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 ^{o}C (212 ^{o}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) (C8SO4), 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 a electrolyte), amino acid (non - electrolytes) and solvent is great significant due to their wide-ranging use in many industrial purpose 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 incorporates 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 ϕ_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.

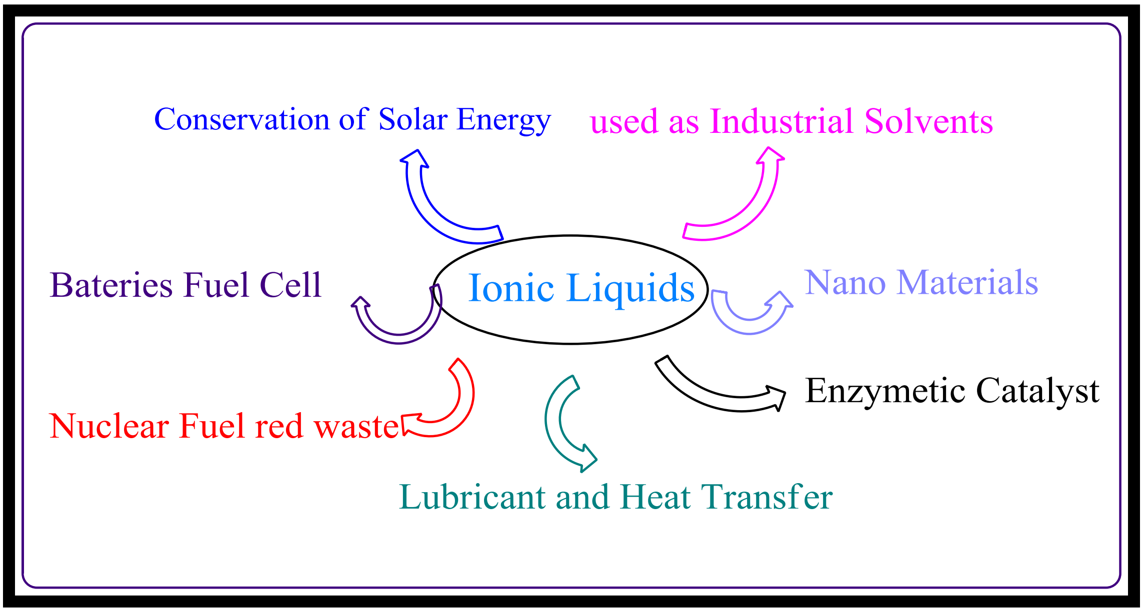
The computational study, surface tension measurement also give the type of interaction associated in molecules in solution system.

Limiting molar conductance (Λ_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

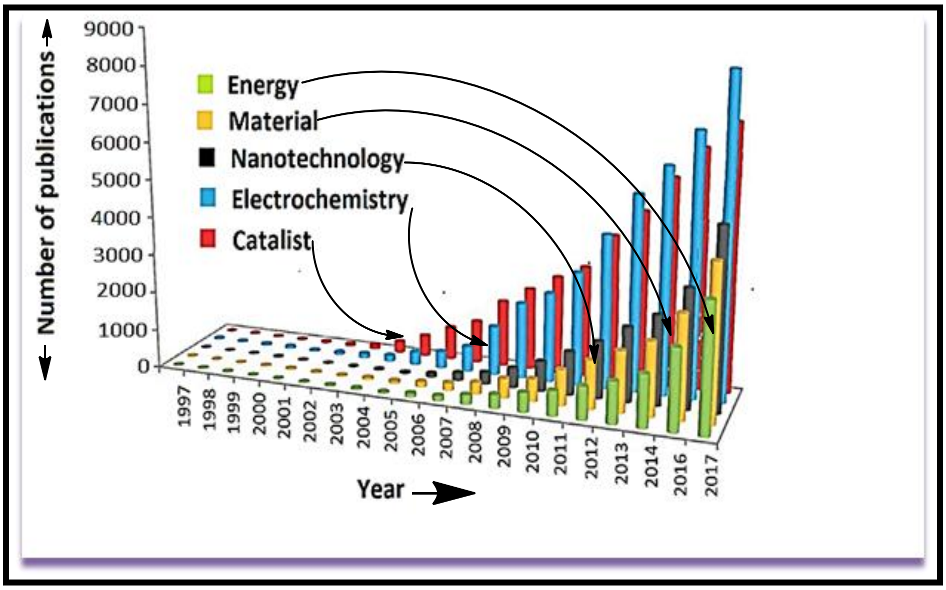
This chapter encloses the *objective, utility and applications of the research work*, the important of electrolytes/solute molecules and solvents used and methods of investigation. This also occupies the summary of the works done connected with the thesis.

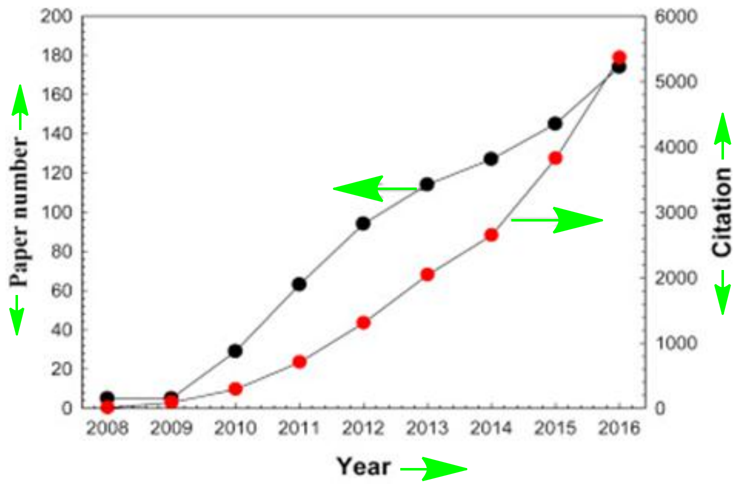


CHAPTER-II

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.



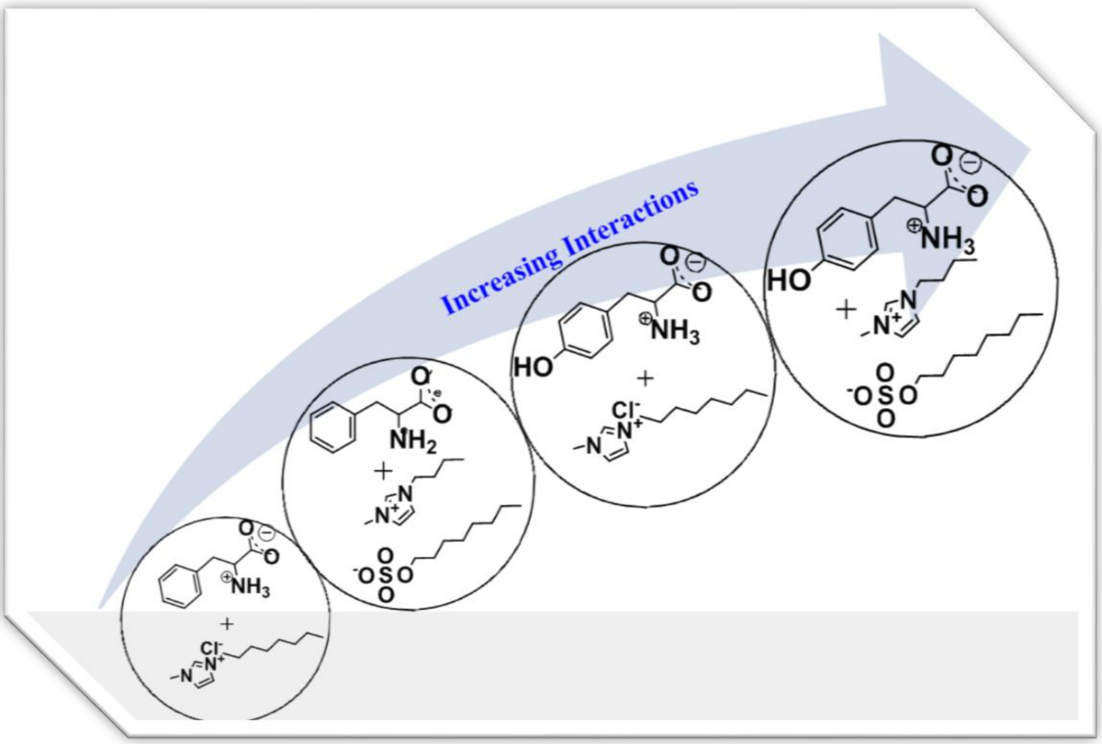


CHAPTER-III

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

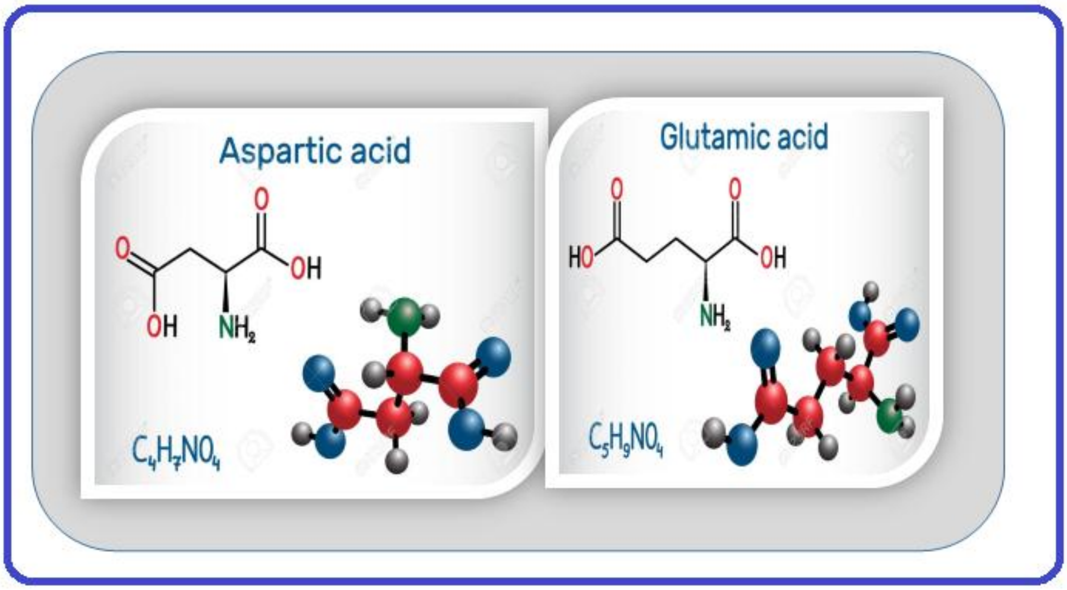
The chapter deals with the precise measurements on electrical conductance (Λ) steady state fluorescence , UV visible spectroscopy, determination of association constant , Gibbs free energy ,study of proton NMR of solutions of an ionic liquid (ILs) , L-Tyrosine, L-Phenyl alanine and their binary mixtures 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(Λ), in the solution systems. From limiting apparent molar volume, (Φv°) experimental slopes (SV*), viscosity B-

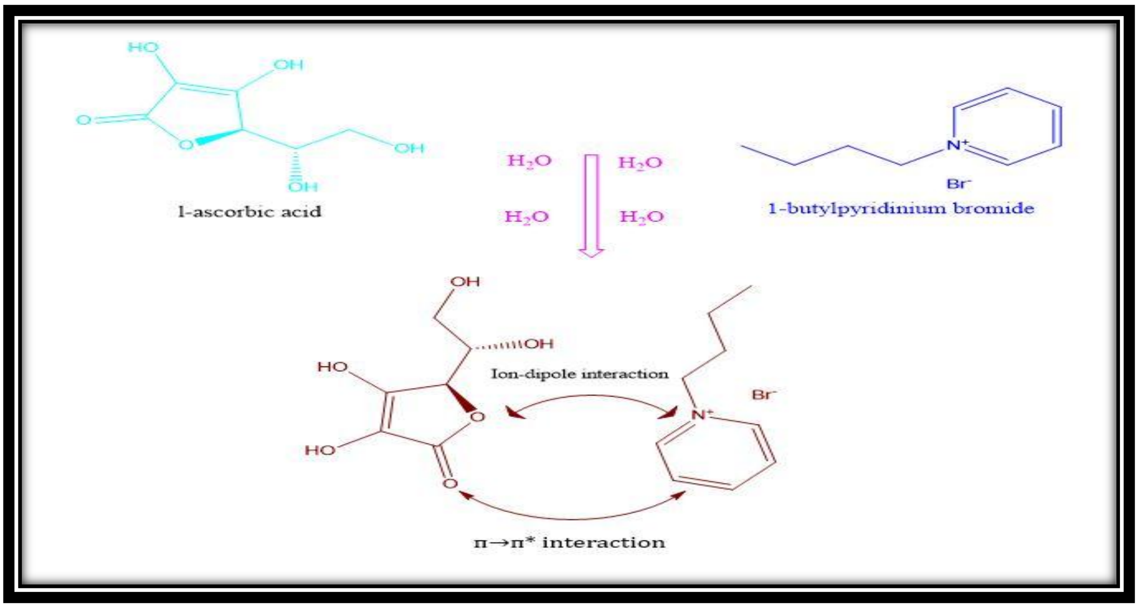
Coefficient data, molar refraction data explained the interaction phenomenon (solute-solvent and solute-solute interactions). Formation of Hydrogen bonding, Dipole-dipole interaction configurational theory, structural aspect, are the powerful forces, for the discussion of the results. The solvation behaviour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



CHAPTER-VI

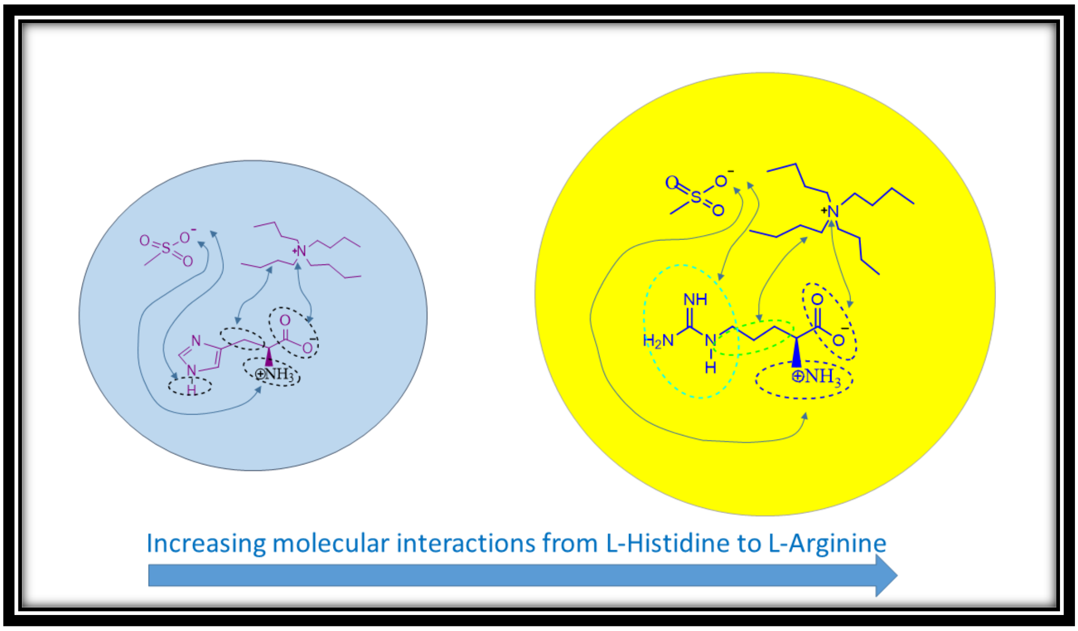
Apparent molar volumes (ϕ_V), viscosity *B*-coefficients, refractive index, specific conductance for L-Ascorbic acid (0.001, 0.003, and 0.005 mol.dm^{-3}) in aqueous ionic liquid, 1-Butylpridiniumbromide ($C_9H_{14}NBr$) solutions were calculated from density of solution. Also viscosity measurements 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 (ϕ_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-Butylpridiniumbromide).



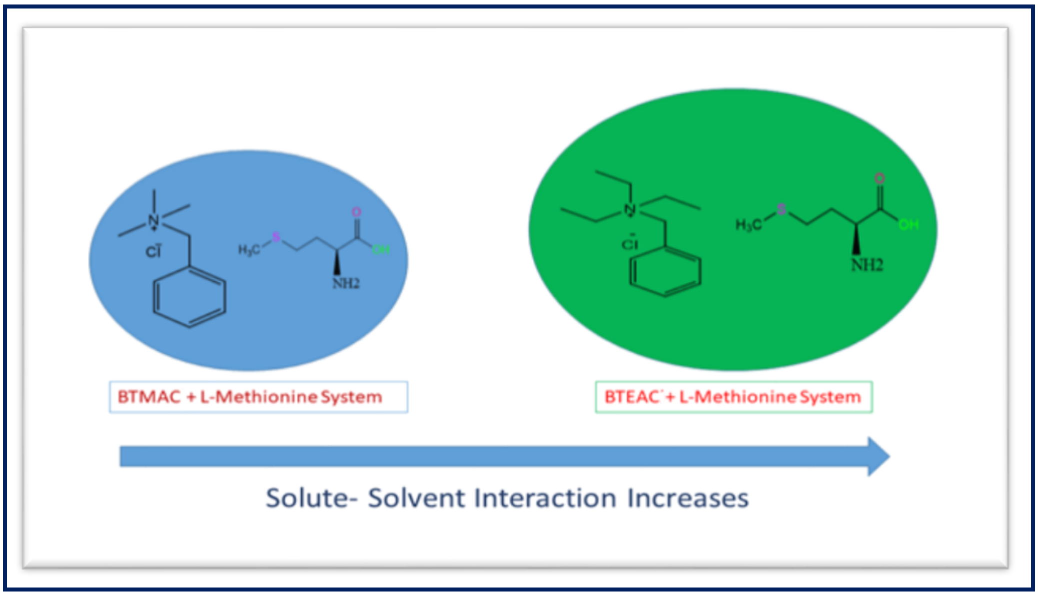
CHAPTER-VII

Custody in mind the uses of amino acids the apparent molar volume (ϕ_V), viscosity *B*-coefficient, Molar conductance (Λ) 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 (ρ), viscosity (η), 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 (ϕ_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, refractmetric, 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 ($\Phi v°$), viscosity B-Coefficient, Molar conductance (ʌ) 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 (ρ), viscosity (η), refractive index (n_D), molar conductance(Λ), surface tension measurements of ionic liquid (Benzyltributylammoniumchloride),solutemolecules,Lglutamine(C5H10N2O3)&Lasparagine(C4H8N2O3) and their ternary mixtures(IL+AA+H2O) 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 (ϕ_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 (ϕ_V^0), slopes (S_V^*), viscosity *A*, *B* coefficients respectively. Spectroscopic technique such as ^{1}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).