.54    | 62.47   | 72.55    | 80.24    |
| 13             | 0.4615              | 33.83  | 46.77    | 56.47    | 55.25   | 66.23    | 73.45    |
| 14             | 0.5714              | 31.91  | 42.32    | 52.72    | 50.48   | 61.41    | 68.93    |
| 15             | 0.6667              | 30.78  | 40.67    | 49.58    | 48.20   | 58.56    | 65.84    |
| 16             | 0.75                | 29.93  | 39.53    | 47.25    | 46.41   | 56.22    | 63.11    |
| 17             | 0.8235              | 29.26  | 38.17    | 46.51    | 45.23   | 54.37    | 62.38    |
| 18             | 0.8889              | 29.18  | 37.22    | 45.11    | 44.66   | 52.64    | 61.46    |
| 19             | 0.9474              | 28.89  | 36.31    | 44.4     | 43.94   | 51.45    | 60.79    |
| 20             | 1.0                 | 27.59  | 35.62    | 43.26    | 43.17   | 50.62    | 59.74    |
| 21             | 1.0476              | 27.19  | 34.03    | 42.54    | 42.65   | 49.51    | 58.01    |
| 22             | 1.0909              | 26.84  | 33.21    | 41.97    | 41.90   | 48.84    | 57.53    |
| 23             | 1.13                | 25.98  | 32.24    | 41.14    | 41.40   | 48.16    | 57.08    |
| 24             | 1.1667              | 25.32  | 31.67    | 40.25    | 40.93   | 47.61    | 56.53    |

<sup>a</sup> Standard uncertainties in temperature (T)=0.01 K

**Table 3** Conductivity values for the [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl IL with L-phe in aqueous at three different temperatures(K<sup>a</sup>)

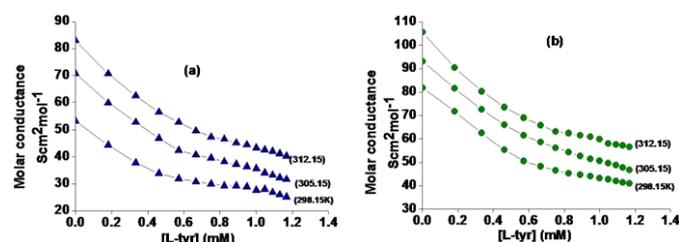
| Total vol.(mL) | Conc. of L-tyr (mM) | Molar conductance (Scm <sup>2</sup> mol <sup>-1</sup> ) of [BMIM][C <sub>8</sub> SO <sub>4</sub> ] |          |          | Molar conductance (Scm <sup>2</sup> mol <sup>-1</sup> ) of [MOIM]Cl |          |          |
|----------------|---------------------|--|----------|----------|---|----------|----------|
|                |                     | 298.15 K   | 305.15 K | 312.15 K | 298.15 K  | 305.15 K | 312.15 K |
| 10             | 0.0                 | 60.35  | 72.27    | 83.62    | 86.92   | 93.55    | 119.34   |
| 11             | 0.1818              | 50.26  | 58.68    | 67.26    | 75.43   | 80.89    | 99.86    |
| 12             | 0.3333              | 42.84  | 50.95    | 59.37    | 67.15   | 72.35    | 87.72    |
| 13             | 0.4615              | 38.19  | 46.15    | 53.82    | 60.27   | 65.51    | 79.59    |
| 14             | 0.5714              | 34.45  | 43.25    | 50.55    | 54.59   | 60.68    | 75.74    |
| 15             | 0.6667              | 32.85  | 40.74    | 47.65    | 50.36   | 57.34    | 71.45    |
| 16             | 0.75                | 31.65  | 38.77    | 45.16    | 46.92   | 53.32    | 68.96    |
| 17             | 0.8235              | 29.45  | 37.41    | 44.46    | 45.45   | 53.56    | 66.75    |
| 18             | 0.8889              | 28.91  | 36.53    | 42.86    | 43.78   | 51.88    | 64.34    |
| 19             | 0.9474              | 28.53  | 35.22    | 41.57    | 42.53   | 50.02    | 62.23    |
| 20             | 1.0                 | 27.42  | 33.49    | 40.53    | 41.47   | 49.19    | 60.15    |
| 21             | 1.0476              | 26.09  | 32.31    | 39.25    | 40.39   | 48.45    | 59.04    |
| 22             | 1.0909              | 25.94  | 31.72    | 38.17    | 39.04   | 47.06    | 58.19    |
| 23             | 1.13                | 25.01  | 30.45    | 37.32    | 38.71   | 46.53    | 57.41    |
| 24             | 1.1667              | 24.62  | 29.91    | 36.05    | 37.47   | 45.25    | 56.95    |

<sup>a</sup> Standard uncertainties in temperature (T)=0.01K

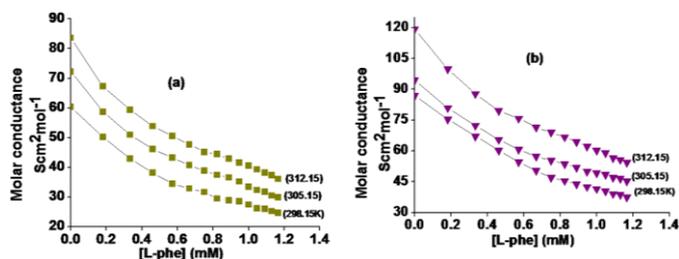
The molar conductivities ( $\Lambda$ ) of aqueous [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl has been monitored with increasing the concentration of L-tyr and L-phe respectively at three different temperatures and have been listed in Table 2 and 3. The Figs. 1 and 2 show the resulting plots of ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-tyr + water) (system 1), ([MOIM]Cl + L-tyr + water) (system 2), ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-phe + water) (system 3) and ([MOIM]Cl + L-phe + water) (system 4) respectively. For each system it has been observed that  $\Lambda$  values increase with increase in temperature and slow addition of AA to ILs solution causes a continuous decrease in molar conductance [32-35].

The decrease in molar conductance may be due to two factors- (i) involvement in non-covalent interactions of ILs with AA(s) [20, 33, 35] and (ii) [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl is an anionic and cationic surface-active ionic liquid (SAILs) respectively [36]. So, they have a positive tendency to form micelles after a certain concentration. Initially as there are no micelles, the free mobile ions of SAILs are accountable for the speedy decrease in  $\Lambda$  values with increasing amino acids content in solutions because of increasing system viscosity as well as the attractions between ILs and AAs with increasing AAs concentration. The strong intermolecular hydrophobic-hydrophobic attraction, and other non-covalent (hydrophilic,  $\pi$ - $\pi$  interactions, columbic attraction etc.) interactions must have been developed with amino acids [37] but after a certain point the ions contribution are less in transport change and leading to level off. As the [BMIM][C<sub>8</sub>SO<sub>4</sub>] SAIL has to some extent more acidic protons and less hindered imidazolium ring protons [31] and long hydrophobic alkyl chain in counter ion part than the [MOIM]Cl, so the former IL must be involved in good interactions than [MOIM]Cl with the amino acids. Apart from these interactions, L-tyr has an extra hydroxyl (-OH) group at para position which helps to bind the ILs more firmly by H-bond than L-phe and involved in strong interactions with the ILs than L-phe. Thus, considering all of these the stability order of interactions follows the order of- (system 1) > (system 2) > (system 3) > (system 4).

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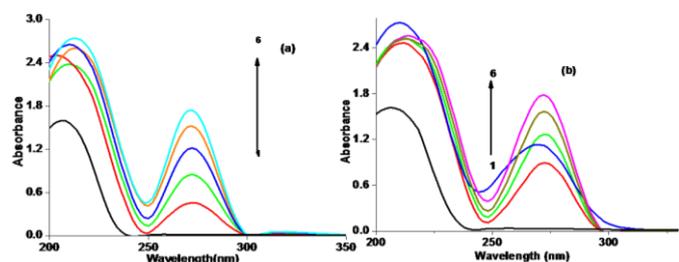
**Fig.1** Molar conductance of (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>] in aqueous solution with L-tyr and (b) [MOIM]Cl in aqueous solution with L-tyr at three different temperatures



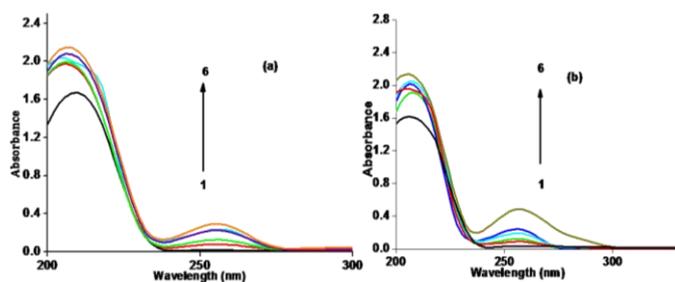
**Fig. 2** Molar conductance of (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>] in aqueous solution with L-phe and (b) [MOIM]Cl in aqueous solution with L-phe at three different temperatures

#### 3.2 UV-Vis Spectroscopy

The UV-vis spectroscopy is a suitable method that not only helps to get the important information about interaction behavior in systems but also provide the binding nature of binding partners [38]. The absorption peak of [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl in aqueous solution by varying concentration of amino acids (i.e. L-tyr and L-phe) are shown in Figs. 3 and 4. The strong absorption peaks for both two imidazolium based ILs appeared at ~210 nm ( $\lambda_{max}$ ) [39]. From Figs. 3 and 4, it is seen that continuous increase in absorption intensity has been occurred due to regular addition of different concentrated amino acids to both the ILs. Such spectral shifts due to the occurrence of  $\pi$ - $\pi$  and C-H $\cdots$  $\pi$  interactions that may involved in the ILs and L-tyr and L-phe.



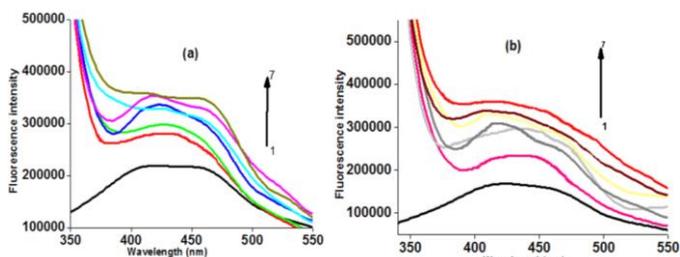
**Fig. 3** Absorption spectra of (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>] and (b) [MOIM]Cl at different concentration of L-tyrosine (1) absence of L-tyrosine, (2) 0.0004 M, (3) 0.0008 M, (4) 0.0012 M, (5) 0.0016 M, (6) 0.0018 M and (7) 0.002 M respectively



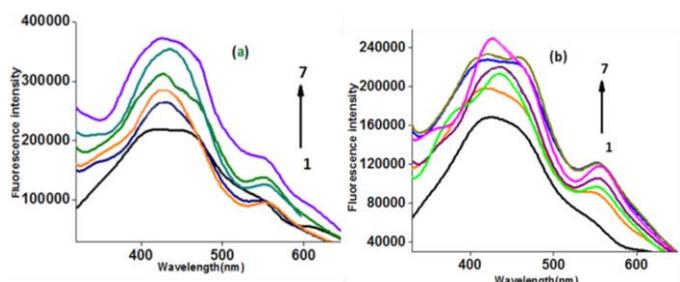
**Fig. 4** Absorption spectra of (a) [BMIM][C<sub>6</sub>SO<sub>4</sub>] and (b) [MOIM]Cl at different concentration of L-phenylalanine (1) absence of L-phenylalanine, (2) 0.0004 M, (3) 0.0008 M, (4) 0.0012 M, (5) 0.0016 M, (6) 0.0018 M and (7) 0.002 M respectively

### 3.3 Steady State Fluorescence Study

The interactions phenomena of the imidazolium ILs with the amino acids have further been further investigated by fluorescence technique [40]. The imidazolium ring of the ILs is responsible for giving significant emission spectra in fluorescence. The emission peaks of both ILs are close enough to each other and appeared at  $\lambda_{\text{max}}^{\text{em}} 420 \text{ nm}$  [41]. This also implies the less contribution of alkyl chain of [BMIM][C<sub>6</sub>SO<sub>4</sub>] and [MOIM]Cl imidazolium based ILs in emission spectra. By keeping constant concentration of ILs in aqueous solution and gradually addition of increase in concentration of amino acids causing the continuous enhancement of the fluorescence intensities of both ILs which indicate that molecular interactions/associations are obviously arising there (Fig. 5-6).



**Fig. 5** Fluorescence spectra of (a) [BMIM][C<sub>6</sub>SO<sub>4</sub>] and (b) [MOIM]Cl at different concentration of L-tyrosine (1) absence of L-tyrosine, (2) 0.0003 M, (3) 0.0006 M, (4) 0.0009 M, (5) 0.0012 M, (6) 0.0015 M and (7) 0.0018 M respectively



**Fig. 6** Fluorescence spectra of (a) [BMIM][C<sub>6</sub>SO<sub>4</sub>] and (b) [MOIM]Cl at different concentration of L-phenylalanine (1) absence of L-phenylalanine, (2) 0.0003 M, (3) 0.0006 M, (4) 0.0009 M, (5) 0.0012 M, (6) 0.0015 M and (7) 0.0018 M respectively

### 3.4 Determination of Association Constant-Spontaneity and Features of Interactions

The association constant in this phenomenon i.e. [BMIM][C<sub>6</sub>SO<sub>4</sub>] / [MOIM]Cl ILs interactions with L-tyr and L-phe have been calculated by Benesi-Hildebrand Eq. (2) [38,39,42] using the absorption and emission spectral (fluorescence) data (Tables 4 and 5). This is very helpful method for quantitative estimation of extent of binding of two binding events.

$$\frac{1}{I - I_0} = \frac{1}{K_a(I - I_0)} \cdot \frac{1}{[\text{AA}]} + \frac{1}{(I - I_0)} \quad (2)$$

where,  $I_0$  and  $I$  are the intensity values of absorption/fluorescence of both IL in absence and presence of AAs respectively.  $I_1$  is the intensity of absorption/fluorescence of ILs due to association with amino acids and  $K_a$  is the association constant.

The double reciprocal plots of  $1/(I - I_0)$  versus  $1/[\text{AA}]$  for all the systems have been shown in Figs. 7 and 8; and all system are within good linear correlation ( $R^2 > 0.900$ ) and suggest the 1:1 interaction is present for each system. The  $K_a$  values have been calculated from the ratio of intercept and slope of each plot. It can be observed from the  $K_a$  value that the association for [BMIM][C<sub>6</sub>SO<sub>4</sub>] is greater with L-tyr than L-phe and least for ([MOIM]Cl + L-phe) system.

<https://doi.org/10.30799/jacs.209.19050203>

Further by using the value of  $K_a$  the free energy changes ( $\Delta G$ ) for the adduct formation of ILs and AAs have been calculated using the following the Eq.(3),

$$\Delta G = -RT \ln K \quad (3)$$

The values of  $\Delta G$  for all adducts have been listed in Tables 4-7 and the negative values be a sign of the feasibility of the adducts formation by interactions. The values of  $K_a$  and  $\Delta G$  make known that (system 1) have greater attraction possibility than the others. In theoretically background, the possibility of such an interaction on for an analogue system is reported earlier [31]. Thus, we can endorse that a stronger H-bond and  $\pi \cdots \pi$  stacking interactions are developed in case of L-tyr than L-phe from S2 side (Scheme 1) that can enhance the stability and can also be attributed for such order of interactions. Further the weak coulombic force of attraction between the positively charged ring cation and the negatively charged AA plays a role in bringing them close to each other.

**Table 4** Data for the Benesi-Hildebrand double reciprocal plot obtained from UV-Vis spectroscopy for aqueous [BMIM][C<sub>6</sub>SO<sub>4</sub>] and [MOIM]Cl ILs with L-tyr system at 298.15K<sup>a</sup>

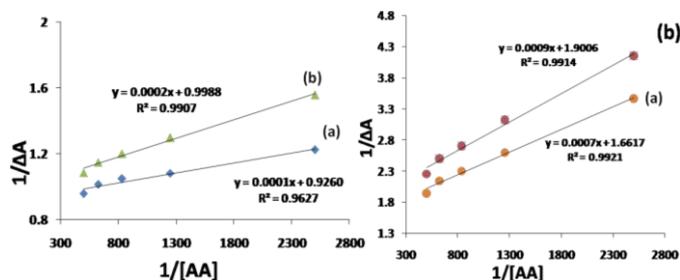
| [BMIM][C <sub>6</sub> SO <sub>4</sub> ] (M) | Conc. of L- tyr (M) | $I_0$   | Intensity (I) | $K_a(\text{M}^{-1})$ | $\Delta G \text{ KJmol}^{-1}$  |
|---|---------------------|---------|---------------|----------------------|--------------------------------|
| $4 \times 10^{-4}$                          | 0.0004              |         | 2.43106       | 9260                 | -22.64                         |
|   | 0.0008              |         | 2.53914       |                      |                                |
|   | 0.0012              |         | 2.56891       |                      |                                |
|   | 0.0016              | 1.61436 | 2.60076       |                      |                                |
|   | 0.002               |         | 2.65974       |                      |                                |
| [MOIM]Cl (M)                                | Conc. of L- tyr (M) | $I_0$   | Intensity (I) | $K_a(\text{M}^{-1})$ | $\Delta G \text{ KJ mol}^{-1}$ |
| $4 \times 10^{-4}$                          | 0.0004              |         | 2.31916       | 4994                 | -21.11                         |
|   | 0.0008              |         | 2.44828       |                      |                                |
|   | 0.0012              | 1.67759 | 2.50968       |                      |                                |
|   | 0.0016              |         | 2.54860       |                      |                                |
|   | 0.002               |         | 2.59924       |                      |                                |

<sup>a</sup> Standard uncertainties in temperature ( $T$ ) = 0.01K

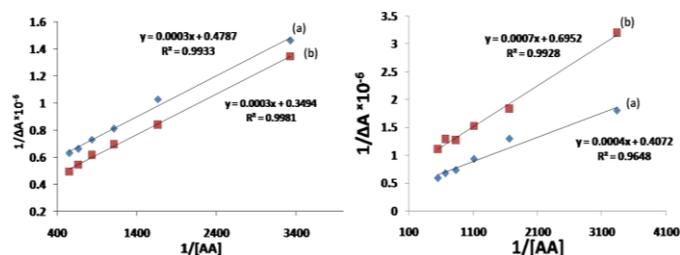
**Table 5** Data for the Benesi-Hildebrand double reciprocal plot obtained from UV-Vis spectroscopy for aqueous [BMIM][C<sub>6</sub>SO<sub>4</sub>] and [MOIM]Cl ILs with L-phe system at 298.15K<sup>a</sup>

| [BMIM][C <sub>6</sub> SO <sub>4</sub> ] (M) | Conc. of L- phe (M) | $I_0$  | Intensity (I) | $K_a(\text{M}^{-1})$ | $\Delta G \text{ KJ mol}^{-1}$ |
|---|---------------------|--------|---------------|----------------------|--------------------------------|
| $4 \times 10^{-4}$                          | 0.0004              |        | 3.45837       | 2373.86              | -19.27                         |
|   | 0.0008              |        | 2.60077       |                      |                                |
|   | 0.0012              | 1.6144 | 2.30684       |                      |                                |
|   | 0.0016              |        | 2.14971       |                      |                                |
|   | 0.002               |        | 1.94121       |                      |                                |
| [MOIM]Cl (M)                                | Conc. of L- phe (M) | $I_0$  | Intensity (I) | $K_a(\text{M}^{-1})$ | $\Delta G \text{ KJ mol}^{-1}$ |
| $4 \times 10^{-4}$                          | 0.0004              |        | 4.14765       | 2111.78              | -18.98                         |
|   | 0.0008              |        | 3.11910       |                      |                                |
|   | 0.0012              |        | 2.69882       |                      |                                |
|   | 0.0016              | 1.6776 | 2.49336       |                      |                                |
|   | 0.002               |        | 2.25789       |                      |                                |

<sup>a</sup> Standard uncertainties in temperature ( $T$ ) = 0.01K



**Fig. 7** Benesi-Hildebrand plot of  $1/\Delta A$  vs.  $1/[\text{AA}]$  in UV-vis spectroscopy for (a) [BMIM][C<sub>6</sub>SO<sub>4</sub>] and (b) [MOIM]Cl in L-tyr and for (c) [BMIM][C<sub>6</sub>SO<sub>4</sub>] and (d) [MOIM]Cl in L-phe at 298.15K<sup>a</sup>



**Fig. 8** Benesi-Hildebrand plot of  $1/\Delta A$  vs.  $1/[\text{AA}]$  in fluorescence spectroscopy for (a) [BMIM][C<sub>6</sub>SO<sub>4</sub>] and (b) [MOIM]Cl in L-tyr and for (c) [BMIM][C<sub>6</sub>SO<sub>4</sub>] and (d) [MOIM]Cl in L-phe at 298.15K<sup>a</sup>

**Table 6** Data for the Benesi-Hildebrand double reciprocal plot obtained from fluorescence spectroscopy for aqueous [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl ILs with L-tyr system at 298.15K<sup>a</sup>

| [BMIM][C <sub>8</sub> SO <sub>4</sub> ] (M) | Conc. of L- tyr (M) | I <sub>0</sub> | Intensity (I) | K <sub>a</sub> (M <sup>-1</sup> ) | ΔG KJmol <sup>-1</sup> |
|---|---------------------|----------------|---------------|-----------------------------------|------------------------|
| 10 x 10 <sup>-4</sup>                       | 0.0003              |                | 270750        |                                   |                        |
|   | 0.0006              |                | 299469        |                                   |                        |
|   | 0.0009              | 202353         | 325637        | 1595                              | -18.28                 |
|   | 0.0012              |                | 339150        |                                   |                        |
|   | 0.0015              |                | 353260        |                                   |                        |
|   | 0.0018              |                | 360658        |                                   |                        |
| [MOIM]Cl (M)                                | Conc. of L- tyr (M) | I <sub>0</sub> | Intensity (I) | K <sub>a</sub> (M <sup>-1</sup> ) | ΔG KJmol <sup>-1</sup> |
| 10 x 10 <sup>-4</sup>                       | 0.0003              |                | 233021        |                                   |                        |
|   | 0.0006              |                | 277888        |                                   |                        |
|   | 0.0009              | 158736         | 302731        | 1164                              | -17.50                 |
|   | 0.0012              |                | 321062        |                                   |                        |
|   | 0.0015              |                | 341268        |                                   |                        |
|   | 0.0018              |                | 360191        |                                   |                        |

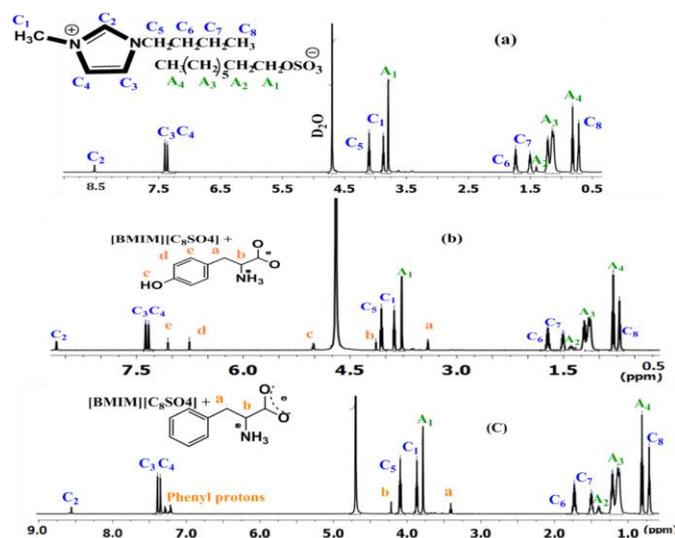
<sup>a</sup> Standard uncertainties in temperature (T)=0.01K**Table 7** Data for the Benesi-Hildebrand double reciprocal plot obtained from fluorescence spectroscopy for aqueous [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl ILs with L-phe system at 298.15K<sup>a</sup>

| [BMIM][C <sub>8</sub> SO <sub>4</sub> ] (M) | Conc. of L- phe (M) | I <sub>0</sub> | Intensity (I) | K <sub>a</sub> (M <sup>-1</sup> ) | ΔG KJmol <sup>-1</sup> |
|---|---------------------|----------------|---------------|-----------------------------------|------------------------|
| 10 x 10 <sup>-4</sup>                       | 0.0003              |                | 257999        |                                   |                        |
|   | 0.0006              |                | 279539        |                                   |                        |
|   | 0.0009              | 202353         | 309878        | 1080                              | -17.32                 |
|   | 0.0012              |                | 338953        |                                   |                        |
|   | 0.0015              |                | 351114        |                                   |                        |
|   | 0.0018              |                | 373406        |                                   |                        |
| [MOIM]Cl (M)                                | Conc. of L- phe (M) | I <sub>0</sub> | Intensity (I) | K <sub>a</sub> (M <sup>-1</sup> ) | ΔG KJmol <sup>-1</sup> |
| 10 x 10 <sup>-4</sup>                       | 0.0003              |                | 190069        |                                   |                        |
|   | 0.0006              |                | 213359        |                                   |                        |
|   | 0.0009              | 158736         | 224236        | 933                               | -16.95                 |
|   | 0.0012              |                | 236632        |                                   |                        |
|   | 0.0015              |                | 237774        |                                   |                        |
|   | 0.0018              |                | 249594        |                                   |                        |

<sup>a</sup> Standard uncertainties in temperature (T)=0.01

### 3.4 NMR Study

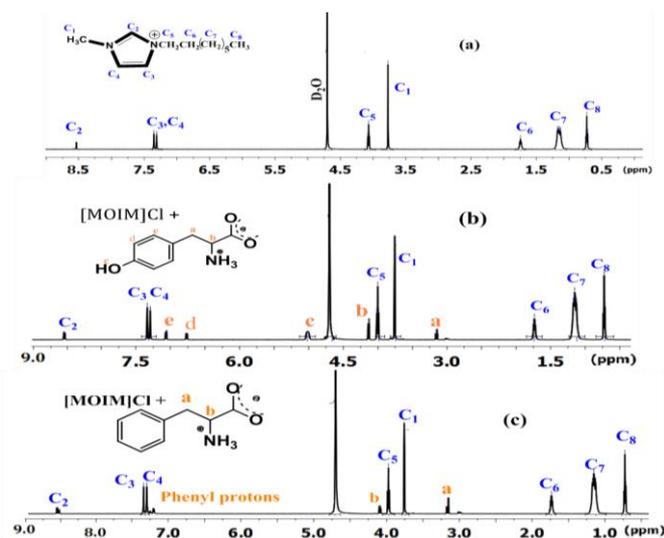
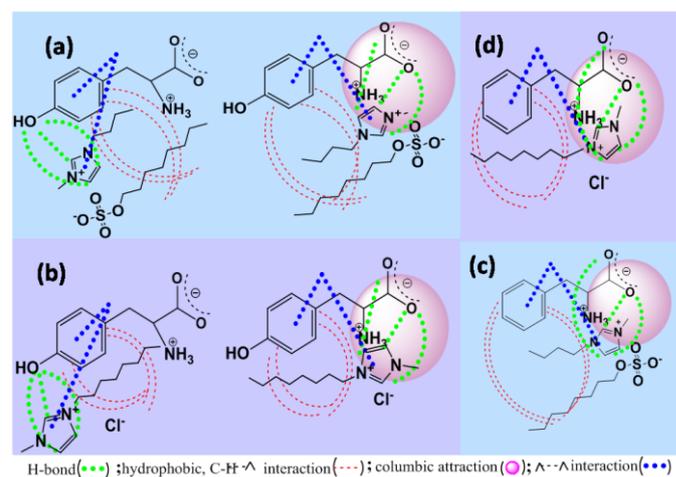
Nuclear magnetic resonance (NMR) is a very effectual technique for studying the changes the electronic environment around the different protons of ILs in presence of various kinds of amino acids [41]. In <sup>1</sup>H NMR the binary mixture of [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl with individual L-tyr and L-phe have been recorded in D<sub>2</sub>O at 298.15 K respectively (Table 8).

**Fig. 9** <sup>1</sup>H NMR spectra of (a) [BMIM][C<sub>8</sub>SO<sub>4</sub>], (b) ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-tyr) system and (c) ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-phe) system in D<sub>2</sub>O at 298.15 K

The chemical shifts of [BMIM][C<sub>8</sub>SO<sub>4</sub>] / [MOIM]Cl depends on the electronic space environment present in their surrounding area. It is found that significant upfield shifts for alkyl protons of the imidazolium ring have been occurred after mixing of amino acids. This indicates the presence of intermolecular hydrophobic- hydrophobic interactions that leading to increase the electron density around the imidazolium ring. It can be seen from chemical shifts that in both ILs the alkyl chain protons attached to imidazolium ring are in good intermolecular interactions with amino acids <https://doi.org/10.30799/jacs.209.19050203>

Cite this Article as: Sukdev Majumder, Mitali Kundu, Raja Ghosh, Ranjoy Das, Nitish Roy, Mahendra Nath Roy, Exploring diverse interactions of some surface-active ionic liquids with amino acids prevalent in aqueous environments by physicochemical contrivance, J. Adv. Chem. Sci. 5(2) (2019) 637–642.

but comparing the protons of imidazolium ring, downfield shift for C<sub>2</sub> proton and upfield shifts for other imidazolium ring protons (C<sub>3</sub>, C<sub>4</sub>) has been observed (Figs. 9 and 10).

**Fig. 10** <sup>1</sup>H NMR spectra of (a) [MOIM]Cl, (b) ([MOIM]Cl + L-tyr) system and (c) ([MOIM]Cl + L-phe) system in D<sub>2</sub>O at 298.15 K**Scheme 2** Schematic representation of interactions between (a) ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-tyr) (b) ([MOIM]Cl + L-tyr) (c) ([BMIM][C<sub>8</sub>SO<sub>4</sub>] + L-phe) and (d) ([MOIM]Cl + L-phe) systems in aqueous solution respectively**Table 8** <sup>1</sup>H NMR chemical shift displacements of [BMIM][C<sub>8</sub>SO<sub>4</sub>] and [MOIM]Cl in interaction with L-tyr and L-phe in D<sub>2</sub>O at 298.15 K<sup>a</sup>

| IL protons                                 | Free IL δ (ppm) | IL with L-tyr δ (ppm) | IL with L-phe δ (ppm) |
|--|-----------------|-----------------------|-----------------------|
| <b>[BMIM][C<sub>8</sub>SO<sub>4</sub>]</b> |                 |                       |                       |
| C1   | 3.892           | 3.881                 | 3.884                 |
| C2   | 8.589           | 8.646                 | 8.598                 |
| C3, C4                                     | 7.358-7.399     | 7.328-7.374           | 7.348-7.392           |
| C5   | 4.091-4.103     | 4.070-4.082           | 4.083-4.095           |
| C6   | 1.726-1.751     | 1.711-1.736           | 1.719-1.744           |
| C7   | 1.486-1.499     | 1.481-1.495           | 1.483-1.489           |
| C8   | 0.710-0.716     | 0.707-0.711           | 0.709-0.714           |
| A1   | 3.794-3.802     | 3.774-3.798           | 3.786-3.800           |
| A2   | 1.376-1.387     | 1.372-1.381           | 1.374-1.383           |
| A3   | 1.123-1.252     | 1.115-1.243           | 1.117-1.248           |
| A4   | 0.818-830       | 0.790-0.815           | 0.787-0.812           |
| <b>[MOIM]Cl</b>                            |                 |                       |                       |
| C1   | 3.771           | 3.756                 | 3.757                 |
| C2   | 8.552           | 8.602                 | 8.590                 |
| C3, C4                                     | 7.310-7.356     | 7.290-7.348           | 7.297-7.353           |
| C5   | 4.057-4.068     | 4.043-4.055           | 4.040-4.056           |
| C6   | 1.738-1.749     | 1.723-1.746           | 1.720-1.748           |
| C7   | 1.129-1.161     | 1.127-1.152           | 1.127-1.153           |
| C8   | 0.717-0.741     | 0.712-0.737           | 0.714-0.740           |

It most probably suggests the orientation for imidazolium ring that allows strong H-bond formation with C<sub>2</sub> proton and weak π...π interactions involving C<sub>3</sub>, C<sub>4</sub> and benzene ring of AA(s). Thus, two opposing

influences i.e. H-bond and  $\pi\cdots\pi$  interactions are possibly responsible for distinct shifts for ring protons [43]. The downfield shift for C<sub>2</sub> proton of [BMIM] cation is larger than the [MOIM] cation C<sub>2</sub> protons, thus it has been concluded that ([BMIM] cation $\cdots$ AA) H-bonding are somewhat stronger than ([MOIM] cation $\cdots$ AA) interactions. Thus all the variations in chemical shifts are perhaps due to contribution of various factors: such as- (i) H-bond interactions between the acidic proton of ring with oxygen atom of amino acids [(C-H)<sub>imidazolium ring</sub> $\cdots$ O<sub>AA</sub>], (ii) aromatic ring current effect: the  $\pi\cdots\pi$  interactions of imidazolium ring with the phenyl ring of amino acid, (iii) weak C-H $\cdots$   $\pi$  between the cation and AA, (iv) hydrophobic interactions, (v) columbic force of attraction are being there [44, 45] (Scheme 2) which are in good agreement with that obtained by our other experiments.

#### 4. Conclusion

The solute-solvent interaction behavior of studied ionic liquid and amino acids in aqueous solution have been determined by conductance measurements at three different temperatures and spectroscopic studies. The ILs and amino acids systems in aqueous solution indicate the non-covalent interactions among them and causing an increase of hydrodynamic radii of ions and a decrease of their ionic mobility, hence we have got the result a decrease in molar conductance. It has been concluded from the association constant values of the selected ILs with AAs obtained by using Uv-vis and fluorescence measurements that among the two ILs, 1-butyl-3-methylimidazolium octylsulphate [BMIM][C<sub>8</sub>SO<sub>4</sub>] interact more firmly with L-tyrosine than L-phenylalanine and in each system both IL and AA have been promoted to each due to non-covalent such as strong hydrophobic- hydrophobic, weak  $\pi\cdots\pi$ , columbic force of attraction, H-bond interactions etc. amongst themselves. The significant chemical shifts of ILs protons in presence of amino acids in <sup>1</sup>HNMR studies also support the results obtained from other spectroscopic and conductance measurements.

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Research Article

## Exploration of Solvation Consequences of Some Biologically Potent Molecules in Aqueous Ionic Liquid Solutions with the Manifestation of Molecular Interactions

Sukdev Majumder<sup>1</sup>, Anuradha Sinha<sup>2</sup>, Lovely Sarkar<sup>3</sup>, Tanusree Ray<sup>3</sup>,  
Vikas Kumar Dakua<sup>4</sup> and Mahendra Nath Roy<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, University of North Bengal, Darjeeling, WB, India.

<sup>2</sup>Department of Chemistry, Islampur College, Islampur, Uttar Dinajpur, WB, India. <sup>3</sup>Department of Chemistry, Siliguri College, Siliguri, WB, India.

<sup>4</sup>Department of Chemistry, Alipurduar College, Alipurduar, WB, India.

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**Abstract:** L-Aspartic and L-Glutamic acid (two solute molecules) interact with an ionic liquid (Benzyl tri-methyl ammonium chloride) in aqueous medium. The interactions have been explained on the basis of some parameters (apparent molar volume, viscosity B-coefficient, molar refraction, specific conductance) at different temperatures and different concentrations from density, viscosity, refractive index, conductance measurements, respectively. Using Masson equation, the experimental slopes and the limiting apparent molar volumes are obtained which explain the solute-solute and solute-solvent interactions. Viscosity parameters, A and B obtained from Jones-Doles equation explained the solute-solute and solute-solvent interactions in the solution. Molar refraction has been calculated from the Lorentz-Lorenz equation. The specific conductance also explained the interaction properties.

**Keywords:** L-Aspartic acid; L-Glutamic acid; Benzyl tri-methyl ammonium chloride; solute-solvent interaction; solute-solute interaction; Amino acids; Ionic liquid.

## 1. INTRODUCTION

Thermodynamic properties of amino acids in aqueous electrolyte solutions can provide valuable information regarding the conformation stability of proteins in these solutions, their

solubility, denaturation, dissociation into subunits, the activity of enzymes, separation and purification, solute–solvent and solute–solute interactions<sup>[1–4]</sup>. In fact, to optimize and control the extraction of bio molecules by ionic liquids (ILs) from aqueous media, knowledge of their thermophysical and thermodynamic properties is required. There are extensive volumetric and viscometric studies of amino acids in aqueous electrolyte solutions<sup>[5–7]</sup>. Consequently, the study of the volumetric properties of amino acids in aqueous ionic liquid solutions will be very useful for obtaining information about various types of interactions occurring in these solutions, which are mostly hydrophobic and electrostatic. Studying these interactions can provide important insight into the conformational stability and unfolding behavior of globular proteins. Thermodynamic properties of amino acids in aqueous solutions containing salts can provide valuable information about solute–solute and solute–solvent interactions. The aqueous solution containing salts affect conformational properties of amino acids and cause denaturation of proteins which is an important biological phenomenon. Therefore, keeping the importance and applicability in view, the systematic thermodynamic investigation of mixtures containing IL and amino acids is undertaken to understand the solvation behavior of these biomolecules<sup>[8]</sup>. Study of transport properties of electrolytes in aqueous media is extremely important to obtain information regarding the solvation and association behaviour of ions in solutions. The electrical conductivity of electrolytes in solvents mainly depends on the concentration of the electrolyte and the viscosity of the solvent. The application of the salt is well understood from the study of ionic solvation. Volumetric, viscometric, refractometric and conductometric techniques render an insight into the molecular interactions that are prevailing in solution and helps in the better understanding of the behaviour of the salt in water.

An ionic liquid (IL) is a salt in the liquid state of melting point below some arbitrary temperature such as 373 K. They have specific intrinsic properties, such as negligible vapour pressure, high thermal stability, large liquid range, ability of dissolving a variety of chemicals, large electrochemical window. They are used as “designer solvents” and “green” replacements for volatile organic solvents used in reactions involving inorganic and biocatalytic reactions, etc. They are also utilized as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells). They are used in analytical equipment. They make up electrolytes in lithium-ion batteries, super capacitors and metal plating baths<sup>[9–14]</sup>. The chemicals used in this study find wide industrial usage. Benzyl tri-methyl ammonium chloride or BTAC is soluble in water and has lyophilic and hydrophilic group. It can be used as phase transfer catalyst in many biphasic organic transitions used in the agrochemicals, polymer and pharmaceutical industries. BTAC can also be used as a corrosion inhibitor in oilfield. L-Aspartic acid and L-Glutamic acid are both water soluble polar aliphatic amino acids having very weak dipole–ion interaction. L-Aspartic acid is an  $\alpha$ -amino acid that is used in the biosynthesis of proteins. Aspartic acid is commonly used to reduce feelings of tiredness, improve athletic performance, and increase the size and strength of muscles. Glutamic acid is an  $\alpha$ -amino acid that is used by almost all living beings in the biosynthesis of proteins. It is also an excitatory neurotransmitter in the vertebrate nervous system.

In the modern technology, the application of the salt is well understood from the study of ionic solvation or ion association. Ionic association of electrolytes in solution depends on the mode of solvation of its ions that in turn depends on the nature of the solvent/solvent mixtures<sup>[15–18]</sup>. The association and solvation behaviour of ions in solution is obtained from the conductance

measurement. Moreover, solvent properties as viscosity and the relative permittivity help in determining the extent of ion association and the solvent-solvent interactions. The volumetric, viscometric, refractometric and conductometric behaviour of solutes has been found to be very useful in elucidating the various interactions occurring in solutions.

In continuation of our investigation, the present work deals with the transport and thermodynamic properties of L-Aspartic acid and L-Glutamic acid in aqueous Benzyl tri-methyl ammonium chloride at 293K, 303K and 313K.

## 2. EXPERIMENTAL SECTION

**2.1. Source and purity of samples:** The studied IL, Benzyl tri-methyl ammonium chloride,  $C_{10}H_{16}ClN$  (M.W. 185.69 g/mole) and amino acids, L-Aspartic acid,  $C_4H_7NO_4$  (M.W. 133.11 g/mole) and L-Glutamic acid,  $C_5H_9NO_4$  (M.W. 147.13 g/mole) of puriss grade were purchased from Sigma Aldrich Germany, SRL India and TLC Japan, respectively and was used as purchased. The purity of mass of taken salts were  $\geq 0.99$ . The amino acids were dried in vacuum over blue silica gel for at least 72 h at room temperature. The other chemicals were used without further purification. Doubly distilled deionized water with a conductivity of approximately  $0.7 \mu S \cdot cm^{-1}$  was used for preparation of the solutions.

**2.2. Apparatus and procedure:** The vibrating-tube Anton Paar Density-Meter (DMA 4500M) was used to measure the density ( $\rho$ ) with a precision of  $0.00001 \times 10^{-3} (kg \cdot m^{-3})$ . The double-distilled water and dry air was used to calibrate the density meter <sup>[19]</sup>. The temperature was kept constant automatically within range  $\pm 0.01 K$ .

The viscosity was measured with the help of suspended Ubbelohde viscometer which was calibrated at room temperature (298K) using doubly distilled water. It was purified with methanol and using viscosity, density data from literature <sup>[20-21]</sup>. The viscometer was dried and cleaned perfectly through hot thermostat and then filled with experimental solution, vertically placed in a glass-walled thermostat (Bose–Panda instruments Pvt. Ltd.) This instrument was maintained to 0.01K. At thermal equilibrium the flow-time were recorded with the help of a stop watch with an accuracy of  $\pm 0.01s$ . The uncertainty for the measurement of viscosity was  $\pm 0.2 \times 10^{-3} mPa \cdot s$ .

Measurement of refractive index has been done with the help of a Digital Refractometer Mettler Toledo instrument. The accuracy for the refractive index measurement was  $\pm 0.0002$  units approximately. The refractometer was calibrated twice using distilled water for measurement of the refractive indices of experimental solutions. The calibration of instrument was made after few seconds of each measurement <sup>[19]</sup>. The light source was light-emitting diode,  $\lambda = 589.3 \text{ nm}$ . The temperature of the solution was maintained during the experiment in a Brookfield Digital TC-500 Thermostatic water bath.

The conductivity measurement was done by Mettler Toledo Instrument (In Lab730 probe cell). The specification of the cell has measurement of conductivity range (0.01-1000 mS/cm). The cell type 4 graphite having a cell constant  $0.56 \text{ cm}^{-1}$ . The calibration of the cell has been done with 0.01 N (NaCl solution). The accuracy of the conductance measurement was  $\pm 0.5\%$ . The specific conductance of the experimental solution having concentration (0.0010, 0.0025, 0.0040, 0.0055, 0.0070, 0.0085) m was reported at 293K, 303K, 313K and was converted into molar conductance by the following equation,  $\Lambda = 1000 \kappa / c$  (where  $c$  is the molar concentration of the studied amino acid solutions in the ionic liquid.  $\kappa$  is the specific conductance of the specified solutions <sup>[22-23]</sup>).

The mixtures were prepared by mixing known volume of solutions in airtight-stoppered bottles. At first, we prepared 0.01m IL, 0.03m IL, 0.05m IL in 250ml water. Then there was preparation of 0.1m L-Aspartic acid and 0.1m L-Glutamic acid in the aqueous ionic liquid solutions. We prepared and used: 20ml, 0.01m IL + 0.01m amino acid in six sets (0.0010m, 0.0025m, 0.0040m, 0.0055m, 0.0070m, 0.0085m by dilution), 0.03m IL + 0.01m amino acid in six sets (0.0010m, 0.0025m, 0.0040m, 0.0055m, 0.0070m, 0.0085m by dilution), 0.05m IL + 0.01m amino acid in six sets (0.0010m, 0.0025m, 0.0040m, 0.0055m, 0.0070m, 0.0085m by dilution) at 293K, 303K, 313K for experimental purpose. Adequate precautions were taken to minimize evaporation losses during the actual measurements. Mass measurements for stock solutions were done on a Mettler AG-285 electronic balance with a precision of  $\pm 0.0003 \times 10^{-3}$  kg. The conversion of molarity into molality was accomplished using experimental density values. The uncertainty in molality of solution is estimated to be  $\pm 0.0001$  mol. kg<sup>-1</sup>.

### 3. RESULTS AND DISCUSSION

Experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of different molality ( $m$ ) of aqueous ionic liquid (BTAC) solution at 293K, 303K and 313K are shown in **Table 1**. **Table 2** gives the experimental values of refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of different molality ( $m$ ) of aqueous ionic liquid (BTAC) solution at 293K, 303K and 313K.

**Table 1:** Experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of different molality ( $m$ ) of aqueous IL (BTAC) solution at 293K, 303K and 313K.

| Conc. of Aq. IL (BTAC) soln. in molality, $m$ (mol.kg <sup>-1</sup> ) | $\rho \times 10^{-3} (\text{kg.m}^{-3})$ |        |        | $\eta (\text{mPa.s})$ |       |       | $R_M$   |         |         |
|---|--|--------|--------|-----------------------|-------|-------|---------|---------|---------|
|   | 293K                                     | 303K   | 313K   | 293K                  | 303K  | 313K  | 293K    | 303K    | 313K    |
| 0.01  | .99840                                   | .99584 | .99239 | 1.064                 | 0.818 | 0.696 | 27.3547 | 27.3800 | 27.4676 |
| 0.03  | .99872                                   | .99614 | .99270 | 1.231                 | 1.010 | 0.892 | 27.3683 | 27.4317 | 27.5117 |
| 0.05  | .99912                                   | .99652 | .99306 | 1.266                 | 1.085 | 0.970 | 27.4246 | 27.4737 | 27.5544 |

**Table 2:** Experimental values of refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of different molality ( $m$ ) of aqueous IL(BTAC) solution at 293K, 303K and 313K.

| Conc. of Aq. IL (BTAC) soln. in molality, $m$ (mol.kg <sup>-1</sup> ) | $n_D$  |        |        | $\kappa (\text{mS/cm})$ |       |       |
|---|--------|--------|--------|-------------------------|-------|-------|
|   | 293K   | 303K   | 313K   | 293K                    | 303K  | 313K  |
| 0.01  | 1.3321 | 1.3315 | 1.3313 | 0.940                   | 1.047 | 1.073 |
| 0.03  | 1.3324 | 1.3322 | 1.3320 | 2.710                   | 2.860 | 2.970 |
| 0.05  | 1.3332 | 1.3330 | 1.3327 | 4.140                   | 5.200 | 5.390 |

**3.1. Density:** In **Table 3** and **Table 4**, the density ( $\rho$ ) values at 0.01m, 0.03m and 0.05m concentrations of aqueous (BTAC) ionic liquid solutions have been reported at 293K, 303K and 313K for different concentrations of L-Aspartic acid and L-Glutamic amino acid solutions, respectively which have been obtained by dilution method.

**Table 3:** Density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of L-Aspartic acid in aqueous (BTAC) ionic liquid solutions at 293K, 303K and 313K.

| Conc. of L-Aspartic acid soln. in molality, m (mol.kg <sup>-1</sup> ) | $\rho \times 10^{-3}$ (kg.m <sup>-3</sup> ) |             |             | $\eta$ (mPa.s) |             |             | $R_M$       |             |             |
|---|---|-------------|-------------|----------------|-------------|-------------|-------------|-------------|-------------|
|   | <u>293K</u>                                 | <u>303K</u> | <u>313K</u> | <u>293K</u>    | <u>303K</u> | <u>313K</u> | <u>293K</u> | <u>303K</u> | <u>313K</u> |
| <b>0.01m IL</b>   |   |             |             |                |             |             |             |             |             |
| 0.0010  | 0.99843                                     | 0.99587     | 0.99242     | 1.071          | 0.825       | 0.704       | 27.3688     | 27.4146     | 27.4819     |
| 0.0025  | 0.99851                                     | 0.99597     | 0.99250     | 1.081          | 0.836       | 0.715       | 27.3890     | 27.4219     | 27.4947     |
| 0.0040  | 0.99857                                     | 0.99603     | 0.99260     | 1.090          | 0.846       | 0.727       | 27.4030     | 27.4272     | 27.5070     |
| 0.0055  | 0.99866                                     | 0.99613     | 0.99272     | 1.100          | 0.857       | 0.740       | 27.4148     | 27.4320     | 27.5112     |
| 0.0070  | 0.99876                                     | 0.99624     | 0.99285     | 1.109          | 0.867       | 0.751       | 27.4195     | 27.4362     | 27.5226     |
| 0.0085  | 0.99887                                     | 0.99638     | 0.99298     | 1.117          | 0.877       | 0.763       | 27.4315     | 27.4398     | 27.5265     |
| <b>0.03m IL</b>   |   |             |             |                |             |             |             |             |             |
| 0.0010  | 0.99875                                     | 0.99617     | 0.99273     | 1.239          | 1.019       | 0.900       | 27.3899     | 27.4459     | 27.5184     |
| 0.0025  | 0.99885                                     | 0.99624     | 0.99281     | 1.249          | 1.032       | 0.915       | 27.4021     | 27.4535     | 27.5312     |
| 0.0040  | 0.99891                                     | 0.99633     | 0.99291     | 1.260          | 1.046       | 0.930       | 27.4079     | 27.4612     | 27.5435     |
| 0.0055  | 0.99901                                     | 0.99644     | 0.99303     | 1.272          | 1.060       | 0.945       | 27.4127     | 27.4668     | 27.5552     |
| 0.0070  | 0.99911                                     | 0.99656     | 0.99317     | 1.282          | 1.074       | 0.960       | 27.4174     | 27.4723     | 27.5588     |
| 0.0085  | 0.99924                                     | 0.99669     | 0.99332     | 1.292          | 1.088       | 0.975       | 27.4216     | 27.4765     | 27.5697     |
| <b>0.05m IL</b>   |   |             |             |                |             |             |             |             |             |
| 0.0010  | 0.99915                                     | 0.99655     | 0.99309     | 1.273          | 1.093       | 0.979       | 27.4312     | 27.4878     | 27.5686     |
| 0.0025  | 0.99923                                     | 0.99662     | 0.99316     | 1.285          | 1.108       | 0.997       | 27.4365     | 27.4934     | 27.5741     |
| 0.0040  | 0.99931                                     | 0.99672     | 0.99326     | 1.297          | 1.123       | 1.015       | 27.4418     | 27.4981     | 27.5789     |
| 0.0055  | 0.99942                                     | 0.99684     | 0.99338     | 1.310          | 1.138       | 1.033       | 27.4462     | 27.5023     | 27.5831     |
| 0.0070  | 0.99954                                     | 0.99698     | 0.99351     | 1.322          | 1.153       | 1.051       | 27.4504     | 27.5059     | 27.5870     |
| 0.0085  | 0.99968                                     | 0.99709     | 0.99367     | 1.334          | 1.169       | 1.068       | 27.4540     | 27.5103     | 27.5900     |

**Table 4:** Density ( $\rho$ ), viscosity ( $\eta$ ) and molar refraction ( $R_M$ ) of L-Glutamic acid in aqueous (BTAC) ionic liquid solutions at 293K, 303K and 313K.

| Conc. of L-Glutamic acid soln. in molality (mol.kg <sup>-1</sup> ) | $\rho \times 10^{-3}$ (kg.m <sup>-3</sup> ) |             |             | $\eta$ (mPa.s) |             |             | $R_M$       |             |             |
|--|---|-------------|-------------|----------------|-------------|-------------|-------------|-------------|-------------|
|  | <u>293K</u>                                 | <u>303K</u> | <u>313K</u> | <u>293K</u>    | <u>303K</u> | <u>313K</u> | <u>293K</u> | <u>303K</u> | <u>313K</u> |
| <b>0.01m IL</b>  |   |             |             |                |             |             |             |             |             |
| 0.0010   | 0.99844                                     | 0.99588     | 0.99243     | 1.073          | 0.827       | 0.706       | 30.2369     | 30.2897     | 30.3201     |
| 0.0025   | 0.99852                                     | 0.99596     | 0.99255     | 1.086          | 0.840       | 0.721       | 30.2593     | 30.3122     | 30.3498     |
| 0.0040   | 0.99861                                     | 0.99606     | 0.99262     | 1.099          | 0.853       | 0.735       | 30.2731     | 30.3340     | 30.3643     |
| 0.0055   | 0.99871                                     | 0.99617     | 0.99274     | 1.111          | 0.866       | 0.750       | 30.2865     | 30.3472     | 30.3855     |
| 0.0070   | 0.99881                                     | 0.99629     | 0.99287     | 1.124          | 0.880       | 0.765       | 30.3000     | 30.3601     | 30.3982     |
| 0.0085   | 0.99892                                     | 0.99642     | 0.99301     | 1.136          | 0.892       | 0.781       | 30.3132     | 30.3727     | 30.4105     |
| <b>0.03m IL</b>  |   |             |             |                |             |             |             |             |             |
| 0.0010   | 0.99876                                     | 0.99618     | 0.99274     | 1.241          | 1.023       | 0.903       | 30.2437     | 30.2972     | 30.3356     |
| 0.0025   | 0.99889                                     | 0.99627     | 0.99286     | 1.256          | 1.041       | 0.923       | 30.2646     | 30.3276     | 30.3566     |
| 0.0040   | 0.99896                                     | 0.99637     | 0.99295     | 1.270          | 1.059       | 0.942       | 30.2790     | 30.3405     | 30.3791     |
| 0.0055   | 0.99908                                     | 0.99649     | 0.99310     | 1.285          | 1.078       | 0.960       | 30.3001     | 30.3540     | 30.3918     |
| 0.0070   | 0.99920                                     | 0.99662     | 0.99325     | 1.300          | 1.097       | 0.979       | 30.3130     | 30.3660     | 30.4038     |
| 0.0085   | 0.99930                                     | 0.99677     | 0.99334     | 1.313          | 1.117       | 0.998       | 30.3182     | 30.3783     | 30.4155     |
| <b>0.05m IL</b>  |   |             |             |                |             |             |             |             |             |
| 0.0010   | 0.99916                                     | 0.99656     | 0.99310     | 1.278          | 1.096       | 0.983       | 30.2564     | 30.3048     | 30.3433     |
| 0.0025   | 0.99924                                     | 0.99665     | 0.99323     | 1.294          | 1.118       | 1.007       | 30.2787     | 30.3360     | 30.3726     |
| 0.0040   | 0.99933                                     | 0.99676     | 0.99331     | 1.311          | 1.141       | 1.032       | 30.2925     | 30.3479     | 30.3868     |
| 0.0055   | 0.99944                                     | 0.99689     | 0.99345     | 1.329          | 1.162       | 1.055       | 30.3057     | 30.3605     | 30.4074     |
| 0.0070   | 0.99957                                     | 0.99703     | 0.99360     | 1.347          | 1.185       | 1.080       | 30.3186     | 30.3727     | 30.4195     |
| 0.0085   | 0.99971                                     | 0.99717     | 0.99377     | 1.364          | 1.209       | 1.109       | 30.3311     | 30.3850     | 30.4309     |

**Table 5** and **Table 6** give the apparent molar volume ( $\Phi_v$ ) of L-Aspartic acid and L-Glutamic acid solution, respectively in 0.01m, 0.03m and 0.05m aqueous ionic liquid (BTAC) solution at different temperatures (293K, 303K, 313K). The apparent molar volumes ( $\Phi_v$ ) were determined from the solution densities using the following equation:

$$\Phi_v = M / \rho_0 - 1000 (\rho - \rho_0) / c \rho_0 \quad (1)$$

where,  $M$  is the molar mass of the solute,  $c$  is the molarity of the solution,  $\rho$  and  $\rho_0$  are the densities of the solution and solvent, respectively. It was observed that  $\Phi_v$  values are positive and decreases with increase in concentration of L-Aspartic acid and L-Glutamic acid solutions. However, it increases with increase in temperature at lower concentration of the amino acids but the trend changes as concentration of amino acid increases in solution. The  $\Phi_v$  values also increase with increase in concentration of the aqueous IL solutions at lower concentration of the amino acids but again the trend changes at higher concentration of the amino acid solutions. It was further observed that L-Glutamic acid have  $\Phi_v$  values higher than that of L-Aspartic acid.

**Table 5:** Apparent molar volume, ( $\Phi_v$ ) and  $(\eta/\eta^0 - 1)/\sqrt{m}$  of L-Aspartic acid solution in 0.01m, 0.03m and 0.05m aqueous BTAC solution at different temperatures (293K, 303K, 313K).

| Conc. of L-Aspartic acid soln. in molality, m (mol.kg <sup>-1</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1)/\sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) |
|---|---|--|---|--|---|--|
| <b>0.01m IL</b>   | <b>293K</b>   |  | <b>303K</b>   |  | <b>313K</b>   |  |
| 0.0010  | 103.2104  | 0.206  | 103.4017  | 0.270  | 103.6557  | 0.357  |
| 0.0025  | 93.5224   | 0.319  | 89.9481   | 0.437  | 89.4333   | 0.542  |
| 0.0040  | 90.6615   | 0.386  | 85.9802   | 0.540  | 81.4533   | 0.702  |
| 0.0055  | 86.0340   | 0.456  | 80.6564   | 0.642  | 75.4453   | 0.851  |
| 0.0070  | 81.6876   | 0.505  | 76.1683   | 0.715  | 69.2768   | 0.943  |
| 0.0085  | 77.9260   | 0.540  | 69.7073   | 0.781  | 64.5830   | 1.043  |
| <b>0.03m IL</b>   | <b>293K</b>   |  | <b>303K</b>   |  | <b>313K</b>   |  |
| 0.0010  | 103.4883  | 0.202  | 103.9725  | 0.278  | 104.2297  | 0.280  |
| 0.0025  | 89.8144   | 0.290  | 93.2958   | 0.432  | 89.4194   | 0.512  |
| 0.0040  | 85.6325   | 0.372  | 85.9687   | 0.562  | 81.0517   | 0.671  |
| 0.0055  | 80.5762   | 0.447  | 78.8222   | 0.667  | 73.7893   | 0.799  |
| 0.0070  | 77.3832   | 0.494  | 73.2053   | 0.756  | 66.2024   | 0.909  |
| 0.0085  | 73.2205   | 0.537  | 68.5227   | 0.836  | 60.3699   | 1.008  |
| <b>0.05m IL</b>   | <b>293K</b>   |  | <b>303K</b>   |  | <b>313K</b>   |  |
| 0.0010  | 103.7505  | 0.172  | 104.0310  | 0.231  | 104.4923  | 0.291  |
| 0.0025  | 90.1393   | 0.298  | 93.2756   | 0.420  | 93.4597   | 0.555  |
| 0.0040  | 85.9127   | 0.387  | 83.4487   | 0.551  | 83.9379   | 0.732  |
| 0.0055  | 78.6512   | 0.468  | 75.1641   | 0.657  | 75.4340   | 0.874  |
| 0.0070  | 73.1665   | 0.528  | 67.6419   | 0.748  | 69.2737   | 0.997  |
| 0.0085  | 67.8722   | 0.582  | 66.0784   | 0.838  | 62.2337   | 1.094  |

**Table 6:** Apparent molar volume, ( $\Phi_v$ ) and  $(\eta/\eta^0 - 1) / \sqrt{m}$  of L-Glutamic acid solution in 0.01m, 0.03m and 0.05m in aqueous (BTAC) solution at different temperatures (293K, 303K, 313K).

| Conc. of L-Glutamic acid soln. in molality, m (mol.kg <sup>-1</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1) / \sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1) / \sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | $\Phi_v \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $(\eta/\eta^0 - 1) / \sqrt{m}$ (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) |
|---|---|--|---|--|---|--|
|   |   |  |   |  |   |  |
| <b>0.01m IL</b>   | <b>293K</b>   |  | <b>303K</b>   |  | <b>313K</b>   |  |
| 0.0010  | 107.2332  | 0.265  | 107.4054  | 0.346  | 107.6381  | 0.451  |
| 0.0025  | 99.2768   | 0.413  | 99.4066   | 0.536  | 90.0886   | 0.717  |
| 0.0040  | 94.6775   | 0.520  | 92.2638   | 0.674  | 89.8522   | 0.833  |
| 0.0055  | 90.9240   | 0.595  | 87.3579   | 0.789  | 83.3127   | 1.045  |
| 0.0070  | 88.7094   | 0.672  | 85.9177   | 0.905  | 78.6931   | 1.184  |
| 0.0085  | 86.1094   | 0.733  | 79.0880   | 0.980  | 74.2348   | 1.324  |
| <b>0.03m IL</b>   | <b>293K</b>   |  | <b>303K</b>   |  | <b>313K</b>   |  |
| 0.0010  | 107.2117  | 0.254  | 107.7843  | 0.402  | 107.6172  | 0.385  |
| 0.0025  | 93.8334   | 0.405  | 95.3694   | 0.612  | 90.6933   | 0.694  |
| 0.0040  | 92.1572   | 0.500  | 89.7329   | 0.766  | 87.3052   | 0.833  |
| 0.0055  | 87.3538   | 0.591  | 83.6384   | 0.907  | 81.7615   | 1.027  |
| 0.0070  | 84.2631   | 0.699  | 78.6561   | 1.029  | 72.7915   | 1.164  |
| 0.0085  | 80.1998   | 0.722  | 73.0749   | 1.148  | 67.0805   | 1.287  |
| <b>0.05m IL</b>   | <b>293K</b>   |  | <b>303K</b>   |  | <b>313K</b>   |  |
| 0.0010  | 107.5815  | 0.296  | 107.7584  | 0.318  | 107.9944  | 0.418  |
| 0.0025  | 99.2207   | 0.441  | 95.9558   | 0.607  | 90.6812   | 0.762  |
| 0.0040  | 94.7233   | 0.560  | 87.4871   | 0.812  | 84.7603   | 1.007  |
| 0.0055  | 89.0525   | 0.670  | 80.1161   | 0.956  | 76.2246   | 1.180  |
| 0.0070  | 82.9417   | 0.762  | 74.3435   | 1.099  | 69.8954   | 1.355  |
| 0.0085  | 80.1718   | 0.838  | 69.6760   | 1.238  | 63.5114   | 1.550  |

For the analysis of the interactions occurring here, the knowledge of the limiting apparent molar volumes are important. The limiting apparent molar volumes ( $\Phi_v^0$ ) were calculated using a least-squares treatment to the plots of ( $\Phi_v$ ) versus  $\sqrt{c}$  using the following Masson equation [24]:

$$\Phi_v = \Phi_v^0 + S_v^* \sqrt{c} \quad (2)$$

where,  $\Phi_v^0$  is the limiting apparent molar volume at infinite dilution and  $S_v^*$  is the experimental slope. **Table 8(a)** and **Table 8(b)** gives the limiting apparent molar volumes ( $\Phi_v^0$ ) and the experimental slopes ( $S_v^*$ ) of L-Aspartic acid and L-Glutamic acid solutions, respectively in BTAC at different temperatures. In **Fig. 1(a)** and **Fig. 1(b)** we see the variation of  $\Phi_v^0$  values of L-Aspartic acid and L-

Glutamic acid solutions, respectively at 0.01m, 0.03m and 0.05m of the IL at (293, 303 and 313) K. The  $\Phi_v^0$  values are positive and seem to increase with the increase in concentration of BTAC and also with the increase in temperature for both the amino acids. But  $S_v^*$  values are negative and decreases with the increase in concentration of the IL and with rise in temperature. Also it is observed that L-Glutamic acid have higher  $\Phi_v^0$  and  $S_v^*$  values than L-Aspartic acid at all conditions.

**Table-7(a):** Refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of L-Aspartic acid in aqueous IL (BTAC)solution at 293K, 303K and 313K.

| Conc. of L-Aspartic acid soln. in molality, (mol.kg <sup>-1</sup> ) | $n_D$  |        |        | $\kappa$ (mS/cm) |      |      |
|---|--------|--------|--------|------------------|------|------|
|   | 293K   | 303K   | 313K   | 293K             | 303K | 313K |
| <b>0.01m IL</b>   |        |        |        |                  |      |      |
| 0.0010  | 1.3323 | 1.3320 | 1.3316 | 1.05             | 1.15 | 1.19 |
| 0.0025  | 1.3326 | 1.3321 | 1.3318 | 1.09             | 1.20 | 1.24 |
| 0.0040  | 1.3328 | 1.3322 | 1.3320 | 1.16             | 1.25 | 1.28 |
| 0.0055  | 1.3330 | 1.3323 | 1.3321 | 1.19             | 1.29 | 1.32 |
| 0.0070  | 1.3331 | 1.3324 | 1.3323 | 1.25             | 1.34 | 1.37 |
| 0.0085  | 1.3333 | 1.3326 | 1.3324 | 1.29             | 1.39 | 1.42 |
| <b>0.03m IL</b>   |        |        |        |                  |      |      |
| 0.0010  | 1.3327 | 1.3325 | 1.3322 | 2.91             | 3.13 | 3.21 |
| 0.0025  | 1.3329 | 1.3327 | 1.3324 | 2.99             | 3.18 | 3.26 |
| 0.0040  | 1.3330 | 1.3329 | 1.3326 | 3.08             | 3.23 | 3.31 |
| 0.0055  | 1.3331 | 1.3330 | 1.3328 | 3.15             | 3.31 | 3.38 |
| 0.0070  | 1.3332 | 1.3331 | 1.3329 | 3.24             | 3.35 | 3.45 |
| 0.0085  | 1.3333 | 1.3332 | 1.3331 | 3.33             | 3.42 | 3.56 |
| <b>0.05m IL</b>   |        |        |        |                  |      |      |
| 0.0010  | 1.3334 | 1.3332 | 1.3330 | 4.29             | 5.28 | 5.46 |
| 0.0025  | 1.3336 | 1.3333 | 1.3331 | 4.38             | 5.36 | 5.59 |
| 0.0040  | 1.3337 | 1.3335 | 1.3333 | 4.45             | 5.42 | 5.84 |
| 0.0055  | 1.3338 | 1.3336 | 1.3334 | 4.49             | 5.48 | 6.10 |
| 0.0070  | 1.3340 | 1.3338 | 1.3336 | 4.53             | 5.55 | 6.46 |
| 0.0085  | 1.3341 | 1.3339 | 1.3337 | 4.63             | 5.61 | 6.65 |

**Table-7(b):** Refractive index ( $n_D$ ) and specific conductance ( $\kappa$ ) of L-Glutamic acid in aqueous IL (BTAC)solution at 293K, 303K and 313K.

| Conc. of L-Glutamic acid soln. in molality, m (mol.kg <sup>-1</sup> ) | $n_D$       |             |             | $\kappa$ (mS/cm) |             |             |
|---|-------------|-------------|-------------|------------------|-------------|-------------|
|   | <u>293K</u> | <u>303K</u> | <u>313K</u> | <u>293K</u>      | <u>303K</u> | <u>313K</u> |
| <b>0.01m IL</b>   |             |             |             |                  |             |             |
| 0.0010  | 1.3321      | 1.3318      | 1.3309      | 1.01             | 1.09        | 1.16        |
| 0.0025  | 1.3324      | 1.3321      | 1.3313      | 1.04             | 1.12        | 1.22        |
| 0.0040  | 1.3326      | 1.3324      | 1.3315      | 1.07             | 1.14        | 1.25        |
| 0.0055  | 1.3328      | 1.3326      | 1.3318      | 1.09             | 1.16        | 1.27        |
| 0.0070  | 1.3330      | 1.3328      | 1.3320      | 1.12             | 1.18        | 1.33        |
| 0.0085  | 1.3332      | 1.3330      | 1.3322      | 1.14             | 1.21        | 1.37        |
| <b>0.03m IL</b>   |             |             |             |                  |             |             |
| 0.0010  | 1.3323      | 1.3320      | 1.3312      | 2.89             | 3.06        | 3.11        |
| 0.0025  | 1.3326      | 1.3324      | 1.3315      | 2.95             | 3.09        | 3.15        |
| 0.0040  | 1.3328      | 1.3326      | 1.3318      | 3.01             | 3.12        | 3.23        |
| 0.0055  | 1.3331      | 1.3328      | 1.3320      | 3.07             | 3.15        | 3.31        |
| 0.0070  | 1.3333      | 1.3330      | 1.3322      | 3.13             | 3.18        | 3.40        |
| 0.0085  | 1.3334      | 1.3332      | 1.3324      | 3.19             | 3.22        | 3.48        |
| <b>0.05m IL</b>   |             |             |             |                  |             |             |
| 0.0010  | 1.3326      | 1.3322      | 1.3314      | 4.27             | 5.17        | 5.35        |
| 0.0025  | 1.3329      | 1.3326      | 1.3318      | 4.33             | 5.20        | 5.51        |
| 0.0040  | 1.3331      | 1.3328      | 1.3320      | 4.37             | 5.23        | 5.74        |
| 0.0055  | 1.3333      | 1.3330      | 1.3323      | 4.40             | 5.25        | 5.98        |
| 0.0070  | 1.3335      | 1.3332      | 1.3325      | 4.46             | 5.27        | 6.32        |
| 0.0085  | 1.3337      | 1.3334      | 1.3327      | 4.49             | 5.30        | 6.44        |

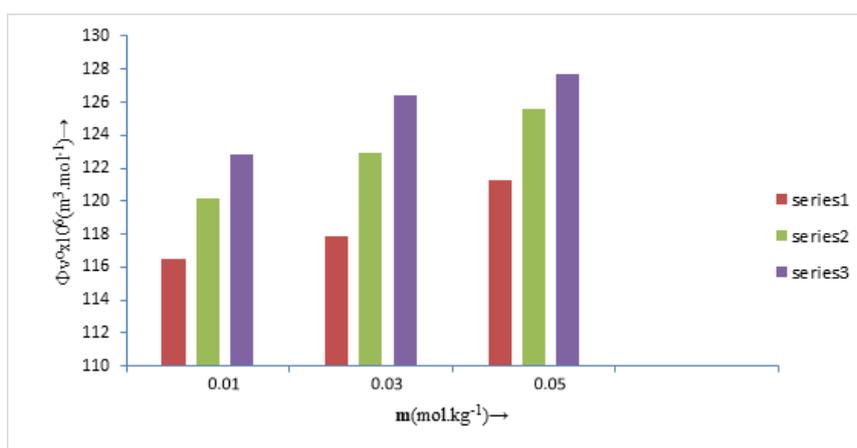
**Table 8(a):** Limiting apparent molar volumes ( $\Phi_V^0$ ), Limiting molar refraction ( $R_M^0$ ), experimental slopes ( $S_V^*$ ), viscosity A, B-coefficients of L-Aspartic acid solution in IL at different temperatures.

| Temperature(K)  | $\Phi_V^0 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $R_M^0$ | $S_V^* \times 10^6$ (m <sup>3</sup> .mol <sup>-3/2</sup> .kg <sup>1/2</sup> ) | B (kg <sup>1/2</sup> .mol <sup>-1/2</sup> ) | A (kg.mol <sup>-1</sup> ) |
|-----------------|---|---------|---|---|---------------------------|
| <b>0.01m IL</b> |   |         |   |   |                           |
| 293             | 116.46  | 27.338  | -414.32   | 5.5734                                      | 0.0346                    |
| 303             | 120.14  | 27.403  | -537.18   | 8.4410                                      | 0.0073                    |
| 313             | 122.83  | 27.458  | -646.61   | 11.588                                      | -0.0262                   |
| <b>0.03m IL</b> |   |         |   |   |                           |
| 293             | 117.86  | 27.375  | -492.49   | 5.7079                                      | 0.0131                    |
| 303             | 122.92  | 27.422  | -590.73   | 9.3383                                      | -0.0283                   |
| 313             | 126.43  | 27.491  | -717.09   | 12.034                                      | -0.0982                   |
| <b>0.05m IL</b> |   |         |   |   |                           |

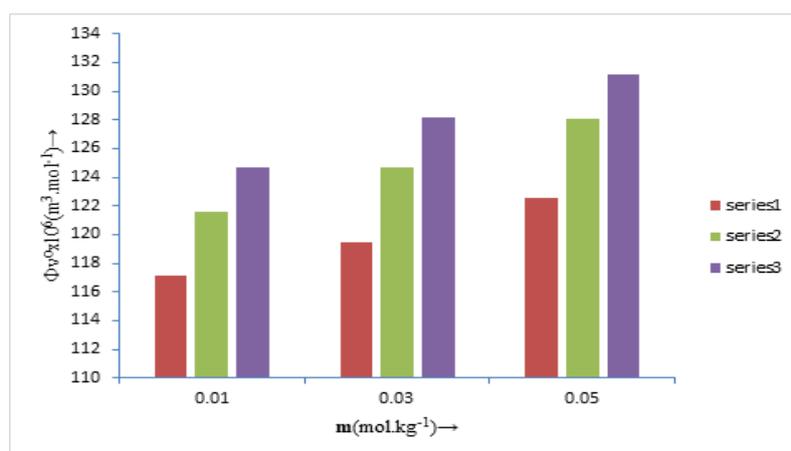
|     |        |        |         |        |         |
|-----|--------|--------|---------|--------|---------|
| 293 | 121.30 | 27.418 | -575.68 | 6.8645 | -0.0479 |
| 303 | 125.59 | 27.475 | -666.95 | 9.9933 | -0.0860 |
| 313 | 127.70 | 27.557 | -698.76 | 13.322 | -0.1218 |

**Table 8(b):** Limiting apparent molar volumes ( $\Phi_v^0$ ), Limiting molar refraction ( $R_M^0$ ), experimental slopes ( $S_v^*$ ), viscosity A, B-coefficients of L-Glutamic acid solution in IL at different temperatures.

| Temperature(K)  | $\Phi_v^0 \times 10^6$<br>( $m^3 \cdot mol^{-1}$ ) | $R_M^0$ | $S_v^* \times 10^6$ ( $m^3 \cdot mol^{-3/2} \cdot kg^{1/2}$ ) | B ( $kg^{1/2} \cdot mol^{-1/2}$ ) | A ( $kg \cdot mol^{-1}$ ) |
|-----------------|--|---------|---|-----------------------------------|---------------------------|
| <b>0.01m IL</b> |  |         |   |                                   |                           |
| 293             | 117.17   | 30.197  | -344.26   | 7.7232                            | 0.0237                    |
| 303             | 121.57   | 30.245  | -450.23   | 7.8217                            | 0.0073                    |
| 313             | 124.71   | 30.273  | -551.01   | 9.1001                            | -0.0062                   |
| <b>0.03m IL</b> |  |         |   |                                   |                           |
| 293             | 119.47   | 30.201  | -429.65   | 10.602                            | 0.0055                    |
| 303             | 124.65   | 30.258  | -555.52   | 12.331                            | -0.0030                   |
| 313             | 128.15   | 30.292  | -654.62   | 15.045                            | -0.1542                   |
| <b>0.05m IL</b> |  |         |   |                                   |                           |
| 293             | 122.55   | 30.217  | -459.38   | 14.278                            | -0.0079                   |
| 303             | 128.09   | 30.268  | -640.65   | 14.745                            | -0.0665                   |
| 313             | 131.15   | 30.298  | -734.15   | 18.372                            | -0.1669                   |

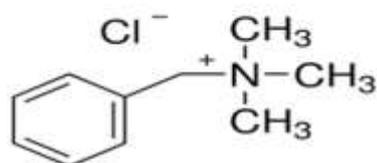


**Fig. 1(a):** Variation of limiting apparent molar volume ( $\Phi_v^0$ ) of L-Aspartic acid solution at 0.01m, 0.03m and 0.05m of the aqueous IL solutions at 293K(Series1), 303K(Series2) and 313K(Series3).



**Fig. 1(b):** Variation of limiting apparent molar volume ( $\Phi_v^0$ ) of L-Glutamic acid solution at 0.01m, 0.03m and 0.05m of the aqueous IL solutions at 293K(Series1), 303K(Series2) and 313K(Series3).

$\Phi_v^0$  values indicate the extent of solute-solvent interaction. A perusal of **Table 8(a)** and **Table 8(b)** reveals that the  $\Phi_v^0$  values are positive and is maximum for L-Glutamic acid in 0.05m aqueous ionic liquid solution at 313K indicating highest solute-solvent interaction here and minimum for L-Aspartic acid in 0.01m aqueous ionic liquid solution at 293K, indicating that the solute-solvent interaction is the least here. This is probably due to the release of a number of the solvent molecules from loose solvation layers during the solute-solvent interactions [25]. Also the higher  $\Phi_v^0$  values of L-Glutamic acid indicates that it interacts more with BTAC than L-Aspartic acid under any conditions. On the contrary, the  $S_v^*$  indicates the extent of solute-solute interaction. The values of  $S_v^*$  show that the extent of solute-solute interaction is highest in L-Glutamic acid 0.01m IL solution at 293K and minimum in 0.05m IL solution at 313K. Here again the higher values of  $S_v^*$  in L-Glutamic acid indicates that it exhibits better interaction among itself than L-Aspartic acid molecules under any conditions. Possible reasons for this behavior could be the structural orientation of the larger alkyl group of L-Glutamic acid than L-Aspartic acid as depicted by their molecular structures in **Scheme 1**. A quantitative comparison of the magnitude of  $\Phi_v^0$  values shows that it is much greater in magnitude than  $S_v^*$  values for the solutions. This suggests that strong solute-solvent interactions dominate over the weak solute-solute interactions in all the solutions [26-27]. There is hydrophobic hydration, or the caging effect of water molecules [28] which reflects hydrophobic interactions in the amino acids that cause volume contractions. Similar linear correlations have been observed earlier for homologous series of amino acids in aqueous electrolytes [29].

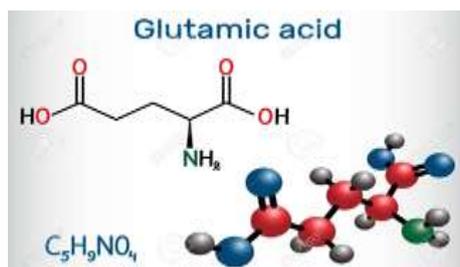


(a)



(b)

(a)Molecular structure of Benzyl tri-methyl ammonium chloride (IL)(b)Molecular structure of L-Aspartic acid



Molecular structure of L-Glutamic acid

**Scheme 1:** Molecular structures of the Ionic Liquid and Amino Acids

Temperature dependency of the limiting apparent molar volume ( $\Phi_v^0$ ) were studied between the temperature range 293K to 313K and the results obtained were found to follow the following polynomial equation <sup>[30]</sup>:

$$\Phi_v^0 = a_0 + a_1T + a_2T^2 \quad (3)$$

where,  $a_0$ ,  $a_1$  and  $a_2$  are the empirical coefficients depending on the nature of solute and mass fraction (W) of co-solvent whereas T is the temperature in Kelvin scale. **Table 9** shows the empirical coefficient values ( $a_0$ ,  $a_1$  and  $a_2$ ) of L-Aspartic acid solution & L-Glutamic acid in different concentration of the IL (0.01m, 0.03m, 0.05m) at 293K, 303K, 313K.

**Table 9:** The empirical coefficient values ( $a_0$ ,  $a_1$  and  $a_2$ ) of L-Aspartic acid solution & L-Glutamic acid in different concentration of the IL (0.01, 0.03m, 0.05m) at 293K, 303K and 313K.

| Conc. of aq. IL soln. in molality, m (mol.kg <sup>-1</sup> ) | L-Aspartic acid  |   |   | L-Glutamic acid  |   |   |
|--|--|---|---|--|---|---|
|  | $a_0 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $a_1 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-1</sup> ) | $a_2 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-2</sup> ) | $a_0 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> ) | $a_1 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-1</sup> ) | $a_2 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-2</sup> ) |
|  | <b>293K</b>  | <b>303K</b>   | <b>313K</b>   | <b>293K</b>  | <b>303K</b>   | <b>313K</b>   |
| 0.01   | -1890.7  | 12.636  | -0.0198   | -2420.5  | 16.025  | -0.0252   |
| 0.03   | -2982.8  | 19.643  | -0.0310   | -3223.1  | 21.230  | -0.0336   |
| 0.05   | -4071.0  | 27.062  | -0.0436   | -4686.2  | 30.918  | -0.0496   |

First derivative of Equation (3) gives the values of limiting apparent molar expansibilities ( $\Phi_E^0$ ) which have been calculated for various temperatures and listed in **Table 10(a)** and **Table 10(b)** for L-Aspartic acid and L-Glutamic acid solutions, respectively.

$$\Phi_E^0 = (\delta\Phi_v^0 / \delta T)_P = a_1 + 2a_2T \quad (4)$$

Limiting apparent molar expansibilities ( $\Phi_E^0$ ) for all the systems are found positive except for 0.05m IL at 313K in both the amino acids signifying the absence of caging or packing effect in the other solutions except this one. The solute–solvent interaction studied so far is now at a state that, it may be

structure-breaker or synergistic structure-maker interaction. In this connection, Hepler developed a way to examine the nature of the solute–solvent interaction taking place in the solution phase [31]. According to Hepler, values of  $(\delta\Phi_E^0/\delta T)_P$  in the expression given below, determines whether, it is structure-breaker or structure-maker interaction [32]:

$$(\delta\Phi_E^0/\delta T)_P = (\delta^2\Phi_v^0/\delta T^2)_P = 2a_2 \quad (5)$$

Generally, positive or small negative values of  $(\delta\Phi_E^0/\delta T)_P$  strongly suggests structure-making rather than structure-breaking interaction. Here, the small negative values listed in **Table 10(a)** and **Table 10(b)** respectively for L-Aspartic acid and L-Glutamic acid solutions in IL (BTAC) at different temperatures confirms the mode of solute–solvent interaction is structure-making and as supported earlier the structure-making effect is strongest in 0.05m aqueous IL solution at 313K for both the amino acids and the effect being greater in L-Glutamic acid solutions with highest packing or caging effect.

**Table 10(a):** Values of limiting molar expansibilities ( $\Phi_E^0$ ) for L-Aspartic acid solution in IL(BTAC) at different temperatures.

| Conc. of aq. IL soln. in molality, m (mol.kg <sup>-1</sup> ) | $\Phi_E^0 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-1</sup> ) |        |         | $(\delta\Phi_E^0/\delta T)_P \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-2</sup> ) |
|--|--|--------|---------|---|
|  | 293K   | 303K   | 313K    |   |
| 0.01   | 1.0332   | 0.6372 | 0.2412  | -0.0396   |
| 0.03   | 1.4770   | 0.8570 | 0.2370  | -0.0620   |
| 0.05   | 1.5124   | 0.6404 | -0.2316 | -0.0872   |

**Table 10(b):** Values of limiting molar expansibilities ( $\Phi_E^0$ ) for L-Glutamic acid solution in IL(BTAC) at different temperatures.

| Conc. of aq. IL soln. in molality, m (mol.kg <sup>-1</sup> ) | $\Phi_E^0 \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-1</sup> ) |        |         | $(\delta\Phi_E^0/\delta T)_P \times 10^6$ (m <sup>3</sup> .mol <sup>-1</sup> .K <sup>-2</sup> ) |
|--|--|--------|---------|---|
|  | 293K   | 303K   | 313K    |   |
| 0.01   | 0.2578   | 0.7538 | 0.2498  | -0.0504   |
| 0.03   | 1.5404   | 0.8684 | 0.1964  | -0.0672   |
| 0.05   | 1.8524   | 0.8604 | -0.1316 | -0.0992   |

**3.2. Viscosity:** In aqueous electrolytic solutions the extent of ionic hydration and structural interactions [33-35] within the ionic hydration cospheres [36] can be explored easily by studying viscosity coefficient with varying concentration and temperature of the aqueous solution. Experimental values of viscosity ( $\eta$ ) of different molality of aqueous ionic liquid (BTAC) solution at 293K, 303K and 313K have been given in **Table 1**. Viscosity ( $\eta$ ) values of L-Aspartic acid and L-Glutamic acid in aqueous (BTAC) ionic liquid, IL solution at 293K, 303K and 313K are given in **Table 3** and **Table 4**, respectively. The results show that the viscosity of the solutions increases with increasing molality of IL. This is due to the fact that upon increasing the molality of the ionic liquid, the number of

collisions among the molecules also increases, resulting in a loss of kinetic energy. Therefore, the molecules tend to stick together with increasing viscosity.

Viscosity data so obtained were analysed with the help of Jones-Dole equation <sup>[37]</sup>.

$$\eta_r = \eta / \eta^0 = 1 + A \sqrt{c} + Bc \quad (6)$$

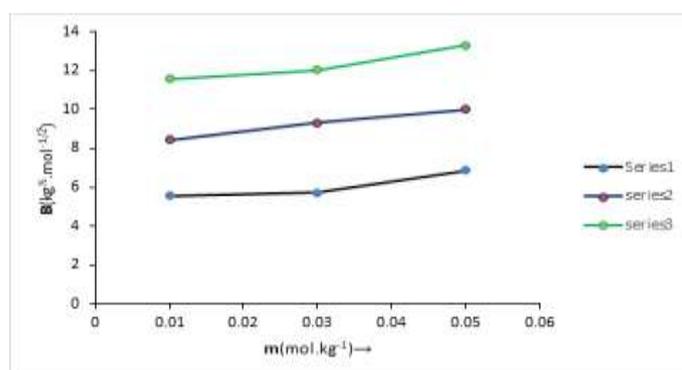
where,  $\eta$  and  $\eta^0$  are viscosities of solution and solvent respectively,  $c$  is the concentration of solution in molality. In **Table 5** and **Table 6**, respectively  $(\eta / \eta^0 - 1) / \sqrt{m}$  values of L-Aspartic acid and L-Glutamic acid solutions have been shown in 0.01m, 0.03m and 0.05m in aqueous IL (BTAC) solution at different temperatures (293K, 303K, 313K).

The  $(\eta / \eta^0 - 1) / \sqrt{m}$  values are positive and seem to increase with increase in concentration of the amino acid in solutions and with increase in temperature from 293K to 313K. However, the  $(\eta / \eta^0 - 1) / \sqrt{m}$  values are found to decrease and then increase as we increase the concentration of aqueous IL solution from 0.01m to 0.03m to 0.05m for 293K and 313K but trend changes for 303K. Same trend is noted for both L-Aspartic acid and L-Glutamic acid but the  $(\eta / \eta^0 - 1) / \sqrt{m}$  values are greater in L-Glutamic acid under all conditions. This is possibly due to stronger hydrophobic-hydrophobic interactions for longer alkyl chains of L-Glutamic acid.

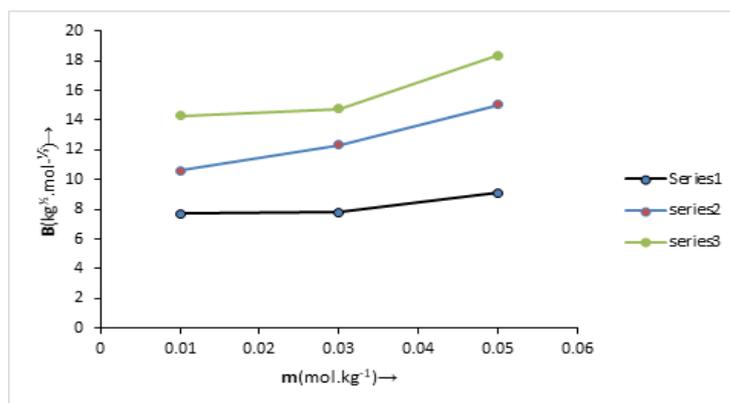
Rearrangement of the above Equation (6) gives following:

$$(\eta_r - 1) / \sqrt{c} = A + B\sqrt{c} \quad (7)$$

Here, viscosity A-coefficient is a constant, also known as Falkenhagen coefficient <sup>[25]</sup>, stands for long-range coulombic forces, so represents the solute-solute interaction in solution, while B-coefficient is an adjustable parameter, which is the measure of the effective hydrodynamic volume, reflects the solute-solvent interaction. Magnitude of viscosity B-coefficient depends on the shape, size and partial molar entropies of the ions. According to the Jones-Dole equation from the plots of  $(\eta_r - 1) / \sqrt{c}$  vs  $\sqrt{c}$ , the viscosity A, B-coefficients obtained by linear least-square analysis, are reported in **Table 8(a)** and **Table 8(b)** for L-Aspartic acid and L-Glutamic acid solutions at (293, 303 and 313)K, respectively. **Fig. 2(a)** and **Fig. 2(b)** shows the variation of B values of L-Aspartic acid and L-Glutamic acid, respectively against 0.01m IL, 0.03m IL and 0.05m IL solutions at different temperatures.



**Fig. 2(a):** Variation of B values of L-Aspartic acid against 0.01m IL, 0.03m IL and 0.05m IL solutions at 293K(Series1), 303K(Series2) and 313K(Series3).



**Fig. 2(b):** Variation of B values of L-Glutamic acid against 0.01m IL, 0.03m IL and 0.05m IL solutions at 293K(Series1), 303K(Series2) and 313K(Series3).

The viscosity  $B$ -coefficient is an empirical constant which depends on size and shape effects as well as structural effects induced by solute+solvent interactions [7]. In all cases the viscosity  $B$ -coefficients are larger in the aqueous ionic liquid solutions which indicates promotion of the liquid structure in the presence of an ionic liquid, thus supporting the conclusions obtained from volumetric properties. From **Table 8(a)** and **Table 8(b)** it is evident that the values of the  $B$ -coefficient are positive, thereby suggesting the presence of strong solute-solvent interactions, that strengthened with an increase in the solvent viscosity value, in accordance with the results obtained from  $\Phi_v^0$  values explained earlier. The values of the  $A$ -coefficient are found to very small as compared to  $B$ -coefficients. These results indicate the presence of very weak solute-solute interactions. These results are in outstanding agreement with those obtained from  $S_v^*$  values. The extent of solute-solvent interaction obtained from the  $B$ -coefficient occurs into the local vicinity of the solute molecules in the solutions. The higher  $B$ -coefficient values for higher viscosity values is due to the solvated solute molecules associated by the solvent molecules all around because of the formation of associated molecule by solute-solvent interactions [38]. Further, these types of interactions are strengthened with rise in temperatures. It shows that the solute-solvent interaction increases with increase in temperature and the concentration of the IL solutions with more interaction between L-Glutamic acid and aqueous BTAC solutions. The replacement of water molecules by more co-solvent molecules from the solvation sphere brings solute and co-solvent closer thereby increasing viscosity  $B$ -coefficients and accounts for the higher solute-solvent interaction. The overall viscometric studies show that, viscosity  $B$ -coefficients are positive and greater than viscosity  $A$ -coefficient, suggesting solute-solvent interaction predominant over the solute-solute interaction.

Extensive study of the viscosity  $B$ -coefficient such that, its first derivative over temperature is an upgradation of viscosity  $B$ -coefficient in predicting the nature of solute-solvent interaction as structure-maker or structure-breaker. The value of  $dB/dT$  is a measure of activation energy required for the viscous flow in solution.

This is the reason, why the measure of  $dB/dT$  is indicative towards the structure making or structure breaking ability than sign or magnitude of the  $B$ -coefficient [39-41]. Viscosity  $B$ -coefficients of L-Aspartic acid and L-Glutamic acid solutions along with  $dB/dT$  values in different concentrations of IL at (293, 303 and 313) K are given in **Table 11(a)** and **Table 11(b)**, respectively. The small positive value of  $dB/dT$  signifies structure-making (kosmotropic) whereas the larger positive value identifies it as structure-breaking (chaotropic). Here the small positive  $dB/dT$  values indicate the amino acids to behave as structure-maker in the aqueous ionic liquid solution.

**Table 11(a):** Viscosity B-coefficients of L-Aspartic acid along with dB/dT values in different concentrations of IL at (293, 303 and 313) K.

| Temperature (K) | 0.01m IL |  | 0.03m IL |  | 0.05m IL |  | dB/dT  |
|-----------------|----------|--|----------|--|----------|--|--------|
|                 | B        |  | B        |  | B        |  |        |
| 293             | 5.5734   |  | 5.7079   |  | 6.8645   |  | 0.3007 |
| 303             | 8.441    |  | 9.3383   |  | 9.9983   |  | 0.3165 |
| 313             | 11.588   |  | 12.034   |  | 13.322   |  | 0.3229 |

**Table 11(b):** Viscosity B-coefficients of L-Glutamic acid along with dB/dT values in different concentrations of IL at (293, 303 and 313) K.

| Temperature (K) | 0.01m IL |  | 0.03m IL |  | 0.05m IL |  | dB/dT  |
|-----------------|----------|--|----------|--|----------|--|--------|
|                 | B        |  | B        |  | B        |  |        |
| 293             | 7.7232   |  | 7.8217   |  | 9.1001   |  | 0.3277 |
| 303             | 10.602   |  | 12.331   |  | 15.045   |  | 0.3462 |
| 313             | 14.278   |  | 14.745   |  | 18.372   |  | 0.4636 |

**3.3. Refractive Index:** Optical data of refractive index of the studied systems has provided interesting information allied to molecular interactions, structure of solutions in these assay. The refractive index of mixing can be interconnected by the application of a composition dependent polynomial equation and molar refraction,  $R_M$  in solution.

The molar refraction  $R_M$  can be evaluated from the Lorentz–Lorenz relation <sup>[42]</sup>:

$$R_M = \{(n_D^2 - 1) / (n_D^2 + 2)\} (M/\rho) \quad (8)$$

where  $R_M$ ,  $n_D$ ,  $M$  and  $\rho$  are the molar refraction, the refractive index, the molar mass and the density of the solution, respectively. The refractive index of a substance is defined as the ratio  $c_o/c$ , where  $c$  is the speed of light in the medium and  $c_o$  is the speed of light in vacuum. Stated more simply, the refractive index of a compound describes its ability to refract light as it moves from one medium to another and thus, the higher the refractive index of a compound, the more the light is refracted <sup>[43]</sup>. As stated by Deetlefs et al. the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser <sup>[44]</sup>. Generally, refractive index of a system is the ability to refract light and hence it can simultaneously measure the compactness of that system.

**Table 1** and **Table 2** gives the experimental values of molar refraction ( $R_M$ ) and refractive index ( $n_D$ ) of different molality of aqueous IL (BTAC) solution at 293K, 303K and 313K, respectively. **Table 3** and **Table 4** show the molar refraction ( $R_M$ ) variation of L-Aspartic acid and L-Glutamic acid, respectively in aqueous (BTAC) ionic liquid, IL solution at 293K, 303K and 313K. **Table 7(a)** and **Table 7(b)** displays the refractive index ( $n_D$ ) of L-Aspartic acid and L-Glutamic acid solutions in aqueous IL (BTAC) solution at 293K, 303K and 313K, respectively.

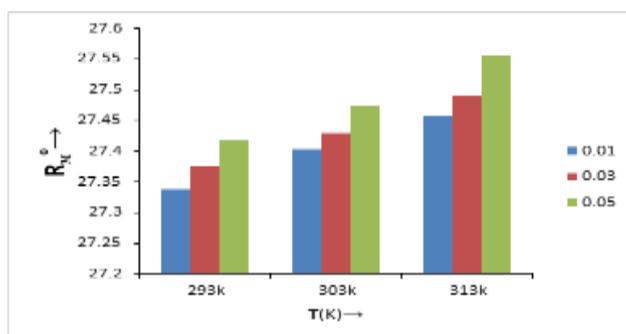
Hence, it is observed that the refractive index ( $n_D$ ) decrease but the molar refraction ( $R_M$ ) increases with increase in temperature. However, both the parameters show an increase with increase in

concentration of the amino acids and IL solutions. Again L-Glutamic acid have higher values than L-Aspartic acid. This is in good agreement with the volumetric and viscometric results attained here. The higher refractive index shows that the molecules are more tightly packed in the solution.

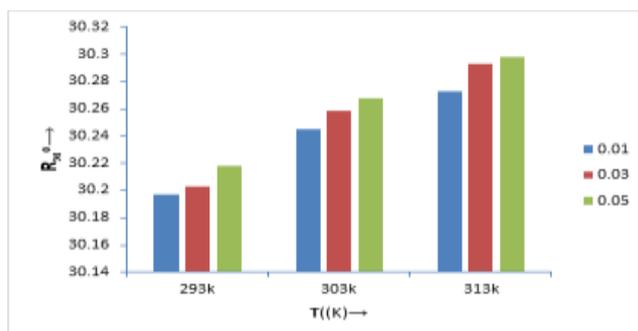
The limiting molar refraction, ( $R_M^0$ ) listed in **Table 8(a)** and **Table 8(b)** can be calculated using the following equation-

$$R_M = R_M^0 + R_S \sqrt{m} \quad (9)$$

where, 'm' is the molality of solution and  $R_M^0$  is the limiting molar refraction that signifies solute-solvent interaction. So, this measurement operates as an expensive tool for studying the molecular interaction in solution. Gradual increase in the values of  $R_M^0$  as shown in **Fig.3(a)** and **Fig. 3(b)** with rise in mass fraction of co-solvent and temperature also signifies that solute-solvent interaction predominant over solute-solute interactions.



**Fig. 3(a):** Variation of  $R_M^0$  values of L-Aspartic acid solution against 293K, 303K and 313K in aqueous solution of IL at 0.01m(Series1), 0.03m(Series2) and 0.05m(Series3).



**Fig. 3(b):** Variation of  $R_M^0$  values of L-Glutamic acid solution against 293K, 303K and 313K in aqueous solution of IL at 0.01m(Series1), 0.03m(Series2) and 0.05m(Series3).

**3.4. Electrical Conductance:** Experimental values of specific conductance ( $\kappa$ ) of different molality of aqueous IL (BTAC) solution at 293K, 303K and 313K are given in **Table 2**. **Table 7(a)** and **Table 7(b)** show the specific conductance ( $\kappa$ ) of L-Aspartic acid and L-Glutamic acid in aqueous IL (BTAC)solution at 293K, 303K and 313K, respectively. **Table 12** shows the molar conductance ( $\Lambda$ ) of L-Aspartic acid and L-Glutamic acid solution in (0.01m, 0.03m, 0.05m) IL at 293K, 303K and 313K. **Fig. 4(a)** and **Fig. 4(b)** gives the variation of molar conductance ( $\Lambda$ ) with different concentrations of L-Aspartic acid in aqueous (0.01m, 0.03m, 0.05m) BTAC (IL) solution at 293K, 303K, 313K. The specific conductance ( $\kappa$ ) values increase with increase in temperature and increase in concentration of aqueous IL solution and the amino acid solutions but the molar conductance ( $\Lambda$ ) values decrease with the increase in concentration of amino acid solutions. However, the values are lesser in L-Glutamic acid solutions under all conditions.

**Table-12:** Molar conductance ( $\Lambda$ ) of L-Aspartic acid and L-Glutamic acid solution in (0.01m, 0.03m, 0.05m) IL at 293K, 303K and 313K.

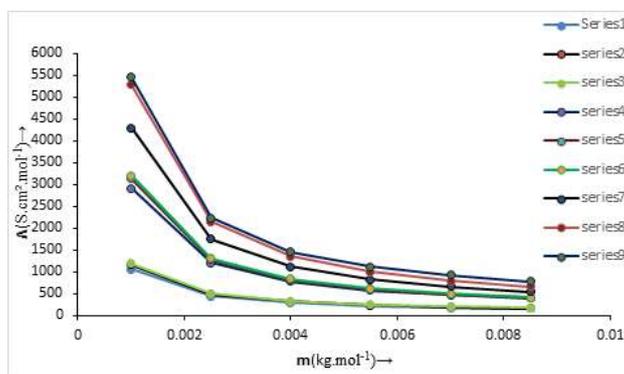
| Concentration of amino acid solutions in molality, $m$ (mol.kg <sup>-1</sup> ) | Molar Conductance of L-Aspartic acid solution $\Lambda$ (S.cm <sup>2</sup> .mol <sup>-1</sup> ) |         |         | Molar conductance of L-Glutamic acid solution $\Lambda$ (S.cm <sup>2</sup> .mol <sup>-1</sup> ) |         |         |
|--|---|---------|---------|---|---------|---------|
|  | 293K  | 303K    | 313K    | 293K  | 303K    | 313K    |
| <b>0.01m IL</b>  |   |         |         |   |         |         |
| 0.0010   | 1053.00   | 1152.00 | 1195.00 | 1010.00   | 1090.00 | 1160.00 |
| 0.0025   | 437.60  | 480.40  | 495.20  | 416.00  | 448.00  | 488.00  |
| 0.0040   | 291.00  | 312.75  | 318.75  | 267.50  | 285.00  | 312.50  |
| 0.0055   | 218.00  | 227.45  | 240.00  | 198.18  | 210.90  | 230.90  |
| 0.0070   | 177.85  | 191.57  | 195.28  | 160.00  | 168.57  | 190.00  |
| 0.0085   | 151.64  | 163.17  | 167.06  | 134.117   | 142.35  | 161.18  |
| <b>0.03m IL</b>  |   |         |         |   |         |         |
| 0.0010   | 2910.00   | 3130.00 | 3210.00 | 2890.00   | 3060.00 | 3110.00 |
| 0.0025   | 1198.80   | 1272.00 | 1304.00 | 1180.0  | 1236.00 | 1260.00 |
| 0.0040   | 770.50  | 810.00  | 827.50  | 752.50  | 780.00  | 807.50  |
| 0.0055   | 573.09  | 610.81  | 614.54  | 558.18  | 572.72  | 601.82  |
| 0.0070   | 462.88  | 478.57  | 492.85  | 447.14  | 454.29  | 485.65  |
| 0.0085   | 391.76  | 402.35  | 411.76  | 375.29  | 378.82  | 409.41  |
| <b>0.05m IL</b>  |   |         |         |   |         |         |
| 0.0010   | 4290.00   | 5280.00 | 5460.00 | 4270.00   | 5170.00 | 5350.00 |
| 0.0025   | 1752.00   | 2144.00 | 2236.00 | 1760.00   | 2080.00 | 2204.00 |
| 0.0040   | 1112.50   | 1352.00 | 1460.00 | 1092.50   | 1307.50 | 1435.00 |
| 0.0055   | 816.36  | 996.36  | 1109.09 | 800.00  | 954.54  | 1087.27 |
| 0.0070   | 651.42  | 792.88  | 922.88  | 637.14  | 752.85  | 902.85  |
| 0.0085   | 544.70  | 660.00  | 782.35  | 528.23  | 623.53  | 757.64  |

The molar conductance ( $\Lambda$ ) has been obtained from the specific conductance ( $\kappa$ ) value using the following equation <sup>[38]</sup>:

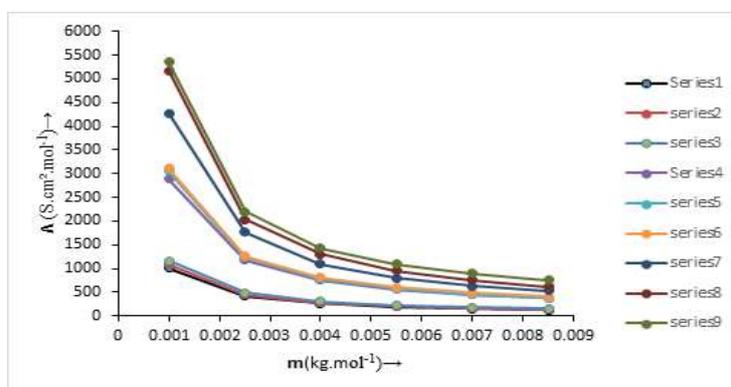
$$\Lambda = (1000 \kappa) / C \quad (10)$$

Linear conductivity curves ( $\Lambda$  vs.  $C$ ) were obtained for the amino acids in IL solutions and extrapolation of  $\sqrt{C} = 0$  was used to evaluate the limiting molar conductance for the IL. The amino

acids have terminal carboxylic (-COOH) group on both ends. IL has benzyl trimethyl ammonium cation and chloride anion. The terminal  $-\text{COO}^-$  functional group of the amino acids interact with the  $\text{N}^+$  centre of benzyl trimethyl ammonium ring through ion-dipole interaction. The molecular structure of the amino acids, L-Aspartic acid and L-Glutamic acid, and the ionic liquid, Benzyl tri-methyl ammonium chloride shown in **Scheme 1** gives an overview.



**Fig. 4(a):** Variation of molar conductance ( $\Lambda$ ) with different concentrations of L-Aspartic acid in aqueous (0.01m,0.03m,0.05m) BTAC (IL) solution at 293K, 303K, 313K. 0.01m at 293K(Series1), 0.01m at 303K(Series2), 0.01m at 313K(Series3) 0.03m at 293K(Series4), 0.03m at 303K(Series5), 0.03m at 313K(Series6) 0.05m at 293K(Series7), 0.05m at 303K(Series8), 0.05m at 313K(Series9)



**Fig. 4(b):** Variation of molar conductance ( $\Lambda$ ) with different concentrations of L-Glutamic acid in aqueous (0.01m,0.03m,0.05m) BTAC (IL) solution at 293K, 303K, 313K. 0.01m at 293K(Series1), 0.01m at 303K(Series2), 0.01m at 313K(Series3) 0.03m at 293K(Series4), 0.03m at 303K(Series5), 0.03m at 313K(Series6) 0.05m at 293K(Series7), 0.05m at 303K(Series8), 0.05m at 313K(Series9)

Another contributing factor in the amino acids is the carboxylic (-O-) atom. The lone pair donating tendency of carboxylic oxygen increases with the increase in +I effect of alkyl group of the studied amino acids. Thus +I effect in L-Glutamic acid is greater than in L-Aspartic acid. Hence, the interaction is more prominent in L-Glutamic acid due to the presence of more lone pair availability of oxygen atom, making the interaction strong with IL. So the free ions are more available for L-Aspartic acid giving higher conductance values than L-Glutamic acid.

#### 4. CONCLUSIONS

Density, viscosity, refractive index and conductance measurements provide the information about ion-dipole interaction and show that the solute-solvent interaction between BTAC ionic liquid and L-Aspartic acid and L-Glutamic amino acid systems is higher than the solute-solute interaction. This is resulted by hydrophobic interactions which lead to volume contraction. The physico-chemical methodologies, describes the mode of interaction in solution. Calculation of limiting apparent molar volume, limiting molar refraction, viscosity B-coefficient and molar conductance makes it possible to identify the interaction as predominant solute-solvent interaction and indicate the predominance of solute-solvent interaction than the solute-solute interaction. The values of  $(\delta\Phi_E^0/\delta T)_P$  and  $(dB/dT)$  have been calculated to provide the information that the solute-solvent interaction is structure-making. The extent of solvation is highest in L-Glutamic acid at 0.05m 313K and lowest in L-Aspartic acid at 0.01m 293K. The derived parameters obtained by analyzing various equations supplemented with experimental data sustain the same finale as discussed and explained above.

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**Conflicts of interest:** The authors declare no conflict of interest.

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**Corresponding author: Mahendra Nath Roy**

<sup>1</sup>Department of Chemistry, University of North Bengal, Darjeeling, WB, India.

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## Physicochemical Investigation of Diverse Interactions of Some Biologically Potent Molecules Prevalent in Aqueous Ionic Liquid Solutions at Different Temperatures

Sukdev Majumder<sup>1</sup>, Kanak Roy<sup>2</sup>, Sanjoy Barman<sup>2</sup>, Mahendra Nath Roy<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, University of North Bengal, Darjeeling, West Bengal, India, <sup>2</sup>Department of Chemistry, Alipurduar College, Alipurduar, West Bengal, India

### ABSTRACT

Densities, viscosities, conductivity, and refractive indices of L-ascorbic acid in aqueous solutions of an ionic liquid, 1-butylpyridinium bromide, have been measured at five different temperatures ranging from 293.15K to 313.15K. Some important parameters have been derived from the above physicochemical experiments, namely, limiting apparent molar volume ( $\phi_V^0$ ) and viscosity *B*-coefficients using extended Masson equation and Jones-Dole equation, respectively. Lorentz-Lorenz equation has used to evaluate molar refractive index ( $R_M$ ) and limiting molar index ( $R_M^0$ ). Specific conductivity measurement applied to ascertain ionic nature of the system.

**Key words:** Solute-co-solute interactions, Apparent molar volume, Viscosity *B*-coefficient, Molar refraction, Conductivity study

### 1. INTRODUCTION

Ionic liquids (ILs) are organic solvents that are liquids at or near room temperature in their pure state. They have been widely used in a number of fields in both academia and industry and exhibit many useful advantages such as a low melting point (<373 K), are liquid over a wide temperature range, and have suitable viscosity, thermal stability, and ability to dissolve a variety of chemicals, and most importantly, negligible vapor pressure [1,2]. ILs have been proposed as green and benign replacements for traditional volatile organic solvents, and a rising number of applications in the fields of catalysis, chemical reactions, separations, electrochemistry, nanoscience, and biosciences far studied [3,4].

Vitamin C, which is also known as L-ascorbic acid (AA), is highly polar and readily soluble in water. Vitamin C can help to prevent and treat scurvy and the common cold. It is essential for the synthesis of collagen, neurotransmitters, and creatinine [5]. Due to the great importance of Vitamin C in human beings, the volumetric and viscometric investigation of the solutes has gained increased significance in several areas of analytical chemistry such as pharmaceutical and food applications. As the body fluid is always circulating, it is interesting to study the transport properties of vitamins in aqueous solutions at different temperatures. Water is a very simple molecule but very complicated to understand especially when it is mixed with other solutes. Hence, it was believed to study the effect of dissolution of L-AA on the structure of aqueous ILs medium at different temperatures.

Measurements of density, viscosity and refractive index, and conductivity of aqueous IL solution of L-ascorbic have not been made over significant temperature and concentration ranges. These measurements are important for elucidation of ion-solvent, ion-ion, and solvent-solvent interactions in aqueous ternary (H<sub>2</sub>O + IL + L-AA) systems. The nature and degree of molecular interactions indifferent

solutions depend upon the nature of the medium, extent of solvation taking place in solution, and also the structure and size of the solute molecule [6-10].

Therefore, in the present study, we have endeavored to make ascertain nature of the interaction of solute itself (L-AA) and with co-solute 1-butylpyridinium bromide (IL) in  $w_I=0.001, 0.003, \text{ and } 0.005$  mass fraction of aqueous medium at different temperatures (298.15–313.15) K with 5 intervals to explain various noncovalent interactions prevailing in the ternary systems under investigation.

### 2. EXPERIMENTAL SECTION

#### 2.1. Source and Purity of Materials

1-butylpyridinium bromide and L-AA were purchased from Sigma-Aldrich. The mass fractions purity of both was  $\geq 0.99$ . The reagents were always placed in the desiccators over P<sub>2</sub>O<sub>5</sub> to keep them in dry atmosphere. These chemicals were used as received without further purification. The provenance and purity of the chemical used have been depicted in Table 1.

#### 2.2. Apparatus and Procedure

Solubility of the 1-butylpyridinium bromide and L-AA in water (deionized and doubly distilled water) has been checked surely, before start of the experimental work and perceived that L-AA is soluble in all

**\*Corresponding author:**

E-mail: mahendraroy2002@yahoo.co.in

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proportion of aqueous IL solution. The mother solutions of L-AA were prepared by mass (Mettler Toledo AG-285 with uncertainty 0.0003 g) and then the working solutions (six sets) were prepared by mass dilution. The conversion of molarity into molality [11] has been done using experimental density values of respective solutions.

The densities ( $\rho$ ) of the experimental solutions were measured using (DMA 4500M) vibrating u-tube Anton Paar digital density meter with a precision of  $\pm 0.00005 \text{ g}\cdot\text{cm}^{-3}$  maintained at  $\pm 0.01 \text{ K}$  of the desired temperature. The calibration was carried out by passing deionized, triply distilled water and dry air [12].

A Brookfield DV-III Ultra Programmable Rheometer with fitted spindle size-42 is used to measure the viscosity ( $\eta$ ). The detailed description has already been described earlier [12].

Refractive index ( $n_D$ ) was measured with the help of a Digital Refractometer Mettler Toledo instrument. The light source was LED,  $\lambda=589.3 \text{ nm}$ . The refractometer was calibrated twice using distilled water and after every few measurements, calibration was checked [13]. The uncertainty of refractive index measurement was  $\pm 0.0002$  units.

Measurements of conductivity were carried out in a Systronics-308 conductivity meter (accuracy  $\pm 0.01\%$ ) using a dip-type dipping conductivity cell, CD-10, having a cell constant of approximately  $(0.1 \pm 0.001) \text{ cm}^{-1}$ . Measurements of experimental solutions were completed in a water bath maintained within  $T = (298.15 \pm 0.01) \text{ K}$  [14].

### 3. RESULTS AND DISCUSSION

The physical parameters of binary mixtures in different mass fractions ( $w_1=0.001, 0.003, 0.005$ ) of aqueous ILs solutions at five different temperatures (293.15K, 298.15K, 303.15K, 308.15K, and 313.15K) and at 1.013 bar have been reported in Table 2. The experimental measured values of density and viscosity of L-AA as a function of concentration (molality) in different mass fractions of aqueous ILs mixture at above-mentioned temperatures have been listed in Table 3.

#### 3.1. Apparent Molar Volume

Volumetric properties, such as apparent molar volume ( $\varphi_V$ ) and limiting apparent molar volume ( $\varphi_V^0$ ), contemplate significant tools for the understanding of interactions taking place in solution systems. The apparent molar volume can be regarded to be the sum of the geometric volume of the central solute molecule and changes in the solvent volume due to its interaction with the solute around the peripheral or co-sphere. Therefore, the apparent molar volumes ( $\varphi_V$ ) have been determined from the solution densities using the suitable equation [13] and the values are given in Table 4.

$$\varphi_V = M/\rho - 1000 (\rho - \rho_0)/m\rho\rho_0 \quad (1)$$

Where  $M$  is the molar mass of the L-AA,  $m$  is the molality of the solution,  $\rho$  and  $\rho_0$  are the density of the solution and aqueous ILs mixture, respectively.

The values of  $\varphi_V$  are positive and large for all the systems, signifying strong solute-co-solute interactions. The apparent molar volumes ( $\varphi_V$ ) are found to decrease with increasing concentration (molality,  $m$ ) of AA in the same mass fraction of aqueous ILs at same temperature. It is also found that apparent molar volumes ( $\varphi_V$ ) increase with both increasing temperature as well as mass fraction of aqueous IL solution and varied with  $\sqrt{m}$  and could be least-squares fitted to the extended Masson equation [15] from where limiting molar volume,  $\varphi_V^0$  (infinite dilution partial molar volume) have been estimated, and the values have been represented in Table 5.

$$\varphi_V = \varphi_V^0 + S_V^* \sqrt{m} \quad (2)$$

**Table 1:** Source and purity of the chemicals

| Chemical name             | Source        | Mass fraction purity | Purification method |
|---------------------------|---------------|----------------------|---------------------|
| 1-butylpyridinium bromide | Sigma-Aldrich | $\geq 0.99$          | Used as procured    |
| L-ascorbic acid           | Sigma-Aldrich | $\geq 0.99$          | Used as procured    |

**Table 2:** Experimental values of density ( $\rho$ ), viscosity ( $\eta$ ), and refractive index ( $n_D$ ) at various temperature and at pressure 1.013 bar of different mass fraction ( $w_1$ ) of aq. IL mixtures\*

| Aq. IL mixture ( $w_1$ ) | Temperature/ K | $\rho \times 10^{-3} / \text{kg}\cdot\text{m}^{-3}$ | $\eta / \text{mP}\cdot\text{s}$ | $n_D$  |
|--------------------------|----------------|---|---------------------------------|--------|
| 0.001                    | 293.15         | 0.399890  | 1.130                           | 1.3322 |
|                          | 298.15         | 0.99789   | 1.022                           | 1.3323 |
|                          | 303.15         | 0.99650   | 0.924                           | 1.3322 |
|                          | 308.15         | 0.99496   | 0.855                           | 1.3321 |
|                          | 313.15         | 0.99321   | 0.803                           | 1.3320 |
| 0.003                    | 293.15         | 0.99814   | 1.132                           | 1.3324 |
|                          | 298.15         | 0.99710   | 1.024                           | 1.3324 |
|                          | 303.15         | 0.99658   | 0.933                           | 1.3323 |
|                          | 308.15         | 0.99525   | 0.864                           | 1.3322 |
|                          | 313.015        | 0.99340   | 0.807                           | 1.3321 |
| 0.005                    | 293.15         | 0.99320   | 1.141                           | 1.3325 |
|                          | 298.15         | 0.99828   | 1.029                           | 1.3325 |
|                          | 303.15         | 0.99650   | 0.937                           | 1.3324 |
|                          | 308.15         | 0.99534   | 0.869                           | 1.3323 |
|                          | 313.15         | 0.99243   | 0.813                           | 1.3322 |

\*Standard uncertainties  $u$  are:  $u(\rho) = 0.002 \text{ kg}\cdot\text{m}^{-3}$ ,  $u(\eta) = 0.02 \text{ mP}\cdot\text{s}$ ,  $u(n_D) = 0.0002$ , and  $u(T) = 0.01 \text{ K}$ , (0.68 level of confidence)

$\varphi_V^0$  is the apparent molar volume at infinite dilution and  $S_V^*$  is the experimental slope. At infinite dilution, solute molecule is surrounded only by the solvent molecules and remains an infinite distance from each other. Consequently, that  $\varphi_V^0$  is unaffected by itself interaction of AA molecules and it is a measure only of the solute-co-solute (AA-IL) interaction.

Scrutiny of Table 5 shows that  $\varphi_V^0$  are large and positive for all L-AA at all the studied temperatures, suggesting the presence of strong solute-co-solute interaction (Scheme 1). Comparing  $\varphi_V^0$  with  $S_V^*$  values show that the magnitude of  $\varphi_V^0$  is  $> S_V^*$ , suggesting that solute-co-solute interactions predominate over itself interaction of solute molecules in all solutions at all studied temperatures. Since the  $S_V^*$  values signify the solute-solute interactions so the small values of  $S_V^*$  indicates very less interactions associate with the L-ascorbic acid molecules in aqueous solutions. It has been observed from the table 5 that all the values of  $S_V^*$  are negative at all studied temperature and are very small which indicates very poor force of interactions involve in L-ascorbic acid molecules.

The variation of  $\varphi_V^0$  with temperature is fitted to a polynomial of the following

$$\varphi_V^0 = a_0 + a_1 T + a_2 T^2 \quad (3)$$

Where  $T$  is the temperature in K and  $a_0$ ,  $a_1$ , and  $a_2$  are the empirical coefficients depending on the solute, mass fraction of co-solute IL.

**Table 3:** Experimental values of density ( $\rho$ ) and viscosity ( $\eta$ ), L-ascorbic acid in different mass fractions of aqueous IL acid mixture ( $w_1$ ) at five different temperatures and at pressure 1.013 bar\*

| $a/m\cdot\text{mol}\cdot\text{kg}^{-1}$ | $\rho\times 10^{-3}/\text{kg}\cdot\text{m}^{-3}$ | $\eta\text{mP}\cdot\text{s}$ | $a/m\cdot\text{mol}\cdot\text{kg}^{-1}$ | $\rho\times 10^{-3}/\text{kg}\cdot\text{m}^{-3}$ | $\eta\text{mP}\cdot\text{s}$ | $a/m\cdot\text{mol}\cdot\text{kg}^{-1}$ | $\rho\times 10^{-3}/\text{kg}\cdot\text{m}^{-3}$ | $\eta\text{mP}\cdot\text{s}$ |
|---|--|------------------------------|---|--|------------------------------|---|--|------------------------------|
| $w_1=0.001$                             |  |                              | $w_1=0.003$                             |  |                              | $w_1=0.005$                             |  |                              |
| T=                                      | 293.15 K   |                              |   | 293.15 K   |                              |   | 293.15 K   |                              |
| 0.010                                   | 0.99905  | 1.136                        | 0.010                                   | 0.99916  | 1.138                        | 0.010                                   | 0.99943  | 1.145                        |
| 0.025                                   | 1.00005  | 1.141                        | 0.025                                   | 1.00016  | 1.141                        | 0.025                                   | 1.00022  | 1.151                        |
| 0.040                                   | 1.00103  | 1.148                        | 0.040                                   | 1.00118  | 1.148                        | 0.040                                   | 1.00125  | 1.157                        |
| 0.055                                   | 1.00209  | 1.152                        | 0.055                                   | 1.00223  | 1.152                        | 0.055                                   | 1.00231  | 1.162                        |
| 0.070                                   | 1.00317  | 1.158                        | 0.070                                   | 1.00330  | 1.158                        | 0.070                                   | 1.00333  | 1.166                        |
| 0.085                                   | 1.00415  | 1.164                        | 0.085                                   | 1.00432  | 1.166                        | 0.085                                   | 1.00435  | 1.173                        |
| T=                                      | 298.15 K   |                              |   | 298.15 K   |                              |   | 298.15 K   |                              |
| 0.010                                   | 0.99798  | 1.028                        | 0.010                                   | 0.99824  | 1.029                        | 0.010                                   | 0.99837  | 1.033                        |
| 0.025                                   | 0.99887  | 1.033                        | 0.025                                   | 0.99899  | 1.034                        | 0.025                                   | 0.99915  | 1.038                        |
| 0.040                                   | 0.99988  | 1.038                        | 0.040                                   | 0.99997  | 1.041                        | 0.040                                   | 1.00005  | 1.045                        |
| 0.055                                   | 1.0009   | 1.045                        | 0.055                                   | 1.00102  | 1.046                        | 0.055                                   | 1.00111  | 1.052                        |
| 0.070                                   | 1.00197  | 1.050                        | 0.070                                   | 1.00208  | 1.052                        | 0.070                                   | 1.00223  | 1.056                        |
| 0.085                                   | 1.00298  | 1.057                        | 0.085                                   | 1.00316  | 1.058                        | 0.085                                   | 1.00342  | 1.062                        |
| T=                                      | 303.15 K   |                              |   | 303.15 K   |                              |   | 303.15 K   |                              |
| 0.010                                   | 0.99659  | 0.930                        | 0.010                                   | 0.99666  | 0.938                        | 0.010                                   | 0.99676  | 0.941                        |
| 0.025                                   | 0.99746  | 0.936                        | 0.025                                   | 0.9975   | 0.943                        | 0.025                                   | 0.99757  | 0.946                        |
| 0.040                                   | 0.99847  | 0.941                        | 0.040                                   | 0.99857  | 0.948                        | 0.040                                   | 0.9986   | 0.952                        |
| 0.055                                   | 0.99948  | 0.948                        | 0.055                                   | 0.99959  | 0.953                        | 0.055                                   | 0.99968  | 0.958                        |
| 0.070                                   | 1.00053  | 0.954                        | 0.070                                   | 1.00075  | 0.962                        | 0.070                                   | 1.00073  | 0.964                        |
| 0.085                                   | 1.00152  | 0.962                        | 0.085                                   | 1.00084  | 0.968                        | 0.085                                   | 1.00089  | 0.971                        |
| T=                                      | 303.15 K   |                              |   | 308.15 K   |                              |   | 308.15 K   |                              |
| 0.010                                   | 0.99503  | 0.861                        | 0.010                                   | 0.99529  | 0.869                        | 0.010                                   | 0.99538  | 0.871                        |
| 0.025                                   | 0.99584  | 0.866                        | 0.025                                   | 0.99599  | 0.874                        | 0.025                                   | 0.996  | 0.877                        |
| 0.040                                   | 0.99683  | 0.871                        | 0.040                                   | 0.99696  | 0.880                        | 0.040                                   | 0.99703  | 0.882                        |
| 0.055                                   | 0.99789  | 0.875                        | 0.055                                   | 0.99797  | 0.886                        | 0.055                                   | 0.99808  | 0.888                        |
| 0.070                                   | 0.99892  | 0.885                        | 0.070                                   | 0.99908  | 0.894                        | 0.070                                   | 0.99928  | 0.896                        |
| 0.085                                   | 0.99991  | 0.892                        | 0.085                                   | 1.00013  | 0.901                        | 0.085                                   | 1.00038  | 0.903                        |
| T=                                      | 313.15K  |                              |   | 313.15K  |                              |   | 313.15K  |                              |
| 0.010                                   | 0.99326  | 0.809                        | 0.010                                   | 0.99344  | 0.812                        | 0.010                                   | 0.99346  | 0.817                        |
| 0.025                                   | 0.99404  | 0.814                        | 0.025                                   | 0.99408  | 0.817                        | 0.025                                   | 0.99411  | 0.823                        |
| 0.040                                   | 0.99502  | 0.820                        | 0.040                                   | 0.99515  | 0.822                        | 0.040                                   | 0.99519  | 0.829                        |
| 0.055                                   | 0.99605  | 0.826                        | 0.055                                   | 0.99613  | 0.828                        | 0.055                                   | 0.99624  | 0.836                        |
| 0.070                                   | 0.99708  | 0.833                        | 0.070                                   | 0.99722  | 0.836                        | 0.070                                   | 0.99735  | 0.844                        |
| 0.085                                   | 0.99807  | 0.842                        | 0.085                                   | 0.99832  | 0.844                        | 0.085                                   | 0.99847  | 0.850                        |

\*Standard uncertainties  $u$  are:  $u(\rho)=0.00002\text{ kg}\cdot\text{m}^{-3}$ ,  $u(\eta)=0.02\text{ mP}\cdot\text{s}$ , and  $u(T)=0.01\text{K}$  (0.68 level of confidence). <sup>a</sup>Molality has been expressed per kg (IL+water) solvent mixture

Values of coefficients of the above equation for the in aqueous IL mixtures are reported in Table 6.

The limiting apparent molar expansibilities,  $\varphi_E^0$ , can be evaluated by the following equation,

$$\varphi_E^0 = (\delta\varphi_V^0/\delta T)_P = a_1 + 2a_2T \tag{4}$$

The limiting apparent molar expansibilities,  $\varphi_E^0$ , change in magnitude with the change of temperature. The values of  $\varphi_E^0$  for different

solutions of studied L-AA at ( $T=293.15\text{K}-313.15\text{K}$ ) are reported in Table 7.

All the values of  $\varphi_E^0$  shown in the Table 7 are positive for L-ascorbic acid in aqueous solutions of ionic liquid at different mass fraction and at different studied temperatures. This fact helps to explain the absence of caging or packing effect for the IL in solution [16].

The long-range structure-making and breaking capacity of the solute in the mixed system can be determined by examining the sign of  $(\delta\varphi_E^0/$

**Table 4:** Apparent molar volume ( $\Psi_V$ ) and  $(\eta_r-1)/\sqrt{m}$  of L-Ascorbic acid in different mass fraction ( $w_1$ ) of aqueous IL mixtures at five different temperatures\*

| <sup>a</sup> molality/<br>mol·kg <sup>-1</sup> | $\Psi_V \times 10^6 /$<br>m <sup>3</sup> mol <sup>-1</sup> | $(\eta_r-1)/\sqrt{m} /$<br>kg <sup>1/2</sup> mol <sup>-1/2</sup> | <sup>a</sup> molality/<br>mol·kg <sup>-1</sup> | $\Psi_V \times 10^6 /$<br>m <sup>3</sup> mol <sup>-1</sup> | $(\eta_r-1)/\sqrt{m} /$<br>kg <sup>1/2</sup> mol <sup>-1/2</sup> | <sup>a</sup> molality/<br>mol·kg <sup>-1</sup> | $\Psi_V \times 10^6 /$<br>m <sup>3</sup> mol <sup>-1</sup> | $(\eta_r-1)/\sqrt{m} /$<br>kg <sup>1/2</sup> mol <sup>-1/2</sup> |
|--|--|--|--|--|--|--|--|--|
| <b>w<sub>1</sub>=0.001</b>                     |  |  | <b>w<sub>1</sub>=0.003</b>                     |  |  | <b>w<sub>1</sub>=0.005</b>                     |  |  |
| T=293.15 K                                     |  |  | T=293.15 K                                     |  |  | T=293.15 K                                     |  |  |
| 0.010  | 161.3074   | 0.10   | 0.010  | 164.2890   | 0.10   | 0.010  | 165.2465   | 0.10   |
| 0.025  | 130.2733   | 0.15   | 0.025  | 131.4611   | 0.15   | 0.025  | 140.2315   | 0.15   |
| 0.040  | 123.0157   | 0.20   | 0.040  | 122.7562   | 0.20   | 0.040  | 127.9780   | 0.20   |
| 0.055  | 118.2601   | 0.23   | 0.055  | 118.2516   | 0.23   | 0.055  | 121.8612   | 0.23   |
| 0.070  | 115.2568   | 0.26   | 0.070  | 115.3915   | 0.26   | 0.070  | 118.9343   | 0.26   |
| 0.085  | 114.4912   | 0.29   | 0.085  | 114.1324   | 0.29   | 0.085  | 117.0449   | 0.29   |
| T=298.15 K                                     |  |  | T=298.15 K                                     |  |  | T=298.15 K                                     |  |  |
| 0.010  | 165.4707   | 0.10   | 0.010  | 166.4314   | 0.10   | 0.010  | 167.4118   | 0.10   |
| 0.025  | 136.3732   | 0.15   | 0.025  | 142.3587   | 0.15   | 0.025  | 142.2825   | 0.15   |
| 0.040  | 126.0911   | 0.20   | 0.040  | 130.5747   | 0.20   | 0.040  | 130.2784   | 0.20   |
| 0.055  | 121.2318   | 0.23   | 0.055  | 123.9409   | 0.23   | 0.055  | 123.0563   | 0.23   |
| 0.070  | 117.7392   | 0.26   | 0.070  | 120.0063   | 0.26   | 0.070  | 117.9590   | 0.26   |
| 0.085  | 116.1897   | 0.29   | 0.085  | 117.2309   | 0.29   | 0.085  | 113.8659   | 0.29   |
| T=303.15 K                                     |  |  | T=303.15 K                                     |  |  | T=303.15 K                                     |  |  |
| 0.010  | 167.6947   | 0.10   | 0.010  | 168.6877   | 0.10   | 0.010  | 171.6834   | 0.10   |
| 0.025  | 138.1137   | 0.15   | 0.025  | 139.7137   | 0.15   | 0.025  | 140.1794   | 0.15   |
| 0.040  | 127.1993   | 0.20   | 0.040  | 126.6911   | 0.20   | 0.040  | 127.1490   | 0.20   |
| 0.055  | 122.2345   | 0.23   | 0.055  | 121.6820   | 0.23   | 0.055  | 120.3674   | 0.23   |
| 0.070  | 118.8225   | 0.26   | 0.070  | 116.8140   | 0.26   | 0.070  | 116.7937   | 0.26   |
| 0.085  | 117.3267   | 0.29   | 0.085  | 114.0258   | 0.29   | 0.085  | 112.1710   | 0.29   |
| T=308.15 K                                     |  |  | T=308.15 K                                     |  |  | T=308.15 K                                     |  |  |
| 0.010  | 169.9583   | 0.10   | 0.010  | 172.9363   | 0.10   | 0.010  | 172.9211   | 0.10   |
| 0.025  | 141.4943   | 0.15   | 0.025  | 147.1081   | 0.15   | 0.025  | 150.3231   | 0.15   |
| 0.040  | 129.8377   | 0.20   | 0.040  | 133.8415   | 0.20   | 0.040  | 134.3368   | 0.20   |
| 0.055  | 123.2543   | 0.23   | 0.055  | 127.0749   | 0.23   | 0.055  | 126.7021   | 0.23   |
| 0.070  | 119.9223   | 0.26   | 0.070  | 121.7701   | 0.26   | 0.070  | 120.1852   | 0.26   |
| 0.085  | 118.2437   | 0.29   | 0.085  | 119.0530   | 0.29   | 0.085  | 117.1584   | 0.29   |
| T=313.15K                                      |  |  | T=313.15K                                      |  |  | T=313.15K                                      |  |  |
| 0.010  | 172.2706   | 0.10   | 0.010  | 173.2509   | 0.10   | 0.010  | 174.2580   | 0.10   |
| 0.025  | 143.7050   | 0.15   | 0.025  | 149.7550   | 0.15   | 0.025  | 149.7513   | 0.15   |
| 0.040  | 131.4999   | 0.20   | 0.040  | 132.9996   | 0.20   | 0.040  | 132.7442   | 0.20   |
| 0.055  | 125.0295   | 0.23   | 0.055  | 127.0351   | 0.23   | 0.055  | 125.5640   | 0.23   |
| 0.070  | 121.3304   | 0.26   | 0.070  | 122.0384   | 0.26   | 0.070  | 120.5955   | 0.26   |
| 0.085  | 119.4161   | 0.29   | 0.085  | 118.6930   | 0.29   | 0.085  | 117.2690   | 0.29   |

\*Standard uncertainties  $u$  are:  $u(T) = 0.01K$ , the accuracy of  $\varphi_V$  is  $1.01 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$  and  $(\eta_r-1)/\sqrt{m}$  is  $0.002 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  (0.68 level of confidence). <sup>a</sup>Molality has been expressed per kg of (IL+water) solvent mixture

$(\delta T)_P$  developed by Hepler [17].

$$(\delta\varphi_E^0/\delta T)_P = (\delta^2\varphi_V^0/\delta T^2)_P = 2a_2 \tag{5}$$

The positive sign or small negative of  $(\delta\varphi_E^0/\delta T)_P$  signifies the molecule is a structure-maker; otherwise, it is a structure-breaker [18]. The perusal of Table 6 shows that  $(\delta\varphi_E^0/\delta T)_P$  values of AA are all positive under investigation. It shows the more symmetric rearrangement of

the interacting molecules (AAandIL) with the formation of H-bonding, van der Waal forces, dipole-dipole interactions, etc. This symmetric arrangement is signifying the molecules of AA and IL is interacting with structure-making tendency in all of the studied solution systems. Table 6 also showing the positively magnitude of  $(\delta\varphi_E^0/\delta T)_P$  values in of L-AA is depicting this structure-making tendency.

### 3.2. Viscosity

The experimental viscosity data for studied systems are listed in Table 3. The relative viscosity ( $\eta_r$ ) has been calculated using the extended Jones-Dole equation [19] for non-electrolytes.

$$(\eta/\eta_0 - 1)/\sqrt{m} = (\eta_r - 1)/\sqrt{m} = A + B \cdot \sqrt{m} \quad (6)$$

Where  $\eta_r = \eta/\eta_0$  is the relative viscosity,  $\eta$  and  $\eta_0$  are the viscosities of ternary solutions (AA + IL) and solvent (aqueous IL), respectively, and  $m$  is the molality of L-AA in ternary solutions. Where  $A$  is known as Falkenhagen coefficient [20] as it is determined by the ionic attraction theory of Falkenhagen-Vernon and  $B$  is empirical constants known as viscosity  $B$ - coefficients, which are specifying to the interaction of solute itself and/or with co-solute molecules, respectively. The values of  $A$ - and  $B$ -coefficients are estimated by the least-square polynomial method by plotting  $(\eta_r - 1)/\sqrt{m}$  against  $\sqrt{m}$  with second order and reported in Table 4. It is observed from Table 4, the values of the  $A$ -coefficient are found to decrease with an increase in temperature. This fact indicates the presence of very weak solute-solute interaction and also in excellent agreement with those obtained from  $S_V^*$  values.

**Table 5:** Limiting apparent molar volume ( $\phi_V^0$ ), experimental slope ( $S_V^*$ ), viscosity  $A$ - and  $B$ -coefficient of L-ascorbic acid in different mass fraction ( $w_I$ ) of aqueous IL mixtures at five different temperatures\*

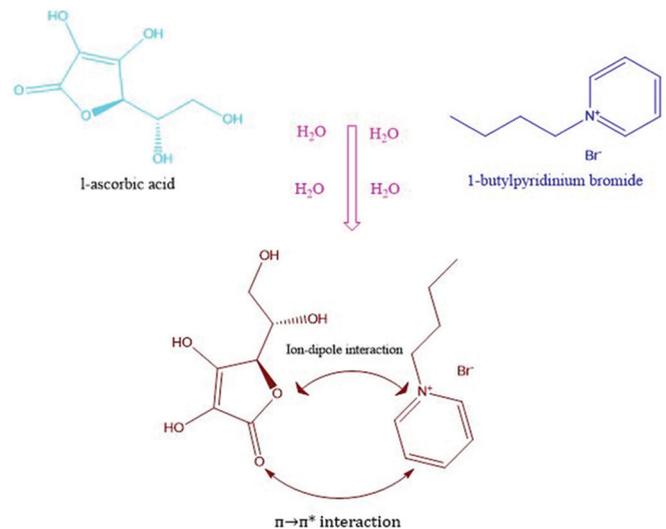
| Mass fraction ( $w_I$ ) | T/K    | $\phi_V^0 \times 10^6 / \text{m}^3 \text{mol}^{-1}$ | $S_V^* \times 10^6 / \text{m}^3 \text{mol}^{-3/2} \text{kg}^{1/2}$ | $B/\text{kg mol}^{-1}$ | $A/\text{kg}^{-1/2} \text{mol}^{-1/2}$ |
|-------------------------|--------|---|--|------------------------|--|
| 0.001                   | 293.15 | 174.80  | -228.31  | 0.52                   | 0.03                                   |
|                         | 298.15 | 181.69  | -244.93  | 0.58                   | 0.05                                   |
|                         | 303.15 | 184.34  | -251.01  | 0.64                   | 0.02                                   |
|                         | 308.15 | 188.46  | -261.69  | 0.73                   | 0.04                                   |
|                         | 313.15 | 191.45  | -267.62  | 0.78                   | 0.01                                   |
| 0.003                   | 293.15 | 178.73  | -244.21  | 0.63                   | 0.01                                   |
|                         | 298.15 | 185.87  | -251.03  | 0.69                   | 0.03                                   |
|                         | 303.15 | 188.56  | -274.23  | 0.76                   | 0.05                                   |
|                         | 308.15 | 192.86  | -276.06  | 0.81                   | 0.02                                   |
|                         | 313.15 | 195.14  | -283.01  | 0.88                   | 0.03                                   |
| 0.005                   | 293.15 | 183.3   | -245.13  | 0.71                   | 0.03                                   |
|                         | 298.15 | 189.22  | -271.58  | 0.77                   | 0.01                                   |
|                         | 303.15 | 193.16  | -295.63  | 0.83                   | 0.04                                   |
|                         | 308.15 | 198.09  | -292.71  | 0.93                   | 0.01                                   |
|                         | 313.15 | 198.68  | -296.67  | 0.99                   | 0.05                                   |

\*Standard uncertainties values of  $u$  are:  $u(T) = 0.01\text{K}$

**Table 6:** Values of various coefficients and standard deviation of equation-3 for L-ascorbic acid in different aqueous IL solutions\*

| Aqueous IL Mixture ( $w_I$ ) | $a_0 \times 10^6 / \text{m}^3 \text{mol}^{-1}$ | $a_1 \times 10^6 / \text{m}^3 \text{mol}^{-1} \text{K}^{-1}$ | $a_2 \times 10^6 / \text{m}^3 \text{mol}^{-1} \text{K}^{-2}$ | $(\delta\phi_E^0 / \delta T) / P \times 10^6 / \text{m}^3 \text{mol}^{-1} \text{K}^{-2}$ |
|------------------------------|--|--|--|--|
| 0.001                        | -1720  | 11.76  | -0.018   | -0.03  |
| 0.003                        | -2181.40                                       | 14.84  | -0.023   | -0.02  |
| 0.005                        | -2585.5  | 17.54  | -0.027   | -0.05  |
| Average standard deviation   | 2.1  | 0.001  | 0.0002   | 0.0001   |

The valuable information about the solvation of the solvated solutes and their effects on the structure of the co-solute IL in the local vicinity of the solute (L-AA) molecules in solutions have been obtained from viscosity  $B$ -coefficient [21]. It is found from Table 4; the values of  $B$ -coefficient are positive and much higher than  $A$ -coefficient which signifies solute-co-solute interaction is dominant over solute-solute and co-solute-co-solute interaction. It is also observed that the positive magnitude of viscosity  $B$ -coefficient increases with increasing temperature and also increases with an increase in mass fraction of aqueous IL which suggests that solute-co-solute interaction is strengthened with a rise in temperature as well as the mass fraction of aqueous IL mixture. These results are in good agreement with those obtained from limiting apparent molar volume  $\phi_V^0$  values.



**Scheme 1:** Plausible solute-co-solute interaction

**Table 7:** Limiting apparent molar expansibilities ( $\phi_E^0$ ) for L-ascorbic acid in different mass fraction of aqueous IL ( $w_I$ ) at different temperature

| Aqueous IL mixture ( $w_I$ ) | $\phi_E^0 \times 10^6 / \text{m}^3 \text{mol}^{-1} \text{K}^{-1}$ |         |         |         |         |
|------------------------------|---|---------|---------|---------|---------|
| T/K                          | 293.15  | 298.15  | 303.15  | 308.15  | 313.15  |
| 0.001                        | 1.15497   | 0.97397 | 0.79297 | 0.61197 | 0.43097 |
| 0.003                        | 1.24284   | 1.01084 | 0.77884 | 0.54684 | 0.31484 |
| 0.005                        | 1.36212   | 1.08612 | 0.81012 | 0.53412 | 0.25812 |
| Average standard deviation   | 0.003   | 0.003   | w0.002  |         |         |

**Table 8:** Values of  $dB/dT$ ,  $A_1$ ,  $A_2$  coefficients for the L-Ascorbic acid in different mass fraction of aqueous IL acid ( $w_I$ ) at studied temperatures\*

| Aqueous IL mixture ( $w_I$ ) | $dB/dT$ | $A_1$  | $A_2$ |
|------------------------------|---------|--------|-------|
| 0.001                        | 0.043   | -6.943 | 0.023 |
| 0.002                        | 0.028   | -7.869 | 0.024 |
| 0.003                        | 0.039   | -8.573 | 0.039 |
| Average standard deviation   | 0.001   | 0.003  | 0.002 |

\*Standard uncertainties values of  $u$  are:  $u(T) = 0.01\text{K}$

**Table 9:** Refractive index ( $n_D$ ) and molar refraction ( $R_M$ ) of L-ascorbic acid in different mass fraction of aqueous solutions at different temperatures and at pressure 1.013 bar\*

| <sup>a</sup> molality/<br>mol·kg <sup>-1</sup> | $n_D$  | $R_M \times 10^6 /$<br>m <sup>3</sup> mol <sup>-1</sup> | <sup>a</sup> molality/<br>mol·kg <sup>-1</sup> | $n_D$  | $R_M \times 10^6 /$<br>m <sup>3</sup> mol <sup>-1</sup> | <sup>a</sup> molality/<br>mol·kg <sup>-1</sup> | $n_D$  | $R_M \times 10^6 /$<br>m <sup>3</sup> mol <sup>-1</sup> |
|--|--------|---|--|--------|---|--|--------|---|
| <b>w1=0.001</b>                                |        |   | <b>w1=0.003</b>                                |        |   | <b>w1=0.005</b>                                |        |   |
| T=293.15K                                      |        |   | T=293.15K                                      |        |   | T=293.15K                                      |        |   |
| 0.010  | 1.3326 | 36.2241   | 0.010  | 1.3328 | 36.2398   | 0.010  | 1.3331 | 36.2597   |
| 0.025  | 1.3327 | 36.1977   | 0.025  | 1.3329 | 36.2135   | 0.025  | 1.333  | 36.2212   |
| 0.040  | 1.3329 | 36.1820   | 0.040  | 1.333  | 36.1864   | 0.040  | 1.3331 | 36.1938   |
| 0.055  | 1.3331 | 36.1634   | 0.055  | 1.3332 | 36.1682   | 0.055  | 1.3333 | 36.1752   |
| 0.070  | 1.3333 | 36.1442   | 0.070  | 1.3334 | 36.1493   | 0.070  | 1.3336 | 36.1679   |
| 0.085  | 1.3336 | 36.1384   | 0.085  | 1.3337 | 36.1421   | 0.085  | 1.3338 | 36.1509   |
| T=298.15K                                      |        |   | T=298.15K                                      |        |   | T=298.15K                                      |        |   |
| 0.010  | 1.3325 | 36.2530   | 0.010  | 1.3327 | 36.2633   | 0.010  | 1.3329 | 36.2784   |
| 0.025  | 1.3327 | 36.2405   | 0.025  | 1.3328 | 36.2460   | 0.025  | 1.333  | 36.2600   |
| 0.040  | 1.3329 | 36.2236   | 0.040  | 1.333  | 36.2302   | 0.040  | 1.3332 | 36.2471   |
| 0.055  | 1.3331 | 36.2064   | 0.055  | 1.3332 | 36.2120   | 0.055  | 1.3333 | 36.2186   |
| 0.070  | 1.3333 | 36.1875   | 0.070  | 1.3334 | 36.1934   | 0.070  | 1.3335 | 36.1978   |
| 0.085  | 1.3335 | 36.1707   | 0.085  | 1.3336 | 36.1741   | 0.085  | 1.3337 | 36.1745   |
| T=303.15K                                      |        |   | T=303.15K                                      |        |   | T=303.15K                                      |        |   |
| 0.010  | 1.3324 | 36.2936   | 0.010  | 1.3326 | 36.3109   | 0.010  | 1.3328 | 36.3271   |
| 0.025  | 1.3325 | 36.2719   | 0.025  | 1.3327 | 36.2902   | 0.025  | 1.3329 | 36.3075   |
| 0.040  | 1.3327 | 36.2550   | 0.040  | 1.3329 | 36.2711   | 0.040  | 1.3331 | 36.2898   |
| 0.055  | 1.3330 | 36.2480   | 0.055  | 1.333  | 36.2440   | 0.055  | 1.3332 | 36.2605   |
| 0.070  | 1.3332 | 36.2297   | 0.070  | 1.3334 | 36.2415   | 0.070  | 1.3334 | 36.2422   |
| 0.085  | 1.3334 | 36.2136   | 0.085  | 1.3336 | 36.2203   | 0.085  | 1.3337 | 36.2265   |
| T=308.15K                                      |        |   | T=308.15K                                      |        |   | T=308.15K                                      |        |   |
| 0.010  | 1.3322 | 36.3307   | 0.010  | 1.3324 | 36.3410   | 0.010  | 1.3326 | 36.3576   |
| 0.025  | 1.3323 | 36.3111   | 0.025  | 1.3325 | 36.3254   | 0.025  | 1.3327 | 36.3449   |
| 0.040  | 1.3326 | 36.3047   | 0.040  | 1.3327 | 36.3099   | 0.040  | 1.3329 | 36.3272   |
| 0.055  | 1.3328 | 36.2860   | 0.055  | 1.333  | 36.3028   | 0.055  | 1.3331 | 36.3087   |
| 0.070  | 1.333  | 36.2683   | 0.070  | 1.3332 | 36.2823   | 0.070  | 1.3333 | 36.2849   |
| 0.085  | 1.3333 | 36.2620   | 0.085  | 1.3334 | 36.2639   | 0.085  | 1.3335 | 36.2647   |
| T=313.15K                                      |        |   | T=313.15K                                      |        |   | T=313.15K                                      |        |   |
| 0.010  | 1.3320 | 36.3755   | 0.010  | 1.3321 | 36.3789   | 0.010  | 1.3322 | 36.3881   |
| 0.025  | 1.3321 | 36.3569   | 0.025  | 1.3322 | 36.3654   | 0.025  | 1.3323 | 36.3742   |
| 0.040  | 1.3324 | 36.3509   | 0.040  | 1.3325 | 36.3561   | 0.040  | 1.3325 | 36.3546   |
| 0.055  | 1.3326 | 36.3332   | 0.055  | 1.3327 | 36.3402   | 0.055  | 1.3328 | 36.3461   |
| 0.070  | 1.3329 | 36.3253   | 0.070  | 1.333  | 36.3301   | 0.070  | 1.3331 | 36.3353   |
| 0.085  | 1.3332 | 36.3190   | 0.085  | 1.3333 | 36.3198   | 0.085  | 1.3334 | 36.3242   |

\*Standard uncertainties  $u$  are:  $u(n_D)=0.02$  and  $u(T)=0.01K$  (0.68 level of confidence), <sup>a</sup>Molality has been expressed per kilogram of (IL+water) solvent mixture

It is observed from Table 4 that the values of the  $B$ -coefficient of AA increase with temperature, that is, the  $dB/dT$  values are positive. From Table 8, the small positive  $dB/dT$  values for the L-AA behave almost as structure-maker.

Furthermore, it is attractive to observe that there is a linear correlation between viscosity  $B$ -coefficients of the studied L-AA with the limiting apparent molar volumes ( $\varphi_V^0$ ) in different mass fraction of aqueous IL solutions. From the above fact, it means

$$B = A_1 + A_2 \varphi_V^0 \tag{7}$$

The coefficients  $A_1$  and  $A_2$  are listed in Table 8. As both viscosities,  $B$ -coefficient and limiting apparent molar volumes define the solute-solvent interaction in solution. The linear variation of viscosity  $B$ -coefficient and limiting apparent molar volume ( $\varphi_V^0$ ) reflects the positive slope (or  $A_2$ ).

It is evident from this study that there is a strong interaction between L-AA and IL and it becomes stronger with a rise in temperature. As

molecules of L-AA are engaged with the IL molecules, the interaction among the IL molecules becomes less effective. We have obtained the derived parameters such as limiting apparent molar volume ( $\phi_V^0$ ) and viscosity  $B$ -coefficient by interpolation and presented in Table 5. The positive and significant magnitude of  $\phi_V^0$  and  $B$ -coefficient from Table 5 clearly indicates that the limiting apparent molar volume ( $\phi_V^0$ ), viscosity  $B$ -coefficient is increasing with increasing mass fraction of IL, which indicates the positive effect of the interaction of AA with IL

### 3.3. Refractive Index

The measurement of refractive index is also an appropriate method for inspecting the molecular interaction present in solution. The molar refraction ( $R_M$ ) can be appraised from the Lorentz-Lorenz relation [22]. The refractive index of a substance is defined as the ratio  $c/c_0$ , where  $c$  and  $c_0$  are the velocity of light in the medium and in a vacuum, respectively. Stated more simply that the refractive index of

a compound describes its capability to refract light as it passes from one medium to another, and thus, the higher the refractive index of a compound, the more the light is refracted [23]. As stated by Deetlefs *et al.* [24], the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser. Hence, a perusal of Tables 9 and 10, we found that the refractive index and the molar refraction are higher for the studied AA and in all the mass fraction of aqueous IL, indicating to the fact that the molecules are more tightly packed in the solution.

The limiting molar refraction ( $R_M^0$ ) estimated from the following equation (14) and presented in Table 10.

$$R_M = R_M^0 + R_S \sqrt{m} \quad (8)$$

Accordingly, we found that the higher values of refractive index and  $R_M^0$  which representing the fact that the molecules of AA and are more tightly packed and greater solute-solvent interaction with IL molecules than solute-solvent interaction. This is also in good agreement with the results obtained from apparent molar volume and viscosity  $B$ -coefficients discussed above.

**Table 10:** Limiting molar refraction ( $R_M^0$ ) of L-ascorbic acid in different temperatures and in different mass fraction of aqueous IL solutions at pressure 1.013 bar\*

| Aq. IL mixtures (w1) | $R_M^0 \times 10^6 / \text{m}^3 \text{mol}^{-1}$ |         |         |         |         |
|----------------------|--|---------|---------|---------|---------|
|                      | 293.15K  | 298.15K | 303.15K | 308.15K | 313.15K |
| 0.001                | 36.27  | 36.30   | 36.33   | 36.37   | 36.40   |
| 0.003                | 36.29  | 36.31   | 36.36   | 36.38   | 36.41   |
| 0.005                | 36.31  | 36.34   | 36.38   | 36.41   | 36.42   |

### 3.4. Conductivity Study

The conductivity study of the L-AA for the interaction (solute-co-solute) in the aqueous solution of IL has been done at five different temperatures. Transport phenomena, molecular, and ionic interaction in the ternary system gives some valuable information [25]. The specific conductivities ( $k$ ) of aqueous IL solution have been monitored with increasing the concentration of L-AA at five different temperatures and tabulated in Table 11. Consequently, it has been observed that molar

**Table 11:** Specific conductivity ( $k$ ) of L-ascorbic acid in different temperatures and in different mass fraction of aqueous IL solutions at pressure 1.013 bar\*

| Added L-Ascorbic acid/mL | Total volume/mL | Conc. L-ascorbic acid solution/mM | Specific Conductivity/mS $\text{cm}^{-1}$ |         |         |         |         |
|--------------------------|-----------------|-----------------------------------|---|---------|---------|---------|---------|
|                          |                 |                                   | 293.15K                                   | 298.15K | 303.15K | 308.15K | 313.15K |
| 0                        | 10              | 0.001                             | 0.11                                      | 0.14    | 0.15    | 0.22    | 0.23    |
| 1                        | 11              | 0.003                             | 0.37                                      | 0.41    | 0.42    | 0.44    | 0.39    |
| 2                        | 12              | 0.003                             | 0.47                                      | 0.44    | 0.47    | 0.48    | 0.50    |
| 3                        | 13              | 0.004                             | 0.53                                      | 0.48    | 0.50    | 0.49    | 0.57    |
| 4                        | 14              | 0.004                             | 0.57                                      | 0.49    | 0.61    | 0.51    | 0.63    |
| 5                        | 15              | 0.005                             | 0.61                                      | 0.51    | 0.66    | 0.55    | 0.67    |
| 6                        | 16              | 0.005                             | 0.64                                      | 0.53    | 0.67    | 0.60    | 0.69    |
| 7                        | 17              | 0.005                             | 0.67                                      | 0.54    | 0.71    | 0.65    | 0.73    |
| 8                        | 18              | 0.006                             | 0.69                                      | 0.59    | 0.74    | 0.69    | 0.74    |
| 9                        | 19              | 0.006                             | 0.70                                      | 0.62    | 0.76    | 0.74    | 0.76    |
| 10                       | 20              | 0.006                             | 0.72                                      | 0.63    | 0.78    | 0.76    | 0.78    |
| 11                       | 21              | 0.007                             | 0.73                                      | 0.64    | 0.79    | 0.77    | 0.79    |
| 12                       | 22              | 0.007                             | 0.74                                      | 0.66    | 0.80    | 0.78    | 0.79    |
| 13                       | 23              | 0.007                             | 0.76                                      | 0.68    | 0.82    | 0.79    | 0.80    |
| 14                       | 24              | 0.007                             | 0.77                                      | 0.69    | 0.82    | 0.79    | 0.82    |
| 15                       | 25              | 0.007                             | 0.78                                      | 0.70    | 0.83    | 0.80    | 0.83    |
| 16                       | 26              | 0.007                             | 0.78                                      | 0.72    | 0.85    | 0.81    | 0.85    |
| 17                       | 27              | 0.007                             | 0.79                                      | 0.73    | 0.85    | 0.85    | 0.86    |
| 18                       | 28              | 0.008                             | 0.80                                      | 0.74    | 0.85    | 0.86    | 0.87    |
| 19                       | 29              | 0.008                             | 0.81                                      | 0.75    | 0.86    | 0.87    | 0.88    |
| 20                       | 30              | 0.008                             | 0.81                                      | 0.78    | 0.87    | 0.88    | 0.90    |

conductivity ( $\Lambda$ ) values increases with an increase in temperatures and gradual addition of L-AA to the IL solution causes a continuous decrease in molar conductivity of the solution. The mobility of the ionic species in solution playing an important role in spite of a growing number of ionic species with added L-AA solution; as a result, the molar conductivity decreases [26,27]. It may be due to the growth of solute-solvent interaction governed by the dipole-dipole, ion-dipole, and hydrophobic – hydrophobic interaction in solution mixtures between the solute and solvent molecules.

#### 4. CONCLUSION

In the summary of this study, there is a strong interaction between L-ascorbic and IL and it becomes stronger with a rise in temperature. As molecules of L-ascorbic and IL have engaged each other, solute-co-solute interaction is much greater than the solute-solute and solvent-solvent interactions in the ternary system.

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**\*Bibliographical Sketch**

Dr. Mahendra Nath Roy, FRSC (London), is a Professor in the Department of Chemistry, University of North Bengal, India. His research interests are in the areas of Host-Guest Inclusion Complexes, Nano Particles, Solution Thermodynamics, Surfactant and Polymer Chemistry. Prof. Roy supervised / supervising 62 Ph.Ds reviewed 49 Ph.D Theses and many referred research papers and authored over 380 research articles and books in Chemistry. He has received the “award of One Time Grant” under basic scientific research” from University Grants Commission, “Prof. Suresh C. Ameta Award “from Indian Chemical Society, “CRSI Bronze Medal 2017” from Chemical Research Society of India and “Shiksha Ratna Award 2018” from the Government of West Bengal “Panchanan Barma Sadbhabona” Award from SODAR Social Organization and “BestProfessor in Chemistry” from Dewang Mehta National Education Awards-2019 for his Outstanding Contribution and Excellencies in Teaching and Chemical Research throughout his career. Recently Dr. Roy is the Vice-Chancellor of Alipurduar University.