

**PHYSICO-CHEMICAL STUDIES ON INTERACTIONS
OF BIOLOGICALLY-ACTIVE SOLUTES AND IONIC
SALTS IN SOME INDUSTRIALLY IMPORTANT
SOLVENT MEDIA**

A Thesis submitted to the
UNIVERSITY OF NORTH BENGAL

For the Award of

**DOCTOR OF PHILOSOPHY (Ph.D.)
In
CHEMISTRY**

By

Ishani Banik, M.Sc. in Chemistry

Guide



DR. MAHENDRA NATH ROY
Professor of Physical Chemistry

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NORTH BENGAL**

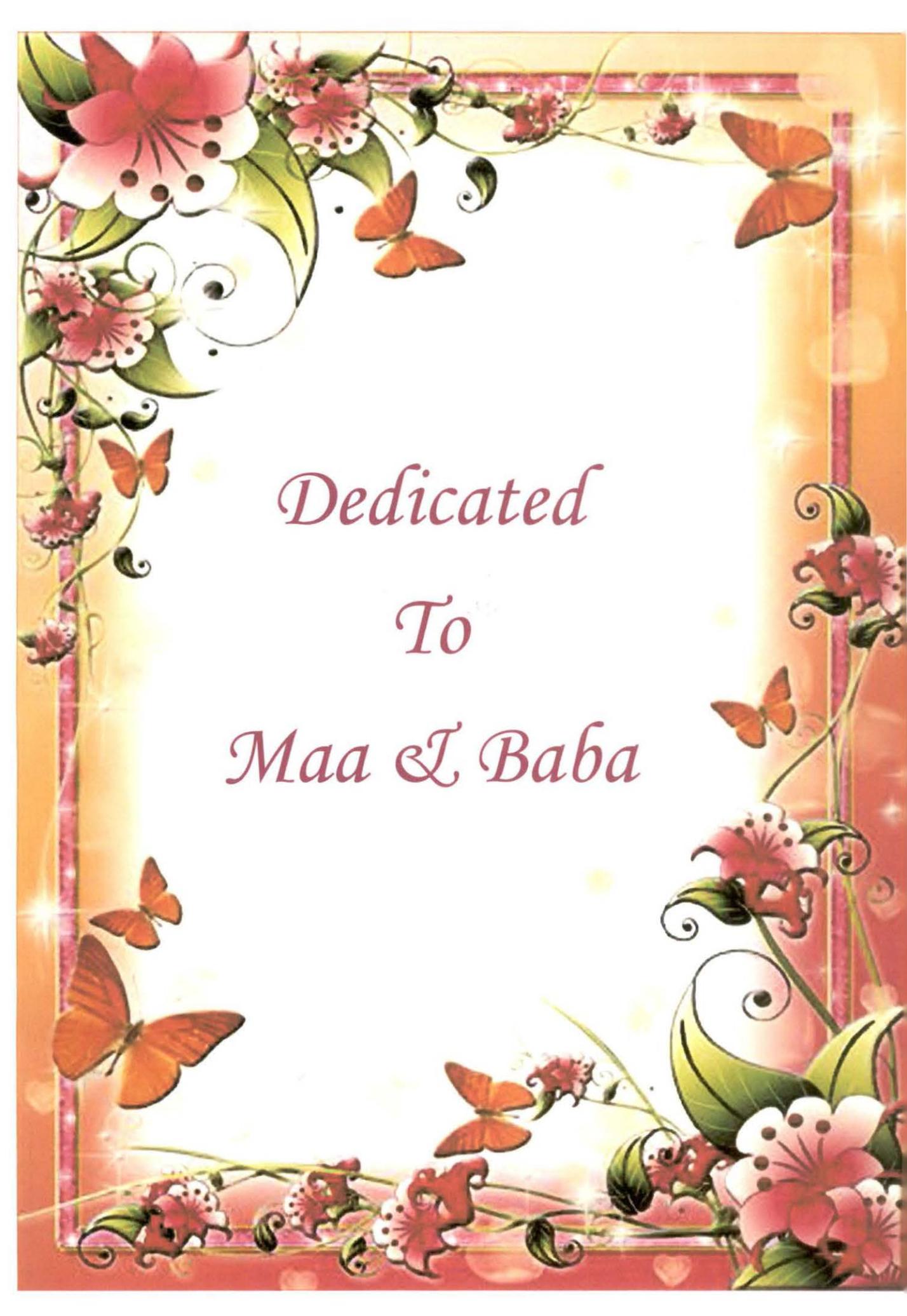
DARJEELING-734013

November, 2014

Th
541.34
B217 p

278436

31 MAR 2016



Dedicated
To
Maa & Baba

DECLARATION

I declare that the thesis entitled “**PHYSICO-CHEMICAL STUDIES ON INTERACTIONS OF BIOLOGICALLY-ACTIVE SOLUTES AND IONIC SALTS IN SOME INDUSTRIALLY IMPORTANT SOLVENT MEDIA**” has been prepared by me under the 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.

Ishani Banik

Ms. ISHANI BANIK,

Department of Chemistry,
University of North Bengal,
Darjeeling: 734013,
West Bengal, India

DATE: *17-11-2014*

UNIVERSITY OF NORTH BENGAL

Prof. M. N. ROY

M. Sc., Ph. D., DSA

DEPARTMENT OF CHEMISTRY

E-mail: mahendraroy2002@yahoo.co.in



Phone : 0353 2776381

Mobile: 094344 96154

Fax: +91 353 2699001

Darjeeling-734 013, INDIA

November, 2014

CERTIFICATE

I certify that Ms. Ishani Banik has prepared the thesis entitled "PHYSICO-CHEMICAL STUDIES ON INTERACTIONS OF BIOLOGICALLY-ACTIVE SOLUTES AND IONIC SALTS IN SOME INDUSTRIALLY IMPORTANT SOLVENT MEDIA", for the award of PhD degree of the University of North Bengal, under my guidance. She has carried out the work at the Department of Chemistry, University of North Bengal.

Mahendra Nath Roy

DR. MAHENDRA NATH ROY,

Professor of Chemistry,

Department of Chemistry,

University of North Bengal,

Darjeeling: 734013

Dr. M. N. Roy, Professor

Department of Chemistry

University of North Bengal

Darjeeling-734013, W.B. India

DATE: 17-11-2014

ABSTRACT

Physico-chemical studies of electrolytes play a very important role in understanding the solute-solute/ion-ion, solute-solvent/ion-solvent and solvent-solvent interactions in solutions. In order to explore the strength and nature of the interactions, the studies on thermodynamic, transport properties of electrolytes, acoustic and optical properties involving in one or more solutes in pure and mixed solvent systems are highly useful. The main objective of the research work is to explore these interactions prevailing in many electrolytic and in many other solution systems where the solvents may be both aqueous and non aqueous. Moreover, knowledge of the Physico-chemical and thermodynamic properties are very important for the proper planning of industrial processes and has great relevance in theoretical and applied areas of research in Chemistry.

A material is said to be biologically-active if it has an interaction or effect on living organism. "Biologically-active compounds" are extra nutritional constituents that typically occur in small quantities in foods. They are being intensively studied to evaluate their effects on health. Biologically-active solutes find great application in pharmaceutical and cosmetic products including medicinal industries. The word "salt" is a general chemical term that refers to ionic compounds formed when an acid reacts with a base. Today, salt continues to be of major economic importance, with thousands of uses in addition to flavoring and preserving food. An ionic liquid (IL) is a salt in the liquid state whose melting point is below some arbitrary temperature, such as 100 °C (212 °F). Ionic liquids have wide range of industrial applications. They used in chemical industry, pharmaceuticals, cellulose processing, gas handling, gas treatment, solar thermal energy, nuclear fuel processing, food and bi-products, waste recycling, batteries etc.

Solution chemistry is an important branch of physical chemistry that studies the change in properties that arise when one substance dissolves in another substance. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. The mixing of different solute or solvent with another solvent/solvent mixtures gives rise to solutions that generally do not behave ideally.

In 'Solution Chemistry' broadly three types of approaches have been made to estimate the extent of solvation. The approaches involves the studies of viscosity, conductance, etc., of electrolytic solutions and the derivation of various factors associated with ionic solvation, the second is the thermodynamic approach 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 spectroscopic measurements where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature.

In recent years there have been increasing interests in the behavior of electrolytes in non- aqueous and mixed solvents with a view to investigating solute-solute/ion-ion and solute-solvent/ion-solvent interactions under varied conditions. However, different sequence of solubility, difference in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have open vistas for physical chemists and interests in these organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry .

Studies of transport properties of electrolytes, along with thermodynamic and acoustic studies, give very valuable information regarding molecular interactions in solutions. The influence of these interactions may be sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in such diverse areas as organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extraction. Knowledge of ion-solvent interactions in aqueous, non-aqueous solutions and mixed solvents is very important in many practical problems concerning energy transport, heat transport, mass transport and fluid flow. The proper understanding of the solute-solvent interactions would form the origin of explaining quantitatively the influence of the solvent and the degree of interaction of ions in solvents and thus pave the way for real understanding of the different phenomena related with solution chemistry.

The major aims of the research work are:

- ❖ To understand the nature and strength of various interactions, their influence on structural and dynamic properties of biologically active solutes and ionic salts in pure and mixed solvent systems.

Abstract

- ❖ To investigate the physico-chemical properties of biologically-active solutes and ionic salts in pure and mixed solvent systems.
- ❖ To study the transport properties of ionic salts along with thermodynamic and acoustic ones to characterize molecular interactions in solutions.

It is thus apparent that the real understanding of the molecular interactions is a difficult task. The aspect embraces a wide range of topics but we have embraced on a series of investigations based on the volumetric, viscometric, interferometric and conductometric behavior to study the chemical nature of the structure of solutes and solvents and their mutual interactions in solution. Therefore, a number of conductometric and related studies of different electrolytes in non-aqueous solvents, have been made for their optimal use in high-energy batteries and for understanding organic reaction mechanisms.

CHOICE OF SOLVENTS, SOLUTES AND ELECTROLYTES USED

Nitromethane, formamide, N-methylformamide, 1,3-dioxolane, methanol, acetonitrile, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulphoxide along with water, considered as a universal solvent, have been chosen as main solvent in this research work because these solvents are industrially very important and by mixing these solvents we could obtain a wide variation of viscosities and dielectric constants giving us an optimum environment for the study.

Amino acids (glycine, L-alanine, L-valine,), carbohydrates (D-glucose, D-mannitol, D-sucrose), ascorbic acid (vitamin C), Nicotinic acid (vitamin B₃) were considered as solutes. The study of these solutes is of great interest because of their wide use as solvents solubilizing agents in pharmaceutical, cosmetics and medicinal industries.

The electrolytes used are tetrabutylammonium tetrafluoroborate, tetrabutylammonium perchlorate, tetrabutylphosphonium tetrafluoroborate, tetrabutylphosphonium methanesulfonate. These electrolytes are used as reference and supporting electrolytes and are used as non-aqueous electrolytes in electrochemical applications.

METHODS OF INVESTIGATION

The existence of free ions, solvated ions, ion-pairs and triple-ions in aqueous and non-aqueous media depends upon the concentrations of the solvent systems. Hence the study of various interactions and equilibrium of ions in different concentration regions are of immense importance to the technologist and theoretician as most of the chemical processes occurs in these systems.

It is of interest to employ different experimental techniques to get a better insight into the phenomena of solvation and different interactions prevailing in solution. We have, therefore, employed five important methods, namely conductometry, viscometry, densitometry, Ultrasonic Interferometry and Refractometry to probe the problem of solvation phenomena.

PHYSICO-CHEMICAL PARAMETERS AND THEIR SIGNIFICANCE

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent/ion-solvent and solute-solute/ion-ion interactions in solution. The sign and magnitude of partial molar volume (ϕ_v^0) also provides information about the nature and magnitude of ion-solvent interaction while the experimental slope (S_v^*) provides information about ion-ion interactions. Viscosity B-coefficient obtained from the viscosity values indicates the extent of ion-solvent interaction in a solution. From experimental speed of sound values, limiting apparent molar adiabatic compressibility (ϕ_K^0) and the experimental slope (S_K^*) can be estimated. These parameters also give an idea about the ion-solvent and ion-ion interaction in the solution.

The transport properties in most cases are studied using the conductance data, especially conductance at infinite dilution. Limiting molar conductance (Λ_0) gives an idea about the ion-solvent interaction in the solution. Association constant (K_A) obtained from the conductance study gives an idea about the solvation of the ions.

SUMMARY OF WORKS DONE

CHAPTER I

This chapter contains the object and applications of the research work, the reasons for choosing the main solvents and solutes and methods of investigation. This also includes a summary of the works associated with the thesis.

CHAPTER II

This chapter contains the general introduction of the thesis and forms a background of the works embodied in the thesis. A brief review of notable works in the field of ion-solvent interaction has been given. Various derived parameters dependent on density, viscosity, ultrasonic speed of sound, refractive indices and conductance along with their importance in solution chemistry has been discussed.

CHAPTER III

This chapter contains the experimental section which mainly involves the structure, source, purification and application of the solvents and solutes used in the research work and the details of the instruments used for the study.

CHAPTER IV

This chapter includes the apparent molar volume (ϕ_V), viscosity B -coefficient, molal refraction (R) and adiabatic compressibility (ϕ_K) of L-Glycine, L-Alanine, and L-Valine have been determined in 0.010, 0.03, 0.05 mol-dm⁻³ aqueous ascorbic acid solutions at 298.15 K from density (ρ), viscosity (η), refractive index (n_D) and speed of sound (u) respectively. The limiting apparent molar volumes (ϕ_V^0) and experimental slopes (S_V^*), derived from the Masson equation, have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The viscosity data were analyzed using the Jones-Dole equation and the derived parameters A and B have also been interpreted in terms of solute-solute and solute-solvent interactions respectively in the solutions. Molal refractions (R) have been calculated using the Lorentz-Lorenz equation. Limiting apparent molar adiabatic

compressibilities (ϕ_k^0) of these amino acids at infinite dilution were evaluated and discussed.

CHAPTER V

Density (ρ) and viscosity (η) measurements of bio-active solutes (D-glucose, D-mannitol and D-sucrose) in aqueous nicotinic acid, (Vitamin B₃) at 298.15, 308.15 and 318.15 K have been carried out. Using these properties, the apparent molar volume (ϕ_V), the partial molar volume (ϕ_V^0), the partial molar volume of transfer ($\Delta\phi_V^0$) of carbohydrates from water to aqueous nicotinic acid solution were calculated. A plausible mechanism for the reaction of carbohydrates in aqueous nicotinic acid is also suggested along with the interaction of the product with water. The viscosity *B*-coefficients of Jones-Dole equation and the molar refraction (*R*) of the solutions have been computed for the interpretation of solute-solvent interactions. The structure-making or breaking capacity of carbohydrates in the solution has been discussed. All these parameters are used to study solute-solvent and solute-solute interactions in the aforementioned mixtures.

CHAPTER VI

In this chapter electrolytic conductivities (Λ), densities (ρ), viscosities (η) and ultrasonic speed (*u*) of an ionic liquid (IL) Tetrabutylphosphonium Tetrafluoroborate [Bu₄PBF₄] have been studied in dimethylsulfoxide (DMSO), dimethylacetamide (DMA), and dimethylformamide (DMF) at 298.15 K. The limiting molar conductivity (Λ_0), the association constant (K_A), and the distance of closest approach of ions (*R*) have been evaluated using the Fuoss conductance equation (1978). The molar conductivities observed were explained by the formation of ion-pairs ($M^+ + X^- \leftrightarrow MX$). The Walden product is obtained and discussed. Ion-solvent interactions have been interpreted in terms of apparent molar volumes (ϕ_V) and viscosity *B*-coefficients which are obtained from the results supplemented with densities and viscosities, respectively. The limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) derived from the Masson equation and viscosity *A* and *B* coefficients using the Jones-Dole equation have been interpreted in terms of ion-ion

Abstract

and ion-solvent interactions respectively. The adiabatic compressibility (β) has been evaluated using the ultrasonic speed (u) values. Finally values of the limiting partial molar adiabatic compressibility (ϕ_x^0) are calculated and discussed.

CHAPTER VII

This chapter entails the qualitative and quantitative analyses of molecular interaction prevailing in ionic liquid tetrabutylphosphonium methanesulfonate [Bu₄PMS] in dimethyl sulfoxide (DMSO), N,N- dimethyl formamide (DMF) and N,N-dimethyl acetamide (DMA) probed by electrical conductances and Fourier transform infrared (FT-IR) measurements have been reported at 298.15 K. Corresponding conductance data have been analysed using the Fuoss conductance-concentration equation (1978) for ion pair formation. The limiting ionic conductances (λ_o^\pm) have been estimated from the appropriate division of the limiting molar conductivity value of tetrabutylammonium tetraphenylborate [Bu₄NBPh₄] as the "reference electrolyte". The diffusion coefficient (D) has been obtained from Stokes-Einstein relation and the ionic mobility (i) for [Bu₄P]⁺ and MS⁻ using appropriate equation. The results have been discussed in terms of dipole-dipole interactions, hydrogen bond formation and structural aspect of the solvents and configurational theory. The FT-IR spectra have also been studied to predict the interactions occurring in the system.

CHAPTER VIII

In this chapter qualitative and quantitative analyses of molecular interaction prevailing in ionic salt-organic solvent media, probed by electrical conductances have been reported. Tetrabutylammonium tetrafluoroborate [Bu₄NBF₄] in acetonitrile (CH₃CN), methanol (CH₃OH), dimethylsulfoxide (DMSO) and 1,3-dioxolane (1,3-DO) have been studied at 298.15 K. The extent of interaction is expressed in terms of the association constant (K_A) and shows the interaction to be a function of viscosity. Limiting molar conductances (Λ_o), association constants (K_A), and the association diameter (R) for ion-pair formation have been analyzed using the Fuoss conductance-concentration equation (1978). The observed molar conductivities were explained by the formation of ion-pairs ($M^+ + X^- \leftrightarrow MX$, K_p) and

triple-ions ($2M^+ + X^- \leftrightarrow M_2X^+$; $M^+ + 2X^- \leftrightarrow MX_2^-$, K_T). The Walden product is obtained and discussed. The deviation of the conductometric curves (Λ vs \sqrt{c}) from linearity for the electrolyte in 1, 3-dioxolane indicates triple-ion formation, and therefore the corresponding conductance data have been analyzed by using the Fuoss-Kraus theory of triple-ions. The limiting ionic conductances (λ_o^\pm) have been calculated from the appropriate division of the limiting molar conductivity value of tetrabutylammonium tetraphenylborate [Bu_4NBPh_4] as the "reference electrolyte" method along with a numerical evaluation of ion-pair and triple-ion formation constants ($K_P \approx K_A$ and K_T). The results have been interpreted in terms of solvent properties and configurational theory.

CHAPTER IX

In these chapter Molecular interactions of tetrabutylammonium salts prevailing in organic solvent media have been analyzed, both qualitatively and quantitatively, using conductometric studies and validating the results with Fourier transform infrared (FT-IR) measurements. From conductometric studies of tetrabutylammonium tetrafluoroborate [Bu_4NBF_4] and tetrabutylammonium perchlorate [Bu_4NClO_4] in nitromethane (NM), N-methyl formamide (NMF), and formamide (FA) at 298.15 K, it is revealed that high molecular interaction is mainly because of ion-dipole interactions, which is evidenced from the FT-IR measurements. The 1978 Fuoss conductance-concentration equation in terms of the limiting molar conductance (Λ_o), the association constant (K_A), and the association diameter (R) was used to interpret the conductance data. Tetrabutylammonium tetraphenylborate [Bu_4NBPh_4] as the "reference electrolyte" was used to estimate the ionic contributions to the limiting molar conductance. The degree of interaction is articulated in terms of the association constant (K_A), which illustrates that viscosity of the solvent plays an important role in the ion-dipole interaction. The ionic interaction obtained is highest in the case of [Bu_4NBF_4] and FA in comparison to the other systems. The consequences have been considered in terms of dipole-dipole interactions, hydrogen bond formation, structural feature, and configurational theory. The FT-IR spectroscopic studies of the variational intensity of characteristic bands of the solvents have been undertaken, and the solvation

Abstract

phenomenon is evidenced by the change of band intensities owing to the occurrence of the electrolytes.

CHAPTER X

This chapter contains the concluding remarks of the works related to the thesis.

PREFACE

The work in the thesis entitled **"PHYSICO-CHEMICAL STUDIES ON INTERACTIONS OF BIOLOGICALLY-ACTIVE SOLUTES AND IONIC SALTS IN SOME INDUSTRIALLY IMPORTANT SOLVENT MEDIA"** was initiated under the supervision of Dr. Mahendra Nath Roy, Prof. of Chemistry in the Department of Chemistry, University of North Bengal. This research was realized within the framework of the Programme: "University Grants Commission for sanctioning Research Fellowship Major Research Project, Ref. No. RP/5032/FCS/2011)".

The work is an attempt to explore molecular interaction in aqueous and non-aqueous electrolytic and non-electrolytic solutions by studying their physico-chemical, transport, acoustic and spectral properties.

During the course of my research, I was privileged to participate in several meets and seminars across the country. I was highly inspired by listening and interacting with distinguished experts and scientists. I was even fortunate enough to publish the works in the thesis in International Journals of repute.

In keeping with general practice 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.

I hope that I will be given more challenges in my life so that the knowledge that the knowledge that I have earned during my work can be put into action in the future.

ACKNOWLEDGEMENT

First of all, I would like to express my deepest sense of gratitude and inner sentiments to my respected teacher and supervisor, Dr. Mahendra Nath Roy, Professor, Department of Chemistry, University of North Bengal, Darjeeling, India. Throughout my research period, I have received constant guidance, valuable suggestions, inspiration and constructive criticism from him. I am deeply indebted to him for his keen interest, strong motivation, constant encouragement and sympathetic consideration. The trust, support and 'the freedom to create' that he has provided throughout the work is very much appreciated. Without his loving care, dependable guidance, and precious supervision, it would have been impossible for me to bring the present contour to this thesis.

I also express my profound sense of gratitude to the honourable faculty members, Department of Chemistry, University of North Bengal for their priceless assistance and continued inspiration during the course of my research. I am grateful to the University authority for providing laboratory facilities, especially University Scientific Instrumentation Centre, University of North Bengal for helping me in my research.

The inspiration, encouragement and whole-hearted cooperation that I received from my husband, Mr. Rakesh Sarkar, is most elegantly acknowledged. He deserves a special mention for showing utmost patience and providing me unconditional support and encouragement to pursue my interests. No word is enough to pay my sincere gratitude to my father Sri Dipak Banik and mother Smt.

Chandana Banik and my sister Ms. Sayani Banik, for their contributions to my carrier building and whose inspiration went a long way to the completion of this thesis.

My special thanks go to Dr. Rajani Dewan, Mr. Palash Chakraborti, Mr. Saptarshi Basak, Mr. Milan Chandra Roy and Mr. Deepak Ekka and of all my research laboratory staff for their valuable assistance and cooperation during my 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.

Finally, I would also like to record my thankfulness to the University Grants Commission for sanctioning Research Fellowship Major Research Project, Ref. No. RP/5032/FCS/2011) and financial assistance in order to continue this research work. I am also thankful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (No. F 540 / 27 / DRS / 2007, SAP-1) and the '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 my research works.

Ishani Banik
ISHANI BANIK

Research Scholar
Department of Chemistry
University of North Bengal
Darjeeling: 734013, WB, INDIA

TABLE OF CONTENTS

TOPIC	PAGE NO.
Declaration	
Certificate	
Abstract	
Preface	
Acknowledgement	
List of Tables	1-7
List of Figures	8-12
List of Appendices	13
<i>Appendix A: List of Publications</i>	
<i>Appendix B: List of Seminars/Symposiums/Conferences Attended</i>	
CHAPTER I	14-29
Necessity of the Research Work	
1.1. Object, Scope and Application of the Research Work	
1.2. Choice and importance of Solvents and Solutes Used	
1.3. Methods of Investigation	
References	
CHAPTER II	30-118
General Introduction(Review of the Earlier Works)	
2.1. Importance of Solution Chemistry	
2.2. Interactions in Solution Phase	
2.3. Density	
2.4. Viscosity	

2.5. Ultrasonic Speed

2.6. Conductance

2.7. Refractive Index

References

CHAPTER III

119-151

Experimental Section

3.1. Name, Structure, Physical properties, Purification and Applications of the Solvents and Solutes Used in the Research Work

3.2. Experimental Methods

References

CHAPTER IV

152-171

Study of solute-solvent interaction of some bio-active solutes prevailing in aqueous ascorbic acid solution

4.1. Introduction

4.2. Experimental Methods

4.3. Results and Discussions

4.4. Conclusion

References

Tables

Figures

***Published in *J. Mol. Liquids*, 169 (2012) 8-14**

CHAPTER V

172-207

Structural Effects of Three Carbohydrates in Nicotinic acid/ Water Mixed Solvents

5.1. Introduction

5.2. Experimental Section

5.3. Results and Discussion

5.4. Conclusions

References

Tables

Figures

Communicated in *J. Mol. Liquids

CHAPTER VI

208-229

Physics and chemistry of an ionic liquid in some industrially important solvent media probed by physicochemical techniques

6.1. Introduction

6.2. Experimental Section

6.3. Results and Discussion

6.4. Conclusions

References

Tables

Figures

***Published in *J. Chem. Thermodynamics*, 57 (2013) 230-237**

CHAPTER VII

230-249

Study of Assorted Interactions of an Ionic liquid in Significant Solvent Systems Using Compensated Equation of Fuoss Conductance and Vibrational Mode

7.1. Introduction

7.2. Experiments

7.3. Results and Discussion

7.4. Conclusions

References

Tables

Figures

* Published in *Ionics*, 20 (2014) 1001-1009

CHAPTER VIII

250-275

Probing subsistence of ion-pair and triple-ion of an ionic salt in liquid environments by means of conductometric contrivance

8.1. Introduction

8.2. Experimental

8.3. Results and Discussion

8.4. Conclusions

References

Tables

Figures

*Published in *J. Chem. Thermodynamics*, 63 (2013) 52-59

Table of Contents

CHAPTER IX	276-305
Role of Anions (Tetrafluoroborate, Perchlorate) of Tetrabutylammonium Salts in Determining Solvation Effects Prevailing in Industrially Essential Solvents Probed by Conductance and FT-IR Spectra	

9.1. Introduction

9.2. Experimental Section

9.3. Results and Discussion

9.4. Conclusion

References

Tables

Figures

*Published in *J. Chem. Eng. Data*, 58 (2013) 3378-3386.

CHAPTER X	306-310
Concluding Remarks	

BIBLIOGRAPHY	311-333
INDEX	334-336

LIST OF TABLES

CHAPTERS	TABLES	PAGE NO.
Chapter IV	<p>Table 1. The values of density (ρ), viscosity (η), refractive index (n_D), and speed of sound (u) in different mass fraction of ascorbic acid at 298.15 K.</p> <p>Table 2. Experimental values of densities (ρ), viscosities (η), refractive Index (n_D), and ultrasonic Speed (u) of L-Glycine, L-Alanine and L-Valine in different mass fraction of ascorbic acid at 298.15 K.</p> <p>Table 3. Molality, apparent molar volume (ϕ_v), $(\eta/\eta_0 - 1)/m^{1/2}$, molar refraction ($R$), adiabatic compressibility (β) and apparent molal adiabatic compressibility (ϕ_k) of L-Glycine, L- Alanine, and L-Valine in ascorbic acid at 298.15 K.</p> <p>Table 4. Limiting apparent molar volumes (ϕ_v^0), experimental slopes (S_v^*), A, B coefficients, limiting partial adiabatic compressibility (ϕ_k^0), and experimental slope (S_k^*) of L-Glycine, L-Alanine, and L-Valine in aqueous ascorbic acid at 298.15 K.</p>	161-167
Chapter V	<p>Table 1. Values of density (ρ), viscosity (η), at 298.15, 308.15, 318.15 K and refractive index (n_D) at 298.15 K in different mass fraction (w_1) of aqueous NA</p> <p>Table 2. Experimental values of density (ρ) and viscosity (η) at 298.15 K, 308.15 K, 318.15 K and Refractive index (n_D) at 298.15 K of carbohydrates in different mass fraction of aqueous NA (w_1).</p>	186-201

Table 3. Molality (m), apparent molar volume (ϕ_V) and $(\eta_r - 1)/\sqrt{m}$ at 298.15 K, 308.15 K, 318.15 K and molar refraction (R) at 298.15 K of carbohydrates in different mass fraction of aqueous NA (w_1).

Table 4. Partial molar volumes (ϕ_V^0), experimental slopes (S_V^*), viscosity A - and B -coefficients of carbohydrates with their standard deviation in different mass fraction of aqueous NA (w_1) at 298.15 K, 308.15 K and 318.15 K respectively.

Table 5. Values of $\phi_V^0(\text{aq})$, $\Delta\phi_V^0$, $B(\text{aqueous})$, ΔB , v_{AB} , and v_{ABA}/v_{BAB} for carbohydrates in different mass fraction of aqueous NA (w_1) at 298.15 K, 308.15 K and 318.15 K respectively

Table 6. Values of empirical coefficients (a_0 , a_1 , and a_2) of Equation 4 for carbohydrates in different mass fraction of aqueous NA (w_1).

Table 7. Limiting apparent molar expansibilities (ϕ_E^0) for carbohydrates in different mass fraction of aqueous NA (w_1) at 298.15 K, 308.15 K and 318.15 K respectively.

Table 8. Values of dB/dT , A_1 and A_2 coefficient of equation 8 for the carbohydrates in different mass fraction of aqueous NA (w_1).

Table 9. Values of \bar{V}_1^0 , $\mu^{0\#}$, $T\Delta S^\#$, $\Delta H^\#$, for carbohydrates in different mass fraction of aqueous NA (w_1) at 298.15 K, 308.15 K and 318.15 K respectively.

<p>Chapter VI</p>	<p>Table 1. Sample provenance and purity</p> <p>Table 2. Values of density (ρ), viscosity (η), refractive index (n_D), Speed of sound (u), and relative permittivity (ϵ_r) of the pure solvents studied at T = 298.15 K.</p> <p>Table 3. The molar conductance (Λ) and corresponding concentration (c) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K.</p> <p>Table 4. Limiting molar conductivity (Λ_0), the association constant (K_A), the distance of closest approach of ions (R), Standard Deviations δ, Walden Product ($\Lambda_0\eta_0$) and Gibbs free energy change (ΔG°) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K.</p> <p>Table 5. Limiting Ionic Conductance (λ_0^\pm), Ionic Walden Product ($\lambda_0^\pm\eta_0$), Stokes' Radii (r_s), Crystallographic Radii (r_c), ionic viscosity B-coefficients (B_x) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K.</p> <p>Table 6. Experimental values of Molarity (c), Densities (ρ), Apparent Molar Volume (ϕ_V), Limiting Apparent Molar Volume (ϕ_V^0) and Experimental Slope (S_V^*) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K.</p> <p>Table 7. Experimental values of Molarity (c), Viscosities (η), $(\eta_r - 1)/\sqrt{c}$, Viscosity A, B-coefficients of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K.</p>	<p>221-225</p>
--------------------------	---	-----------------------

	<p>Table 8. Experimental Values of Molarity (c), Speed of Sound (u), Adiabatic Compressibility (β) and Apparent Molar Adiabatic Compressibility (ϕ_K), Limiting Apparent Molar Adiabatic Compressibility (ϕ_K^0), and Experimental Slopes (S_K^*) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K.</p>	
Chapter VII	<p>Table 1. Sample description.</p> <p>Table 2. Values of Density (ρ), Viscosity (η) and Dielectric constant (ϵ_r) of pure solvents at $T = 298.15$ K.</p> <p>Table 3. Limiting molar conductivity (Λ_0), the association constant (K_A), the distance of closest approach of ions (R), standard deviations δ of experimental Λ from equation 1, Walden product ($\Lambda_0\eta$) and Gibb's energy change (ΔG°) of $[\text{Bu}_4\text{PMS}]$ in studied solvent systems at $T = 298.15$ K.</p> <p>Table 4. Limiting ionic conductance (λ_0^\pm), ionic Walden product ($\lambda_0^\pm\eta$), Stokes' radii (r_s) and crystallographic radii (r_c) of $[\text{Bu}_4\text{PMS}]$ in studied at $T = 298.15$ K.</p> <p>Table 5. Diffusion Coefficient (D) and ionic mobility (i) of $[\text{Bu}_4\text{P}]^+$ and MS^- in studied solvents at 298.15 K.</p> <p>Table 6. Stretching frequencies of the functional groups present in the pure solvent and change of frequency after addition of IL, $[\text{Bu}_4\text{PMS}]$ in the solvents.</p>	243-245

Chapter VIII	<p>Table 1. Sample description.</p> <p>Table 2. Values of density (ρ), viscosity (η) and dielectric constant (ϵ) of CH₃CN, CH₃OH, DMSO, and 1,3-DO at $T = 298.15$ K and atmospheric pressure</p> <p>Table 3. Molar conductance (Λ) and the corresponding concentration (c) of [Bu₄NBF₄] in CH₃CN, CH₃OH, DMSO and 1, 3-DO at $T = 298.15$ K and atmospheric pressure</p> <p>Table 4. Limiting molar conductivity (Λ_0), the association constant (K_A), the distance of closest approach of ions (R), standard deviations δ of experimental Λ from Equation (2), Walden product ($\Lambda_0\eta_0$) and Gibbs energy change (ΔG°) of [Bu₄NBF₄] in CH₃CN, CH₃OH and DMSO at $T = 298.15$ K and atmospheric pressure.</p> <p>Table 5. Limiting ionic conductance (λ_0^\pm), ionic Walden product ($\lambda_0^\pm\eta_0$), Stokes' radii (r_S) and crystallographic radii (r_C) of [Bu₄NBF₄] in CH₃CN, CH₃OH, and DMSO at $T = 298.15$ K and atmospheric pressure.</p> <p>Table 6. The calculated limiting molar conductance of ion-pair (Λ_0), limiting molar conductance of triple-ion (Λ_0^T), slope and intercept of Equation (13) of [Bu₄NBF₄] in 1, 3-DO at $T = 298.15$ K and atmospheric pressure.</p> <p>Table 7. Salt concentration at the minimum conductivity (c_{\min}) along with the ion-pair formation</p>	265-269
--------------	--	---------

	<p>constant (K_P), triple-ion formation constant (K_T) of $[Bu_4NBF_4]$ in 1, 3-DO at $T = 298.15$ K and atmospheric pressure.</p> <p>Table 8. Salt concentration (c_{min}) at the minimum conductivity (Λ_{min}), the ion-pair fraction (α), triple-ion fraction (α_T), ion-pair concentration (C_P) and triple-ion concentration (C_T) of $[Bu_4NBF_4]$ in 1,3-DO at $T = 298.15$ K and atmospheric pressure.</p> <p>Table 9. Salt concentration (c), the ion-pair fraction (α), triple-ion fraction (α_T), ion-pair concentration (C_P) and triple-ion concentration (C_T) of $[Bu_4NBF_4]$ in 1, 3-DO at 298.15 K and atmospheric pressure.</p>	
Chapter IX	<p>Table 1. Values of Density (ρ), Viscosity (η) and Relative Permittivity (ϵ_r) of Studied Pure Solvents at $T = 298.15$ K and $P = 0.1$ MPa^a</p> <p>Table 2. Molar Conductance (Λ) and the Corresponding Concentration (c) of the Studied Electrolytes in Different Solvents at $T = 298.15$ K and $T = 0.1$ MPa^a</p> <p>Table 3. Limiting Molar Conductivity (Λ_0), the Association Constant (K_A), the Distance of Closest Approach of Ions (R), Standard Deviations δ of Experimental Λ from Eq 1, Walden Product ($\Lambda_0\eta$), Gibb's energy change (ΔG^0) and A-coefficient of Electrolytes in Different Studied Solvents at $T = 298.15$ K.</p> <p>Table 4. Limiting Ionic Conductance (λ_0^\pm), Ionic Walden Product ($\lambda_0^\pm\eta$), Stokes' Radii (r_s) and</p>	293-298

	<p>Crystallographic Radii (r_c) of Ammonium Based Electrolytes in Different Studied Solvents at $T = 298.15$ K.</p> <p>Table 5. Diffusion Coefficient (D_{\pm}) and Ionic Mobility (i_{\pm}) of Electrolytes in Different Studied Solvents at 298.15 K</p> <p>Table 6. IR Vibration Data of the Functional Groups Present in the Pure Solvent and Change of Frequency after Addition of Electrolytes $[\text{Bu}_4\text{NClO}_4]$ and $[\text{Bu}_4\text{NBF}_4]$ in the Solvents.</p>	
--	--	--

LIST OF FIGURES

CHAPTERS	FIGURES	PAGE NO.
Chapter IV	<p>Figure 1. The plots of limiting apparent molar volumes (ϕ_v^0) for L-Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of ascorbic acid in aqueous mixture at 298.15K</p> <p>Figure 2. The plots of viscosity B-coefficient for L-Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of ascorbic acid in aqueous mixture at 298.15K</p> <p>Figure 3. The plots of limiting partial adiabatic compressibility (ϕ_k^0) for L-Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of ascorbic acid in aqueous mixture at 298.15K</p>	168-169
Chapter V	<p>Figure 1. Plot of partial molar volume (ϕ_v^0) of D-glucose, D-mannitol, D-sucrose as a function of mass fraction of nicotinic acid in different binary mixtures of nicotinic acid (1)+water (2); at 298.15 K (-◆-), 308.15 K (-■-), and 318.15 K (-▲-) respectively</p> <p>Figure 2. Plot of standard transfer volume ($\Delta\phi_v^0$), and deviation of viscosity B-coefficient (ΔB), from water to aqueous nicotinic acid solutions for D-glucose at different temperatures. Solid lines for $\Delta\phi_v^0$ at 298.15 K (-◆-), 308.15 K (-▲-), 308.15 K (-●-) and dotted lines for ΔB at 298.15 K (-◇-), 308.15 K (-△-), 318.15 K (-○-) respectively</p>	202-204

Figure 3. Plot of standard transfer volume ($\Delta\phi_V^0$), and deviation of viscosity B -coefficient (ΔB), from water to aqueous nicotinic acid solutions for D-mannitol at different temperatures. Solid lines for $\Delta\phi_V^0$ at 298.15 K (-◆-), 308.15 K (-▲-), 308.15 K (-●-) and dotted lines for ΔB at 298.15 K (-◇-), 308.15 K (-△-), 318.15 K (-○-) respectively

Figure 4. Plot of standard transfer volume ($\Delta\phi_V^0$), and deviation of viscosity B - coefficient (ΔB), from water to aqueous nicotinic acid solutions for D-sucrose at different temperatures. Solid lines for $\Delta\phi_V^0$ at 298.15 K (-◆-), 308.15 K (-▲-), 308.15 K (-●-) and dotted lines for ΔB at 298.15 K (-◇-), 308.15 K (-△-), 318.15 K (-○-) respectively

Figure 5. Plot of $(\partial\phi_E^0/\partial T)_p$ for D-glucose (-◆-), D-mannitol (-▲-), D-sucrose (-●-), and dB/dT for D-glucose (-◇-), D-mannitol (-△-), D-sucrose (-○-), against different mass fraction (w_1) of aq. NA at studied temperature (T)

Chapter VI

Figure 1. Plots of values of limiting molar conductivity (Λ_0) and Walden Product ($\Lambda_0\eta_0$) of the salt $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA, DMF at 298.15 K.

Figure 2. Plots of values of Association constant (K_A) and Gibbs free energy change (ΔG°) of the salt $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K.

Figure 3. Plots of values of ionic Walden product ($\lambda_0^\pm\eta_0$) for $[\text{Bu}_4\text{P}]^+$ (■), for $[\text{BF}_4]^-$ (◆), and ionic viscosity

226-227

	<i>B</i> -coefficients (B_{\pm}) for $[\text{Bu}_4\text{P}]^+$ (\blacktriangle), for $[\text{BF}_4]^-$ (\times) in DMSO, DMA, DMF at 298.15 K respectively.	
Chapter VII	<p>Figure 1. Plot of molar conductance (Λ) and the square root of molar concentration (\sqrt{c}) of $[\text{Bu}_4\text{PMS}]$ in DMSO (<i>black diamond</i>), DMA (<i>black triangle</i>), and DMF (<i>black circle</i>), respectively, at $T = 298.15$ K.</p> <p>Figure 2. Stretching frequency of C-O in DMF (<i>black solid line</i>) and $[\text{Bu}_4\text{PMS}] + \text{DMF}$ (<i>red solid line</i>).</p> <p>Figure 3. Stretching frequency of C-O in DMA (<i>black solid line</i>) and $[\text{Bu}_4\text{PMS}] + \text{DMA}$ (<i>red solid line</i>).</p> <p>Figure 4. Stretching frequency of S=O in DMSO (<i>black solid line</i>) and $[\text{Bu}_4\text{PMS}] + \text{DMSO}$ (<i>red solid line</i>).</p>	246-247
Chapter VIII	<p>Figure 1. Plots of molar conductance, Λ, and the square root of concentration (\sqrt{c}), of $[\text{Bu}_4\text{NBF}_4]$ in CH_3CN ($-\blacktriangle-$), CH_3OH ($-\blacksquare-$), DMSO ($-\blacklozenge-$) at $T = 298.15$ K.</p> <p>Figure 2. Plots of values of Gibbs energy change, ΔG°, ($-\blacklozenge-$) and Association constant, K_A, ($-\blacktriangle-$) of $[\text{Bu}_4\text{NBF}_4]$ in CH_3CN, CH_3OH and DMSO 298.15 K.</p> <p>Figure 3. Plots of values of limiting molar conductivity, Λ_0, ($-\blacksquare-$) and Walden Product, $\Lambda_0\eta_0$, ($-\blacktriangle-$) of $[\text{Bu}_4\text{NBF}_4]$ in CH_3CN, CH_3OH and DMSO at 298.15 K.</p> <p>Figure 4. Plot of values of Molar conductance (Λ) and the square root of concentrations (\sqrt{c}) of $[\text{Bu}_4\text{NBF}_4]$ in 1,3-DO at 298.15 K.</p> <p>Figure 5. Plots of values of limiting ionic conductance, λ_0^\pm, for $[\text{Bu}_4\text{N}]^+$ ($-\blacklozenge-$), for $[\text{BF}_4]^-$ ($-\blacklozenge-$)</p>	270-272

	<p>■—) and ionic Walden product, $\lambda_o^\pm \eta_o$, for $[\text{Bu}_4\text{N}]^+$ (— ▲—), for $[\text{BF}_4]^-$ (—●—), in CH_3CN, CH_3OH and DMSO at 298.15 K respectively.</p>	
<p>Chapter IX</p>	<p>Figure 1. Plot of molar conductance (Λ) and the square root of molar concentration (\sqrt{c}) for $[\text{Bu}_4\text{NBF}_4]$ in nitromethane (\blacklozenge), N-methylformamide (\blacksquare), formamide (\blacktriangle), for $[\text{Bu}_4\text{NClO}_4]$ in nitromethane (\diamond), N-methylformamide (\square), and formamide (Δ) respectively, at $T = 298.15$ K.</p> <p>Figure 2. Plot of limiting molar conductance (Λ_o) for $[\text{Bu}_4\text{NBF}_4]$ (\blacklozenge), $[\text{Bu}_4\text{NClO}_4]$ (\blacktriangle), and Walden Product ($\Lambda_o \eta$) for $[\text{Bu}_4\text{NBF}_4]$ (\diamond), $[\text{Bu}_4\text{NClO}_4]$ (Δ), in nitromethane, N-methylformamide and formamide respectively at $T = 298.15$ K</p> <p>Figure 3. Plot of limiting ionic conductance (λ_o^\pm) for BF_4^- (\blacksquare), ClO_4^- (\blacktriangle) and ionic Walden Product ($\lambda_o^\pm \eta$) for BF_4^- (\square), ClO_4^- (Δ) in nitromethane, N-methylformamide and formamide respectively at $T = 298.15$ K.</p> <p>Figure 4. Plot of association constant (K_A) for $[\text{Bu}_4\text{NBF}_4]$ (\blacklozenge), $[\text{Bu}_4\text{NClO}_4]$ (\blacktriangle), and Gibb's energy change (ΔG°) for $[\text{Bu}_4\text{NBF}_4]$ (\diamond) and $[\text{Bu}_4\text{NClO}_4]$ (Δ), in nitromethane, N-methylformamide, and formamide respectively at $T = 298.15$ K.</p> <p>Figure 5. Plot of diffusion coefficient (D_\pm) for BF_4^- (\blacksquare), ClO_4^- (\blacktriangle) and ionic mobility (i_\pm) for BF_4^- (\square), ClO_4^- (Δ), in nitromethane, N-methylformamide, and formamide, respectively, at $T = 298.15$ K.</p> <p>Figure 6. IR vibration data of -N-O in nitromethane</p>	<p>299-304</p>

	<p>(black solid line) and in {[Bu₄NClO₄] and nitromethane} (red solid line), {[Bu₄NBF₄] and nitromethane} (blue solid line)</p> <p>Figure 7. IR vibration data of C=O in N-methylformamide (black solid line) and in {[Bu₄NClO₄] and N-methylformamide} (red solid line) and {[Bu₄NBF₄] and N-methylformamide } (blue solid line).</p> <p>Figure 8. IR vibration data of C=O in formamide (black solid line) and in {[Bu₄NClO₄] and formamide} (red solid line) and {[Bu₄NBF₄] and formamide} (blue solid line).</p>	
--	--	--

LIST OF APPENDICES

APPENDIX A:

LIST OF PUBLICATION(S)

A.1. THESIS RELATED PUBLICATIONS

A.2. PUBLICATIONS IN OTHER AREAS

APPENDIX B:

LIST OF

SEMINARS/SYMPOSIUMS/CONFERENCES

ATTENDED

APPENDIX A

LIST OF PUBLICATIONS

A.1. THESIS RELATED PUBLICATIONS:

1. 'Study of solute-solvent interaction of some bio-active solutes prevailing in aqueous ascorbic acid solution'



ELSEVIER

J. Mol. Liquids, 169 (2012) 8-14

2. 'Physics and chemistry of an ionic liquid in some industrially important solvent media probed by physicochemical techniques'



ELSEVIER

J. Chem. Thermodynamics, 57 (2013) 230-237

3. 'Probing subsistence of ion-pair and triple-ion of an ionic salt in liquid environments by means of conductometric contrivance'



ELSEVIER

J. Chem. Thermodynamics, 63 (2013) 52-59

4. 'Role of Anions (Tetrafluoroborate, Perchlorate) of Tetrabutylammonium Salts in Determining Solvation Effects Prevailing in Industrially Essential Solvents Probed by Conductance and FT-IR Spectra.'



J. Chem. Eng. Data, 58 (2013) 3378-3386

APPENDIX A

5. Study of assorted interactions of an ionic liquid in significant solvent systems using compensated equation of Fuoss conductance and vibrational mode



Ionics, 20 (2014) 1001-1009

A.2. PUBLICATIONS IN OTHER AREAS:

1. 'Physics and chemistry of lithium halides in 1,3-dioxolane and its binary mixtures with acetonitrile probed by conductometric, volumetric, viscometric, refractometric and acoustic study'



ELSEVIER

Thermochimica Acta, 547 (2012) 89-98

2. 'Probing molecular interactions of ionic liquid in industrially important solvents by means of conductometric and spectroscopic approach'



ELSEVIER

Thermochimica Acta, 559 (2013) 46-51

APPENDIX B

LIST OF SEMINARS/SYMPOSIUMS/CONVENTIONS ATTENDED

1. **Chemical Research Society of India**, Eastern Zonal Meeting 2011 and Celebration of the International year of Chemistry 2011, July 22-24, 2011 organized by Department of Chemistry, University of North Bengal, Darjeeling.
2. **Science Academies' Lecture Workshop on Recent Trends in Chemistry**, November 11-12, 2011, organized by the Department of Chemistry, University of North Bengal, Darjeeling.
3. **Science Academies' Lecture Workshop on Modern Trends in Chemistry and Chemistry Education**, November 22-23, 2012, organized by the Department of Chemistry, University of North Bengal, Darjeeling-734-013, West Bengal.
4. **15th CRSI National Symposium in Chemistry** held at Banaras Hindu University, Varanasi during February 1-3, 2013, organized by Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi.
5. **Workshop on Intellectual Property and Innovation Management in Knowledge Era**, organized by National Research Development Corporation (NRDC), New Delhi, and University of North Bengal (NBU), Siliguri, on 12th February, 2013, at University of North Bengal, Siliguri, West Bengal.
6. **National Seminar on Frontiers in Chemistry-2013**, held at the Department of Chemistry, University of North Bengal, on February 28th, 2013, Sponsored by University Grants Commission, New Delhi, and organized by Department of Chemistry, University of North Bengal.
7. **Workshop on Diversities and Frontiers in Chemistry (State University Network)**, held at the Department of Chemistry, University of North Bengal during August 07-08, 2013 and organized by Department of Chemistry, Jadavpur University, Kolkata & Department of Chemistry, University of North Bengal, Siliguri.
8. **International Seminar on 5th Asian Conference on Colloid and Interface Science**, held at Department of chemistry, University of North Bengal, Darjeeling during November 20-23, 2013 and organized by the Asian Society for Colloid and Surface Science and Department of Chemistry, University of North Bengal, Darjeeling, India.

CHAPTER I

NECESSITY OF THE RESEARCH WORK

1.1. OBJECT, SCOPE AND APPLICATION OF THE RESEARCH WORK

A material is said to be biologically active if it has an interaction or effect on living organism. Pharmacological activity is usually taken to describe beneficial effects, i.e. the effects of drug candidates. The main kind of biological activity is a substance's toxicity. "Bioactive compounds" are extra nutritional constituents that typically occur in small quantities in foods. They are being intensively studied to evaluate their effects on health. Bioactive compounds will reduce the risk of many diseases, including cancer, chronic diseases such as cardiovascular disease. Recent findings have established that cardiovascular disease is a disease of inflammation, and consequently is amenable to intervention via molecules that have anti-inflammatory effects. In addition, research demonstrating adverse effects of oxidants on atherogenesis raises the possibility that antioxidants can confer cardioprotective effects. This review provides an overview of research approaches that can be used to unravel the biology and health effects of bioactive compounds. Because of the number of bioactive compounds and the diversity of likely biological effects, numerous and diverse experimental approaches must be taken to increase our understanding of the biology of bioactive compounds. Recognizing the complexity of this biology, sophisticated experimental designs and analytical methodologies must be employed to advance the field. The discovery of novel health effects of bioactive compounds will provide the scientific basis for future efforts to use biotechnology to modify/fortify foods and food components as a means to improve public health. There is sufficient evidence to recommend consuming food sources rich in bioactive compounds. From a practical perspective, this translates to recommending a diet rich in a variety of fruits, vegetables, whole grains, legumes, oils, and nuts. In the body under physiological conditions, many vital functions are regulated by pulsed or transient release of bioactive substances at a specific time and site. Thus,

to mimic the function of living systems, it is important to develop new drug delivery devices to achieve pulsed delivery of a certain amount of a bioactive compound at predetermined time intervals. The ability to deliver bioactive compounds and/or therapeutic agents to a patient in a pulsatile or staggered release profile has been a major goal in drug delivery research over the last two decades. Rice bran has been recognized as an excellent source of bioactive compounds, but only a small amount is consumed by humans. The limitation of using rice bran in a food industry is its rough texture and low concentration of bioactive compounds, when incorporated into food products. Various methods have been developed to enhance the level of bioactive components in food materials, including thermal, alkali, acid and chemical treatments. Many bioactive compounds have been discovered. These compounds vary widely in chemical structure and function. Many biologically active molecules are chiral, including the naturally occurring amino acids (the building blocks of proteins) and sugars. In biological systems, most of these compounds are of the same chirality: most amino acids are L and sugars are D. Typical naturally occurring proteins, made of L amino acids, are known as left-handed proteins, whereas D amino acids produce right-handed proteins. Amino acid serves as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, and toiletries. It is used as a source of energy for muscle tissue, the brain, and central nervous system, in strengthening the immune system by producing antibodies. It has been used as a source for the production of glucose in order to stabilize blood sugar levels over lengthy periods. In sickle-cell disease, valine substitutes for the hydrophilic amino acid glutamic acid in hemoglobin. Because valine is hydrophobic, the hemoglobin does not fold correctly. Ascorbic acid, commonly known as vitamin C, is also able to regenerate other antioxidants as vitamin E. Vitamin C is required for the synthesis of collagen, the intercellular "cement" which gives the structure of muscles, vascular tissues, bones, and tendon. Vitamin C with Zn is also important for the healing of wounds. It is also needed for the metabolism of bile acids which may have implications for blood cholesterol levels and gallstones. Ascorbic acid and its sodium, potassium, and calcium salts are commonly used as antioxidants food additives. Vitamin C plays an important role for the synthesis of several important peptide hormones neurotransmitters and creatinine. It also enhances the eye's ability

and delay the progression of advanced age related muscular degeneration [1]. Carbohydrates are an exceptionally important constituent of biological systems. They play an important role in animal and plant physiology. Carbohydrates are sources of energy for essential metabolic process. Water, the most abundant compound on earth, is widely used in chemistry as a universal solvent. The study of carbohydrates in aqueous solutions has become a subject of increasing attention because of the multidimensional physical, biochemical and industrially useful properties in addition to their significance in the food pharmaceutical and chemical industries [2, 3]. Understanding the behaviour of these effects in dilute solutions is of utmost importance in medicinal and biological systems. The pyridine-monocarboxylic acids are examples of amphiprotic electrolytes that are of considerable biological interest. Nicotinic acid (3-pyridine carboxylic acid), also known as niacin or pellagra-preventing factor, is an important compound which play a crucial role in various physiological effects, biosynthesis, metabolic reactions, and several drug preparations [4].

The word "salt" is a general chemical term that refers to ionic compounds formed when an acid reacts with a base. Salt became an essential part of commercial transactions and was often used as money or barter. Today, salt continues to be of major economic importance, with thousands of uses in addition to flavoring and preserving food. Sodium chloride occurs naturally as the mineral halite, commonly called rock salt, in large underground deposits on every continent. Seawater contains about 3.5 percent dissolved minerals, of which 2.8 percent is sodium chloride and the other 0.7 percent is primarily calcium, magnesium, and sulfate ions. Table salt is pure salt that has been ground into fine particles. Because salt tends to cake in humid climates, an anti-caking agent such as magnesium carbonate or calcium silicate is often added. Salt is used to cure meat and fish by soaking them in brine, rubbing salt onto them, or injecting them with a salt solution. Bacon and cured ham are examples of meats preserved by the use of salt. Salt is also used to make pickles by soaking cucumbers in brine. Both sodium chloride and potassium chloride are essential to the electrolyte balance in body fluids. Good health depends on the proper ratio of potassium ions to sodium ions. Typical values are greater than one. Natural, unprocessed foods have high K^+ / Na^+ weight ratios. Calcium salt is also the fifth-most-abundant dissolved ion in seawater by both

molarity and mass. Calcium is essential for living organisms, in particular in cell physiology, where movement of the calcium ion Ca^{2+} into and out of the cytoplasm functions as a signal for many cellular processes. As a major material used in mineralization of bones and shells, calcium is the most abundant metal by mass in many animals. Lithium salts are chemical salts of lithium used mainly in the treatment of bipolar disorder as mood stabilizers. They are also sometimes used to treat depression and mania. Lithium carbonate, Lithium sulfate, Lithium orotate, Lithium citrate are the most common salts used in this purpose. Lithium is widely distributed in the central nervous system and interacts with a number of neurotransmitters and receptors, decreasing noradrenaline release and increasing serotonin synthesis. Lithium and its compounds have several industrial applications, including heat-resistant glass and ceramics, high strength-to-weight alloys used in aircraft lithium batteries, and lithium-ion batteries. Lithium salt is used in lithium-ion batteries because of its high electrochemical potential. Lithium batteries are not to be confused with lithium-ion batteries, which are high energy-density rechargeable batteries. Other rechargeable batteries include the lithium-ion polymer batteries, lithium-iron phosphate batteries, and the nanowire batteries.

To date, most chemical reactions have been carried out in industrially important solvents. For two millennia, most of our understanding of chemistry has been based upon the behavior of molecules in the solution phase in molecular solvents. Recently, however, a new class of solvent has emerged—ionic liquids. An ionic liquid (IL) is an electrolyte in the liquid state/phase having melting point below some arbitrary temperature, such as 100°C (212°F), which consists of a combination of organic-organic or organic-inorganic cation/anions. Ionic liquid consists of only ions exhibiting non-volatility, high ionic conductivity and catalytic activity. Room temperature Ionic liquids (RTIL) are salts which are already liquid below room temperature [5]. Because of their insignificant vapour pressures, low melting points, good solvent characteristics for organic, inorganic and polymeric materials, adjustable polarity, selective catalytic effects, chemical and thermal stability, non-flammability and high ionic conductivity, ionic liquids have generated significant interest for a wide range of industrial applications [6]. It use as the solvent for extractions and electrolytes for batteries is

attracting increasing attention. Ionic liquid is an environmentally friendly reagent for organic synthesis reactions. ILs finds a variety of industrial applications. Ionic liquids are used in Chemical industry, Pharmaceuticals, Cellulose processing, Gas handling, Gas treatment, Solar thermal energy, Nuclear fuel processing, Food and bi-products, waste recycling, Batteries etc.

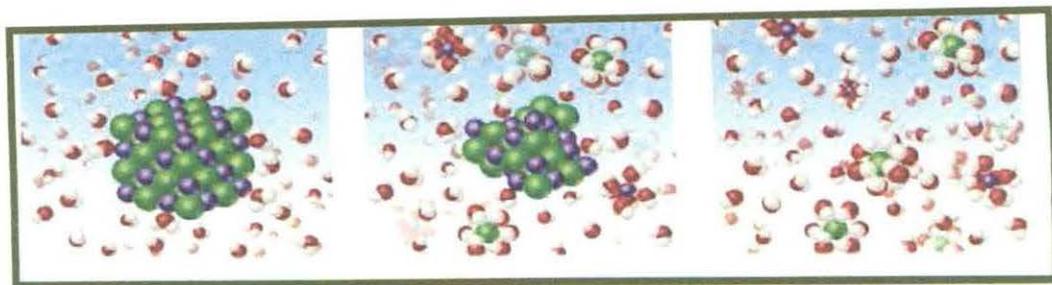
In addition to having a wide range, ionic liquids have the ability to dissolve in both polar and non-polar compounds and perhaps most importantly, they do not evaporate due to their extremely low vapour pressure and thus, cannot lead to fugitive emissions. The chemical and physical properties of ILs can to some extent, be customized by proper selection of the type of cation and anion that compose the ILs, as well as any substituent groups. Because of their insignificant vapour pressures, low melting points, good solvent characteristics for organic, inorganic and polymeric materials, adjustable polarity, selective catalytic effects, chemical and thermal stability, non-flammability and high ionic conductivity, ionic liquids have generated significant interest for a wide range of industrial applications.

A 'solution' is a homogeneous mixture of two or more substances, consisting of ions or molecules, i.e. when a small amount of substance, called solute (solid, liquid or gas), dissolves to a certain limit in a liquid or solid substance (pure, or a mixture itself) called the solvent. In a solution the solute is dispersed uniformly throughout the solvent and substances must have similar intermolecular forces to form solutions. When a soluble solute is introduced into a solvent, the particles of solute can interact with the particles of solvent. In the case of a solid or liquid solute, the interactions between the solute particles and the solvent particles are so strong that the individual solute particles separate from each other and, surrounded by solvent molecules, enter the solution. The relative force of attraction of the solute for the solvent is a major factor in their solubility.

278436

31 MAR 2016





Solution chemistry is an important branch of physical chemistry that studies the change in properties that arise when one substance dissolves in another substance. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. The mixing of different solute or solvent with another solvent/solvent mixtures gives rise to solutions that generally do not behave ideally.

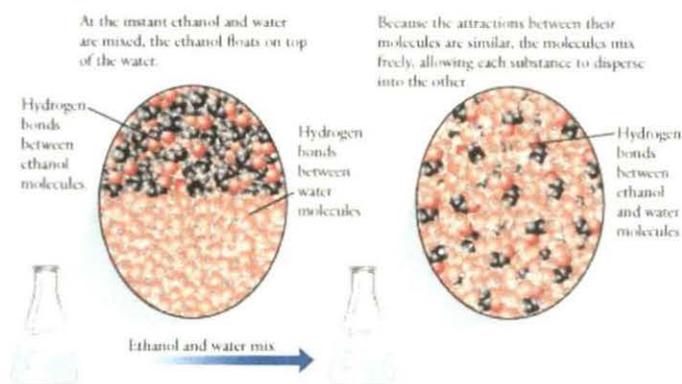
We know matter in three states of aggregation — solid, liquid, and gaseous. Matter in every one of these three states can be dissolved in matter of the same state of aggregation as itself and in both of the other states. Thus, we have solutions of gases in gases, or mixtures of gases which do not act chemically upon one another. The characteristic here is unlimited solubility, the properties of the mixture being the sum of the properties of the constituent gases.

Solutions of gases, liquids, and solids in liquids are the best and longest known types of solutions. Gases dissolve in liquids to only a limited extent, the amount, in keeping with Henry's law, increasing with the pressure to which the gas is subjected. The solubility of a gas in a liquid is directly proportional to its pressure.



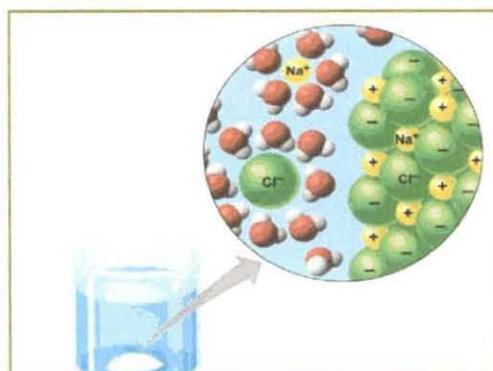
Dissolution of gas in liquid

The presence of intermolecular H-bonding in water and alcohol, after mixing new H-bonding prevails in the mixture due to solvent-solvent interaction. Liquids dissolve in liquids, many of them to an unlimited extent. Liquids which, at ordinary temperatures, have only limited solubility in other liquids, often become infinitely soluble at more elevated temperatures.



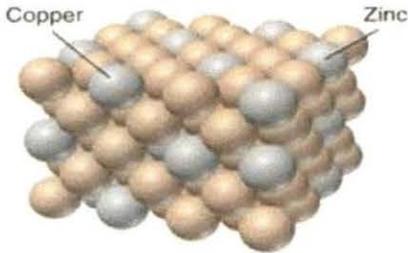
Solution of binary liquids

Solids dissolve in liquids to a limited extent, the amount for any solid being a function of the temperature. An ionic solid such as sodium chloride dissolves in water because of the electrostatic attraction between the cations (Na^+) and the partially negatively charged oxygen atoms of water molecules, and between the anions (Cl^-) and the partially positively charged hydrogen atoms of water.

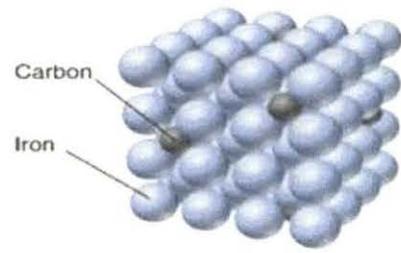


Solubility of solid in liquid

One of the newest and most interesting types of solutions is that of solid in solid. Solid-Solid solutions particularly of metals are sometimes called ALLOYS.

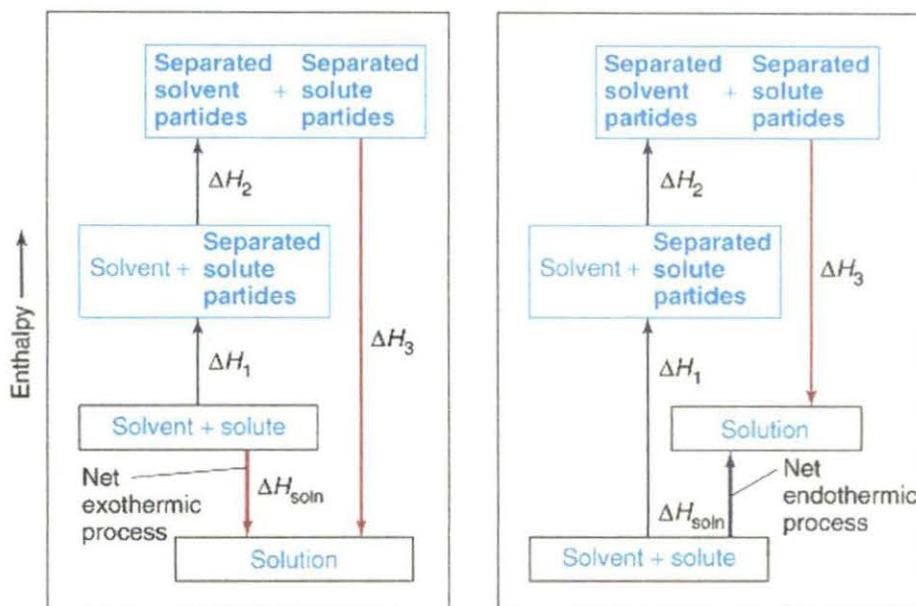
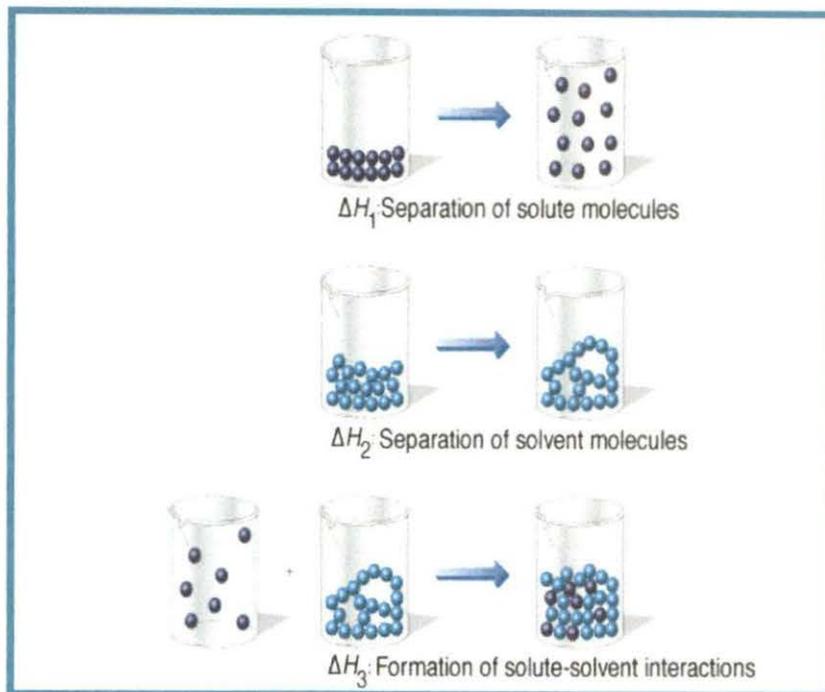


A Brass, a substitutional alloy



B Carbon steel, an interstitial alloy

The process of solubilisation involves the breaking of inter-ionic or intermolecular bonds in the solute, the separation of the molecules of the solvent to provide space in the solvent for the solute, interaction between the solvent and the solute molecule or ion. We understand much of the dissolution phenomenon through its energetic (thermodynamics).



In recent years there has been an increasing interest in the study of physicochemical properties of solvent-solvent [7, 8] and solute-solvent [9, 10] systems. The physicochemical properties play a pivotal role in interpreting the intermolecular interactions among mixed components and efforts in recent years have been directed at

an understanding of such properties at microscopic and macroscopic levels. In order to gain insight into the mechanism of such interactions thermodynamic, transport and acoustic studies on binary and ternary solvent systems are highly useful. The excess thermodynamic properties of the mixtures correspond to the difference between actual property and the property if the system behaves ideally. Thus these properties provide important information about the nature and strength of intermolecular forces operating among mixed components. Also physico-chemical properties involving excess thermodynamic functions have relevance in carrying out engineering applications in the process industries and in the design of industrial separation processes.

The properties, both physical and chemical, of a solution (liquid) is a result of the strength of their intermolecular forces and the forces between molecules arises from the same source: differing charges on adjacent molecules that lead to electrostatic attractions and governed by coulombs law. Partial charges acquired by molecules results in dipole-dipole forces, dipole-induced dipole forces, hydrogen bonding, etc and are collectively termed as intermolecular forces. Intermolecular forces in a solution control their thermodynamic properties and the understanding of the solvation thermodynamics is essential to the characterization and interpretation of any process carried out in the liquid phase. These thermodynamic properties are quantities which are either an attribute of an entire system or are functions of position which is continuous and does not vary rapidly over microscopic distances, except in cases where there are abrupt changes at boundaries between phases of the system. Therefore, the studies on the thermodynamic along with the transport properties of a solution would give a clear idea about the nature of the forces existing within the constituents of a solution.

The object of this introductory chapter is to call attention to the significance of solvents and the study made on various interaction prevailing in liquid systems by studying their thermodynamic and transport properties.

The bearing of solution on natural processes was early recognized. It was clearly seen that without solution there would be no chemistry. This was summarized by the alchemists in the terse generalization, "Corpora non agunt nisi soluta," or in the equally

concise, "Menstrua non agunt nisifluida." These generalizations are a little too broad in the light of what was known about solutions at the time when they were written.

In solution chemistry the way for proper understanding of the different phenomena regarding the molecular interactions forms the basis of explaining quantitatively the influence of the solvent and the extent of interactions of ions in solvents. Estimates of ion-solvent interactions can be had thermodynamically and also from the measurement of partial molar volumes, viscosity B - coefficient and limiting ionic conductivity studies. Estimates of single-ion values enable us to refine our model of ion solvent interactions. Acceptable values of ion-solvent interactions would enable the chemists to choose solvents that will enhance (i) the rates of chemical reactions, (ii) the solubility of minerals in leaching operations or (iii) reverse the direction of equilibrium reactions. The importance and uses of the chemistry of electrolytes in non aqueous and mixed solvents are now well recognized.

The importance and uses of the chemistry of electrolytes in non-aqueous and mixed solvents are now well recognized. The applications and implications of the studies of reaction in non-aqueous and mixed solvents have been summarized by Meck [11] Franks [12] Popovych [13] Bates [14] Parker [15] Criss and Salomon [16], Marcus [17] and others [18].

In spite of vast collections of data on the different electrolytic and non electrolytic solutions in water, the structure of water and the different types of interactions that water undergoes with electrolytes are yet to be properly understood. However, the studies on properties of aqueous solutions have provided sufficient information on the thermodynamic properties of different electrolytes and non-electrolytes, the effects of variation in ionic structure, ionic mobility and common ions along with a host of other properties [12]. The behavior of electrolytes or solutes in non-aqueous and mixed solvents with a view to investigate solute-solute and solute-solvent interactions under varied conditions. However, different sequence of solubility, difference in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have opened vistas for physical chemists and interest in these organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry [19]. Research on non-aqueous electrolyte

solutions has manifested their wide applications in many fields. Non-aqueous electrolyte solutions are actually competing with other ion 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. High-energy primary and secondary batteries, wet double-layer capacitors and super capacitors, electro deposition and electroplating are some devices and processes for which the use of non-aqueous electrolyte solutions had brought the biggest success [20, 21].

Drug transport across biological cells and membranes is dependent on physicochemical properties of drugs. But direct study of the physico-chemical properties in physiological media such as blood, intracellular fluids is difficult to accomplish. One of the well-organized approaches is the study of molecular interactions in fluids by thermodynamic methods as thermodynamic parameters are convenient for interpreting intermolecular interactions in solution phase. Also the study of thermodynamic properties of drug in a suitable medium can be correlated to its therapeutic effects [22, 23].

1.2. CHOICE AND IMPORTANCE OF SOLVENTS AND SOLUTES USED

Nitromethane, formamide, N-methylformamide, 1,3-dioxolane, methanol, acetonitrile, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulphoxide along with water, considered as a universal solvent, have been chosen as main solvent in this research work because these solvents are industrially very important and by mixing these solvents we could obtain a wide variation of viscosities and dielectric constants giving us an optimum environment for the study.

Amino acids viz., glycine, L-alanine, L-valine, carbohydrates (D-glucose, D-mannitol, D-sucrose), ascorbic acid (vitamin C), tetrabutylammonium tetrafluoroborate, tetrabutylammonium perchlorate, tetrabutylphosphonium tetrafluoroborate, tetrabutylphosphonium methanesulfonate, lithium hexafluoroarsenate were considered as solutes.

The study of these solutes is of great interest because of their wide use as solvents, solubilizing agents in pharmaceutical, cosmetics and medicinal industries.

1.3. METHODS OF INVESTIGATION

The existence of free ions, solvated ions, ion-pairs and triple-ions in aqueous and non-aqueous media depends upon the concentrations of the solvent systems. Hence, the study of various interactions and equilibrium of ions in different concentration regions are of immense importance to the technologist and theoretician as most of the chemical processes occurs in these systems.

It is of interest to employ different experimental techniques to get a better insight into the phenomena of solvation and different interactions prevailing in solution. We have, therefore, employed five important methods, namely, densitometry, viscometric, conductometric, ultrasonic interferometer and refractometric to probe the problem of solvation phenomena.

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent/ion-solvent and solute-solute/ion-ion interactions in solution. The sign and magnitude of partial molar volume (ϕ_v^0) also provides information about the nature and magnitude of ion-solvent interaction while the experimental slope (S_v^*) provides information about ion-ion interactions [24]. Viscosity B-coefficient obtained from the viscosity values indicates the extent of ion-solvent interaction in a solution. From experimental speed of sound values, limiting apparent molar adiabatic compressibility (ϕ_K^0) and the experimental slope (S_K^*) can be estimated. These parameters also give an idea about the ion-solvent and ion-ion interaction in the solution.

The change in viscosity by the addition of electrolyte solutions is attributed to interionic and ion-solvent effects. The B-coefficients are also separated into ionic components by the 'reference electrolyte' method and from the temperature dependence of ionic values, a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, structure-breaking or structure-making, polarization, etc. may be given.

The transport properties in most cases are studied using the conductance data, especially the conductance at infinite dilution. Conductance data obtained as a function of concentration can be used to study the ion-association with the help of appropriate equations.

REFERENCES

- [1]. M. N. Roy, R. K. Das, A. Bhattacharjee, *Russian J. Phys.Chem A*. 84 (2010) 2201.
- [2]. R. N. Goldberg, Y. B. Tewari, *J. Phys. Chem. Ref. Data*. 18 (1989) 809.
- [3]. J. Boerio Goates, *J. Chem. Thermodyn.* 23 (1991) 403.
- [4]. S. Budavari, The Merck Index, An Encyclopedia of Chemicals, *Drugs and Biologicals*. 12th edn, p. 1120. Merck, Whitehouse Station, N.J. (1996).
- [5]. Joan F. Brennecke, Edward J. Maginn, *AIChE Journal*. 47 (2001) 2384.
- [6]. N. H. Kim, S. V. Malhotra, M. Xanthos, *Microporous and Mesoporous Materials* 96 (2006) 29.
- [7]. A. J. Queimade, I. M. Marrucho, J. A. P. Coutinho, E. H. Stenby, *Int. J. Thermophys.* 26 (2005) 47.
- [8]. N. N. Wankhede, M. K. Lande, B. R. Arbad, *J. Chem. Eng. Data*. 55 (2005) 969.
- [9]. A. Sinha, M. N. Roy, *J. Chem. Eng. Data*. 51 (2006) 1415.
- [10]. L. H. Blanco, E. F. Vargas, *J. Soln. Chem.* 35 (2006) 21.
- [11]. D. K. Meck, *The Chemistry of Non-Aqueous Solvents*, Ed. J. J. Lagowski, Vol-10, Chapter 1, Academic, New York, (1976).
- [12]. F. Franks, *Physico-Chemical Processes in Mixed Aqueous Solvents*, Heinemann Educational Books Ltd. (1967).
- [13]. O. Popovych, *Crit. Rev. Anal. Chem.* 1 (1970) 73.
- [14]. R. G. Bates, *Solute-Solvent Interactions*, Eds. J. J. Coetzee, C.D. Ritchie, Marcel Dekker, New York, (1999).
- [15]. A. J. Parker, *Electrochim. Acta*. 21 (1976) 671.
- [16]. C. M. Criss, M. Salomon, *J. Chem. Edu.* 53 (1976) 763.
- [17]. Y. Marcus, *Ion Solvation*, Wiley, Chinchester, (1986).
- [18]. R. R. Dogonadze, E. Kalman, A. A. Kornyshev, J. Ulstrup, *The Chemical Physics of Solvation*, Elsevier, Amsterdam, (1988).
- [19]. A. K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, (1973).
- [20]. Y. Marcus, *Ion Properties*, Dekker, New York, (1998),

- [21]. A. F. D. Namor, M. A. L. Tanco, M. Solomon, J. C. Y. Ng, *J. Phys. Chem.* 98 (1994) 11796.
- [22]. E.L. Herric, J.G. Brewer, *J. Chem. Eng. Data.* 14 (1969) 55.
- [23]. P.K. Gessner, M.P. Shakarjian, *J. Pharm. Exptal. Therap.* 235 (1988) 32.
- [24]. P. Pradhan, R.S. Sah, M.N. Roy, *J. Mol. Liq.* 144 (2009) 149.

CHAPTER II

GENERAL INTRODUCTION (REVIEW OF THE EARLIER WORKS)

2.1. IMPORTANCE OF SOLUTION CHEMISTRY

Solution chemistry is an important branch of physical chemistry that studies the change in properties that arise when one substance dissolves in another substance. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. One of the interesting facts 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 to an extent whereas the solute molecules are also modified. In 'Solution Chemistry' broadly three types of approaches have been made to estimate the degree of solvation. The first is the solvational approach involving the studies of viscosity, conductance, etc., of electrolytes and the derivation of various factors associated with ionic solvation [1], the second is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors related with solvation can be revealed [2] and the third is to use spectroscopic measurements where the spectral solvent shifts or the chemical shifts find out their qualitative and quantitative nature [3].

The extent of ion-solvation is dependent upon the interactions taking place between solute-solute, solute-solvent, solvent-solvent species. The assesment of ion-pairing in these systems is important because of its effect on the ionic conductivity and hence on the ionic mobility of the ions in solution. This explains the spurt in research in solution chemistry to elucidate the exact nature of these interactions through experimental studies involving conductometry, densitometry, viscometry, interferrometry, refractometry and other suitable methods and to interpret the experimental data collected. The majority of the reactions occurring in solutions are either chemical or biological in nature. The solvent only provides an inert medium for chemical reactions. The significance of solute-solvent interactions was realized only recently as a result of extensive studies in aqueous, non-aqueous and mixed

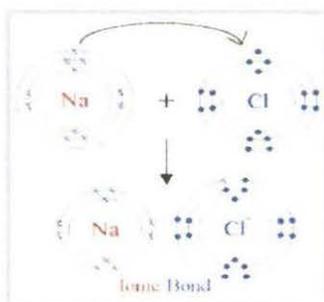
solvents [4-6]. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute, solute-solvent and solvent-solvent interactions are elucidated and thus the present research work is intimately related to the studies of solute-solute, and solvent-solvent interactions in some industrially important liquid systems.

2.1.1. FORCES BINDING ATOMS IN A MOLECULE

Interactions between two or more molecules are called intermolecular interactions, while the interactions between the atoms within a molecule are called intramolecular interactions. Intermolecular interactions occur between all types of molecules or ions in all states of matter. In a molecule the forces binding atoms are due to chemical bonding. The energy required to break a bond is called the bond-energy. For example the average bond-energy for O-H bonds in water is 463kJ/mol. The forces holding molecules together are generally called intermolecular forces. The energy required to break molecules apart is much smaller than a typical bond-energy, but intermolecular forces play important roles in determining the properties of a substances. Intermolecular forces are particularly important in terms how molecules interact and form biological organisms or even life. This link gives an excellent introduction to the interactions between molecules.

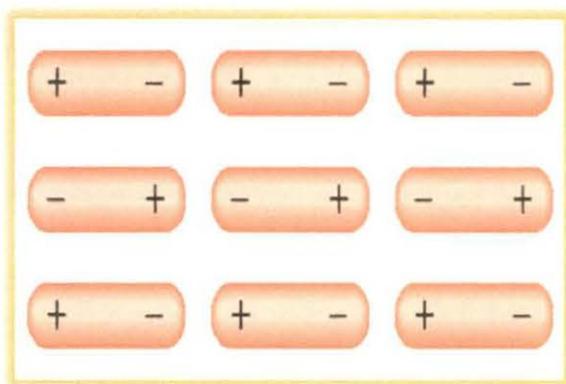
In general, intermolecular forces can be divided into several categories. The well-known types are:

a. Strong ionic attraction: It has relations to properties of solids. The more ionic compound has the higher lattice energy. The following result can be explained by way of ionic attraction: LiF, 1036; LiI, 737; KF, 821; MgF_2 , 2957 kJ/mol.



b. Intermediate dipole-dipole forces:

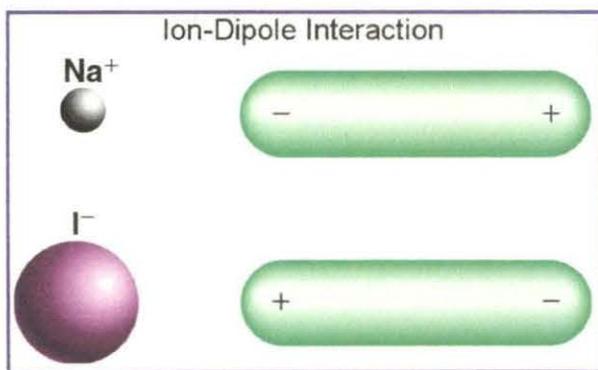
Molecules with permanent dipoles can interact with other polar molecules through dipole-dipole interactions. Again this is electrostatic in nature. The molecular dipole vector points towards high electron density. Permanent dipoles results from atom with different electro negativity.



Orientation of Polar molecules in a solid

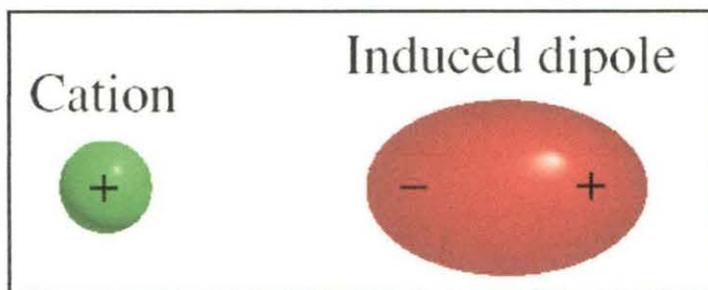
Substances, whose molecules have dipole moment, have higher melting point or boiling point than those of similar molecular mass, having no dipole moment.

c. Ion-dipole forces: Attractive forces between ion and a polar molecule.



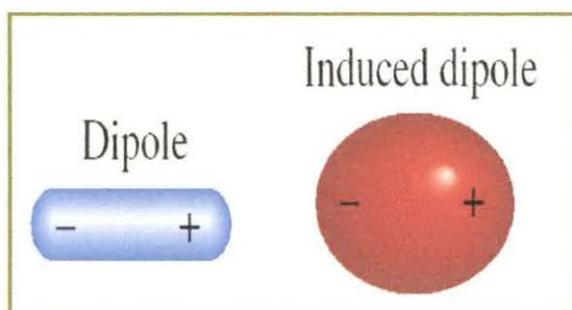
d. Weak London dispersion forces or van der Waal's force:

Attractive forces that arise as a result of temporary dipoles induced in atoms or molecules. Dispersion forces (weak intermolecular forces of attraction) also known as London forces or induced dipoles.



Ion-induced dipole interaction

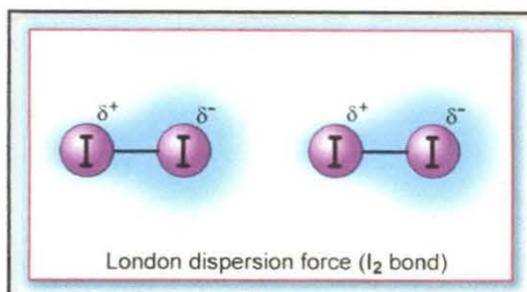
A molecule with a permanent dipole can induce a dipole in a second molecule that is located nearby in space. The strength of the interaction depends on the dipole moment of the first molecule and the polarizability of the second. Dipole-induced dipole interactions are always attractive and can contribute as much as 0.5 kcal/mole to stabilization.



Dipole-induced dipole interaction

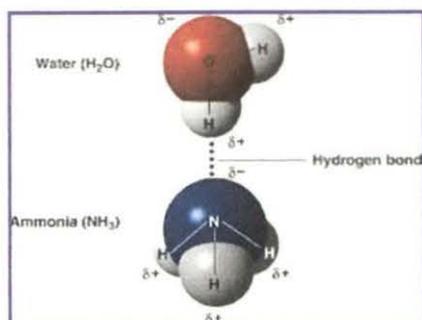
We could discount intermolecular interactions between gas-phase molecules because these molecules are mostly far apart and moving rapidly relative to each other. In the liquid phases, all molecules interact with one another. The stronger the interaction between a molecule and a pure liquid, the greater will be the solubility of the molecule in the liquid.

In general, the heavier the molecule, the stronger the Vander Waal's force of interaction. For example, the boiling points of inert gases increase as their atomic masses increases due to stronger London dispersion interactions.

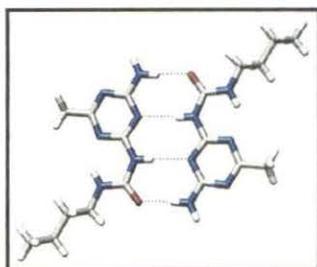


e. Hydrogen bond: Hydrogen bond is the attractive interaction between polar molecules in which hydrogen is bound to highly electronegative atom, such as nitrogen, oxygen or fluorine (thus the name "hydrogen bond," which should not be confused with a covalent bond to hydrogen). The hydrogen must be covalently bonded to another electronegative atom to create the bond. These bonds can occur between molecules (*intermolecularly*), or within different parts of a single molecule (*intramolecularly*). The hydrogen bond (5 to 30 kJ/mole) is stronger than a van der Waals interaction, but weaker than covalent or ionic bonds. This type of bond occurs in both inorganic molecules such as water and organic molecules such as DNA. Hydrogen bonds are essentially electrostatic in nature, although the energy can be decomposed into additional contributions from polarization, exchange repulsion, charge transfer, and mixing.

Certain substances such as H₂O, HF, NH₃ form hydrogen bonds, and the formation of which affects properties (m.p, b.p, solubility) of substance.

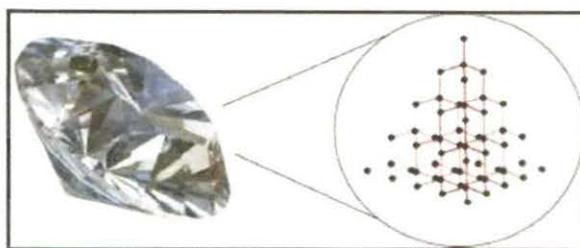


Other compounds containing OH and NH₂ groups also form hydrogen bonds. Molecules of many organic compounds such as alcohols, acids, amines, and amino acids contain these groups, and thus hydrogen bonding plays an important role in biological science.



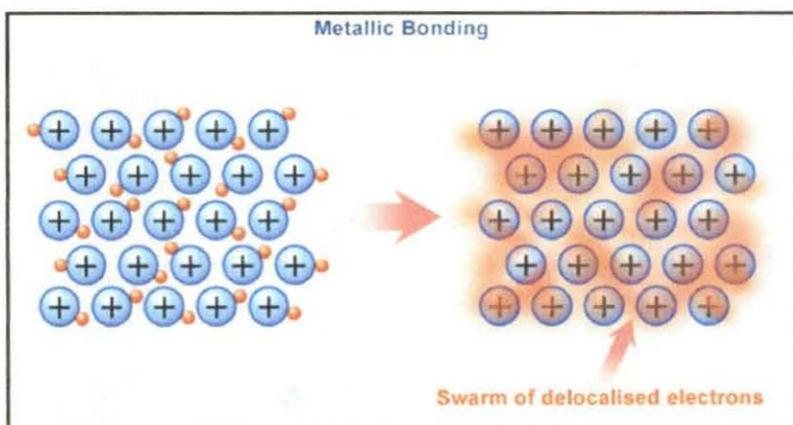
Intermolecular hydrogen bonding in a self-assembled dimer complex

f. Covalent bonding: Covalent bond is a chemical bond that involves the sharing of electrons pairs between atoms. Covalent is really intramolecular force rather than intermolecular force. Covalent bonds are strong, and their enthalpies are on the order of 100 kcal/mole (400 kjoule/mole). It is mentioned here, because some solids are formed due to covalent bonding. For example, in diamond, silicon, quartz etc., the all atoms in the entire crystal are linked together by covalent bonding. These solids are hard, brittle, and have high melting points. Covalent bonding holds atoms tighter than ionic attraction.



Covalent Bonding in Diamond

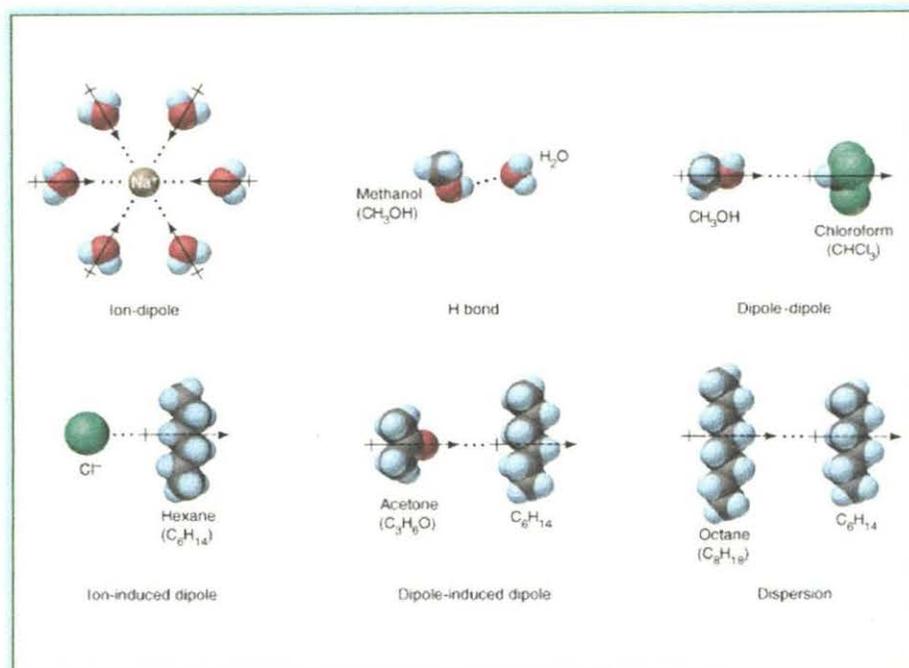
g. Metallic bonding: A metallic bond is the reaction between molecules within metals called reactive force of alkali. The metallic bond involves the sharing of free electrons among a metal atoms lattice. The metallic bonds may be compared to molten salts. The positive ions and the electrons in the metal have a heavy attractive force between metallic bond. Hence metals frequently have high point of boiling or melting.



The outer electrons are so weakly bound to metal atoms that they are free to roam across the entire metal. Having lost their outer electrons, individual metal atoms are more like positive ions in a swarm of communal electrons. The electron swarm is responsible for the ability of metals to conduct heat and electricity, as well as their shine. And the layered alignment of the positive ions is behind both the hardness and the malleability of metals.

The division into types is for convenience in their discussion. Of course all types can be present simultaneously for many substances. Usually, intermolecular forces are discussed together with "The States of Matter". Intermolecular forces also

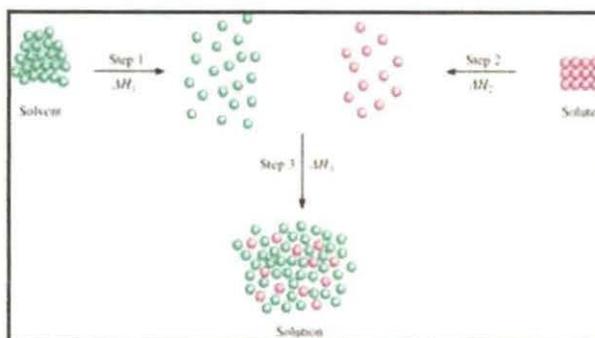
play important roles in solutions. A summary of the interactions is illustrated in the following diagram:



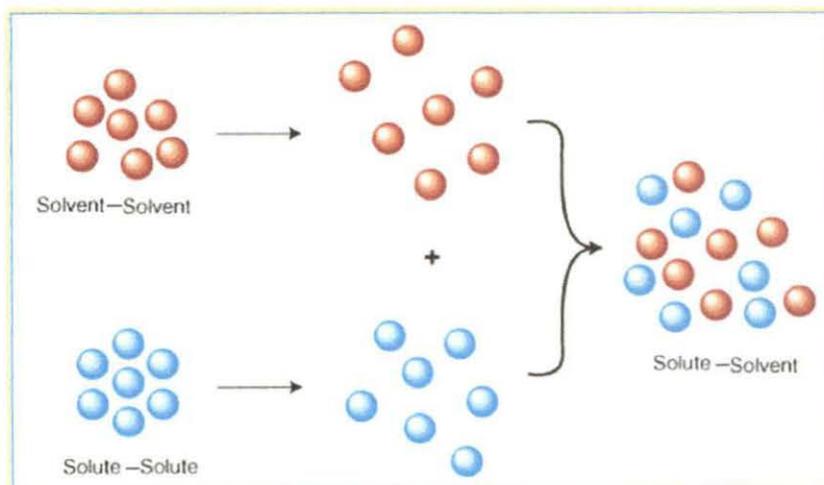
Intermolecular forces are also important in determining the solubility of a substance. "Like" intermolecular forces for solute and solvent will make the solute soluble in the solvent. In this regard ΔH_{soln} is sometimes negative and sometimes positive. Furthermore, solubility is affected by (a) Energy of attraction (due Ion-dipole force) affects the solubility. (b) Lattice energy (energy holding the ions together in the lattice. (c) Charge on ions: larger charge means higher lattice energy and (d) Size of the ion: large ions mean smaller lattice energy.

2.2. INTERACTIONS IN SOLUTION PHASE

There are three types of interactions in the solution process:

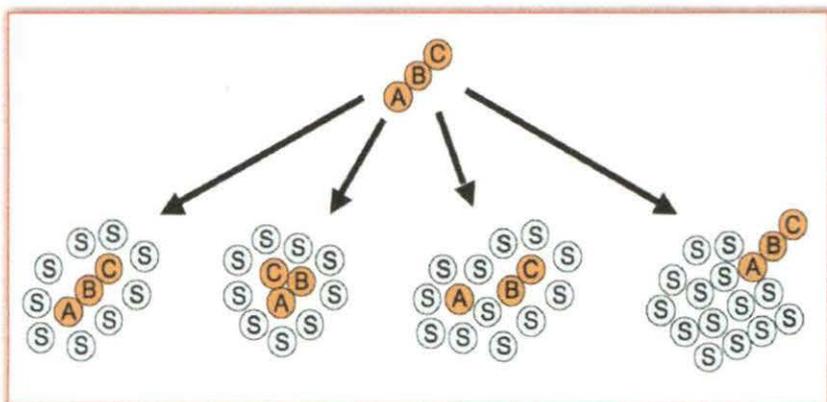


- Solvent – solvent interactions:** energy required to break weak bonds between solvent molecules.
- Solute – solute interactions:** energy required to break intermolecular bonds between the solute molecules.
- Solute – solvent interactions:** ΔH is negative since bonds are formed between them.



For liquid systems, the macroscopic properties are usually quite well known, whereas the microscopic structure is often much less studied. The liquid phase is

characterized by local order and long-range disorder, and to study processes in liquids, it is therefore valuable to use methods that probe the local surrounding of the constituent particles. The same is also true for solvation processes: a local probe is important to obtain insight into the physical and chemical processes going on.

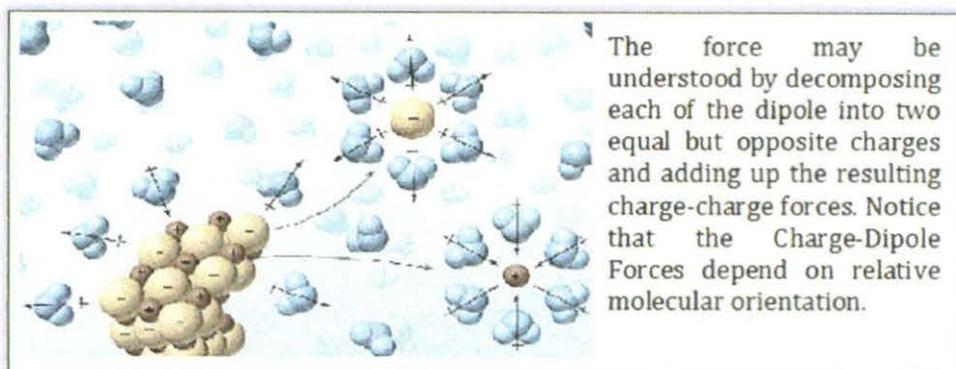


Schematic figure of possible processes after solvation of a molecule.

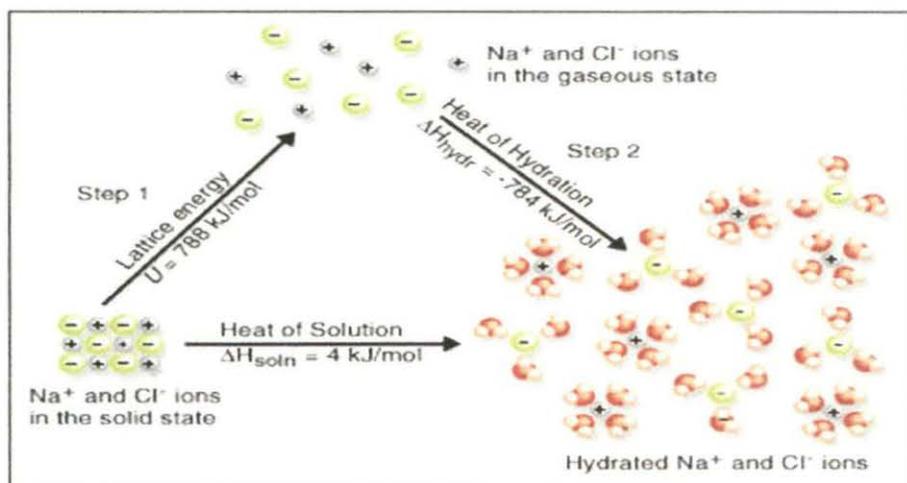
A molecule ABC may after solvation by solvent molecule S for instance remain essentially unchanged (left), it may change its geometric conformation (center left), it may dissociate, for instance into ionic fragments (center right), or it may migrate to the surface, with a hydrophobic end sticking out (right).

2.2.1. INVESTIGATION ON DIFFERENT KIND OF INTERACTIONS

When salt is dissolved in water, the ions of the salt dissociate from each other and associate with the dipole of the water molecules. This result in a solution called an electrolyte.



This means that the forces can be attractive or repulsive depending on whether like or unlike charges are closer together. On average, dipoles in a liquid orient themselves to form attractive interactions with their neighbours, but thermal motion makes some prompt configurations unfavourable.



Therefore, if a salt crystal is put in water, the polar water molecules are attracted to ions on the crystal surfaces. The water molecules gradually surround and isolate the surface ions. The ions become hydrated. They gradually move away from the crystal into solution. This separation of ions from each other is called dissociation. The surrounding of solute particles by solvent particles 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 acts 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 afford 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 possible by separating these functions into ionic contributions to determine the contributions due to cations and anions in the solute-solvent interactions. Thus ion-solvent interactions show a very important role to know the physico-chemical properties of solutions.

One of the causes for the intricacies in solution chemistry is that the structure of the solvent molecule is not known with certainty. The introduction of a solute also modifies the solvent structure to an uncertain magnitude whereas the solute molecule is also modified and the interplay of forces like solute-solute, solute-solvent and solvent-solvent interactions become predominant though the isolated picture of any of the forces is still not known completely to the solution chemist.

The problems of ion-solvent interactions which are closely akin to ionic solvations can be studied from different angles using almost all the available physico-chemical techniques.

The ion-solvent interactions can also be studied from the thermodynamic point of view where the changes of free energy, enthalpy and entropy, etc. associated with a particular reaction can be qualitatively and quantitatively evaluated using various physico-chemical techniques from which conclusions regarding the factors associated with the ion-solvent interactions can be worked out.

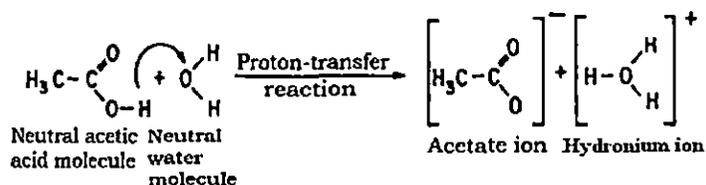
Similarly, the ion-solvent interactions can be studied using solvational approaches involving the studies of different properties such as, density, viscosity, ultrasonic speed, refractive index and conductance of electrolytes and various derived factors associated with ionic solvation.

We shall particularly dwell upon the different aspects of these thermodynamic, transports, acoustic and optical properties as the present research work is intimately related to the studies of ion-ion, ion-solvent and solvent-solvent interactions.

2.2.2. ION-SOLVENT INTERACTION

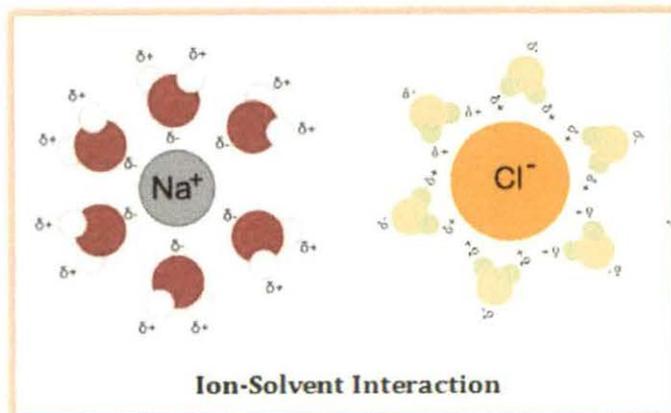
Ion-solvation is a phenomenon of primary interest in many contexts of chemistry because solvated ions are omnipresent on Earth. Hydrated ions occur in aqueous solution in many chemical and biological systems [7]. Solvated ions appear in high concentrations in living organisms, where their presence or absence can fundamentally alter the functions of life. Ions solvated in organic solvents or mixtures of water and organic solvents are also very common [8]. The exchange of solvent molecules around ions in solutions is fundamental to the understanding of the reactivity of ions in solution [9]. Solvated ions also play a key role in electrochemical applications, where for instance the conductivity of electrolytes depends on ion-solvent interactions [10].

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



The chemical method of producing ionic solutions

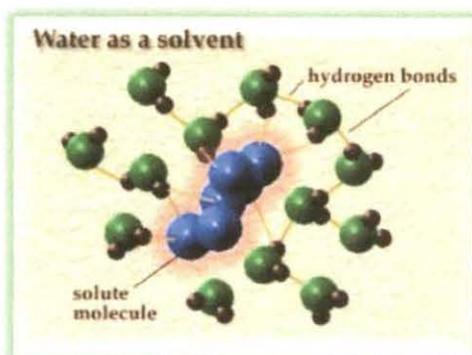
The second one involves dissociation of a solid lattice of ions such as the lattice of sodium chloride. In the ion formation, the solvent colliding with the walls of the crystal gives the ions in the crystal lattice a better deal energetically than they have within the lattice. It entices them out and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



Ions orient dipoles. The spherically symmetrical electric field of the ion may tear 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. The majority of reactions occurring in solutions are chemical or biological in nature. It was presumed earlier that the solvent only provides an inert medium for chemical reactions. The significance of ion-solvent interactions was realized after extensive studies in aqueous, non-aqueous and mixed solvents [11-20].

Most chemical processes of individual and 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 unsolvated rate for collision. The solvent governs the movement and energy of the reacting species to such an extent that a reaction suffers 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. But still our knowledge of molecular interactions in water is extremely limited. Moreover, the uniqueness of water as a solvent has been questioned [21, 22] and it has been realized that the studies of other solvent media like non-aqueous and mixed solvents would be of great 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 [20] donor-acceptor properties [23, 24] hard and soft acid-base principles [25] etc. As a result, the different solvents show a wide divergence of properties ultimately influencing their thermodynamic, transport and acoustic properties in presence of electrolytes and non-electrolytes in these solvents. The determination of thermodynamic, transport and acoustic properties of different electrolytes or non-electrolytes in various solvents would thus provide important information in this direction. Henceforth, in the development of theories of electrolytic solutions, much attention has been devoted to the controlling forces-‘ion-solvent interactions’ in infinitely dilute solutions wherein ion-ion interactions are almost absent. By separating these functions into ionic contributions, it is possible to determine the contributions due to cations and anions in the solute-solvent interactions. Thus ion-

solvent interactions play a key role to understand the physico-chemical properties of solutions.

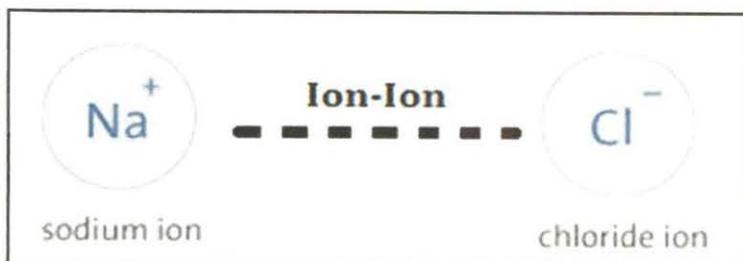
One of the causes for the intricacies in solution chemistry is the uncertainty about the structure of the solvent molecules in solution. The introduction of a solute modifies the solvent structure to an uncertain magnitude, the solvent molecule and the interplay of forces like solute-solute, solute-solvent also modify the solute molecule and solvent-solvent interactions become predominant, though the isolated picture of any of the forces is still not known completely to the solution chemist. Ion-solvent interactions can be studied by spectrometry [26, 27]. The spectral solvent shifts or the chemical shifts can determine the qualitative and quantitative nature of ion-solvent interactions. But even qualitative or quantitative apportioning of the ion-solvent interactions into the various possible factors is still an uphill task.

It is thus apparent that the real understanding of the ion-solvent interaction is a difficult task. The aspect embraces a wide range of topics but we concentrated only on the measurement of transport properties like viscosity, conductance etc. and such thermodynamic properties as apparent and partial molar volumes and apparent molal adiabatic compressibility.

2.2.3. ION-ION INTERACTION

Ion-solvent interactions are only a part of the story of an ion related to its environment. The surrounding of an ion sees not only solvent molecules but also other ions. The mutual interactions between these ions constitute the essential part 'ion-ion interactions'. The degree of ion-ion interactions affects the properties of solution and depends on the nature of electrolyte under investigation. Ion-ion interactions, in general, are stronger than ion-solvent interactions. Ion-ion interaction in dilute electrolytic solutions is now theoretically well understood, but ion-solvent interactions or ion-solvation still 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,

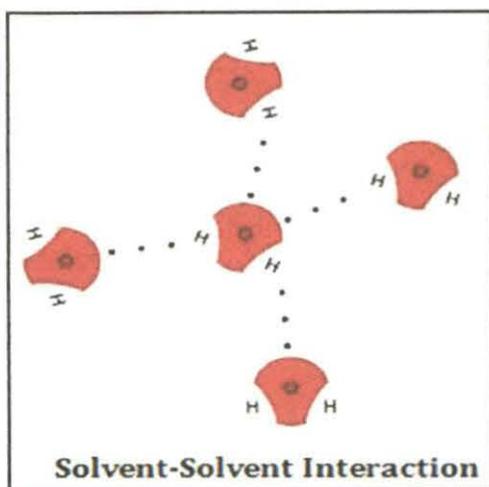
solute-solvent and solvent-solvent interactions are elucidated and thus the present dissertation is intimately related to the studies of solute-solute, solute-solvent and solvent-solvent interactions in some solvent media.



Ion-Ion Interaction

2.2.4. SOLVENT-SOLVENT INTERACTION (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. Theories of perturbation type have been extended from their successful applicability in pure solvents to mixed solvents. L. Jones and Devonshire [28] 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 [29] extended the above approach to solvent mixtures. Random mixing of solvents was their main assumption provided the molecules have similar sizes. Prigogine and Bellemans [30] 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.* [31] 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.



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 structural contributions are mostly 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 assumption is not a concrete one, as evident from some studies [32, 33]. It is observed in many systems that there is no simple correlation between the strength of interaction and the observed properties. Rastogi *et al.* [34] therefore suggested that the observed excess property is a combination of an interaction and non-interaction part. The non-interaction part 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. Based on the principle of corresponding states as suggested by Pitzer [35], L. Huggins [36] 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 thermodynamic properties of the pure components.

Recently, Rowlinson *et al.* [37-39] 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 [40]. A more successful approach is due to Flory who made the use of certain features of cell theory [41-43] 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 [44] combined both Prigogine and Flory theories to a unified one for rationalizing various contributions of free volume, internal pressure, etc. to the excess thermodynamic properties. Recently, Heintz [45-47] and coworkers suggested a theoretical model 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). It combines the effect of association with non-associative intermolecular interaction occurring in solvent mixtures based on equation of state developed originally by Flory *et al.* [41-43]. Subsequently the ERAS model has been successfully applied by many workers [48-50] to describe the excess thermodynamic properties of alkanol-amine mixtures. Recently, a new symmetrical reformation on the Extended Real Association (ERAS) model has been described in the literature [51]. The symmetrical-ERAS (S-ERAS) model makes it possible to describe excess molar enthalpies and excess molar volumes of binary mixtures containing very similar compounds described by extremely small mixing functions. The symmetrical Extended Real Associated Solution Model (S-ERAS) is, in fact, a simple continuation of the ERAS model. It was developed in order to widen its applicability to the thermodynamic properties of systems that could not be satisfactorily described by the equations of the ERAS model [51, 52]. Gepert *et al.* [53] applied this model for studying some binary systems containing alcohols.

2.3. DENSITY

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. The physicochemical properties of liquid mixtures have attracted much attention from both theoretical and engineering applications points of view. Many engineering applications require quantitative data on the density of liquid mixtures. They also provide information about the nature and molecular interactions between liquid mixture components.

The volumetric information includes 'Density' as a function of weight, volume and mole fraction and excess volumes of mixing. One of the well-recognized approaches to the study of molecular interactions in fluids is the use of thermodynamic methods. Thermodynamic properties are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in the solution phase. Fundamental properties such as enthalpy, entropy and Gibbs energy represent the macroscopic state of the system as an average of numerous microscopic states at a given temperature and pressure. An interpretation of these macroscopic properties in terms of molecular phenomena is generally difficult. Sometimes higher derivatives of these properties can be interpreted more effectively in terms of molecular interactions. The volumetric information may be of immense importance in this regard. Various concepts regarding molecular processes in solutions like electrostriction [54], hydrophobic hydration [55], micellization [56] and co-sphere overlap during solute-solvent interactions [57] have been derived and interpreted from the partial molar volume data of many compounds.

2.3.1. APPARENT AND PARTIAL MOLAR VOLUMES

The molar volume of a pure substance can be calculated using density data. 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 entry 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 influence of the ion's electric field, i.e., electrostriction. Electrostriction is a general phenomenon and whenever there are electric fields of the order of 10^9 - 10^{10} V m⁻¹, the compression of ions and molecules is likely to be significant. The effective volume of an ion in solution, the partial molar volume, can be determined from a directly obtainable quantity-

apparent molar volume (ϕ_V). The apparent molar volumes, (ϕ_V), of the solutes can be calculated by using the following relation [58].

$$\phi_V = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \quad (1)$$

where M is the molar mass of the solute, c is the molarity of the solution; ρ_0 and ρ are the densities of the solvent and the solution respectively. The partial molar volumes, ϕ_{2V} , can be obtained from the equation [59]:

$$\phi_{2V} = \phi_V + \frac{(1000 - c\phi_V)}{2000 + c^{3/2} \left(\frac{\partial \phi_V}{\partial \sqrt{c}} \right)} c^{1/2} \left(\frac{\partial \phi_V}{\partial \sqrt{c}} \right) \quad (2)$$

The extrapolation of the apparent molar volume of electrolyte to infinite dilution and the expression of the concentration dependence of the apparent molar volume have been made by four major equations over a period of years – the Masson equation [60], the Redlich-Meyer equation [61], the Owen-Brinkley equation [62], and the Pitzer equation [32]. Masson found that the apparent molar volume of electrolyte, ϕ_V , vary with the square root of the molar concentration by the linear equation:

$$\phi_V = \phi_V^0 + S_V^* \sqrt{c} \quad (3)$$

where, ϕ_V^0 is the apparent molar volume (equal to the partial molar volume) at infinite dilution and S_V^* the experimental slope. The majority of ϕ_V data in water [63] and nearly all ϕ_V data in non-aqueous [64–68] solvents have been extrapolated to infinite dilution through the use of equation (3).

The temperature dependence of ϕ_V^0 or various investigated electrolytes in various solvents can be articulated by the general equation as follows:

$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \quad (4)$$

where a_0 , a_1 and a_2 are the coefficients of a particular electrolyte and T is the temperature in Kelvin.

The limiting apparent molar expansibilities (ϕ_E^0) can be calculated by the following equation:

$$\phi_E^0 = \left(\delta \phi_v^0 / \delta T \right)_p = a_1 + 2a_2 T \quad (5)$$

The limiting apparent molar expansibilities (ϕ_E^0) change in magnitude with the change of temperature. During the past few years, different workers emphasized that S_v^* is not the sole criterion for determining the structure-making or breaking tendency of any solute. Helper [69] developed a technique of examining the sign of $\left(\delta \phi_E^0 / \delta T \right)_p$ for the solute in terms of long-range structure-making and breaking capacity of the electrolytes in the mixed solvent systems. The general thermodynamic expression used is as follows:

$$\left(\delta \phi_E^0 / \delta T \right)_p = \left(\delta^2 \phi_v^0 / \delta T^2 \right)_p = 2a_2 \quad (6)$$

If the sign of $\left(\delta \phi_E^0 / \delta T \right)_p$ is positive or small negative the electrolyte is a structure maker and when the sign of $\left(\delta \phi_E^0 / \delta T \right)_p$ is negative, it is a structure breaker. Redlich and Meyer [61] have shown that an equation (3) cannot be any more than a limiting law where for a given solvent and temperature, the slope S_v^* should depend only upon the valence type. They suggested the equation:

$$\phi_v = \phi_v^0 + S_v \sqrt{c} + b_v c \quad (7)$$

$$\text{where } S_v = Kw^{3/2} \quad (8)$$

S_v is the theoretical slope, based on molar concentration, including the valence factor where

$$w = 0.5 \sum_i Y_i Z_i^2 \quad (9)$$

$$\text{and } K = N^2 e^2 \left(\frac{8\pi}{1000 \epsilon^3 RT} \right)^{1/2} \left[\left(\frac{\partial \ln \epsilon}{\partial p} \right)_T - \frac{\beta}{3} \right] \quad (10)$$

In equation (10), K is the compressibility of the solvent and the other terms having their usual significance.

The Redlich-Meyer's extrapolation equation [61] adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies [61-72] on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation. Thus, for polyvalent electrolytes, the more complete Owen-Brinkley equation [62] can be used to aid in the extrapolation to infinite dilution and to adequately represent the concentration dependency of ϕ_V . The Owen-Brinkley equation [62] which includes the ion-size parameter, a (cm), is given by:

$$\phi_V = \phi_V^0 + S_V \tau (\kappa a) \sqrt{c} + 0.5 w_V \theta (\kappa a) c + 0.5 K_V c \quad (11)$$

where the symbols have their usual significance. However, this equation is not widely used for non-aqueous solutions.

Recently, the Pitzer formalism has been used by Pogue and Atkinson [73] to fit the apparent molal volume data. The Pitzer equation for the apparent molar volume of a single salt $M \gamma_M M \gamma_X$ is :

$$\phi_V = \phi_V^0 + V |Z_M Z_X| A_V |2b \ln \left(I + bI^{1/2} \right) + 2\gamma_M \gamma_X RT \left[m B_{MX}^2 + m^2 (\gamma_M \gamma_X)^{1/2} C_{MX}^V \right] \quad (12)$$

where the symbols have their usual significance.

2.3.2. IONIC LIMITING PARTIAL MOLAR VOLUMES

The individual partial ionic volumes provide information relevant to the general question of the structure near the ion, i.e., its solvation. The calculation of the ionic limiting partial molar volumes in organic solvents is, however, a difficult one. At present, however, most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods originally developed for aqueous solutions to non-aqueous electrolyte solutions. In the last few years, the

method suggested by Conway *et al.* [74] has been used more frequently. These authors used the method to determine the limiting partial molar volumes of the anion for a series of homologous tetra alkyl ammonium chlorides, bromides and iodides in aqueous solution. They plotted the limiting partial molar volume $\phi_{vR_4NX}^0$ for a series of these salts with a halide ion in common as a function of the formula weight of the cation, $M_{R_4N^+}$ and obtained straight-lines for each series. Therefore, they suggested the following equation:

$$\phi_{vR_4NX}^0 = bM_{R_4N^+} + \phi_{vX^-}^0 \quad (13)$$

The extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions $\phi_{vX^-}^0$.

Uosaki *et al.* [75] used this method for the separation of some literature values and of their own $\phi_{vR_4NX}^0$ values into ionic contributions in organic electrolyte solutions.

Krumgalz [76] applied the same method to a large number of partial molar volume data for non-aqueous electrolyte solutions in a wide temperature range.

2.3.3. EXCESS MOLAR VOLUMES

The excess molar volumes, V^E are calculated from the molar masses M_i and the densities of pure liquids and the mixtures according to the following equation [77, 78]

$$V^E = \sum_{i=1}^n x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (14)$$

where ρ_i and ρ are the density of the i^{th} component and density of the solution mixture respectively. V^E is the resultant of contributions from several opposing effects. These may be divided arbitrarily into three types, namely, chemical, physical and structural. Physical contributions, which are nonspecific interactions between the real species present in the mixture, contribute a positive term to V^E . The chemical or specific intermolecular interactions result in a volume decrease, thereby contributing negative V^E values. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume [17]. These phenomena are the results

of difference in energies of interaction between molecules being in solutions and packing effects. Disruption of the ordered structure of pure component during formation of the mixture leads to a positive effect observed on excess volume while an order formation in the mixture leads to negative contribution.

2.4. VISCOSITY

As fundamental and important properties of liquids, viscosity and volume could also provide a lot of information on the structures and molecular interactions of liquid mixtures. Viscosity and volume are different types of properties of one liquid, and there is a certain relationship between them. So by measuring and studying them together, relatively more realistic and comprehensive information could be expected to be gained. The relationship between them could also be studied. The viscometric information includes 'Viscosity' as a function of composition on the basis of weight, volume and mole fraction; comparison of experimental viscosities with those calculated with several equations and excess Gibbs free energy of viscous flow. Viscosity, one of the most important transport properties is used for the determination of ion-solvent interactions and studied extensively [79, 80]. Viscosity is not a thermodynamic quantity, but viscosity of an electrolytic solution along with the thermodynamic property, $\phi_{v,2}^0$, i.e., the partial molar volume, gives a lot of information and insight regarding ion-solvent interactions and the nature of structures in the electrolytic solutions.

2.4.1. VISCOSITY OF PURE LIQUIDS AND LIQUID MIXTURES

Since the molecular motion in liquids is controlled by the influence of the neighbouring molecules, the transport of momentum in liquids takes place, in sharp contrast with gases at ordinary pressures, not by the actual movement of molecules but by the intense influence of intermolecular force fields. It is this aspect of the mechanism of momentum transfer which forms the basis of the procedures for predicting the variations in the viscosity of liquids and liquid mixtures.

2.4.2. EARLY THEORETICAL CONSIDERATIONS ON LIQUID VISCOSITY

The theoretical development of liquid viscosity in early stages has been reviewed Andrade [81] and Frenkel [82]. By considering the forces of collision to be the only important factor and assuming 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. Andrade [81] developed equations which checked well against data on mono atomic metals at the melting point. Frenkel [82] considered the molecules of a liquid to be spheres moving with an average velocity with respect to the surrounding medium and using Stokes' law and Einstein's relation for self-diffusion-coefficient, arrived at a complicated expression for liquid viscosity with only limited applicability. Furth [83] assumed the momentum transfer to take place by the irregular Brownian movement of the holes [84] which were linked to clusters in a gas and thus, in analogy with the gas theory of viscosity and with assumption of the equipartition law of energy, showed that for liquids:

$$\eta = 0.915 \frac{RT}{V} \left(\frac{m}{\sigma} \right) e^{\frac{A}{RT}} \quad (15)$$

where η , V and m are viscosity, volume and mass, respectively, T is the temperature, R is the universal gas constant, σ is the surface tension and A is the work function at the melting point. He compared his theory with experiment as well as with the theories of Andrade [82] and Ewell and Eyring [85] Auluck, De and Kothari [86] further modified the theory and successfully explained the variations of the viscosity with pressure. A critical review of these simple theories and their abilities to explain momentum transport in liquids is given by Eisenschitz [87].

2.4.3. THE CELL LATTICE THEORY AND LIQUID VISCOSITY

A model related to in the literature by various names such as cell, lattice, cage, free volume or one particle model was introduced by Lennard- Jones and Devonshire [88, 89] and further expanded by Pople [90]. Eisenschitz employing this model developed a theory of viscosity by considering the motion of the representative molecules to be Brownian and their distribution according to the

Smoluchowski equation. Even with certain assumptions, the final expression showed shortcomings most of which were later overcome in a subsequent publication [91].

2.4.4. STATISTICAL MECHANICAL APPROACH TO LIQUID VISCOSITY

The distribution functions for the liquid molecules were obtained on the basis of statistical mechanical theory mainly by the efforts of Kirkwood [92, 93] Mayer and Montroll [94], Mayer [95], Born and Green [96] and the considerations on the basis of the general kinetic theory led Born and Green [96, 97] to develop a viscosity equation which provided explanation for several empirical equations [80, 81, 83] proposed for liquid viscosity. In this connection the theoretical contributions of Kirkwood and coworkers [84, 98-104] Zwanzig *et al.*, [105] Rice and coworkers [106-109] Longuet-Higgins and Valleeu [110] and Davis and Coworkers [111, 112] are worth mentioning.

2.4.5. PRINCIPLE OF CORRESPONDING STATES AND LIQUID VISCOSITY

The principle of the corresponding states has been applied to liquids in the same way as to gases [113] the basic assumption being that the intermolecular potential between two molecules is a universal function of the reduced intermolecular separation. This assumption is a good approximation for spherically symmetric mono atomic non-polar molecules. For complicated molecules, the principle becomes increasingly crude. In general, more parameters are introduced in the corresponding state correlations on somewhat empirical grounds in the hope that such modification in some way compensates the shortcomings of the above stated assumption. In this connection the studies by Rogers and Brickwedde [114], Boon and Thomaes [115-117] Boon, Legros and Thomaes [118], and Hollman and Hijmans [119] are worth mentioning.

2.4.6. THE REACTION RATE THEORY FOR VISCOUS FLOW

Considering viscous flow as a chemical reaction in which a molecule moving in a plane occasionally acquires the activation energy necessary to slip over the potential barrier to the next equilibrium position in the same plane. Eyring [120] showed that the viscosity of the liquid is given by:

$$\eta = \frac{\lambda_1 h F_n}{\kappa \lambda^2 \lambda_2 \lambda_3 F_a^*} \exp \frac{\Delta E_{act}}{kT} \quad (16)$$

where λ is the average distance between the equilibrium positions in the direction of motion, λ_1 is the perpendicular distance between two neighbouring layers of molecules in relative motion, λ_2 is the distance between neighbouring molecules in the same direction and λ_3 is the distance from molecule to molecule in the plane normal to the direction of motion. The transmission coefficient (κ) is the measure of the chance that a molecule having once crossed the potential barrier will react and not recross in the reverse direction, F_n is the partition function of the normal molecules, F_a^* that of the activated molecule with a degree of freedom corresponding to flow, ΔE_{act} is the energy of activation for the flow process, h is Planck's constant and k is Boltzmann constant. Ewell and Eyring argued that for a molecule to flow into a hole, it is not necessary that the latter be of the same size as the molecule. Consequently they assume that ΔE_{act} is a function of ΔE_{vap} for viscous flow because ΔE_{vap} is the energy required to make a hole in the liquid of the size of a molecule. Utilizing the idea and certain other relations [84, 120] finally gets

$$\eta = \frac{N_A h (2\pi mkT)^{\frac{1}{2}}}{Vh} \frac{bRTV^{\frac{1}{3}}}{N_A^{\frac{1}{3}} \Delta E_{vap}} \exp \frac{\Delta E_{vap}}{nRT} \quad (17)$$

where n and b are constants. It was found that the theory could reproduce the trend in temperature dependence of η but the computed values are greater than the observed values by a factor of 2 or 3 for most liquids. Kincaid, Eyring and Stearn [121, 122] have summarized all the working relations.

2.4.7. THE SIGNIFICANT STRUCTURE THEORY AND LIQUID VISCOSITY

Eyring and coworkers [123-126] improved the “holes in solid” model theory [122-127] to picture the liquid state by identifying three significant structures. In brief, a molecule has solid like properties for the short time it vibrates about an equilibrium position and then it assumes instantly the gas like behaviour on jumping into the neighbouring vacancy. The above idea of significant structures leads to the following relation for the viscosity of liquid [128, 129].

$$\eta = \frac{V_s}{V} \eta_s + \frac{V - V_s}{V} \eta_g \quad (18)$$

where 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 while η_s and η_g are the viscosity contributions from the solid-like and gas-like degrees of freedom, respectively. The expressions for η_s and η_g are given by Carlson, Eyring and Ree [129]. Eyring and Ree [130] have discussed in detail the evaluation of η_s from the reaction rate theory of Eyring [120] assuming that a solid molecule can jump into all neighbouring empty sites. The expression for η_s takes the following form [131]

$$\eta_s = \frac{N_A h}{Z \kappa} \cdot \frac{V}{V_s} \cdot \frac{6}{2^2} \cdot \frac{1}{V - V_s} \cdot \frac{1}{1 - e^{-\theta/T}} \exp \frac{a' E_s V_s}{(V - V_s) RT} \quad (19)$$

where N_A is Avogadro's number, Z is the number of nearest neighbours, θ is the Einstein characteristic temperature, E_s is the energy of sublimation and a' is the proportionality constant. On the other hand, the term η_g is obtained from the kinetic theory of gases [131] by the relation:

$$\eta_g = \frac{2}{3d^2} \left(\frac{mkT}{\pi^3} \right)^{\frac{1}{2}} \quad (20)$$

where d is the molecular diameter and m is the molecular mass.

2.4.8. VISCOSITY OF ELECTROLYTIC SOLUTIONS

The viscosity relationships of electrolytic solutions are highly complicated. Because ion-ion and ion-solvent interactions are occurring in the solution and separation of the related forces is a difficult task. But, from careful analysis, vivid and valid conclusions can be drawn regarding the structure and the nature of the solvation of the particular system. As viscosity is a measure of the friction between adjacent, relatively moving parallel planes of the liquid, anything that increases or decreases the interaction between the planes will raise or lower the friction and thus, increase or decrease the viscosity. If large spheres are placed in the liquid, the planes will be keyed together in increasing the viscosity. Similarly, increase in the average degree of hydrogen bonding between the planes will increase the friction between the planes, thereby viscosity. An ion with a large rigid co-sphere for a structure-promoting ion will behave as a rigid sphere placed in the liquid and increase the inter-planar friction. Similarly, an ion increasing the degree of hydrogen bonding or the degree of correlation among the adjacent solvent molecules will increase the viscosity. Conversely, ions destroying correlation would decrease the viscosity. In 1905, Grüneisen [132] performed the first systematic measurement of viscosities of a number of electrolytic solutions over a wide range of concentrations. He noted non-linearity and negative curvature in the viscosity concentration curves irrespective of low or high concentrations. In 1929, Jones and Dole [133] suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations (c):

$$\frac{\eta}{\eta_0} = \eta_r = 1 + A\sqrt{c} + Bc \quad (21)$$

The above equation can be rearranged as:

$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} \quad (22)$$

where A and B are constants specific to ion-ion and ion-solvent interactions. The equation is applicable equally to aqueous and non-aqueous solvent systems where there is no ionic association and has been used extensively. The term $A\sqrt{c}$, originally

ascribed to Grüneisen effect, arose from the long-range coulombic forces between the ions. The significance of the term had since then been realized due to the development Debye-Hückel theory [134] of inter-ionic attractions in 1923. The A -coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory [135-137] and is given by the Falkenhagen Vernon [137] equation:

$$A_{Theo} = \frac{0.2577 \Lambda_o}{\eta_o (\epsilon T)^{0.5} \lambda_+^o \lambda_-^o} \left[1 - 0.6863 \left(\frac{\lambda_+^o \lambda_-^o}{\Lambda_o} \right)^2 \right] \quad (23)$$

where the symbols have their usual significance. In very accurate work on aqueous solutions [138], A -coefficient has been obtained by fitting η_r to equation (22) and compared with the values calculated from equation (23), the agreement was normally excellent. The accuracy achieved with partially aqueous solutions was however poorer [139]. A -coefficient suggesting that should be calculated from conductivity measurements. Crudden *et al.* [140] suggested that if association of the ions occurs to form an ion pair, the viscosity should be analysed by the equation:

$$\frac{\eta_r - 1 - A\sqrt{\alpha c}}{\alpha c} = B_i + B_p \left(\frac{1-\alpha}{\alpha} \right) \quad (24)$$

where A , B_i and B_p are characteristic constants and α is the degree of dissociation of ion pair. Thus, a plot of $(\eta_r - 1 - A\sqrt{\alpha c}/\alpha c)$ against $(1-\alpha)/\alpha$, when extrapolated to $(1-\alpha)/\alpha = 0$ gave the intercept B_i . However, for the most of the electrolytic solutions both aqueous and nonaqueous, the equation (22) is valid up to 0.1 (M) [141, 142] within experimental errors.

At higher concentrations the extended equation (25), involving an additional coefficient D , originally used by Kaminsky, has been used by several workers [143, 144] and is given below:

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc + Dc^2 \quad (25)$$

The coefficient D cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, equation (22) is used by the most of the workers.

The plots of $(\eta/\eta_0 - 1)/\sqrt{c}$ against \sqrt{c} for the electrolytes should give the value of A - coefficient. But sometimes, the values come out to be negative or considerably scatter and also deviation from linearity occur [142,145-147]. Thus, instead of determining A - coefficient from the plots or by the least square method, the A - coefficient are generally calculated using Falkenhagen-Vernon equation (23). A - coefficient should be zero for non-electrolytes. According to Jones and Dole, the A - coefficient probably represents the stiffening effect on the solution of the electric forces between the ions, which tend to maintain a space-lattice structure [133]. The B - coefficient may be either positive or negative and it is actually the ion-solvent interaction parameter. It is conditioned by the ions and the solvent and cannot be calculated a priori. The B - coefficients are obtained as slopes of the straight lines using the least square method and intercepts equal to the A values.

The factors influencing B - coefficients are [148, 149]:

- (1) The effect of ionic solvation and the action of the field of the ion in producing long-range order in solvent molecules, increase η or B - value.
- (2) The destruction of the three dimensional structure of solvent molecules (i.e., structure breaking effect or depolymeriation effect) decreases η values.
- (3) High molal volume and low dielectric constant, which yield high B -values for similar solvents.
- (4) Reduced B -values are obtained 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.

2.4.9. VISCOSITIES AT HIGHER CONCENTRATION

It had been found that the viscosity at high concentrations (1M to saturation) can be represented by the empirical formula suggested by Andrade:

$$\eta = A \exp \frac{b}{r} \quad (26)$$

The several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration range [150-155] and the equation suggested by Angell [156-158] based on an extension of the free volume theory of transport phenomena in liquids and fused salts to ionic solutions is particularly noteworthy. The equation is:

$$\frac{1}{\eta} = A \exp \left[-\frac{K_1}{N_o - N} \right] \quad (27)$$

where N represents the concentration of the salt in eqv. litre⁻¹, A and K_1 are constants supposed to be independent of the salt composition and N_o is the hypothetical concentration at which the system becomes glass. The equation was recast by Majumder *et al.* [158-160] introducing the limiting condition, that is $N \rightarrow 0$, $\eta \rightarrow \eta_o$; which is the viscosity of the pure solvent.

Thus, we have:

$$\ln \eta / \eta_o = \ln \eta_{Rel} = \frac{K_1 N}{N_o(N_o - N)} \quad (28)$$

Equation (28) predicts a straight line passing through the origin for the plot of $\ln \eta_{Rel}$ vs. $N/(N_o - N)$ if a suitable choice for N_o is made. Majumder *et al.* tested the equation (28) by using literature data as well as their own experimental data. The best choice for N_o and K_1 was selected by a trial and error methods. The set of K_1 and N_o producing minimum deviations between η_{Rel}^{Exp} and η_{Rel}^{Theo} was accepted.

In dilute solutions, $N \ll N_o$ and we have:

$$\eta_{Rel} = \exp \left(\frac{K_1 N}{N_o^2} \right) \cong 1 + \frac{K_1 N}{N_o^2} \quad (29)$$

Equation (29) is nothing but the Jones-Dole equation with the ion-solvent interaction term represented as $B = K_1/N_o^2$. The arrangement between B -values determined in this way and using Jones-Dole equation has been found to be good for several electrolytes.

Further, the equation (28) can be written in the form:

$$\frac{N}{\ln \eta_{Rel}} = \frac{N_o^2}{K_1} - \left(\frac{N_o}{K_1} \right) N \quad (30)$$

It closely resembles the Vand's equation [153] for fluidity (reciprocal for viscosity):

$$\frac{2.5c}{2.3 \log \eta_{Rel}} = \frac{1}{V_h} - Qc \quad (31)$$

where c is the molar concentration of the solute and V_h is the effective rigid molar volume of the salt and Q is the interaction constant.

2.4.10. DIVISION OF B -COEFFICIENT INTO IONIC VALUES

The viscosity B -coefficients have been determined by a large number of workers in aqueous, mixed and non-aqueous solvents [161-191]. However, the B -coefficients as determined experimentally using the Jones-Dole equation, does not give any impression regarding ion-solvent interactions unless there is some way to identify the separate contribution of cations and anions to the total solute-solvent interaction. The division of B - values into ionic components is quite arbitrary and based on some assumptions, the validity of which may be questioned. The following methods have been used for the division of B - values in the ionic components:

(1) Cox and Wolfenden [192] carried out the division on the assumption that B_{ion} values of Li^+ and IO_3^- in LiIO_3 are proportional to the ionic volumes which are proportional to the third power of the ionic mobilities. The method of Gurney [193] and also of Kaminsky [143] is based on:

$$B_{K^+} = B_{Cl^-} \text{ (in water)} \quad (32)$$

The argument in favour of this assignment is based on the fact that the B -coefficients for KCl is very small and that the motilities' of K^+ and Cl^- are very similar over the temperature range 288.15 – 318.15 K. The assignment is supported from other thermodynamic properties. Nightingale [194], however preferred RbCl or CsCl to KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron [144] is based on the assumption that the Et_4N^+ ion in water is probably closest to be neither structure breaker nor a structure maker. Thus, they suggest that it is possible to apply with a high degree of accuracy of the Einstein's equation [195],

$$B = 0.0025 \overline{V}_o \quad (33)$$

and by having an accurate value of the partial molar volume of the ion, \overline{V}_o , it is possible to calculate the value of 0.359 for $B_{\text{Et}_4\text{N}^+}$ in water at 298.15 K. Recently, Sacco *et al.* proposed the "reference electrolytic" method for the division of B -values.

Thus, for tetraphenyl phosphonium tetraphenyl borate in water, we have:

$$B_{BPh_4^-} = B_{PPh_4^+} + B_{BPh_4PPh_4}/2 \quad (34)$$

$B_{BPh_4PPh_4}$ (scarcely soluble in water) has been obtained by the following method:

$$B_{BPh_4PPh_4} = B_{NaBPh_4} + B_{PPh_4Br} - B_{NaBr} \quad (35)$$

The values obtained are in good agreement with those obtained by other methods. The criteria adopted for the separation of B - coefficients in nonaqueous solvents differ from those generally used in water. However, the methods are based on the equality of equivalent conductances of counter ions at infinite dilutions.

(a) Criss and Mastroianni assumed $B_{K^+} = B_{Cl^-}$ in ethanol based on equal mobilities of ions [196]. They also adopted $B_{Me_4N^+}^{25} = 0.25$ as the initial value for acetonitrile solutions.

(b) For acetonitrile solutions, Tuan and Fuoss [197] proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer *et al.* [198], $\lambda_{25}^{\circ}(Bu_4N^+) = 61.4$ and $\lambda_{25}^{\circ}(Ph_4B^-) = 58.3$ in acetonitrile.

$$B_{Bu_4N^+} = B_{Ph_4B^-} \quad (36)$$

(c) Gopal and Rastogi [148] resolved the B -coefficient in N-methyl propionamide solutions assuming that $B_{Et_4N^+} = B_{I^-}$ at all temperatures.

(d) In dimethyl sulphoxide, the division of B -coefficients were carried out by Yao and Beunion [147] assuming:

$$B_{[(i-pe)_3BuN^+]} = B_{Ph_4B^-} = 1/2B_{[(i-pe)_3BuNPh_4B]} \quad (37)$$

at all temperatures.

Wide use of this method has been made by other authors for dimethyl sulphoxide, sulfolane, hexamethyl phosphotriamide and ethylene carbonate [199] solutions. The methods, however, have been strongly criticized by Krumgalz [200]. According to him, any method of resolution based on the equality of equivalent conductances for certain ions suffers from the drawback that it is impossible to select any two ions for which $\lambda_o^+ = \lambda_o^-$ in all solvents at all temperatures. Thus, though $\lambda_k^+ = \lambda_{Cl}^-$ at 298.15 K in methanol, but is not so in ethanol or in any other

solvents. In addition, if the mobilities of some ions are even equal at infinite dilution, but it is not necessarily true at moderate concentrations for which the B - coefficient values are calculated. Further, according to him, equality of dimensions of $(i-pe)_3BuN^+$ or $(i-Am)_3BuN^+$ and Ph_4B^- does not necessarily imply the equality of B - coefficients of these ions and they are likely to be solvent and ion-structure dependent. Krumgalz [200, 201] has recently proposed a method for the resolution of B -coefficients. The method is based on the fact that the large tetraalkylammonium cations are not solvated [202, 203] in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic B - values for large tetraalkylammonium ions, R_4N^+ (where $R > Bu$) in organic solvents are proportional to their ionic dimensions. So, we have:

$$B_{R_4NX} = a + br^3R_4N^+ \quad (38)$$

$a=B_x$. B and b is a constant dependent on temperature and solvent nature.

The extrapolation of the plot of B_{R_4NX} ($R > Pr$ or Bu) against r^3 to R_4N to zero cation dimension gives directly B_x in the proper solvent and thus B - ion values can be calculated.

The B -ion values can also be calculated from the equations:

$$B_{R_4N^+} - B_{R_4'N^+} = B_{R_4NX} - B_{R_4'NX} \quad (39)$$

$$\frac{B_{R_4N^+}}{B_{R_4'N^+}} = \frac{r^3_{R_4N^+}}{r^3_{R_4'N^+}} \quad (40)$$

The radii of the tetraalkylammonium ions have been calculated from the conductometric data [204]. Gill and Sharma [182] used Bu_4NBPh_4 as a reference electrolyte. The method of resolution is based on the assumption, like Krumgalz, that Bu_4N^+ and Ph_4B^- ions with large R - groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constant. The ionic radii of Bu_4N^+ (5.00 Å) and Ph_4B (5.35 Å) were, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers. They proposed the equations:

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \left(\frac{5.35}{5.00}\right)^3 \quad (41)$$

$$B_{Bu_4NBPh_4} = B_{Bu_4N^+} + B_{Ph_4B^-} \quad (42)$$

The method requires only the B -values of Bu_4NBPh_4 and is equally applicable to mixed non-aqueous solvents. The B -ion values obtained by this method agree well with those reported by Sacco *et al.* in different organic solvents using the assumption as given below:

$$B_{[(i-Am)_3\text{Bu}_4\text{N}^+]} = B_{\text{Ph}_4\text{B}^-} = 1/2B_{\text{Bu}_4\text{NBPh}_4} \quad (43)$$

Recently, Lawrence and Sacco [185] used tetrabutylammonium tetrabutylborate (Bu_4NBBu_4) as reference electrolyte because the cation and anion in each case are symmetrical in shape and have almost equal Van der Waal's volume. Thus, we have:

$$\frac{B_{\text{Bu}_4\text{N}^+}}{B_{\text{Bu}_4\text{B}^-}} = \frac{V_{W(\text{Bu}_4\text{N}^+)}}{V_{W(\text{Bu}_4\text{B}^-)}} \quad (44)$$

$$B_{\text{Bu}_4\text{N}^+} = \frac{B_{\text{Bu}_4\text{NBPh}_4}}{[1 + V_{W(\text{Bu}_4\text{B}^-)}/V_{W(\text{Bu}_4\text{N}^+)}} \quad (45)$$

A similar division can be made for Ph_4PBPh_4 system.

Recently, Lawrence *et al.* made the viscosity measurements of tetraalkyl (from propyl to heptyl) ammonium bromides in DMSO and HMPT.

The B -coefficients $B_{R_4\text{NBr}} = B_{\text{Br}^-} + a[f_x R_4\text{N}^+]$ were plotted as functions of the Vander Waal's volumes. The B_{Br^-} values thus obtained were compared with the accurately determined B_{Br^-} value using Bu_4NBBu_4 and Ph_4PBPh_4 as reference salts. They concluded that the 'reference salt' method is the best available method for division into ionic contributions.

Jenkins and Pritchett [205] suggested a least square analytical technique to examine additivity relationship for combined ion thermodynamics data, to effect apportioning into single-ion components for alkali metal halide salts by employing Fajan's competition principle [206] and 'volcano plots' of Morris [207]. The principle was extended to derive absolute single ion B coefficients for alkali metals and halides in water. They also observed that $B_{\text{Cs}^+} = B_{\text{I}^-}$ suggested by Krungalz [202] to be more reliable than $B_{\text{K}^+} = B_{\text{Cl}^-}$ in aqueous solutions. However, we require more data to test the validity of this method.

It is apparent that almost all these methods are based on certain approximations and anomalous results may arise unless proper mathematical theory is developed to calculate B -values.

2.4.11. TEMPERATURE DEPENDENCE OF B - ION VALUES

Regularity in the behaviour of B_{\pm} and dB_{\pm}/dT has been observed both in aqueous and non-aqueous solvents and useful generalizations have been made by Kaminsky. He observed that (i) within a group of the periodic table the B -ion values decrease as the crystal ionic radii increase, (ii) within a group of periodic system, the temperature co-efficient of B_{ion} values increase as the ionic radius. The results can be summarized as follows:

$$(i) A \text{ and } dA/dT > 0 \quad (46)$$

$$(ii) B_{ion} < 0 \text{ and } dB_{ion}/dT > 0 \quad (47)$$

characteristic of the structure breaking ions.

$$(iii) B_{ion} > 0 \text{ and } dB_{ion}/dT < 0 \quad (48)$$

characteristic of the structure making ions.

An ion when surrounded by a solvent sheath, the properties of the solvent in the solvational layer may be different from those present in the bulk structure. This is well reflected in the 'Co-sphere' model of Gurney [208], A, B, C Zones of Frank and Wen [209] and hydrated radius of Nightingale [194].

Stokes and Mills gave an analysis of the viscosity data incorporating the basic ideas presented before. The viscosity of a dilute electrolyte solution has been equated to the viscosity of the solvent (η_o) plus the viscosity changes resulting from the competition between various effects occurring in the ionic neighborhood. Thus, the Jones-Dole equation:

$$\eta = \eta_o + \eta^* + \eta^E + \eta^A + \eta^D = \eta_o + \eta(A\sqrt{c} + Bc) \quad (49)$$

where η^* , the positive increment in viscosity is caused by coulombic interaction. Thus,

$$\eta^E + \eta^A + \eta^D = \eta_o Bc \quad (50)$$

B -coefficient can thus be interpreted in terms of the competitive viscosity effects.

Following Stokes, Mills and Krumgalz [200] we can write:

$$B_{Ion} = B_{Ion}^{Einst} + B_{Ion}^{Orient} + B_{Ion}^{Str} + B_{Ion}^{Reinf} \quad (51)$$

whereas according to Lawrence and Sacco:

$$B_{Ion} = B_W + B_{Solv} + B_{Shape} + B_{Ord} + B_{Discord} \quad (52)$$

B_{Ion}^{Einst} is the positive increment arising from the obstruction to the viscous flow of the solvent caused by the shape and size of the ions (the term corresponds to η^E or B_{Shape}). B_{Ion}^{Orient} is the positive increment arising from the alignment or structure making action of the electric field of the ion on the dipoles of the solvent molecules (the term corresponds to η^A or B_{Ord}). B_{Ion}^{Str} is the negative increment related to the destruction of the solvent structure in the region of the ionic co-sphere arising from the opposing tendencies of the ion to orientate the molecules round itself centrosymmetrically and solvent to keep its own structure (this corresponds to η^D or $B_{Discord}$). B_{Ion}^{Reinf} is the positive increment conditioned by the effect of 'reinforcement of the water structure' by large tetraalkylammonium ions due to hydrophobic hydration. The phenomenon is inherent in the intrinsic water structure and absent in organic solvents. B_W and B_{Solv} account for viscosity increases and attributed to the Vander Waals volume and the volume of the solvation of ions. Thus, small and highly charged cations like Li^+ and Mg^{2+} form a firmly attached primary solvation sheath around these ions (B_{Ion}^{Orient} or η^E positive). At ordinary temperature, alignment of the solvent molecules around the inner layer also cause increase in B_{Ion}^{Orient} (η^A), B_{Ion}^{Orient} (η^D) is small for these ions. Thus, B_{Ion} will be large and positive as $B_{Ion}^{Einst} + B_{Ion}^{Orient} > B_{Ion}^{Str}$. However, B_{Ion}^{Einst} and B_{Ion}^{Orient} would be small for ions of greatest crystal radii (within a group) like Cs^+ or I^- due to small surface charge densities resulting in weak orienting and structure forming effect. B_{Ion}^{Str} would be large due to structural disorder in the immediate neighbourhood of the ion due to competition between the ionic field and the bulk structure. Thus, $B_{Ion}^{Einst} + B_{Ion}^{Orient} < B_{Ion}^{Str}$ and B_{Ion} is negative. Ions of intermediate size (e.g., K^+ and Cl^-) have a close

balance of viscous forces in their vicinity, *i.e.*, $B_{Ion}^{Einst} + B_{Ion}^{Orient} = B_{Ion}^{Str}$ so that B is close to zero.

Large molecular ions like tetraalkylammonium ions have large B_{Ion}^{Einst} because of large size but B_{Ion}^{Orient} and B_{Ion}^{Str} would be small, *i.e.*, $B_{Ion}^{Einst} + B_{Ion}^{Orient} \gg B_{Ion}^{Str}$ would be positive and large. The value would be further reinforced in water arising from B_{Ion}^{Reinf} due to hydrophobic hydrations.

The increase in temperature will have no effect on B_{Ion}^{Einst} . But the orientation of solvent molecules in the secondary layer will be decreased due to increase in thermal motion leading to decrease in B_{Ion}^{Str} . B_{Ion}^{Orient} will decrease slowly with temperature as there will be less competition between the ionic field and reduced solvent structure. The positive or negative temperature co-efficient will thus depend on the change of the relative magnitudes of B_{Ion}^{Orient} and B_{Ion}^{Str} .

In case of structure-making ions, the ions are firmly surrounded by a primary solvation sheath and the secondary solvation zone will be considerably ordered leading to an increase in B_{Ion} and concomitant decrease in entropy of solvation and the mobility of ions. Structure breaking ions, on the other hand, are not solvated to a great extent and the secondary solvation zone will be disordered leading to a decrease in B_{Ion} values and increases in entropy of solvation and the mobility of ions. Moreover, the temperature induced change in viscosity of ions (or entropy of solvation or mobility of ions) would be more pronounced in case of smaller ions than in case of the larger ions. So, there is a correlation between the viscosity, entropy of solvation and temperature dependent mobility of ions. Thus, the ionic B -coefficient and the entropy of solvation of ions have rightly been used as probes of ion-solvent interactions and as a direct indication of structure making and structure breaking character of ions. The linear plot of ionic B -coefficients against the ratios of mobility viscosity products at two temperatures (a more sensitive variable than ionic mobility) by Gurney [207] clearly demonstrates a close relation between ionic B -coefficients and ionic mobilities. Gurney also demonstrated a clear correlation between the molar entropy of solution values with B -coefficient of salts. The ionic B

- values show a linear relationship with the partial molar ionic entropies or partial molar entropies of hydration (\bar{S}_h^o) as:

$$\bar{S}_h^o = \bar{S}_{aq}^o - \bar{S}_g^o \quad (53)$$

Where, $\bar{S}_{aq}^o = \bar{S}_{ref}^o + \Delta S^o$, \bar{S}_g^o , is the calculated sum of the translational and rotational entropies of the gaseous ions. Gurney obtained a single linear plot between ionic entropies and ionic B -coefficients for all mono atomic ions by equating the entropy of the hydrogen ion ($S_{H^+}^o$) to $-5.5 \text{ cal. mol}^{-1} \text{ deg}^{-1}$. Asmus [210] used the entropy of hydration to correlate ionic B values and Nightingale [194] showed that a single linear relationship could be obtained with it for both monoatomic and polyatomic ions. The correlation was utilized by Abraham *et al.* [211] to assign single ion B - coefficients so that a plot of ΔS_e^o [212, 213] the electrostatic entropy of solvation or $\Delta S_{I,II}^o$ the entropic contributions of the first and second solvation layers of ions against B points (taken from the works of Nightingale) for both cations and anions lie on the same curve. There are excellent linear correlations between ΔS_e^o and ΔS_I^o and the single ion B - coefficients. Both entropy criteria (ΔS_e^o and $\Delta S_{I,II}^o$) and B - ion values indicate that in water the ions Li^+ , Na^+ , Ag^+ and F^- are not structure makers, and the ions Rb^+ , Cs^+ , Cl^- , Br^- , I^- and ClO_4^- are structure breakers and K^+ is a border line case.

2.4.12. THERMODYNAMICS OF VISCOUS FLOW

Assuming viscous flow as a rate process, the viscosity (η) can be represented from Eyring's [214] approaches as:

$$\eta = A e^{\frac{E_{vis}}{RT}} = \left(\frac{hNA}{V} \right) e^{\frac{\Delta G^*}{RT}} = \left(\frac{hNA}{V} \right) e^{\left(\frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \right)} \quad (54)$$

where E_{vis} = the experimental entropy of activation determined from a plot of $\ln \eta$ against $1/T$. ΔG^* , ΔH^* and ΔS^* are the free energy, enthalpy and entropy of activation, respectively.

Nightingale and Benck [215] dealt in the problem in a different way and calculated the thermodynamics of viscous flow of salts in aqueous solution with the help of the Jones-Dole equation (neglecting the $A c$ term).

Thus, we have:

$$R \left[\frac{d \ln \eta}{d(1/T)} \right] = r \left[\frac{d \ln \eta_0}{d(1/T)} \right] + \frac{R}{(1+Bc)} \cdot \frac{d(1+Bc)}{d(1/T)} \quad (55)$$

$$\Delta E_{\eta(Soln)}^{\ddagger} = \Delta E_{\eta_0(Solv)}^{\ddagger} + \Delta E_V^{\ddagger} \quad (56)$$

ΔE_V^{\ddagger} can be interpreted as the increase or decrease of the activation energies for viscous flow of the pure solvents due to the presence of ions, i.e., the effective influence of the ions upon the viscous flow of the solvent molecules. Feakins *et al.* [216] have suggested an alternative formulation based on the transition state treatment of the relative viscosity of electrolytic solution. They suggested the following expression:

$$B = \frac{(\phi_{v,2}^0 - \phi_{v,1}^0)}{1000} + \phi_{v,2}^0 \frac{(\Delta \mu_2^{0\ddagger} - \Delta \mu_1^{0\ddagger})}{1000RT} \quad (57)$$

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

$$\Delta \mu_1^{0\ddagger} = \Delta G_1^{0\ddagger} = RT \ln(\eta_0 \phi_{v,1}^0 / h N_A) \quad (58)$$

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:

$$\frac{d(\Delta \mu_2^{0\ddagger})}{dT} = -\Delta S_2^{0\ddagger} \quad (59)$$

$$\Delta H_2^{0\ddagger} = \Delta \mu_2^{0\ddagger} + T \Delta S_2^{0\ddagger} \quad (60)$$

2.4.13. EFFECTS OF SHAPE AND SIZE

Stokes and Mills have dealt in the aspect of shape and size extensively. The ions in solution can be regarded to be rigid spheres suspended in continuum. The hydrodynamic treatment presented by Einstein [195] leads to the equation:

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi \quad (61)$$

where ϕ is the volume fraction occupied by the particles. Modifications of the equation have been proposed by (i) Sinha [217] on the basis of departures from spherical shape and (ii) Vand on the basis of dependence of the flow patterns around the neighboring particles at higher concentrations. However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monatomic cations). Thus, we have from equation (61):

$$2.5\phi = A\sqrt{c} + Bc \quad (62)$$

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

$$2.5\phi_{v,1}^0 = B \quad (63)$$

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

$$B_{\pm} = 2.5\phi_{\pm}^0 = \frac{2.5 \times 4 (\pi R_{\pm}^3 N)}{3 \times 1000} \quad (64)$$

assuming that the ions behave like rigid spheres with a effective radii, R_{\pm} moving in a continuum. R_{\pm} , calculated using the equation (64) should be close to crystallographic radii or corrected Stoke's radii if the ions are scarcely solvated and behave as spherical entities. But, in general, R_{\pm} values of the ions are higher than the crystallographic radii indicating appreciable solvation.

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

$$B_{\pm} = \frac{2.5}{1000(\phi_i + n_b\phi_s)} \quad (65)$$

where ϕ_i is the molar volume of the base ion and ϕ_s , the molar volume of the solvent. The equation (65) has been used by a number of workers to study the nature of solvation and solvation number.

2.4.14. VISCOSITY OF NON-ELECTROLYTIC SOLUTIONS

The equations of Vand [218], Thomas [219] and Moulik proposed mainly to account for the viscosity of the concentrated solutions of bigger spherical particles have been also found to correlate the mixture viscosities of the usual nonelectrolytes [220-222]. These equations are:

$$\text{Vand equation:} \quad \ln \eta_r = \frac{\alpha}{1-Q} = \frac{2.5V_h c}{1-QV_h c} \quad (66)$$

$$\text{Thomas equation:} \quad \eta_r = 1 + 2.5V_h + 10.05cV_h^2 c \quad (67)$$

$$\text{Moulik equation:} \quad \eta^2 = I + Mc^2 \quad (68)$$

where η_r is the relative viscosity, α is constant depending on axial ratios of the particles, Q is the interaction constant, V_h is the molar volume of the solute including rigidly held solvent molecules due to hydration, c is the molar concentration of the solutes; I and M are constants. The viscosity equation proposed by Eyring and coworkers for pure liquids on the basis of pure significant 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:

$$\eta_m = \frac{6N_A h}{\sqrt{2}r_m(V_m - V_{Sm})} \left[\sum_i^n \left\{ 1 - \exp\left(\frac{-\theta_i}{T}\right) \right\}^{-x_i} \right] \exp \left[\frac{a_m E_{Sm} V_{Sm}}{RT(V_m - V_{Sm})} \right] + \frac{V_m - V_{Sm}}{V_m} \left[\sum_i^n \frac{2}{3d_i^2} \left(\frac{m_i kT}{\pi^3} \right)^{\frac{1}{2}} x_i \right] \quad (69)$$

where n is 2 for binary and 3 for ternary liquid mixtures. The mixture parameters, r_m , E_{Sm} , V_m , V_{Sm} and a_m were calculated from the corresponding pure component parameters by using the following relations :

$$r_m = \sum_i^n x_i^2 r_i + \sum_{i \neq j} 2x_i x_j r_{ij} \quad (70)$$

$$E_{Sm} = \sum_i^n x_i^2 E_{Si} + \sum_{i \neq j} 2x_i x_j E_{Sij} \quad (71)$$

$$V_m = \sum_i^n x_i V_i \quad V_{Sm} = \sum_i^n x_i V_{Si} \quad a_m = \sum_i^n x_i a_i \quad (72)$$

$$r_{ij} = (r_i r_j)^{\frac{1}{2}} \text{ and } E_{Sij} = (E_{Si} E_{Sj})^{\frac{1}{2}} \quad (73)$$

$$\theta = \frac{h}{\kappa 2\pi} \left(\frac{b}{m}\right)^{\frac{1}{2}} \quad (74)$$

$$b = 2Z\varepsilon \left[22.106 \left(\frac{N_A \sigma^2}{v_S}\right)^4 - 10.559 \left(\frac{N_A \sigma^3}{v_S}\right)^2 \right] \frac{1}{\sqrt{2}\sigma^2} \left(\frac{N_A \sigma^3}{v_S}\right)^{\frac{2}{3}} \quad (75)$$

here σ and ε are Lennard-Jones potential parameters and the other symbols have their usual significance.

For interpolation and limited extrapolation purposes, the viscosities of ternary mixture can be correlated to a high degree of accuracy in terms of binary contribution by the following equations [223-229].

$$\begin{aligned} \eta_m = \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] + x_2 x_3 [A_{23} + \\ B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] + \\ x_3 x_1 [A_{31} + B_{31}(x_1 - x_2) + \\ C_{31}(x_1 - x_2)^2] \end{aligned} \quad (76a)$$

The correlation of ternary is modified to the following form:

$$\begin{aligned} \eta_m = \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] + x_2 x_3 [A_{23} + \\ B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] + x_3 x_1 [A_{31} + B_{31}(x_1 - x_2) + C_{31}(x_1 - x_2)^2] + \\ A_{123}^* x_1 x_2 x_3 \end{aligned} \quad (76b)$$

However, a better result may be obtained using the following relation:

$$\begin{aligned} \eta_m = \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] + x_2 x_3 [A_{23} + \\ B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] + x_3 x_1 [A_{31} + B_{31}(x_1 - x_2) + C_{31}(x_1 - x_2)^2] + \\ x_1 x_2 x_3 [A_{123} + B_{123} x_1^2 (x_2 - x_3)^2 + \\ C_{123} x_1^3 (x_2 - x_3)^3] \end{aligned} \quad (76c)$$

where A_{12} , B_{12} , C_{12} , A_{23} , B_{23} , C_{23} , A_{31} , B_{31} and C_{31} , are constants for binary mixtures; A_{123} , B_{123} and C_{123} are constants for the ternaries; and the other symbols have their usual significance.

2.4.15. VISCOSITY DEVIATION

Viscosity of liquid mixtures can also provide information for the elucidation of the fundamental behaviour of liquid mixtures, aid in the correlation of mixture viscosities with those of pure components, and may provide a basis for the selection of physico-chemical methods of analysis. Quantitatively, as per the absolute reaction rates theory [230], the deviations in viscosities $\Delta\eta$, from the ideal mixture values can be calculated as:

$$\Delta\eta = \eta - \sum_{i=1}^f (x_i \eta_i) \quad (77)$$

where η is the dynamic viscosities of the mixture and $x_i \eta_i$ are the mole fraction and viscosity of i^{th} component in the mixture, respectively.

2.4.16. GIBBS EXCESS ENERGY OF ACTIVATION FOR VISCOUS FLOW

Quantitatively, the Gibbs excess energy of activation for viscous flow ΔG^E can be calculated as [231]:

$$\Delta G^E = RT \left[\ln \eta V - \sum_{i=1}^f (x_i \ln \eta_i V_i) \right] \quad (78)$$

where η and V are the viscosity and molar volume of the mixture; η_i and V_i are the viscosity and molar volume of i^{th} pure component, respectively.

2.4.17. VISCOUS SYNERGY AND ANTAGONISM

Rheology is the branch of science that studies [232] material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products, [233-242] and to establish their stability and even bioavailability, since it has been firmly established that viscosity influences the drug absorption rate in the body [243, 244]. The study of the viscous behavior of pharmaceutical, foodstuffs, cosmetics or industrial products, etc., is essential for

conforming that their viscosity is appropriate for the contemplated use of the products.

Viscous synergy is the term used in the application to the interaction between the components of a system that causes the total viscosity of the system to be greater than the sum of the viscosities of each component considered separately. In contraposition to viscous synergy, viscous antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each component considered separately. If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction [245, 246].

The method most widely used to analyze the synergic and antagonic behavior of the ternary liquid mixtures used here is that developed by Kaletunc- Gencer and Peleg [247] allowing quantification of the synergic and antagonic interactions taking place in the mixtures involving variable proportions of the constituent components. The method compares the viscosity of the system, determined experimentally, η_{exp} , with the viscosity expected in the absence of interaction, η_{cal} , as defined by the simple mixing rule as:

$$\eta_{cal} = \sum_{i=1}^j w_i \eta_i \quad (79)$$

where w_i and η_i are the fraction by weight and the viscosity of the i^{th} component, measured experimentally and i is an integer.

Accordingly, when $\eta_{exp} > \eta_{cal}$, viscous synergy exists, while, when $\eta_{exp} < \eta_{cal}$, the system is said to exhibit viscous antagonism. The procedure is used when Newtonian fluids are involved, since in non-synergy indices are defined in consequence [248].

In order to secure more comparable viscous synergy results, the so-called synergic interaction index (I_S) as introduced by Howell [249] is taken into account:

$$I_S = \frac{\eta_{exp} - \eta_{mix}}{\eta_{mix}} = \frac{\Delta\eta}{\eta_{mix}} \quad (80)$$

When the values of I_S are negative, it is concerned as antagonic interaction index (I_A).

The method used to analyze volume contraction and expansion is similar to that applied to viscosity, i.e., the density of the mixture is determined experimentally, ρ_{exp} , and a calculation is made for ρ_{cal} based on the expression:

$$\rho_{\text{cal}} = \sum_{i=1}^j w_i \rho_i \quad (81)$$

where ρ_i is the experimentally measured density of the i^{th} component. Other symbols have their usual significance.

Accordingly, when $\rho_{\text{exp}} > \rho_{\text{cal}}$, volume contraction occurs, but when $\rho_{\text{exp}} < \rho_{\text{cal}}$, there is volume expansion in the system.

2.5. ULTRASONIC SPEED

In recent years, there has been considerably progress in the determination of thermodynamic, acoustic and transport properties of working liquids from ultrasonic speeds, density and viscosity measurement. The study of ultrasonic speeds and isentropic compressibilities of liquids, solutions and liquid mixtures provide useful information about molecular interactions, association and dissociation. Various parameters like molar isentropic and isothermal compressibilities, apparent molal compressibility, isentropic compressibility, deviation in isentropic compressibility from ideality, etc. can very well be evaluated and studied from the measurement of ultrasonic speeds and densities in solutions. Isentropic compressibilities play a vital role in characterization of binary and ternary liquid mixtures particularly in cases where partial molar volume data alone fail to provide an unequivocal interpretation of the interactions.

2.5.1. APPARENT MOLAL ISENTROPIC COMPRESSIBILITY

Although for a long time attention has been paid to the apparent molal isentropic compressibility for electrolytes and other compounds in aqueous solutions [249-253] measurements in non-aqueous solvents are still scarce. It has been emphasized by many authors that the apparent molal isentropic compressibility data can be used as a useful parameter in elucidating the solute-

solvent and solute-solute interactions. The most convenient way to measure the compressibility of a solvent/solution is from the speed of sound in it.

The isentropic compressibility (β) of a solvent/solution can be calculated from the Laplace's equation [254-256]:

$$\beta = \frac{1}{u^2 \rho} \quad (82)$$

where ρ is the solution density and u is the ultrasonic speed in the solvent/solution. The isentropic compressibility (β) determined by equation (82) is adiabatic, not an isothermal one, because the local compressions occurring when the ultrasound passes through the solvent/solution are too rapid to allow an escape of the heat produced.

The apparent molal isentropic compressibility (ϕ_k) of the solutions was calculated using the relation:

$$\phi_k = M\beta / \rho + 1000(\beta\rho_0 - \beta_0\rho) / m\rho\rho_0 \quad (83)$$

β_0 is the isentropic compressibility of the solvent mixture, M is the molar mass of the solute and m is the molality of the solution.

The limiting apparent isentropic compressibility ϕ_k^0 may be obtained by extrapolating the plots of ϕ_k versus the square root of the molal concentration of the solutes by the computerized least-square method according to the equation.

$$\phi_k = \phi_k^0 + S_k^* \sqrt{m} \quad (84)$$

The limiting apparent molal isentropic compressibility (ϕ_k^0) and the experimental slope S_k^* can be interpreted in terms of solute-solvent and solute-solute interactions respectively. It is well established that the solutes causing electrostriction leads to the decrease in the compressibility of the solution [256, 257]. This is reflected by the negative values of ϕ_k^0 of electrolytic solutions. Hydrophobic solutes often show negative compressibilities due to the ordering induced by them in the water structure. The compressibility of hydrogen-bonded structure, however, varies

depending on the nature of the hydrogen bonding involved. However, the poor fit of the solute molecules [258, 259] as well as the possibility of flexible hydrogen bond formation appear to be responsible for causing a more compressible environment and hence positive ϕ_K^o values have been reported in aqueous non-electrolyte [260] and non-aqueous non-electrolyte [261] solutions.

2.5.2. DEVIATION IN ISENTROPIC COMPRESSIBILITY

The deviation in isentropic compressibility (ΔK_s) can be calculated using the following equation [262-264]:

$$\Delta K_s = K_s - \sum_{i=1}^j x_i K_{s,i} \quad (85)$$

where x_i , $K_{s,i}$ are the mole fraction and isentropic compressibility of i^{th} component in the mixture, respectively. The observed values of ΔK_s can be qualitatively explained by considering the factors, namely (i) the mutual disruption of associated species present in the pure liquids, (ii) the formation of weak bonds by dipole-induced dipole interaction between unlike molecules, and (iii) geometrical fitting of component molecules into each other structure. The first factor contributes to positive ΔK_s values, whereas the remaining two factors lead to negative ΔK_s values [265]. The resultant values of ΔK_s for the mixtures are due to the net effect of the combination of (i) to (iii) [266].

Moreover, the excess or deviation properties ($V_m^E, \Delta\eta, \Delta G^E$ and ΔK_s) have been fitted to Redlich-Kister [267] polynomial equation using the method of least squares involving the Marquardt algorithm [268] and the binary coefficients, a_i were determined as follows :

$$Y_{i,j}^E = x_1 x_2 \sum_{i=1}^j a_i (x_1 - x_2)^i \quad (86)$$

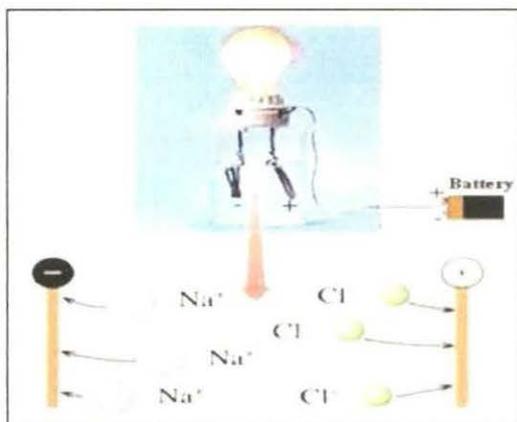
where $Y_{i,j}^E$ refers to an excess or deviation property and x_1 and x_2 are the mole fraction of the solvent 1 and solvent 2, respectively. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation (σ). The standard deviation (σ) was calculated using,

$$\sigma = \left[\frac{(Y_{\text{exp}}^E - Y_{\text{cal}}^E)^2}{n - m} \right]^{\frac{1}{2}} \quad (87)$$

where n is the number of data points and m is the number of coefficients.

2.6. CONDUCTANCE

One of the most precise and direct technique available to determine the extent of the dissociation constants of electrolytes in aqueous, mixed and non-aqueous solvents is the “conductometric method.” Conductance data in conjunction with viscosity measurements, gives much information regarding ion-ion and ion-solvent interaction.



Dissolved Ions Conduct Electricity

The measurements can be made in a variety of solvents over wide ranges of temperature and pressure and in dilute solutions where interionic theories are not applicable. Conductance measurements together with transference number determinations provide an unequivocal method of obtaining single-ion values. The chief limitations, however, is the colligative-like nature of the information obtained.

The studies of conductance measurements were pursued vigorously during the last five decades, both theoretically and experimentally and a number of important theoretical equations have been derived. We shall dwell briefly on some of these aspects in relation to the studies in aqueous, non-aqueous, pure and mixed solvents. The successful application of the Debye-Hückel theory of interionic

attraction was made by Onsager [269] to derive the Kohlrausch's equation representing the molar conductance of an electrolyte. For solutions of a single symmetrical electrolyte the equation is given by:

$$\Lambda = \Lambda_o - S\sqrt{c} \quad (88)$$

where,

$$S = \alpha\Lambda_o + \beta \quad (89)$$

$$\alpha = \frac{(z^2)k}{3(2+\sqrt{2})\epsilon_r kT\sqrt{c}} = \frac{82.406 \times 10^4 z^3}{(\epsilon_r T)^{\frac{3}{2}}} \quad (90a)$$

$$\beta = \frac{z^2 e F k}{3\pi\eta\sqrt{c}} = \frac{82.487 z^3}{\eta\sqrt{\epsilon_r T}} \quad (90b)$$

The equation took no account for the short-range interactions and also of shape or size of the ions in solution. The ions were regarded as rigid charged spheres in an electrostatic and hydrodynamic continuum, i.e., the solvent [270]. In the subsequent years, Pitts (1953) [271] and Fuoss and Onsager (1957) [272] independently worked out the solution of the problem of electrolytic conductance accounting for both long-range and short-range interactions.

However, the Λ_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 was questioned [273,274]. The original Fuoss-Onsager equation was further modified by Fuoss and Hsia [275] who recalculated the relaxation field, retaining the terms which had previously been neglected.

The results of conductance theories can be expressed in a general form:

$$\Lambda = \frac{\Lambda_o - \alpha\Lambda_o\sqrt{c}}{(1+\kappa\alpha)} \left(\frac{1+\kappa\alpha}{\sqrt{2}} \right) - \frac{\beta\sqrt{c}}{(1+\kappa\alpha)} + G(\kappa\alpha) \quad (91)$$

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

$$\Lambda = \Lambda_o - S\sqrt{c} + Ec \ln c + J_1 c - J_2 \sqrt[3]{c} \quad (92)$$

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 discussed elaborately by Fernandez-Prini [276,277]. Further correction of the equation (92) was made by Fuoss and Accascin. They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \ln c + J_1 c + J_2 \sqrt[3]{c} - F\Lambda c \quad (93)$$

where,

$$Fc = \frac{4\pi R^3 N_A}{3} \quad (94)$$

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 [278].

2.6.1. IONIC ASSOCIATION

The equation (93) successfully represents the behaviour of completely dissociated electrolytes. The plot of Λ against \sqrt{c} (limiting Onsager equation) is used to assign the dissociation or association of electrolytes. Thus, if $\Lambda_{0\text{exp}}$ is greater than $\Lambda_{0\text{theo}}$, i.e., if positive deviation occurs (ascribed to short range hard core repulsive interaction between ions), the electrolyte may be regarded as completely dissociated but if negative deviation ($\Lambda_{0\text{exp}} < \Lambda_{0\text{theo}}$) or positive deviation from the Onsager limiting tangent ($\alpha\Lambda_0 + \beta$) occurs, the electrolyte may be regarded to be associated. Here the electrostatic interactions are large so as to cause association between cations and anions. The difference in $\Lambda_{0\text{exp}}$ and $\Lambda_{0\text{theo}}$ would be considerable with increasing association [279].

Conductance measurements help us to determine the values of the ion-pair association constant, K_A for the process:



$$K_A = \frac{(1-\alpha)}{\alpha^2 c \gamma_{\pm}^2} \quad (96)$$

$$\alpha = 1 - \alpha^2 K_A c \gamma_{\pm}^2 \quad (97)$$

where γ_{\pm} is the mean activity coefficient of the free ions at concentration αc

For strongly associated electrolytes, the constant, K_A and Λ_0 has been determined using Fuoss-Kraus equation [280] or Shedlovsky's equation [281].

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda_0} + \frac{K_A}{\Lambda_0^2} \cdot \frac{c \gamma_{\pm}^2 \Lambda}{T(z)} \quad (98)$$

where $T(z) = F(z)$ (Fuoss-Kraus method) and $1/T(z) = S(z)$ (Shedlovsky's method).

$$F(z) = 1 - z(1 - z(1 - \dots))^{\frac{1}{2}} \quad (99a)$$

and

$$\frac{1}{T(z)} = S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \dots \quad (99b)$$

A plot of $T(z)/\Lambda$ against $c \gamma_{\pm}^2 \Lambda / T(z)$ should be a straight line having $1/\Lambda_0$ for its intercept and K_A/Λ_0^2 for its slope. Where K_A is large, there will be considerable uncertainty in the determined values of Λ_0 and K_A from equation (98).

The Fuoss-Hsia [274] conductance equation for associated electrolytes is given by:

$$\Lambda = \Lambda_0 - S\sqrt{\alpha c} + E(\alpha c) \ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{\frac{3}{2}} - K_A \Lambda \gamma_{\pm}^2(\alpha c) \quad (100)$$

The equation was modified by Justice [282]. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

$$\Lambda = \alpha(\Lambda_0 - S\sqrt{\alpha c} + E(\alpha c) \ln(\alpha c) + J_1 R(\alpha c) - J_2 R(\alpha c)^{\frac{3}{2}}) \quad (101)$$

$$\frac{(1-\alpha)}{\alpha^2 c \gamma_{\pm}^2} = K_A \quad (102)$$

$$\ln \gamma_{\pm} = \frac{-k\sqrt{q}}{(1+kR\sqrt{\alpha c})} \quad (103)$$

The conductance parameters are obtained from a least square treatment after setting, $R = q = \frac{e^2}{2\epsilon kT}$ (Bjerrum's critical distance).

According to Justice the method of fixing the J -coefficient by setting, $R = q$ clearly permits a better value of K_A to be obtained. Since the equation (101) is a series expansion truncated at the $c^{3/2}$ term, it would be preferable that the resulting errors be absorbed as much as possible by J_2 rather than by K_A , whose theoretical interest is greater as it contains 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. The following equation has been proposed by Fuoss [283]:

$$K_A = \frac{4\pi N_A \alpha^3}{3000} \exp\left(\frac{e^2}{\alpha \epsilon kT}\right) \quad (104)$$

In some cases, the magnitude of K_A was too small to permit a calculation of a . The distance parameter was finally determined from the more general equation due to Bjerrum [284].

$$K_A = \frac{4\pi N_A \alpha}{1000} \int_{r=a}^{r=q} r^2 \exp\left(\frac{z^2 e^2}{r \epsilon kT}\right) dr \quad (105)$$

The equations neglect specific short-range interactions except for solvation in which the solvated ion can be approximated by a hard sphere model. The method has been successfully utilized by Douheret [285].

2.6.2. ION SIZE PARAMETER AND IONIC ASSOCIATION

For plotting, equation (93) can be rearranged to the 'A' function as:

$$A_1 = A + S\sqrt{c} - Ec \ln c = A_0 + J_1 c + J_2 \sqrt[3]{c} = A_0 + J_1 c \quad (106)$$

with J_2 term omitted.

Thus, a plot of A_0 vs. c gives a straight line with A_0 as intercept and J_1 as slope and 'a' values can be calculated from J_1 values. The 'a' values obtained by this method for DMSO were much smaller than would be expected from sums of crystallographic radii. One of the reasons attributed to it is that ion-solvent interactions are not included in the continuum theory on which the conductance equations are based.

The inclusion of dielectric saturation results in an increase in 'a' values (much in conformity with the crystallographic radii) of alkali metal salts (having ions of high surface charge density) in sulpholane. The viscosity correction leads to a larger value of 'a' [286] but the agreement is still poor. However, little of real physical significance may be attached to the distance of closest approach derived from J_1 [287]. Fuoss [288] in 1975 proposed a new conductance equation. Later he subsequently put forward another conductance equation in 1978 replacing the old one as suggested by Fuoss and co-workers. He classified the ions of electrolytic solutions in one of the three categories.

(i) Ions finding an ion of opposite charge in the first shell of nearest neighbours (contact pairs) with $r_{ij} = a$. The nearest neighbours to a contact pair are the solvent molecules forming a cage around the pairs.

(ii) Ions with overlapping Gurney's co-spheres (solvent separated pairs). For them $r_{ij} = a + ns$, where n is generally 1 but may be 2, 3 etc.; 's' is the diameter of sphere corresponding to the average volume (actual plus free) per solvent molecule.

(iii) Ions finding no other unpaired ion in a surrounding sphere of radius R , the diameter of the co-sphere (unpaired ions). Thermal motions and interionic forces establish a steady state, represented by the following equilibria:



Solvent separated ion-pair Contact ion-pair Neutral molecule

Contact pairs of ionogens may rearrange to neutral molecules $A^+B^- = AB$, e.g., H_3O^+ and CH_3COO^- . Let γ be the fraction of solute present as unpaired ($r > R$) ions. If $c\gamma$ is the concentration of unpaired ion and α is the fraction of paired ions ($r \leq R$), then the concentration of unpaired ion and $c(1-\alpha)(1-\gamma)$ and that of contact pair is $\alpha c(1-\gamma)$.

The equilibrium constants for eq. 107 are:

$$K_R = \frac{(1-\alpha)(1-\gamma)}{c\gamma^2 f^2} \quad (108)$$

$$K_S = \frac{\alpha}{1-\alpha} = \exp\left(\frac{-E_s}{kT}\right) = e^{-\epsilon} \quad (109)$$

Where K_R describes the formation and separation of solvent separated pairs by diffusion in and out of spheres of diameter R around cations and can be calculated by continuum theory; K_S is the constant describing the specific short-range ion-solvent and ion-ion interactions by which contact pairs form and dissociate. E_S is the difference in energy between a pair in the states ($r = R$) and ($r = a$); ϵ is E_S measured in units of kT .

Now,

$$(1-\alpha) = \frac{1}{1+K_S} \quad (110)$$

and the conductometric pairing constant is given by:

$$K_A = \frac{(1-\alpha)}{c\gamma^2 f^2} = \frac{K_R}{1-\alpha} = K_R(1+K_S) \quad (111)$$

The equation determines the concentration, $c\gamma$ of active ions that produce long-range interionic effects. The contact pairs react as dipoles to an external field, X and contribute only to changing current. Both contact pairs and solvent separated pairs are left as virtual dipoles by unpaired ions, their interaction with unpaired ions is, therefore, neglected in calculating long-range effects (activity coefficients, relaxation field ΔX and electrophoresis ($\Delta X \Delta A_e$)). The various patterns can be reproduced by theoretical fractions in the form:

$$A = p \left[A_o \left(\frac{1+\Delta X}{X} \right) + \Delta A_e \right] = p [A_o(1+R_X) + E_L] \quad (112)$$

which is a three parameter equation $A = A(c, A_o, R, E_S), \Delta X / X$ (the relaxation field) and ΔA_e (the electrophoretic counter current) are long range effects due to electrostatic interionic forces and p is the fraction of Gurney co-sphere.

The parameters K_R (or E_S) is a catch-all for all short range effects:

$$p = 1 - \alpha(1 - \gamma) \quad (113)$$

In case of ionogens or for ionophores in solvents of low dielectric constant, α is very near to unity ($-E_S/kT \gg 1$) and the equation becomes:

$$\Lambda = \gamma \left[\Lambda_0 \left(\frac{1 + \Delta X}{X} \right) \right] + \Delta \Lambda_e \quad (114)$$

The equilibrium constant for the effective reaction, $A^+ + B^- + AB$, is then

$$K_A = \frac{(1-\gamma)}{c\gamma^2 f^2} \approx K_R K_S \quad (115)$$

as $K_S \gg 1$. The parameters and the variables are related by the set of equations:

$$\gamma = 1 - \frac{K_R c \gamma^2 f^2}{(1-\alpha)} \quad (116)$$

$$K_R = \left(\frac{4\pi N_A R^3}{3000} \right) \exp\left(\frac{\beta}{R}\right) \quad (117)$$

$$-\ln f = \frac{\beta\kappa}{2(1+\kappa R)}, \quad \beta = \frac{e^2}{\epsilon\kappa T} \quad (118)$$

$$\kappa^2 = 8\pi\beta\gamma\eta = \frac{\pi\beta N_A \gamma c}{125} \quad (119)$$

$$-\varepsilon = \ln \left[\frac{\alpha}{1-\alpha} \right] \quad (120)$$

The details of the calculations are presented in the 1978 paper [288]. The shortcomings of the previous equations have been rectified in the present equation that is also more general than the previous equations and can be used for higher concentrations (0.1 N in aqueous solutions).

2.6.3. LEE-WHEATON CONDUCTANCE EQUATION

As Fuoss 1978 conductance equation contained a boundary condition error, [289, 290] Fuoss introduced a slight modification to his model [291, 292]. According to him, the ion pairs (ion approaching with their Gurney co-sphere) are divided into two categories- contact pairs (with no contribution to conductance) and solvent separated ion pairs (which can only contribute to the net transfer of charge). To rectify the boundary errors contained in Fuoss 1978 conductance equation, Lee-Wheaton [293(a)] in the same year described in the derivation of a new conductance equation, based on the Gurney co-sphere model and henceforth the new equation is

referred to as the Lee-Wheaton equation [293(b)]. The conductance data were analyzed by means of the Lee-Wheaton conductance equation [294] in the form:

$$\Lambda = \alpha_i \left[\Lambda_o \{1 + C_1 \beta \kappa + C_2 (\beta \kappa)^2 + C_3 (\beta \kappa)^3\} - \frac{\rho \kappa}{1 + \kappa R} \left\{ 1 + C_4 \beta \kappa + C_5 (\beta \kappa)^2 + \frac{\kappa R}{12} \right\} \right] \quad (121)$$

The mass action law association [295] is

$$K_{A,c} = \frac{(1 - \alpha_i) \gamma_A}{\alpha_i^2 c_i \gamma_{\pm}^2} \quad (122)$$

and the equation for the mean ionic activity coefficient:

$$\gamma_{\pm} = \exp \left[-\frac{q \kappa}{1 + \kappa R} \right] \quad (123)$$

where C_1 to C_5 are least square fitting coefficients as described by Pethybridge and Taba [296], Λ_o is the limiting molar conductivity, $K_{A,c}$, is the association constant, α_i is the dissociation degree, q is the Bjerrum parameter and γ the activity coefficient and $\beta = 2q$. The distance parameter R is the least distance that two free ions can approach before they merge into ion pair. The Debye parameter κ , the Bjerrum parameter q and ρ are defined by the expressions [296]:

$$\kappa = 16000 \pi N_A q c_i \alpha_i \quad (124)$$

$$q = \frac{e^2}{8 \epsilon_o \epsilon_r \kappa T} \quad (125)$$

$$\rho = \frac{F e}{299.79 \times 3 \pi \eta} \quad (126)$$

where the symbols have their usual significance [297].

The equation (118) was resolved by an iterative procedure. For a definite R value the initial value of Λ_o and $K_{A,c}$, were obtained by the Kraus-Bray method [298]. The parameter Λ_o and $K_{A,c}$, were made to approach gradually their best values by a sequence of alternating linearization and least squares optimizations by the Gauss - Siedel method [299] until satisfying the criterion for convergence. The best value of

a parameter is the one when equation (118) is best fitted to the experimental data corresponding to minimum standard deviation (σ_A) for a sequence of predetermined R value and standard deviation (σ_A) was calculated by the following equation:

$$\sigma_A^2 = \sum_{i=1}^n \frac{[A_{i(calc)} - A_{i(obs)}]^2}{n-m} \quad (127)$$

where n is the number of experimental points and m is the number of fitting parameters. The conductance data were analyzed by fixing the distance of closest approach R with two parameter fit ($m=2$). For the electrolytes with no significant minima observed in the σ_A versus R curves, the R values were arbitrarily preset at the centre to centre distance of solvent-separated pair:

$$R=a+d \quad (128)$$

where $a = r_c^+ + r_c^-$, i.e., the sum of the crystallographic radii of the cation and anion and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The definitions of d and related terms are described in the literature [300]. R was generally varied by a step 0.1 Å and the iterative process was continued with equation (118).

2.6.4. LIMITING EQUIVALENT CONDUCTANCE

The limiting equivalent conductance of an electrolyte can be easily determined from the theoretical equations and experimental observations. At infinite dilutions, the motion of an ion is limited solely by the interactions with the surroundings solvent molecules as the ions are infinitely apart. Under these conditions, the validity of Kohlrausch's law of independent migration of ions is almost axiomatic. Thus:

$$\Lambda_0 = \lambda_0^+ + \lambda_0^- \quad (129a)$$

At present, limiting equivalent conductance is the only function which can be divided into ionic components using experimentally determined transport number of ions, i.e.,

$$\lambda_o^+ = t_+ \Lambda_o \text{ and } \lambda_o^- = t_- \Lambda_o \quad (129b)$$

Thus, from accurate value of λ_o of ions it is possible to separate the contributions due to cations and anions in the solute-solvent interactions. However, accurate transference number determinations are limited to few solvents only.

In the absence of experimentally measured transference numbers it would be useful to develop indirect methods to obtain the ionic limiting equivalent conductances in solvents for which experimental transference numbers are not yet available. Various attempts were made to develop indirect methods to obtain the limiting ionic equivalent conductance, in ionic solvents for which experimental transference numbers are not yet available.

The method has been summarized by Krumgalz [301] and some important points are mentioned as follows:

$$(i) \quad \text{Walden equation [302]} \\ (\lambda_o^\pm)_{\text{water}}^{25} \cdot \eta_{o,\text{water}} = (\lambda_o^\pm)_{\text{acetone}}^{25} \cdot \eta_{o,\text{acetone}} \quad (130)$$

$$(ii) \quad (\lambda_{o,\text{pic}} \cdot \eta_o) = 0.267, \quad \lambda_{o,\text{Et}_4\text{N}^+} \cdot \eta_o = 0.269^{[301,302]} \quad (131) \\ \text{based on } \Lambda_{o,\text{Et}_4\text{N}_{\text{pic}}} = 0.563$$

Walden considered the products to be independent of temperature and solvent. However, the $\Lambda_{o,\text{Et}_4\text{N}_{\text{pic}}}$ values used by Walden were found to differ considerably from the data of subsequent more precise studies and the values of (ii) are considerably different for different solvents.

$$(iii) \quad \lambda_o^{25}(\text{Bu}_4\text{N}^+) = \lambda_o^{25}(\text{Ph}_4\text{B}^-) \quad (132)$$

The equality holds well in nitrobenzene and in mixture with CCl_4 but not realized in methanol, acetonitrile and nitromethane.

$$(iv) \quad \lambda_o^{25}(\text{Bu}_4\text{N}^+) = \lambda_o^{25}(\text{Bu}_4\text{B}^-) [303,304] \quad (133)$$

The method appears to be sound as the negative charge on boron in the Bu_4B^- ion is completely shielded by four inert butyl groups as in the Bu_4N^+ ion while this phenomenon was not observed in case of Ph_4B^- .

(v) The equation suggested by Gill [305] is:

$$\lambda_o^{25}(R_4N^+) = \frac{ZF^2}{6\pi N_A \eta_o [r_i - (0.0103\epsilon_o + r_y)]} \quad (134)$$

where Z and r_i are the charge and crystallographic radius of proper ion, respectively; η_o and ϵ_o are solvent viscosity and dielectric constant of the medium, respectively; r_y = adjustable parameter taken equal to 0.85 Å and 1.13 Å for dipolar non-associated solvents and for hydrogen bonded and other associated solvents respectively.

However, large discrepancies were observed between the experimental and calculated values [301(a)]. In a paper, [301(b)] Krumgalz examined the Gill's approach more critically using conductance data in many solvents and found the method reliable in three solvents e.g. butan-1-ol, acetonitrile and nitromethane.

$$(vi) \quad \lambda_o^{25} [(i-Am)_3 BuN^+] = \lambda_o^{25} (Ph_4B^-)^{3051} \quad (135)$$

It has been found from transference number measurements that the $\lambda_o^{25} [(i-Am)_3 BuN^+]$ and $\lambda_o^{25} (Ph_4B^-)$ values differ from one another by 1%.

$$(vii) \quad \lambda_o^{25} (Ph_4B^-) = 1.01 \lambda_o^{25} [(i-Am)_4 B^-]^{306} \quad (136)$$

The value is found to be true for various organic solvents.

Krumgalz suggested a method for determining the limiting ion conductance in organic solvents. The method is based on the fact that large tetraalkyl (aryl) onium ions are not solvated in organic solvents due to the extremely weak electrostatic interactions between solvent molecules and the large ions with low surface charge density and this phenomenon can be utilized as a suitable model for apportioning Λ_o values into ionic components for non-aqueous electrolytic solutions.

Considering the motion of solvated ion in an electrostatic field as a whole, it is possible to calculate the radius of the moving particle by the Stokes equation:

$$r_s = \frac{|z|F^2}{A\pi\eta_o\lambda_o^{\pm}} \quad (137)$$

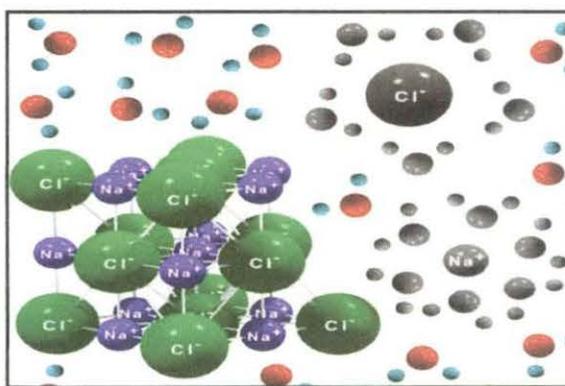
where A is a coefficient varying from 6 (in the case of perfect sticking) to 4 (in case of perfect slipping). Since the r_s values, the real dimension of the non-solvated tetraalkyl (aryl) onium ions must be constant, we have:

$$\lambda_o^\pm \eta_o = \text{constant} \quad (138)$$

This relation has been verified using λ_o^\pm values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i\text{-Am}_4\text{B}^-$, Ph_4As^+ , Ph_4B^- ions and for tetraalkylammonium cation starting with Et_4N^+ . The relationship can be well utilized to determine λ_o^\pm of ions in other organic solvents from the determined λ_o values.

2.6.5. SOLVATION

Various types of interactions exist between the ions in solutions. These interactions result in the orientation of the solvent molecules towards the ion. The number of solvent molecules that are involved in the solvation of the ion is called solvation number. If the solvent is water, this is called hydration number. Solvation region can be classified as primary and secondary solvation regions. Here we are concerned with the primary solvation region. The primary solvation number is defined as the number of solvent molecules which surrender their own translational freedom and remain with the ion, tightly bound, as it moves around, or the number of solvent molecules which are aligned in the force field of the ion.



Solvation phenomena

If the limiting conductance of the ion i of charge Z_i is known, the effective radius of the solvated ion can be determined from Stokes' law. The volume of the solvation shell is given by the equation.

$$V_s = \left(\frac{4\pi}{3} \right) (r_s^3 - r_c^3) \quad (139)$$

where r_c is the crystallographic radius of the ion. The solvation number n_s would then be obtained from

$$n_s = \frac{V_s}{V_0} \quad (140)$$

Assuming Stokes' relation to hold well, the ionic solvated volume can be obtained, because of the packing effects [308], from

$$V_s^o = 4.35r_s^3 \quad (141)$$

where V_s^o is expressed in mol/lit. and r_s in angstroms. However, this method is not applicable to ions of medium size though a number of empirical and theoretical corrections [309-312] have been suggested in order to apply it to most of the ions.

2.6.6. STOKES' LAW AND WALDEN'S RULE

The starting point for most evaluations of ionic conductances is Stokes' law that states that the limiting Walden product (the limiting ionic conductance-solvent viscosity product) for any singly charged, spherical ion is as function only of the ionic radius and thus, under normal conditions, is constant. The limiting conductances λ_i^o of a spherical ion of radius R_i moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

$$\lambda_i^o = \frac{|z_i e| e F}{6\pi\eta_o R_i} = \frac{0.819|z_i|}{\eta_o R_i} \quad (142)$$

where η_o = macroscopic viscosity by the solvent in poise, R_i is in angstroms. If the radius R_i is assumed to be the same in every organic solvent, as would be the case, in case of bulky organic ions, we get:

$$\lambda_o^i \eta_o = \frac{0.819 z_i}{R_i} = \text{constant} \quad (143)$$

This is known as the Walden rule [313]. The effective radii obtained using this equation can be used to estimate the solvation numbers. However, Stokes' radii failed to give the effective size of the solvated ions for small ions.

Robinson and Stokes [314], Nightingale [194] and others [315-317] have suggested a method of correcting the radii. The tetraalkylammonium ions were assumed to be not solvated and by plotting the Stokes' radii against the crystal radii of those large ions, a calibration curve was obtained for each solvent. However, the experimental results indicate that the method is incorrect as the method is based on the wrong assumption of the invariance of Walden's product with temperature. The idea of microscopic viscosity [318] was invoked without much success [319, 320] but it has been found that:

$$\lambda_o^i \eta_o = \text{constant} \quad (144)$$

where p is usually 0.7 for alkali metal or halide ions and $p = 1$ for the large ions [321, 322]. Gill [323] has pointed out the inapplicability of the Zwanzig theory [324] of dielectric friction for some ions in non-aqueous and mixed solvents and has proposed an empirical modification of Stokes' Law accounting for the dielectric friction effect quantitatively and predicts actual solvated radii of ions in solution. This equation can be written as:

$$r_i = \frac{|z| F^2}{6\pi N_A \eta_o \lambda_o^i} + 0.0103D + r_y \quad (145)$$

where r_i is the actual solvated radius of the ion in solution and r_y is an empirical constant dependent on the nature of the solvent [323, 324].

The dependence of Walden product on the dielectric constant led Fuoss to consider the effect of the electrostatic forces on the hydrodynamics of the system. Considering the excess frictional resistance caused by the dielectric relaxation in the solvent caused by ionic motion, Fuoss proposed the relation:

$$\lambda_o^i = \frac{Fe|z_i|}{6\pi R_\infty} \left(\frac{1+A}{\epsilon R_\infty^2} \right) \quad (146)$$

$$\text{or,} \quad R_i = R_\infty + \frac{R}{\infty} \quad (147)$$

where R_∞ is the hydrodynamic radius of the ion in a hypothetical medium of dielectric constant where all electrostatic forces vanish and A is an empirical constant.

Boyd [281] gave the expression:

$$\lambda_o^i = \frac{Fe|z_i|}{6\pi\eta_o r_i \left[\left(1 + \frac{2}{27} \pi\eta_o \right) \cdot \left(\frac{z_i^2 e^2 \tau}{r_i^4 \epsilon_o} \right) \right]} \quad (148)$$

by considering the effect of dielectric relaxation in ionic motion; τ is the Debye relaxation time for the solvent dipoles. Zwanzig [311] treated the ion as a rigid sphere of radius r_i moving with a steady state viscosity, V_i through a viscous incompressible dielectric continuum. The conductance equation suggested by Zwanzig is:

$$\lambda_o^i = \frac{z_i^2 e F}{\left[A_v \pi \eta_o r_i + A_D \left\{ \frac{z_i^2 e^2 (\epsilon_r^\circ - \epsilon_r^\infty) \tau}{\epsilon_r^\circ (2\epsilon_r^\circ + 1) r_i^3} \right\} \right]} \quad (149)$$

where ϵ_r° and ϵ_r^∞ are the static and limiting high frequency (optical) dielectric constants. $A_v = 6$ and $A_D = 3/8$ for perfect sticking and $A_v = 4$ and $A_D = 3/4$ for perfect slipping. It has been found that Born's and Zwanzig's equations are very similar and both may be written in the form:

$$\lambda_o^i = \frac{A r_i^3}{r_i^4 + B} \quad (150)$$

The theory predicts [325] that λ_o^i passes through a maximum of $27^{\frac{1}{4}} A / 4B^{\frac{1}{4}}$ at $r_i = (3B)^{1/4}$. The phenomenon of maximum conductance is well known. The relationship holds good to a reasonable extent for cations in aprotic solvents but fails in case of anions. The conductance, however, falls off rather more rapidly than predicted with increasing radius. For comparison with results in different solvents, the equation (149) can be rearranged as [326]:

$$\frac{z_i^2 eF}{\lambda_o^i \eta_o} = \frac{A_V \pi r_i + A_D z_i^2}{r_i^3} \cdot \frac{e^2 (\epsilon_r^o - \epsilon_r^\infty)}{\epsilon_r^o (2\epsilon_r^o + 1)} \left(\frac{\tau}{\eta_o} \right) \quad (151)$$

$$L^* = A_V \pi r_i + \frac{A_D z_i^2}{r_i^3 P^*} \quad (152)$$

In order to test Zwanzig's theory, the equation (152) was applied for Me_4N^+ and Et_4N^+ in pure aprotic solvents like methanol, ethanol, acetonitrile, butanol and pentanol [325-330]. Plots of L^* against the solvent function P^* were found to be straight line. But, the radii calculated from the intercepts and slopes are far apart from equal except in some cases where moderate success is noted. It is noted that relaxation effect is not the predominant factor affecting ionic mobility and these mobility differences could be explained quantitatively if the microscopic properties of the solvent, dipole moment and free electron pairs were considered the predominant factors in the deviation from the Stokes' law.

It is found that the Zwanzig's theory is successful for large organic cations in aprotic media where solvation is likely to be minimum and where viscous friction predominates over that caused by dielectric relaxation. The theory breaks down whenever the dielectric relaxation term becomes large, i.e., for solvents of high P^* and for ions of small r_i . Like any continuum theory Zwanzig has the inherent weakness of its inability to account for the structural features, [325] e.g.,

(i) It does not allow for any correlation in the orientation of the solvent molecules as the ion passes by and this may be the reason why the equation is not applicable to the hydrogen-bonded solvents [327].

(ii) The theory does not distinguish between positively and negatively charged ions and therefore, cannot explain why certain anions in dipolar aprotic media possess considerably higher molar concentrations than the fastest cations.

The Walden product in case of mixed solvents does not show any constancy but it shows a maximum in case of DMF + water and DMA + water [325-335] mixtures and other aqueous binary mixtures [336-340]. To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts [340] have been made with different models for ion-solvent interactions but no satisfactory expression has been derived taking into account all types of ion-solvent interactions because

(i) it is difficult to include all types of interactions between ions as well as solvents in a single mathematical expression, and

(ii) it is not possible to account for some specific properties of different kinds of ions and solvent molecules.

Ions moving in a dielectric medium experience a frictional force due to dielectric loss arising from ion-solvent interactions with the hydrodynamic force. Though Zwanzig's expression accounts for a change in Walden product with solvent composition but does not account for the maxima. According to Hemmes [341] the major deviations in the Walden products are due to the variation in the electrochemical equilibrium between ions and solvent molecules of mixed polar solvent composition. In cases where more than one types of solvated complexes are formed, there should be a maximum and/or a minimum in the Walden product. This is supported from experimental observations. Hubbard and Onsager [342] have developed the kinetic theory of ion-solvent interaction within the framework of continuum mechanics where the concept of kinetic polarization deficiency has been introduced. However, quantitative expression is still awaited. Further, improvements [343, 344] naturally must be in terms of (i) sophisticated treatment of dielectric saturation, (ii) specific structural effects involving ion-solvent interactions. From the discussion, it is apparent that the problem of molecular interactions is intriguing as well as interesting. It is desirable to explore this problem using different experimental techniques. We have, therefore, utilized four

important methods, viz., volumetric, viscometric, interferometric and conductometric for the physico-chemical studies in different solvent media.

2.6.7. THERMODYNAMICS OF ION-PAIR FORMATION

The standard Gibbs energy changes (ΔG°) for the ion- association process can be calculated from the equation

$$\Delta G^\circ = -RT \ln K_A \quad (153)$$

The values of the standard enthalpy change, ΔH° and the standard entropy change, ΔS° , can be evaluated from the temperature dependence of values as follows,

$$\Delta H^\circ = -T^2 \left[\frac{d(\Delta G^\circ / T)}{dT} \right]_P \quad (154)$$

$$\Delta S^\circ = -T^2 \left[\frac{d(\Delta G^\circ)}{dT} \right]_P \quad (155)$$

The values can be fitted with the help of a polynomial of the type:

$$\Delta G^\circ = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \quad (156)$$

And the coefficients of the fits can be compiled together with the $\sigma\sigma$ % values of the fits. The standard values at 298.15 K are then:

$$\Delta G_{298.15}^\circ = c_0 \quad (157)$$

$$\Delta S_{298.15}^\circ = c_1 \quad (158)$$

$$\Delta H_{298.15}^\circ = c_0 + 298.15c_1 \quad (159)$$

The main factors which govern the standard entropy of ion-association of electrolytes are: (i) the size and shape of the ions, (ii) charge density on the ions, (iii) electrostriction of the solvent molecules around the ions, and (iv) penetration of the solvent molecules inside the space of the ions, and the influence of these factors are discussed later.

The non-columbic part of the Gibbs energy ΔG° can also be calculated using the following equation:

$$\Delta G^\circ = N_A W_{\pm} \quad (160)$$

$$K_A = \left(\frac{4\pi N_A}{1000} \right) \int_a^R r^2 \exp\left(\frac{2q}{r} - \frac{W_{\pm}}{kT} \right) dr \quad (161)$$

where the symbols have their usual significance.

The quantity $2q/r$ is Columbic part of the interionic mean force potential and W_{\pm} is its non-columbic part.

2.6.8. SOLVATION MODELS—SOME RECENT TRENDS

The interactions between particles in chemistry have been based upon empirical laws- principally on Coulomb's law. This is also the basis of the attractive part of the potential energy used in the SchÖdinger equation. Quantum mechanical approach for ion-water interactions was begun by Clementi in 1970. A quantum mechanical approach to solvation can provide information on the energy of the individual ion-water interactions provided it is relevant to solution chemistry, because it concerns potential energy rather than the entropic aspect of solvation. Another problem in quantum approach is the mobility of ions in solution affecting solvation number and coordination number. However, the Clementi calculations concerned stationary models and cannot have much to do with the dynamic solvation numbers. Covalent bond formation enters little into the aqueous calculations; however, with organic solvents the quantum mechanical approaches to bonding may be essential. The trend pointing to the future is thus the molecular dynamics technique. In molecular dynamic approach, a limited number of ions and molecules and Newtonian mechanics of movement of all particles in solution is concerned. The foundation of such a approach is the knowledge of the intermolecular energy of interactions between a pair of particles. Computer simulation approaches may be useful in this regard and the last decade (1990-2000) witnessed some interesting trends in the development of solvation models and computer software. Based on a collection of experimental free energy of solvation data, C.J. Cramer, D.G. Truhlar and co-workers from the University of Minnesota, U.S.A. constructed a series of solvation models (SM1-SM5 series) to predict and calculate the free energy of solvation of a chemical compound [345-349]. These models are applicable to virtually any substance composed of H, C, N, O, F, P, S, Cl, Br

and/or I. The only input data required are, molecular formula, geometry, refractive index, surface tension, Abraham's a (acidity parameter) and b (basicity parameter) values, and, in the latest models, the dielectric constants. The advantage of models like SM5 series is that they can be used to predict the free energy of self-solvation to better than 1 KJ/mole. These are especially useful when other methods are not available. One can also analyze factors like electrostatics, dispersion, hydrogen bonding, etc. using these tools. They are also relatively inexpensive and available in easy to use computer codes.

Galindo *et al.* [350,351] have developed Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to model the thermodynamics and phase equilibrium of electrolytic aqueous solutions. The water molecules are modeled as hard spheres with four short-range attractive sites to account for the hydrogen-bond interactions. The electrolyte is modeled as two hard spheres of different diameter to describe the anion and cation. The Debye-Hückel and mean spherical approximations are used to describe the interactions. Good agreement with experimental data is found for a number of aqueous electrolyte solutions. The relative permittivity becomes very close to unity, especially when the mean spherical approximation is used, indicating a good description of the solvent. E. Bosch *et al.* [352] of the University of Barcelona, Spain, have compared several "Preferential Solvation Models" specially for describing the polarity of dipolar hydrogen bond acceptor-cosolvent mixture.

2.6.9. CONDUCTANCE-SOME RECENT TRENDS

Recently Blum, Turq and coworkers [353,354] have developed a mean spherical approximation (MSA) version of conductivity equations. Their theory starts from the same continuity and hydrodynamic equations used in the more classical treatment; however, an important difference exists in the use of MSA expressions for the equilibrium and structural properties of the electrolytic solutions. Although the differences in the derivation of the classical and MSA conductivity theories seem to be relatively small, it has been claimed that the performance of MSA equation is better with a much wider concentration range than that covered by the classical equations. However, no through study of the performance of the new equation at the experimental uncertainty level of

conductivity measurement is yet available in the literature, except the study by Bianchi *et al.* [355]. They compared the results obtained using the old and new equations in order to evaluate their capacity to describe the conductivity of different electrolytic solutions. In 2000, Chandra and Bagchi [356] developed a new microscopic approach to ionic conductance and viscosity based on the mode coupling theory. Their study gives microscopic expressions of conductance and viscosity in terms of static and dynamic structural factors of charge and number density of the electrolytic solutions. They claim that their new equation is applicable at low as well as at high concentrations and it describes the cross over from low to high concentration smoothly. Debye-Huckel, Onsager and Falkenhagen expressions can be derived from this self-consistent theory at very low concentrations. For conductance, the agreement seems to be satisfactory up to 1 (M).

2.7. REFRACTIVE INDEX

Optical data (refractive index) of electrolyte mixtures 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 other properties [357].

The ratio of the speed of light in a vacuum to the speed of light in another substance is defined as the index of refraction (n_D) for the substance.

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

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

$$\frac{V_A}{V_B} = \frac{\sin\theta_A}{\sin\theta_B} = \frac{n_B}{n_A} \quad (162)$$

Thus, it is not necessary to measure the speed of light in a sample in order to determine its index of refraction. Instead, by measuring the angle of refraction, and knowing the index of refraction of the layer that is in contact with the sample, it is 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 [358] by using, n_D experimental data according to the following expression

$$R = [(n_D^2 - 1)/n_D^2 + 2](M/\rho) \quad (163)$$

where M is the mean molecular weight of the mixture and ρ is the mixture density. n_D can be expressed as the following:

$$n_D = [(2A + 1)/(1 - A)]^{0.5} \quad (164)$$

where A is given by:

$$A = \left[\left\{ \frac{(n_1^2 - 1)}{(n_1^2 + 2)} (1/\rho_1) \right\} - \left\{ \frac{(n_1^2 - 1)}{(n_1^2 + 2)} (w_2/\rho_1) \right\} + \left\{ \frac{(n_2^2 - 1)}{(n_2^2 + 2)} (w_2/\rho_2) \right\} \right] \rho \quad (165)$$

where n_1 and n_2 are the pure component refractive indices, w_j the weight fraction, ρ the mixture density, and ρ_1 and ρ_2 the pure component densities.

The molar refractivity deviation is calculated by the following expression:

$$\Delta R = R - \phi_1 R_1 - \phi_2 R_2 \quad (166)$$

where ϕ_1 and ϕ_2 are volume fractions and R , R_1 , and R_2 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:

$$\Delta n_D = n_D - x_1 n_{D1} - x_2 n_{D2} \quad (167)$$

where Δn_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 fraction.

The computed deviations of refractive indices of the binary mixtures are fitted using the following Redlich-Kister expression [359].

$$\Delta n_{Dew} = w_e w_w \sum_{p=0}^S B_p (w_e w_w)^p \quad (168)$$

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:

$$n_{Ds,sol} = n_{Dsol} + \sum_{i=1}^N A_i m^i \quad (169)$$

where $n_{Ds,sol}$ is the refractive index of the salt + solvent system and n_{Dsol} is the refractive index of the solvent respectively, m is the molality of the salt in the solution, A_i are the fitting parameters, and N is the number of terms in the polynomial.

For the ternary systems of the salt + solvent-1 + solvent-2 solutions a polynomial expansion [360]. Similar to that obtained for the salt + solvent solutions was used to represent ternary refractive indices:

$$n_D = n_{Dw} + \sum_{l=1}^P C_l m^l \quad (170)$$

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

There is no general rule that states how to calculate a refractivity deviation function. However, the molar refractivity is isomorphic to a volume for which the ideal behavior may be expressed in terms of mole fraction: in this case smaller deviations occur but data are more scattered because of the higher sensitivity of the expression to rounding errors in the mole fraction. For the sake of completeness, both calculations of refractivity deviation function, molar refractivity deviation was fitted to a Redlich and Kister-type expression and the adjustable parameters and the

relevant standard deviation δ are calculated for the expression in terms of volume fractions and in terms of mole fractions, respectively.

From the discussion, it is apparent that the problem of molecular interactions is intriguing as well as interesting. It is desirable to attack this problem using different experimental techniques. We have, therefore, utilized five important methods, *viz.*, volumetric, viscometric, interferometric, conductometric and refractometric for the physico-chemical studies in different solvent systems.

REFERENCES

- [1]. (a) J. D. Pandey and A. Yasmin, *Proc. Ind. Acad. Sci.* 109 (1997) 289.
(b) J. D. Pandey, Y. Akhtar and A. K. Sharma, *Ind. J. Chem.* 37A (1998) 1094.
- [2]. J. I. Kim, *J. Phys. Chem.* 82 (1978) 191.
- [3]. W. Kemp, *Organic spectroscopy*, 3rd (ELBS) Ed., Macmillan Press, Hampshire, U.K., (1993).
- [4]. H.S. Harned, B.B. Owen, *The physical chemistry of Electrolytes Solutions*, 3rd ed., Reinhold Publishing Co., New work, (1958).
- [5]. J.E. Gordon, *The Organic Chemistry of Electrolyte Solutions*, Wiley Interscience, (1975).
- [6]. B.E. Conway, R.G. Barradas, *Chemical Physics of Ionic Solutions*, Wiley, New York (1966).
- [7]. D.T. Richens, *The Chemistry of Aqua Ions*; Wiley, New York (1997).
- [8]. K. Ibuki, M. Nakahara, *J. Phys. Chem.* 94 (1990) 8370.
- [9]. A. Henni, J.H. Jonathan, T. Paitoon, A. Chakma, *J. Chem. Eng. Data.* 48 (2003) 1062.
- [10]. J. Burgess, *Metal Ions in Solutions*; Ellis Horwood, New York (1978).
- [11]. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York (1958).
- [12]. J. J. Lagowski, *The Chemistry of Non-Aqueous Solvents*, Academic, New York (1966).
- [13]. B.E. Conway, R.G. Barradas, *Chemical Physics of Ionic Solutions*, Wiley, New York (1966).
- [14]. J.S. Muishead-Gould, K.J. Laidler, *Chemical Physics of Ionic Solutions*, Wiley, New York (1966).
- [15]. J.F. Coetzee, C.D. Ritchie, *Solute-Solvent Interactions*, Marcel Dekker, New York (1969).
- [16]. R.G. Bates, *J. Electroanal. Chem.* 29 (1972) 1.
- [17]. G.S. Kell, C.M. Daries, J. Jarynski, *Water and Aqueous Solutions, Structure, Thermodynamics and Transport process*, Wiley, New York (1972).

- [18]. E.S. Amis, J.F. Hinton, *Solvent effects on Chemical Phenomena*, Academic, New York (1973).
- [19]. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York (1973).
- [20]. J.E. Gordon, *The Organic Chemistry of Electrolyte Solutions*, Wiley- Interscience, New York (1975).
- [21]. F. Franks, *Physico-Chemical processes in Mixed Aqueous Solvents*, Heinemann, London (1967).
- [22]. F. Franks, *Water—A Comprehensive Treatise*, Plenum Press, New York (1973).
- [23]. V. Gutmann, *Electrochim. Acta.* 21 (1967) 661.
- [24]. U. Mayer, V. Gutmann, *Adv. Inorg.Chem. Radiochem.* 17 (1975) 189.
- [25]. R.G. Pearson, *Hard and Soft Acids and Bases*, Strondsburgh (1973).
- [26]. G.R. Behbehani, M. Dillon, J. Symth, W.E. Waghorne, *J. Solution Chem.* 31 (2002) 811.
- [27]. C. Guha, J.M. Chakraborty, S. Karanjai, B. Das, *J. Phys. Chem. B.* 107 (2003) 12814.
- [28]. L. Jones, J.F. Devonshire, *A. F. Proc. Royal Soc.* (1937).
- [29]. I. Prigogine, S. Garikian, *Physica.* 16 (1950) 239.
- [30]. I. Prigogine, A. Belleman, *J. Phys. Chem.* 21 (1953) 561.
- [31]. A.J. Treszczanowicz, G.C. Benson, *Fluid Phase Equilib.* 23 (1985) 117.
- [32]. Wen-Lu Weng, *J. Chem. Eng. Data.* 45 (2000) 606.
- [33]. P.S. Nikam, S.J. Kharat, *J. Chem. Eng. Data.* 50 (2005) 455.
- [34]. R.P. Rastogi, J. Nath, J. Mishra, *J. Phys. Chem.* 71 (1967) 1277.
- [35]. K.S. Pitzer, G. Mayora, *J. Phys. Chem.* 77 (1973) 2300.
- [36]. D. Cook, L-Higgins, *H. C. Proc. Royal. Soc.* A209 (1951) 28.
- [37]. J.S. Rowlinson, *Liquid and Liquid Mixtures*, Scientific Publications, London (1959).
- [38]. J.S. Rowlinson, *Proc. Royal. Soc.* A214 (1952) 192.
- [39]. J.L. Lebowitz, J. S. Rowlinson, *J. Chem. Phys.* 41 (1964) 133.
- [40]. J.A. Barker, D.J. Henderson, *J. Phys. Chem.* 47 (1967) 4714.
- [41]. P.J. Flory, R.A. Orwoll, A. Vrij, *J. Am. Chem. Soc.* 86 (1964) 3507.
- [42]. P.J. Flory, A. Abe, *J. Am. Chem. Soc.* 86 (1964) 3563.
- [43]. P.J. Flory, *J. Am. Chem. Soc.* 87 (1965) 1833.

- [44]. D. Patterson, G. Delmas, *Discuss. Faraday Soc.* 49 (1970) 98.
- [45]. A. Heintz, *Ber. Bunsenges. J. Phys.chem.* 89 (1985) 172.
- [46]. H. Funke, M. Wetzel, A. Heintz, *J. Pure. Appl. Chem.* 61 (1989) 1429.
- [47]. A. Heintz, D. Papaioannou, *Thermochimica Acta.* 310 (1998) 69.
- [48]. A. Heintz, P.K. Naicker, S.P. Verevkin, R. Pfestrof, B. Bunsenges, *Phys. Chem.* 102 (1998) 953.
- [49]. S. Villa, N. Riesco, I. Garcia de la Fuente, J.A. Gonzalz, J.C. Cobos, *Fluid Phase Equilib.* 216 (2004) 123.
- [50]. S.L. Oswal, *J. Thermochim. Acta.* 425 (2005) 59.
- [51]. A. Pineiro, A. Amigo, R. Bravo, P. Brocos, *Fluid Phase Equilib.* 173 (2000) 211.
- [52]. A. Pineiro, *Fluid Phase Equilib.* 216 (2004) 245.
- [53]. M. Gepert, B. Stachowska, *J. Sol. Chem.* 35 (2006) 425.
- [54]. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolyte Solutions*, Reinhold Publishing Corporation, New York (1943).
- [55]. C. Tanford, *Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Wiley-Interscience, New York (1980).
- [56]. E. Vikingstad, *Aggregation Process in Solutions*, Elsevier, Amsterdam (1983).
- [57]. J.E. Desnoyers, M. Arel, H. Perron, C. Jolicoenn, *J. Phys. Chem.* 73 (1969) 3346.
- [58]. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York (1973).
- [59]. D.K. Hazra, B. Das, *J. Chem. Eng. Data.* 36 (1991) 403.
- [60]. D.O. Masson, *Phil. Mag.* 8 (1929) 218.
- [61]. O. Redlich, D.M. Meyer, *Chem. Rev.* 64 (1964) 221.
- [62]. B.B. Owen, S.R. Brinkley, *J. Ann. N. Y. Acad. Sci.* 51 (1949) 753.
- [63]. F.J. Millero, *Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes*, Wiley- Interscience, New York (1972).
- [64]. R. Gopal, M.A. Siddiqi, *J. Phys. Chem.* 73 (1969) 3390.
- [65]. J. Padova, I. Abrahmen, *J. Phys. Chem.* 71 (1967) 2112.
- [66]. R. Gopal, D.K. Agarwal, R. Kumar, *Bull. Chem. Soc. Jpn.* 46 (1973) 1973.
- [67]. R. Gopal, P.P. Rastogi, *Z. Phys. Chem. (N.F.)* 69 (1970) 1.
- [68]. B. Das, D.K. Hazra, *J. Chem. Eng. Data.* 36 (1991) 403.
- [69]. L. G. Hepler, *Can. J. Chem.* 47 (1969) 4617.

- [70]. L.G. Hepler, J.M. Stokes, R.H. Stokes, *Trans. Faraday Soc.* 61 (1965) 20.
- [71]. F.H. Spedding, M.J. Pikal, B.O. Ayres, *J. Phys. Chem.* 70 (1966) 2440.
- [72]. L.A. Dunn, *Trans. Faraday Soc.* 64 (1968) 2951.
- [73]. R. Pogue, G. Atkinson, *J. Chem. Eng. Data.* 33 (1988) 370.
- [74]. B.E. Conway, R.E. Verral, J.E. Desnoyers, *Trans. Faraday Soc.* 62 (1966) 2738.
- [75]. K. Uosaki, Y. Koudo, N. Tokura, *Bull. Chem. Soc. Jpn.* 45 (1972) 871.
- [76]. B.S. Krungalz, *J. Chem. Soc. Faraday Trans. I.* 76 (1980) 1887.
- [77]. A.W. Quin, D.F. Hoffmann, P. Munk, *J. Chem. Eng. Data.* 37 (1992) 55.
- [78]. Z. Atik, *J. Sol. Chem.* 33 (2004) 1447.
- [79]. R.H. Stokes, R. Mills, *Viscosity of Electrolytes and Related Properties*, Pergamon, Great Britain (1965).
- [80]. F. Vaslow, *Water and Aqueous Solutions*, Wiley- Interscience, New York (1972).
- [81]. E.N.da C. Andrade, *Phil. Mag.* 17 (1934) 698.
- [82]. J. Frankel, *Kinetic Theory of Liquids*, Dover Publications, New York (1955).
- [83]. R. Furth, *Proc. Camb. Phil. Soc.* 37 (1941) 281.
- [84]. R. Furth, *Proc. Camb. Phil. Soc.* 37 (1941) 252.
- [85]. R.H. Ewell, H. Eyring, *J. Chem. Phys.* 5 (1937) 726.
- [86]. F.C. Auluck, S.C. De, D.S. Kothari, *Proc. Natl. Inst. Sci.* 10(4) (1944) 397.
- [87]. R. Eisenschitz, *Proc. Roy. Soc.* 215A (1952) 29.
- [88]. J.E. Lennard-Jones, A.F. Devonshire, *Proc. Roy. Soc.* 163A (1937) 53.
- [89]. J.E. Lennard-Jones, A.F. Devonshire, *Proc. Roy. Soc.* 165A (1938) 1.
- [90]. J.A. Pople, *Proc. Roy. Soc.* 215A (1952) 67.
- [91]. R. Eisenchitz, *Proc. Phys. Soc.* 62A (1949) 41.
- [92]. J.G. Kirkwood, *J. Chem. Phys.* 14 (1946) 180.
- [93]. J.G. Kirkwood, *Theory of Liquids*, Science Publishers, New York (1968).
- [94]. J.E. Mayer, E. Montroll, *J. Chem. Phys.* 9 (1941) 2.
- [95]. J.E. Mayer, *J. Chem. Phys.* 15 (1947) 187.
- [96]. M. Born, H.S. Green, *Proc. Roy. Soc.* 188A (1946) 10.
- [97]. M. Born, H.S. Green, *Proc. Roy. Soc.* 190A (1947) 455.
- [98]. J.G. Kirkwood, F.P. Buff, M.S. Green, *J. Chem. Phys.* 17 (1949) 988.
- [99]. J.G. Kirkwood, *J. Chem. Phys.* 3 (1935) 300.
- [100]. J.G. Kirkwood, *J. Chem. Phys.* 7 (1939) 919.

- [101]. J.G. Kirkwood, Z.W. Salsburg, *Faraday Soc. Discuss.* 15 (1953) 25.
- [102]. J.G. Kirkwood, E.M. Boggs, *J. Chem. Phys.* 10 (1942) 394.
- [103]. J.G. Kirkwood, E.K. Maun, B.J. Alder, *J. Chem. Phys.* 18 (1950) 1040.
- [104]. J.G. Kirkwood, V.A. Lewinson, B.J. Alder, *J. Chem. Phys.* 20 (1952) 929.
- [105]. R.W. Zwanzig, J.G. Kirkwood, K.F. Stripp, I. Oppenheim, *J. Chem. Phys.* 21 (1953) 2050.
- [106]. S.A. Rice, P. Gray, *The Statistical Mechanics of Simple Liquids. An introduction to the theory of equilibrium and Non-equilibrium Phenomena*, Interscience Publishers, New York (1965).
- [107]. S.A. Rice, *The Kinetic Theory of Dense Fluids, Colloquium Lecturers in Pure and Applied Science*, No. 9 Mobil Oil Corp. Research Lab., Dallas, Texas (1964).
- [108]. S.A. Rice, A.R. Allnatt, *J. Chem. Phys.* 34 (1961) 2144.
- [109]. A.R. Allnatt, S.A. Rice, *J. Chem. Phys.* 34 (1961) 2156.
- [110]. H.C. Longuet-Higgins, J.P. Valleau, *Mol. Phys.* 1 (1958) 284.
- [111]. H.T. Davis, S.A. Rice, J.V. Sengers, *J. Chem. Phys.* 35 (1961) 2210.
- [112]. H.T. Davis, K.D. Luks, *J. Phys. Chem.* 69 (1965) 869.
- [113]. J.O. Hirschfelder, C.F. Curtis, R.B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley and Sons, New York, (1954), reprinted with notes added (1964).
- [114]. J.D. Rogers, F.G. Brickwedde, *Physica.* 32 (1966) 100.
- [115]. J.P. Boon, G. Thomaes, *Physica.* 29 (1963) 208.
- [116]. J.P. Boon, G. Thomaes, *Physica.* 28 (1962) 1074.
- [117]. J.P. Boon, G. Thomaes, *Physica.* 29 (1963) 123.
- [118]. J.P. Boon, J. C. Legros, G. Thomaes, *Physica.* 33 (1967) 547.
- [119]. T.H. Holleman, J. Hijmans, *Physica.* 28 (1962) 604.
- [120]. H. Eyring, *J. Chem. Phys.* 4 (1936) 283.
- [121]. H. Eyring, J.O. Hirschfelder, *J. Phys. Chem.* 41 (1937) 249.
- [122]. J.F. Kincaid, H. Eyring, A.E. Stearn, *Chem. Rev.* 28 (1941) 301.
- [123]. H. Eyring, T. Ree, N. Hirai, *Proc. Natl. Acad. Sci.* 44 (1958) 683.
- [124]. E.J. Fuller, T. Ree, H. Eyring, *Proc. Natl. Acad. Sci.* 45 (1959) 1594.
- [125]. C.M. Carlson, H. Eyring, *Proc. Natl. Acad. Sci.* 46 (1960) 333.
- [126]. T.R. Thomson, H. Eyring, T. Ree, *Proc. Natl. Acad. Sci.* 46 (1960) 336.
- [127]. J. Walter, H. Eyring, *J. Chem. Phys.* 9 (1941) 393.

- [128]. T. Ree, H. Eyring, *Ind. Eng. Chem.* 50 (1958) 1036.
- [129]. C.M. Carlson, H. Eyring, T. Ree, *Proc. Natl. Acad. Sci.* 46 (1960) 649.
- [130]. H. Eyring, T. Ree, *Proc. Natl. Acad. Sci.* 47 (1961) 526.
- [131]. H. Eyring, M.S. John, *Significant Liquid Structures*, John Wiley & Sons, New York (1969).
- [132]. Gruneisen, Wiss, Abhaudl, *Physik-tech. Reich-austatt.* 4 (1905) 239.
- [133]. G. Jones, M. Dole, *J. Am. Chem. Soc.* 51 (1929) 2950.
- [134]. P. Debye, E. Hückel, *Z. Phys. Chem.* 24 (1923) 185.
- [135]. H. Falkenhagen, M. Dole, *Phys. Z.* 30 (1929) 611.
- [136]. H. Falkenhagen, E.L. Vernon, *Phys. Z.* 33 (1932) 140.
- [137]. H. Falkenhagen, E.L. Vernon, *Phil. Mag.* 14 (1983) 537.
- [138]. M. Kaminsky, *Discuss Faraday Soc.* 24 (1957) 171.
- [139]. D. Feakins, D.J. Freemantle, K.G. Lawrence, *J. Chem. Soc. Faraday Trans. I.* 70 (1974) 795.
- [140]. J. Crudden, G.M. Delancy, D. Feakins, P.J. O'Reilly, W. E. Waghorne, K. G. Lawrence, *J. Chem. Soc. Faraday Trans I.* 82 (1986) 2195.
- [141]. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York (1973).
- [142]. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York (1958).
- [143]. M. Kaminsky, *Z. Phys. Chem.* 12 (1957) 206.
- [144]. J. Desnoyers, G. Perron, *J. Solution Chem.* 1 (1972) 199.
- [145]. R.J.M. Bicknell, K.G. Lawrence, D. Feakins, *J. Chem. Soc. Faraday I.* 76 (1980) 637.
- [146]. R.L. Kay, T. Vituccio, C. Zawoyski, D.F. Evans, *J. Phys. Chem.* 70 (1966) 2336.
- [147]. N.P. Yao, D.N. Bennion, *J. Phys. Chem.* 75 (1971) 1727.
- [148]. M. Kaminsky, *Discussions Faraday Soc.* 24 (1957) 171.
- [149]. D. Feakins, K.G. Lawrence, *J. Chem. Soc. A* (1966) 212.
- [150]. V. Vand, *J. Phys. Chem.* 52 (1948) 277.
- [151]. D.G. Thomas, *J. Colloid Sci.* 20 (1965) 267.
- [152]. S.P. Moulik, *J. Ind. Chem. Soc.* 49 (1972) 483.
- [153]. D. England, G. Pilling, *J. Phys. Chem.* 76 (1972) 1902.
- [154]. D.E. Goldsack, R.C. Franchetto, *Can. J. Chem.* 55 (1977) 1062.

- [155]. D.E. Goldsack, R.C. Franchetto, *Can. J. Chem.* 56 (1978) 1442.
- [156]. C.A. Angell, *J. Phys. Chem.* 70 (1966) 2793.
- [157]. C.A. Angell, *J. Chem. Phys.* 46 (1967) 4673.
- [158]. K.R. Chowdhury, D.K. Majumdar, *Electrochim. Acta.* 28 (1983) 23.
- [159]. K.R. Chowdhury, D.K. Majumdar, *Electrochim. Acta.* 28 (1983) 597.
- [160]. K.R. Chowdhury, D.K. Majumdar, *Electrochim. Acta.* 29 (1984) 1371.
- [161]. P.P. Rastogi, *Bull. Chem. Soc. Japan.* 43 (1970) 2442.
- [162]. R. Gopal, P.P. Rastogi, *Z. Phys. Chem. (N.F.)* 69 (1970) 1.
- [163]. C.M. Criss, M.J. Mostroiani, *J. Phys. Chem.* 75 (1971) 2532.
- [164]. K. Tamaski, Y. Ohara, Y. Isomura, *Bull. Chem. Soc. Japan.* 46 (1973) 951.
- [165]. P.P. Deluca, T.V. Rabagay, *J. Phys. Chem.* 79 (1975) 2493.
- [166]. B.N. Prasad, N.P. Singh, M.M. Singh, *Ind. J. Chem.* 14A (1976) 322.
- [167]. B.N. Prasad, M.M. Agarwal, *Ind. J. Chem.* 14A (1976) 343.
- [168]. R.T.M. Bicknell, K.G. Lawrence, M.A. Scelay, D. Feakins, L. Werblan, *J. Chem. Soc. Faraday I.* 72 (1976) 307.
- [169]. J.M. Mcdowall, N. Martinus, C.A. Vincent, *J. Chem. Soc. Faraday I.* 72 (1976) 654.
- [170]. A. Sacco, G. Petrella, M. Castagnola, *J. Phys. Chem.* 80 (1976) 749.
- [171]. R.L. Blokhra, Y.P. Segal, *Ind. J. Chem.* 15A (1977) 36.
- [172]. N.C. Das, P.B. Das, *Ind. J. Chem.* 15A (1977) 826.
- [173]. A. Sacco, G. Petrella, M. Della Monica, M. Castagnola, *J. Chem. Soc. Faraday I.* 73 (1977) 1936.
- [174]. P.K. Mandal, B.K. Seal, A.S. Basu, *Z. Phys. Chem.* 258 (1977) 809.
- [175]. J.I. Kim, *J. Phys. Chem.* 82 (1978) 191.
- [176]. S.K. Vijaylakshamna, *Indian J. Chem.* 17A (1979) 511.
- [177]. A. Sacco, G. Petrella, M.D. Monica, *J. Chem. Soc. Faraday I.* 75 (1979) 2325.
- [178]. P.T. Thomson, M. Durbana, J.L. Turner, R.H. Wood, *J. Sol. Chem.* 9 (1980) 955.
- [179]. K. Kurotaki, S. Kawamura, *J. Chem. Soc. Faraday I.* 77 (1981) 217.
- [180]. N. Martinus, C.A. Vincent, *J. Chem. Soc. Faraday Trans I.* 77 (1981) 141.
- [181]. A. Sacco, A. D. Giglio, A. D. Atti, *J. Chem. Soc. Faraday I.* 77 (1981) 2693.
- [182]. D.S. Gill, A.N. Sharma, *J. Chem. Soc. Faraday I.* 78 (1982) 78475.
- [183]. A. Sacco, G. Petrella, A.D. Atti, M. Castagnolo, *J. Chem. Soc. Faraday I.* 78 (1980) 955.

- [184]. A. Sacco, A.D. Giglio, A.D. Atti, M. Castagnolo, *J. Chem. Soc. Faraday I.* 79 (1983) 431.
- [185]. K.G. Lawrence, A. Sacco, *J. Chem. Soc. Faraday I.* 79 (1983) 615.
- [186]. K. Miyajima, M. Sawada, M. Nakagaki, *Bull. Chem. Soc. Jpn.* 56 (1983) 827.
- [187]. J. Doenech, S. Rivera, *J. Chem. Soc. Faraday I.* 80 (1984) 1249.
- [188]. D. Dasgupta, S. Das, D.K. Hazra, *Bull. Chem. Soc. Jpn.* 62 (1989) 1246.
- [189]. S. Taniewska-Osinska, M. Jozwaik, *J. Chem. Soc. Faraday Trans I.* 85 (1989) 2147.
- [190]. D. Nandi, D.K. Hazra, *J. Chem. Soc. Faraday Trans I.* 85 (1989) 4227.
- [191]. I. Ibulci, M. Nakahara, *J. Phys. Chem.* 94 (1990) 8370.
- [192]. W.M. Cox, J. H. Wolfenden, *Proc. Roy. Soc. London.* 145A (1934) 475.
- [193]. R.W. Gurney, *Ionic Processes in Solution*, Mc Graw Hill, New York (1953).
- [194]. E.R. Nightingale, *J. Phys. Chem.* 63 (1959) 1381.
- [195]. A. Einstein, *Ann. Phys.* 19 (1906) 289.
- [196]. G.S. Benson, A.R. Gordon, *J. Chem. Phys.* 13 (1945) 473.
- [197]. [D.F.T. Tuan, R.M. Fuoss, *J. Phys. Chem.* 67 (1963) 1343.
- [198]. C.H. Springer, J.F. Coetzee, R.L. Key, *J. Phys. Chem.* 78 (1969) 471.
- [199]. G. Petrella, A. Sacco, *J. Chem. Soc. Faraday I.* 74 (1978) 2070.
- [200]. B.S. Krumgalz, *J. Chem. Soc. Faraday I.* 76 (1980) 1275.
- [201]. B.S. Krumgalz, *Russ. J. Phys. Chem.* 46 (1972) 858.
- [202]. B.S. Krumgalz, *Russ. J. Phys. Chem.* 47 (1973) 956.
- [203]. B.S. Krumgalz, *Russ. J. Phys. Chem.* 48 (1974) 1163.
- [204]. B.S. Krumgalz, *Russ. J. Phys. Chem.* 45 (1971) 1448.
- [205]. H.D.B. Jenkins, M.S.F. Pritchett, *J. Chem. Soc. Faraday I.* 80 (1984) 721.
- [206]. K. Fajan, *Naturwissenschaften.* 9 (1921) 729.
- [207]. D.F.C. Morris, *Struct. Bonding.* 6 (1969) 157.
- [208]. R.W. Gurney, *Ionic Processes in Solutions*, Doves, New York (1962).
- [209]. H.S. Frank, W.Y. Wen, *Disc. Farad. Soc.* 24 (1957) 133.
- [210]. Z. Asmus, *Naturforsch.* 4A (1949) 589.
- [211]. M.H. Abraham, J. Liszi, E. Papp, *J. Chem. Soc. Faraday I.* 78 (1982) 197.
- [212]. M.H. Abraham, J. Liszi, L. Meszaros, *J. Chem. Phys.* 70 (1979) 249.
- [213]. M.H. Abraham, J. Liszi, *J. Chem. Soc. Faraday I.* 76 (1980) 1219.

- [214]. S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw Hill, New York (1941).
- [215]. E.R. Nightingale, R.F. Benck, *J. Phys. Chem.* 63 (1959) 1777.
- [216]. D. Feakins, D.J. Freemantle, K.G. Lawrence, *J. Chem. Soc. Faraday I.* 70 (1974) 795.
- [217]. R. Sinha, *J. Phys. Chem.* 44 (1940) 25.
- [218]. V. Vand, *J. Phys. Chem.* 52 (1948) 277.
- [219]. D.G. Thomas, *J. Colloid Sci.* 20 (1965) 267.
- [220]. S.P. Moulik, *J. Phys. Chem.* 72 (1968) 4688.
- [221]. S.P. Moulik, *Electrochim. Acta.* 17 (1972) 1491.
- [222]. S.P. Moulik, *J. Indian Chem. Soc.* 49 (1972) 483.
- [223]. R.J. Fort, W.R. Moore, *Trans. Faraday Soc.* 62 (1966) 1112.
- [224]. G.R. Naidu, P.R. Naidu, *Ind. J. Chem.* 22A (1983) 324.
- [225]. O. Redlich, A.T. Kister, *Ind. Eng. Chem.* 40 (1948) 345.
- [226]. L. Pikkarainen, *J. Chem. Eng. Data.* 28 (1983) 344.
- [227]. L. Pikkarainen, *J. Chem. Eng. Data.* 28 (1983) 381.
- [228]. L.S. Manjeshwar, T. Aminabhavi, *J. Chem. Eng. Data.* 33 (1988) 184.
- [229]. K.P. Rao, K.S. Reddy, *J. Chem. Eng. Data.* 33 (1988) 130.
- [230]. S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw Hill, New York (1941).
- [231]. D.S. Gill, T.S. Kaur, H. Kaur, I.M. Joshi, J. Singh, *J. Chem. Soc. Faraday Trans.* 89 (1993) 1737.
- [232]. J.V. Herraiez, R. Belda, *J. Soln. Chem.* 33 (2004) 117.
- [233]. J. Ferguson, Z. Kemblonski, *Applied Fluid Rheology*, Elsevier, Cambridge (1991).
- [234]. H.A. Barnes, J.F. Hutton, K. Walters, *An Introduction to Rheology*, Elsevier, Amsterdam (1993).
- [235]. C.W. Macosk, *Rheology. Principles, Measurements and Applications* (VCH), New York (1994).
- [236]. M. Garcia-Velarde, *Revista Esp. Fisica.* 9 (1995) 12.
- [237]. R. Shukla, M. Cheryan, *J. Membrane Sci.* 198 (2002) 104.
- [238]. J.M. Resa, C. Gonzalez, J. Lanz, *J. Food Eng.* 51 (2002) 113.
- [239]. M.J. Assael, N.K. Dalaouti, I. Metaxa, *Fluid Phase Equilibria.* 199 (2002) 237.
- [240]. A. Darr, *Technologie Farmaceutica.*, S.A. Acibia, Zaragoza (1979).

- [241]. R. Voight, S.A. Acibia, *Tratado de Tecnología Farmaceutica.*, Zaragoza (1982).
- [242]. C.K. Z'eborg-Mikkelsen, S.E. Quiñones-Cisneros, S.H. Stenby, *Fluid Phase Equilibria*. 1191 (2002) 194.
- [243]. C. Fauli-Trillo, *Tratado de Farmacia Galénica*, S.A. Lujan, Madrid (1993).
- [244]. J. Swarbrik, J.C. Boyland, *Encyclopedia of Pharmaceutical Technology*, Marcel Dekker, NewYork (1993).
- [245]. J. Pellicer, *Sinergia Viscosa*, Valencia, Spain (1997).
- [246]. G. Copetti, R. Lapasin, E.R. Morris, *Proceedings of the Fourth European Rheology Conference*, Seville, Spain (1994).
- [247]. G. Kalentunc-Gencer, M. Peleg, *J. Texture Studies*. 17 (1986) 61.
- [248]. D.D. Christianson, *Hydrocolloidal Interactions with Starches*, Wesport. Conn. (1982).
- [249]. N.K. Howell, *Proceedings of the Seventh International Conference*, Wales (1993)
- [250]. J.G. Mathieson, B.E. Conway, *J. Sol. Chem.* 3 (1974) 455.
- [251]. S. Bhowmik, R.K. Mohanty, *Ind. J. Chem.* 25A (1986) 416.
- [252]. M.V. Kaulgud, K.S. Mohan Rao, *Ind. J. Chem.* 27A (1988) 12.
- [253]. K.J. Patil, A.B. Wazalwar, G.R. Mehta, *Ind. J. Chem.* 27A (1988) 799.
- [254]. M. Iqbal, R.E. Verral, *Can. J. Chem.* 67 (1989) 727.
- [255]. M. Kikuchi, M. Sakurai, K. Nitta, *J. Chem. Eng. Data*. 41 (1996) 1439.
- [256]. B.E. Conway, R.E. Verral, *J. Phys. Chem.* 70 (1966) 3952.
- [257]. K. Gekko, H. Noguchi, *J. Phys. Chem.* 83 (1979) 2706.
- [258]. W.L. Masterson, *J. Chem. Phys.* 22 (1954) 1830.
- [259]. L.G. Hepler, *Can. J. Chem.* 47 (1969) 4613.
- [260]. M.V. Kaulgud, K.J. Patil, *J. Phys. Chem.* 80 (1976) 138.
- [261]. K.J. Patil, G.R. Mehta, R.K. Chandewar, *Ind. J. Chem.* 25A (1986) 1147.
- [262]. C. Lafuente, B. Ginar, A. Villares, I. Gascon, P. Cea, *Int. J. Thermophys.* 25 (2004)1735.
- [263]. G. Douheret, A. Pal, M.I. Davis, *J. Chem. Thermodyn.* 22 (1990) 99.
- [264]. I. Gascon, S. Martin, P. Cea, M.C. Lopez, F.M. Royo, *J. Sol. Chem.* 31 (2002) 905.
- [265]. R. Mehra, M. Pancholi, *J. Ind. Chem. Soc.* 82 (2005) 791.
- [266]. S.L. Oswal, K.D. Prajapati, *J. Chem. Eng. Data*. 43 (1998) 367.
- [267]. K. Hsu-Chen, T. Chein-Hsium, *J. Chem. Eng. Data*. 50 (2005) 608.

- [268]. D.W. Marquardt, *J. Soc. Ind. Appl. Math.* 11 (1963) 431.
- [269]. L. Onsager, *Z. Phys. Chem.* 28 (1927) 277.
- [270]. R.M. Fuoss, *Rev. Pure Appl. Chem.* 18 (1968) 125.
- [271]. E. Pitts, *Proc. Roy. Soc.* 217A (1953) 43.
- [272]. R.M. Fuoss, L. Onsager, *J. Phys. Chem.* 61 (1957) 668.
- [273]. R.M. Fuoss, *Chemical Physics of Ionic Solutions*, Wiley, New York (1966).
- [274]. E. Pitts, R.E. Tabor, J. Daly, *Trans. Faraday Soc.* 65 (1969) 849.
- [275]. (a) R.M. Fuoss, K.L. Hsia, *Proc. Natl. Acad. Sci.* 57 (1967) 1550.
(b) R.M. Fuoss, K.L. Hsia, *J. Am. Chem. Soc.* 90 (1968) 3055.
- [276]. R. Fernandez-Prini, *J.E. Prue. Z. Phys. Chem.* 228 (1965) 373.
- [277]. R. Fernandez-Prini, *J.E. Prue. Z. Phys. Chem.* 228 (1965) 473.
- [278]. D.F. Evans, R.L. Kay, *J. Phys. Chem.* 70 (1966) 366.
- [279]. D. F. Arrington, E. Griswold, *J. Phys. Chem.* 74 (1970) 123.
- [280]. R.M. Fuoss, C.A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 476.
- [281]. T. Shedlovsky, J. Franklin, *Instt.* 225 (1938) 739.
- [282]. (a) J.C. Justice, *J. Chem. Phys.* 65 (1968) 353.
(b) J.C. Justice, R. Bury, C. Treiner, *J. Chem. Phys.* 65 (1968) 1708.
- [283]. R.M. Fuoss, F. Accascina, *Electrolytic Conductance*, Wiley, New York (1959)
- [284]. N.K. Bjerrum, *Dan. Vidensk. Selek. Mat.Fys.Medd.* 7 (1926) 9.
- [285]. M. Tissier, G. Douheret, *J. Soln. Chem.* 7 (1978) 87.
- [286]. R. Fernandez-Prini, *J. Prue, Trans. Faraday Soc.* 62 (1966) 1257.
- [287]. (a) R.M. Fuoss, L. Onsager, *J. Phys. Chem.* 66 (1962) 1722.
(b) R.M. Fuoss, L. Onsager, *J. Phys. Chem.* 67 (1963) 621.
- [288]. R.M. Fuoss, *J. Phys. Chem.* 49 (1975) 525.
- [289]. P.C. Carman, D.P. Laurie, *J. Sol. Chem.* 5 (1976) 457.
- [290]. R.M. Fuoss, *J. Phys. Chem.* 81 (1977) 1829.
- [291]. R.M. Fuoss, *Proc. Nat. Acad. Sci.* 75 (1978) 16.
- [292]. R.M. Fuoss, *J. Phys. Chem.* 82 (1978) 2427.
- [293]. (a) W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday II.* 74 (1978) 743.
(b) W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday II.* 74 (1978) 1456.
- [294]. W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday Trans. I.* 75 (1979) 1128.
- [295]. W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday Trans II.* 74 (1978) 1456.

- [296]. A.D. Pethybridge, S.S. Tara, *J. Chem. Soc. Faraday I.* 76 (1980) 368.
- [297]. M. Bester-Rogac, R. Neueder, J. Barthel, *J. Solution Chem.* 28 (1999) 1071.
- [298]. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York (1964).
- [299]. E. Balaguruswami, *Numerical Methods*, Tata McGraw-Hill Publishing Company, New Delhi (2007).
- [300]. M.N. Roy, B. Sinha, V.K. Dakua, *Pak J. Sci. Ind. Res.* 49 (2006) 153.
- [301]. (a) B.S. Krumgalz, *J. Chem. Soc. Faraday I.* 79 (1983) 571.
(b) B.S. Krumgalz, *J. Chem. Soc. Faraday I.* 81 (1985) 241.
- [302]. P. Walden, H. Ulich, D. Bush, *Z. Phys. Chem.* 123 (1926) 429.
- [303]. R.M. Fuoss, E. Hirsch, *J. Am. Chem. Soc.* 82 (1960) 1018.
- [304]. S. Takezawa, Y. Kondo, N. Tokura, *J. Phys. Chem.* 77 (1973) 2133.
- [305]. (a) D.S. Gill, *J. Chem. Soc. Faraday I.* 77 (1981) 751.
(b) D.S. Gill, N. Kumari, M.S. Chauhan, *J. Chem. Soc. Farada Trans I.* 81 (1985) 687.
- [306]. M.A. Coplan, R.M. Fuoss, *J. Phys. Chem.* 68 (1964) 1177.
- [307]. J.F. Coetzee, G.P. Cunningham, *J. Am. Chem. Soc.* 87 (1965) 2529.
- [308]. R.H. Stokes, R.A. Robinson, *Trans. Faraday Soc.* 53 (1957) 301.
- [309]. M. Born, *Z. Phys. Chem.* 1 (1920) 221.
- [310]. R.H. Boyd, *J. Chem. Phys.* 35 (1961) 1281.
- [311]. R. Zwanzig, *J. Chem. Phys.* 38 (1963) 1603.
- [312]. E.J. Passeron, *J. Phys. Chem.* 68 (1964) 2728.
- [313]. (a) P. Walden, *Z. Phys. Chem.* 55 (1906) 207.
(b) P. Walden, *Z. Phys. Chem.* 78 (1912) 257.
- [314]. R.A. Robinson, R.H. Stokes, *Electrolyte Solutions*, Butterworths, London (1959)
- [315]. R. Gopal, M.M. Hussain, *J. Ind. Chem. Soc.* 40 (1963) 981.
- [316]. L.G. Longsworth, *J. Phys. Chem.* 67 (1963) 689.
- [317]. M. Della Monica, U. Lamauna, L. Seutatore, *J. Phys. Chem.* 72 (1968) 2124.
- [318]. S. Brocus, *J. Chem. Phys.* 28 (1958) 1158.
- [319]. D.G. Miller, *J. Phys. Chem.* 64 (1960) 1598.
- [320]. G.J. Hills, *Chemical Physics of Ionic Solutions*, Wiley, New York (1966).
- [321]. R.H. Stokes, I.A. Weeks, *Aust. J. Chem.* 17 (1964) 304.

- [322]. R.H. Stokes, *The Structure of Electrolytic Solutions*, Wiley, New York (1959).
- [323]. D.S. Gill, *J. Chem. Soc. Faraday Trans. I.* 77 (1981) 751.
- [324]. R. Zwanzig, *J. Chem. Phys.* 52 (1970) 3625.
- [325]. H.S. Franks, *Chemical Physics of Ionic Solutions*, Wiley, New York (1966).
- [326]. G. Atkinson, S.K. Koz, *J. Phys. Chem.* 69 (1965) 128.
- [327]. R.L. Kay, G.P. Cunningham, D.F. Evans, *Hydrogen bonded Solvent Systems*, Taylor and Francis, London (1968).
- [328]. R.L. Kay, B.J. Hales, G.P. Cunningham, *J. Phys. Chem.* 71 (1967) 3925.
- [329]. R.L. Kay, C. Zawoyski, D.F. Evans, *J. Phys. Chem.* 69 (1965) 4208.
- [330]. D. F. Evans, J. L. Broadwater, *J. Phys. Chem.* 72 (1968) 1037.
- [331]. M. Spiro, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York (1973).
- [332]. R. Fernandez-Prini, G. Atkinson, *J. Phys. Chem.* 75 (1971) 239.
- [333]. L. Bahadur, M.V. Ramanamurti, *J. Chem. Soc. Faraday I.* 76 (1980) 1409.
- [334]. L. Bahadur, M.V. Ramanamurti, *J. Electrochem. Soc.* 128 (1981) 339.
- [335]. L. Bahadur, M.V. Ramanamurti, *Can. J. Chem.* 62 (1984) 1051.
- [336]. J.L. Broadwater, R.L. Kay, *J. Phys. Chem.* 74 (1970) 3803.
- [337]. S. Das, D.K. Hazra, *Indian J. Chem.* 274 (1988) 1073.
- [338]. S. Das, D.K. Hazra, *J. Ind. Chem. Soc.* LXV (1988) 100.
- [339]. (a) R.L. Kay, J.L. Broadwater, *Electrochim. Acta.* 16 (1971) 667.
(b) R.L. Kay, J.L. Broadwater, *J. Sol. Chem.* 5 (1976) 57.
- [340]. A.D. Aprano, R.M. Fuoss, *J. Phys. Chem.* 67 (1963) 1704.
- [341]. P. Hemmes, *J. Phys. Chem.*, 78 (1974) 907.
- [342]. J. Hubbard, L. Onsager, *J. Chem. Phys.* 53 (1977) 4850.
- [343]. N. Islam, M.R. Islam, M. Ahmed, *Z. Phys. Chem.* 262 (1981) 129.
- [344]. D.S. Gill, A.N. Sharma, H. Schneider, *J. Chem. Soc. Faraday I.* 78 (1982) 465.
- [345]. C.J. Cramer, D.G. Truhlar, *J. Am. Chem. Soc.* 113 (1991) 8305.
- [346]. D.J. Giesen, J.W. Stores, C.J. Cramer, D.G. Truhlar, *J. Am. Chem. Soc.* 117 (1995) 1057.
- [347]. (a) C.J. Cramer, D.G. Truhlar, *J. Org. Chem.* 61 (1996) 8720.
(b) C.J. Cramer, D.G. Truhlar, *Erratum.* 101 (1999) 309.
- [348]. G.D. Hawkins, C.J. Cramer, D.G. Truhlar, *J. Phys. Chem. B.* 101 (1997) 7147.

- [349]. G.D. Hawkins, C.J. Cramer, D.G. Truhlar, *J. Phys. Chem. B.* 102 (1998) 3257.
- [350]. A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burgess, *J. Chem. Phys.* 106 (1997) 4168.
- [351]. A. Galindo, L.A. Davies, A. Gil-Villegas, G. Jackson, *Mol. Phys.* 93 (1998) 241.
- [352]. M. Roses, C. Rafols, J. Ortega, E. Bosch, *J. Chem. Soc. Perkin Trans. 2* (1995) 1607.
- [353]. O. Bernard, W. Kunz, P. Turq, L. Blum, *J. Phys. Chem.* 96 (1992) 3833.
- [354]. S. Durand-Vidal, P. Turq, O. Bernard, *J. Phys. Chem.* 100 (1996) 17345.
- [355]. H.L. Bianchi, I. Dujovne, R. Fernandez-Prini, *J. Sol. Chem.* 29 (2000) 237.
- [356]. A. Chandra, B. Bagchi, *J. Phys. Chem. B.* 104 (2000) 9067
- [357]. W. Heller, *J. Phys. Chem.* 69 (1965) 1123.
- [358]. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York (1970).
- [359]. O. Redlich, A. Kister, *Ind. Eng. Chem.* 40 (1948) 345.
- [360]. J.F. Comesaña, J.J. Otero, E. Camesella, A. Correa, *J. Chem. Eng. Data.* 46 (2001) 1153.

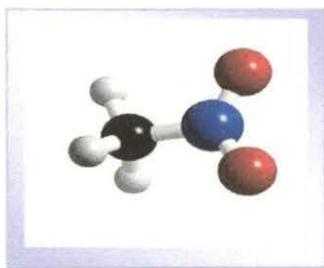
CHAPTER III

EXPERIMENTAL SECTION

3.1. NAME, STRUCTURE, PHYSICAL PROPERTIES, PURIFICATION AND APPLICATIONS OF THE SOLVENTS AND SOLUTES USED IN THE RESEARCH WORK

3.1.1. SOLVENTS

Nitromethane



Nitromethane (NM) is one of the simplest organic nitro compounds. It is a slightly viscous, highly polar liquid.

Appearance:	Liquid
Molecular Formula:	CH₃NO₂
Molecular Weight:	61.04 g/mol
Boiling Point:	244.15 K
Melting Point:	373-376 K
Dielectric Constant:	35.87 at 298.15 K

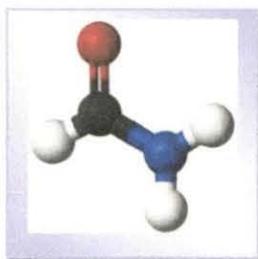
Source: Thomas Baker, India.

Purification: It is dried with CaSO₄ and then distilled [1].

Application: The principle use of nitromethane is as a stabilizer for chlorinated solvents, which are used in dry cleaning, semiconductor processing, and degreasing. It is also used most effectively as a solvent or dissolving agent for acrylate

monomers, such as cyanoacrylates. In more specialized organic synthesis, nitromethane serves as a Michael donor, adding to α , β -unsaturated carbonyl compounds via 1,4-addition in the Michael reaction. Its acidity allows it to undergo deprotonation, enabling condensation reactions analogous to those of carbonyl compounds. It is used widely in the manufacture of pharmaceuticals, pesticides, explosives, fibers, and coatings. It is also used as a racing fuel in Top Fuel drag racing, and as an important component in the fuel for miniature internal combustion engines that are used in radio-controlled models.

Formamide



Formamide (FA), also known as methanamide is an amide derived from formic acid. It is a clear liquid which is miscible with water and has an ammonia-like odor.

Appearance:	Liquid
Molecular Formula:	CH₃NO
Molecular Weight:	45.04 g/mol
Boiling Point:	483 K
Melting Point:	275-276 K
Dielectric Constant:	109.50 at 298.15 K

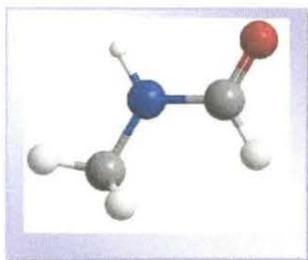
Source: Thomas Baker, India.

Purification: It is dried by 3Å molecular sieves and then distilled [1].

Application: Formamide is used as an ionizing agent. Formamide is chemical feedstock for the manufacture of sulfa drugs, other pharmaceuticals, herbicides, the manufacture of hydrocyanic acid. It has been used as a softener for paper and fiber. It is a solvent for many ionic compounds. It has also been used as a solvent

forresins and plasticizersIt can be used as a cryoprotectant and gel-stabilizer. It is known to destabilize nucleic acid duplexes, making it useful for preparing hybridization buffers for RNA and DNA applications.

N-methylformamide



N-methylformamide (NMF) is a colorless, nearly odorless, organic compound which is a liquid at room temperature. It is highly polar solvent and infinitely soluble in water. In N-methylformamide the partial double bond that exists between the carbonyl carbon and nitrogen, which gives rise to a high rotational barrier. Thus, the molecule is not able to freely rotate around its main axis and the E-configuration is preferred due to steric repulsion of larger substituents.

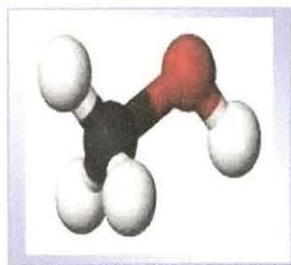
Appearance:	Liquid
Molecular Formula:	C₂H₅NO
Molecular Weight:	59.07 g/mol
Boiling Point:	455.7 K
Melting Point:	269 K
Dielectric Constant:	182.40 at 298.15 K

Source: Thomas Baker, India.

Purification: It is dried with molecular sieves for two days and then distilled [1].

Application: N-methylformamide (NMF) is mainly used as a reagent in various organic syntheses. NMF is a specialized solvent in oil refineries. It is a precursor in specialized amidation reactions where formamide would not be suitable. Formothion is an insecticide which was prepared from N-methylformamide. In the laboratory NMF is used as a ligand in coordination chemistry.

Methanol



Methanol, also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits, is the simplest alcohol, and is a light, volatile, colorless, flammable, liquid with a distinctive odor that is very similar to but slightly sweeter than ethanol (drinking alcohol).

Appearance:	Liquid
Molecular Formula:	CH₃OH
Molecular Weight:	32.04 g/mol
Boiling Point:	176 K
Melting Point:	337.8 K
Dielectric Constant:	32.70 at 298.15 K

Source: Merck, India

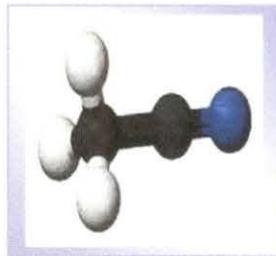
Purification: It was passed through Linde 4Å molecular sieves and then distilled.

Application: The largest use of methyl alcohol by far is in making other chemicals. About 40% of methanol is converted to formaldehyde, and from there into products as diverse as plastics, plywood, paints, explosives, and permanent press textiles. Methanol is a traditional denaturant for ethanol, thus giving the term methylated spirit. Methanol is also used as a solvent, and as an antifreeze in pipelines. In some waste water treatment plants, a small amount of methanol is added to waste water to provide a food source of carbon for the denitrifying bacteria, which converts nitrates to nitrogen to reduce the denitrification of sensitive aquifers. Methanol is

used on a limited basis to fuel internal combustion engines. Methanol is also useful as an energy carrier. It is easier to store than hydrogen, burns cleaner than fossil fuels, and is biodegradable.

Acetonitrile

Acetonitrile is the colorless organic liquid and is the simplest organic nitrile. It is produced mainly as a byproduct of acrylonitrile manufacture.



Appearance:	Liquid
Molecular Formula:	CH₃CN
Molecular Weight:	41.05 g/mol
Boiling Point:	607 K
Melting Point:	628.3 K
Dielectric Constant:	35.94 at 298.15 K

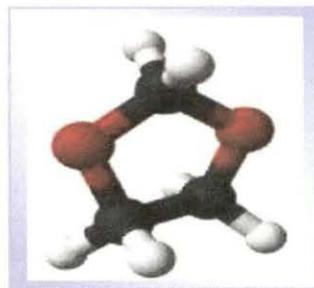
Source: Merck, India.

Purification: It is shaken with silica gel, refluxed with CaH₂ and distilled over P₂O₅ [1].

Application: It is widely used in battery applications because of its relatively high dielectric constant and ability to dissolve electrolytes. For similar reasons it is a popular solvent in cyclic voltammetry. Its low viscosity and low chemical reactivity make it a popular choice for liquid chromatography. Acetonitrile plays a significant role as the dominant solvent used in the manufacture of DNA oligonucleotides from monomers. Industrially, it is used as a solvent in the purification of butadiene and in the manufacture of pharmaceuticals and photographic film. Acetonitrile is a common two-carbon building block in organic synthesis as in the production of pesticides to perfumes.

1,3-dioxolane

Dioxolane or 1,3-dioxolane is a heterocyclic acetal. No unusual toxic effects have been associated with the use of 1,3-dioxolane. The product is not explosive, not spontaneously flammable and has no disagreeable odor. Dioxolanes are a group of organic compounds sharing the dioxolane ring structure.



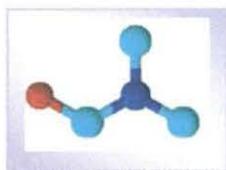
Appearance:	Liquid
Molecular Formula:	C₃H₆O₂
Molecular Weight:	74.08 g/mol
Boiling Point:	178 K
Melting Point:	348 K
Dielectric Constant:	7.34 at 298.15 K

Source: Merck, India.

Purification: It is dried with KOH and then distilled from sodium [1].

Application: It is a very good solvent for pharmaceutical manufacturing, it is used as a replacement for many chlorinated solvents, in lithium battery electrolyte solvent component, as a copolymerization agent with trioxane and formaldehyde for manufacturing polyacetal resins, paint stripper, glue stabilizer, water solubilizing agent for pesticides, herbicides and wood preservatives.

N, N- dimethylformamide



N, N-dimethylformamide is an organic compound with the formula (CH₃)₂NC(O)H. Commonly abbreviated as DMF (though this acronym is sometimes used

for dimethylfuran), this colorless liquid is miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions. Pure dimethylformamide is odorless whereas technical grade or degraded dimethylformamide often has a fishy smell due to impurity of dimethylamine. Its name is derived from the fact that it is a derivative of formamide, the amide of formic acid. DMF is a polar (hydrophilic) aprotic solvent with a high boiling point. It facilitates reactions that follow polar mechanisms, such as S_N2 reactions.

Appearance:	Liquid
Molecular Formula:	C₃H₇NO
Molecular Weight:	73.09 g/mol
Boiling Point:	212.7 K
Melting Point:	425-427 K
Dielectric Constant:	36.71 at 298.15 K

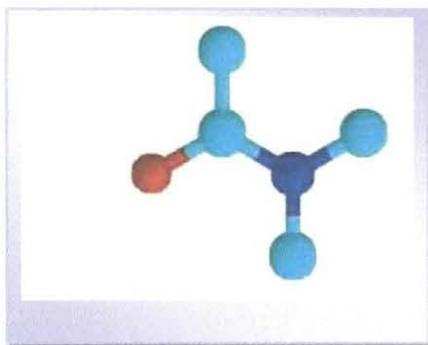
Source: Merck, India

Purification: It was dried by passing through Linde 4Å molecular sieves and then distilled [1].

Application: The primary use of dimethylformamide is as a solvent with low evaporation rate. DMF is used in the production of acrylic fibers and plastics. It is also used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, and in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings [2]. It is used as a reagent in the Bouveault aldehyde synthesis and in the Vilsmeier-Haack reaction, another useful method of forming aldehydes. It is also a common catalyst used in the synthesis of acyl halides, in particular the synthesis of acyl chlorides from carboxylic acids using oxalyl or thionyl chloride [3]. DMF penetrates most plastics and makes them swell. This property makes it very suitable for solid phase peptide synthesis. It also frequently occurs as a component of paint strippers for this purpose. DMF is very effective at separating and suspending carbon nanotubes, and is recommended by the NIST for use in near infrared spectroscopy of such. DMF can be utilized as a

standard in proton NMR allowing for a quantitative determination of an unknown chemical. DMF is used as a solvent to recover olefins such as 1,3-butadiene via extractive distillation. It is also used in the manufacturing of solvent dyes as an important raw material. It is consumed during reaction. Pure acetylene gas cannot be compressed and stored without the danger of explosion. Industrial acetylene gas is, therefore, dissolved in dimethylformamide and stored in metal cylinders or bottles. The casing is also filled with agamassan, which renders it safe to transport and use.

N, N- dimethylacetamide



N,N-

dimethylacetamide is the organic compound with the formula $\text{CH}_3\text{C}(\text{O})\text{N}(\text{CH}_3)_2$. This colorless, water-miscible, high boiling liquid is commonly used as a polar solvent in organic synthesis. DMA, as it often abbreviated, is miscible with

most other solvents, although it is poorly soluble in aliphatic hydrocarbons.

Appearance:	Liquid
Molecular Formula:	$\text{C}_4\text{H}_9\text{NO}$
Molecular Weight:	87.12 g/mol
Boiling Point:	253 K
Melting Point:	438.2 K
Dielectric Constant:	37.78 at 298.15 K

Source: Merck, India

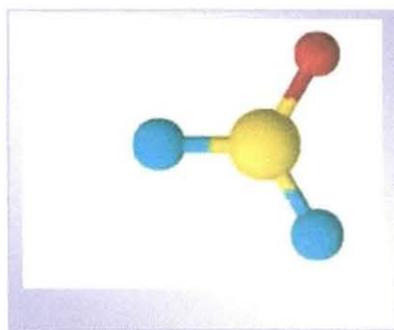
Purification: It was dried by passing through molecular sieves [1].

Application: DMA is useful solvent for reactions involving strong bases such as sodium hydroxide. Dimethylacetamide is commonly used as a solvent for fibers

(e.g., polyacrylonitrile, spandex) or in the adhesive industry [4]. It is also employed in the production of pharmaceuticals and plasticizers as a reaction medium.

Dimethyl sulphoxide

Dimethyl sulfoxide (DMSO) is an organosulfur compound with the formula $(\text{CH}_3)_2\text{SO}$. This colorless liquid is an important polar aprotic solvent that dissolves both polar and non-polar compounds and is miscible in a wide range of organic solvents as well as water. It penetrates the skin very readily, giving it the unusual property for many individuals of being secreted onto the surface of the tongue after contact with the skin and causing a garlic-like taste in the mouth.



Although it has some niche medicinal uses it also has significant known side effects. It has been promoted as a fake cure for cancer and other conditions.

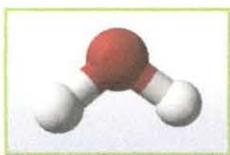
Appearance:	Liquid
Molecular Formula:	$\text{C}_2\text{H}_6\text{SO}$
Molecular Weight:	78.13 g/mol
Boiling Point:	292 K
Melting Point:	462 K
Dielectric Constant:	46.70 at 298.15 K

Source: Merck, India

Purification: It was dried by passing through Linde 4Å molecular sieves.

Application: DMSO is frequently used as a solvent for chemical reactions involving salts, most notably Finkelstein reactions and other nucleophilic substitutions. It is also extensively used as an extractant in biochemistry and cell biology. Because of its ability to dissolve many kinds of compounds, DMSO plays a role in sample management and high-throughput screening operations in drug design. DMSO is used in PCR to inhibit secondary structures in the DNA template or the DNA primers. It is added to the PCR mix before reacting, where it interferes with the self-complementarity of the DNA, minimizing interfering reactions. In medicine, DMSO is predominantly used as a topical analgesic, a vehicle for topical application of pharmaceuticals, as an anti-inflammatory, and an antioxidant [5]. Because DMSO increases the rate of absorption of some compounds through organic tissues, including skin, it can be used as a drug delivery system. It is frequently compounded with antifungal medications, enabling them to penetrate not just skin but also toe and fingernails. It is also used as veterinary medicines.

Water



Water is a ubiquitous chemical substance that is composed of hydrogen and oxygen and is essential for all known forms of life. In typical usage, water refers only to its liquid form or state, but the substance also has a solid state, ice, and a gaseous state, water vapor or steam. Water is a good solvent and is often referred to as the universal solvent.

Appearance:	Liquid
Molecular Formula:	H₂O
Molecular Weight:	18.02 g/mol
Boiling Point:	100 °C
Melting Point:	0°C
Dielectric Constant:	78.35 at 298.15 K

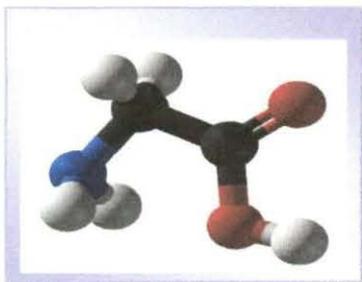
Source: Distilled water.

Purification: Water was first deionised and then distilled in an all glass distilling set along with alkaline KMnO_4 solution to remove any organic matter therein. The doubly distilled water was finally distilled using an all glass distilling set. Precautions were taken to prevent contamination from CO_2 and other impurities. The triply distilled water had specific conductance less than $1 \times 10^{-6} \text{ S.cm}^{-1}$.

Application: Water is also a good solvent due to its polarity. The solvent properties of water are vital in biology, because many biochemical reactions take place only within aqueous solutions (e.g., reactions in the cytoplasm and blood). In addition, water is used to transport biological molecules. The most important use of water in agriculture is for irrigation. Water fit for human consumption is called drinking water. Water is widely used in chemical reactions as a solvent or reactant and less commonly as a solute or catalyst. In inorganic reactions, water is a common solvent, dissolving many ionic compounds. In organic reactions, it is not usually used as a reaction solvent, because it does not dissolve the reactants well and is amphoteric (acidic *and* basic) and nucleophilic. Nevertheless, these properties are sometimes desirable. Also, acceleration of Diels-Alder reactions by water has been observed. Supercritical water has recently been a topic of research.

3.1.2. SOLUTES

Glycine



Glycine is an organic compound with the formula $\text{C}_2\text{H}_5\text{NO}_2$. With only a hydrogen atom as the side chain, glycine is the smallest of the 20 amino acids commonly found in proteins. Glycine is a colorless, sweet-tasting crystalline solid. It is unique among the proteinogenic amino acids and it is not chiral. It can fit into hydrophilic and hydrophobic environments, due

to its single hydrogen atom side chain.

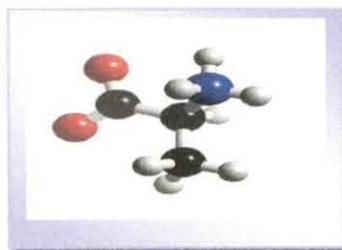
Appearance:	White powder
Molecular Formula:	C₂H₅NO₂
Molecular Weight:	75.07 g/mol
Melting Point:	233^oC

Source: S.D. Fine Chemicals Ltd., Mumbai, India

Purification: Used as purchased

Application: The principal function of glycine is as a precursor to proteins. It is also a building block to numerous natural products. Glycine is an inhibitory neurotransmitter in the central nervous system, especially in the spinal cord, brainstem and retina. Glycine serves as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, and toiletries.

L-alanine



Alanine is a α -amino acid with the chemical formula C₃H₇NO₂. The L-isomer is one of the 22 proteinogenic amino acids, i.e., the building blocks of proteins. It is classified as a non-polar amino acid. Alanine is a non-essential amino acid, meaning it can be manufactured by the human body, and does not need to be obtained directly through the diet.

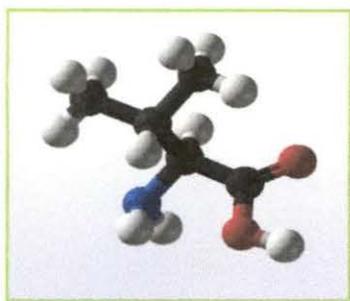
Appearance:	White powder
Molecular Formula:	C₃H₇NO₂
Molecular Weight:	89.09 g/mol
Melting Point:	258^oC

Source: S.D. Fine Chemicals Ltd., Mumbai, India

Purification: Used as purchased

Application: Alanine is used for low blood sugar (hypoglycemia), diarrhea-related dehydration, liver disease, enlarged prostate (benign prostatic hypertrophy, BPH), fatigue, stress, and certain inherited disorders including glycogen storage disease and urea cycle disorders.

L-valine



L-valine is a α -amino acid with the chemical formula $C_5H_{11}NO_2$. The L-valine is one of the 22 proteinogenic amino acids, i.e., the building blocks of proteins. It is one of the most important amino acid.

Appearance:	White powder
Molecular Formula:	$C_5H_{11}NO_2$
Molecular Weight:	117.15 g/mol
Melting Point:	298°C

Source: Loba Chemie, India

Purification: Used as purchased

Application: Valine is needed to keep the body in balance for greater muscle growth and recovery. When it comes to muscle building and energy, valine is perhaps best known for its effects as a balancing agent of our bodies' nitrogen content. Valine has been shown to aid in correcting deficiencies created by drug addictions and as a supplemental treatment for those addictions.

Ascorbic acid



Ascorbic acid ($C_6H_8O_6$) is a naturally occurring organic compound with antioxidant properties. Its appearance is white powder, and it is soluble in water. Ascorbic acid is commonly known as vitamin-C. The name is derived from α - (meaning "no") and scorbutus (scurvy), the disease caused by a deficiency of vitamin-C.

Appearance:	White powder
Molecular Formula:	$C_6H_8O_6$
Molecular Weight:	176.12 g/mol
Melting Point:	190°C

Source: S.D. Fine Chemicals Ltd., Mumbai, India

Purification: Used as purchased

Application: Ascorbic acid and its sodium, potassium, and calcium salts are commonly used as antioxidant food additives. Ascorbic acid is easily oxidized and so is used as a reductant in photographic developer solutions (among others) and as a preservative. In fluorescence microscopy and related fluorescence-based techniques, ascorbic acid can be used as an antioxidant to increase fluorescent signal and chemically retard dye photo bleaching.

Nicotinic acid



Nicotinic acid is an organic compound with the formula $C_6H_5NO_2$. Its appearance is white, translucent crystal powder, and it is soluble in water. Nicotinic acid is commonly known as vitamin B₃.

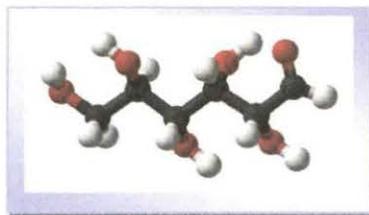
Appearance:	White, translucent crystal
Molecular Formula:	C₆H₅NO₂
Molecular Weight:	123.11 g/mol
Melting Point:	237°C

Source: S.D. Fine Chemicals Ltd., Mumbai, India

Purification: Used as purchased

Application: Nicotinic acid (3-pyridine carboxylic acid), also known as niacin or pellagra-preventing factor, is an important compound which play a crucial role in various physiological effects, biosynthesis, metabolic reactions, and several drug preparations.

D-glucose



Glucose (C₆H₁₂O₆) is a simple monosaccharide found in plants. It is one of the three dietary monosaccharides, along with fructose and galactose that are absorbed directly into the bloodstream during digestion. The chemical D-glucose is sometimes referred to as dextrose, a historical name that derives from dextrorotatory glucose because a solution of D-glucose in water rotates the plane of polarized light to the right (dextro).

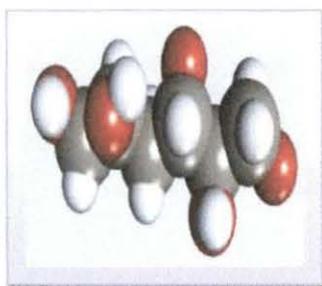
Appearance:	White powder
Molecular Formula:	C₆H₁₂O₆
Molecular Weight:	180.16 g/mol
Melting Point:	146-150°C

Source: S.D. Fine Chemicals Ltd., Mumbai, India

Purification: Used as purchased

Application: Glucose is one of the main products of photosynthesis and fuels for cellular respiration. Glucose is a ubiquitous fuel in biology. It is used as an energy source in most organisms, from bacteria to humans. Use of glucose may be by either aerobic respiration, anaerobic respiration, or fermentation.

D-mannitol



Mannitol (also referred to as mannite or manna sugar) is a white, crystalline solid with the chemical formula $C_6H_{14}O_6$. It was originally isolated from the secretions of the flowering ash and called manna after its resemblance to the Biblical food. Mannitol is classified as a sugar alcohol; that is, it is derived from a sugar (mannose) by

reduction.

Appearance:	White crystalline powder
Molecular Formula:	$C_6H_{14}O_6$
Molecular Weight:	182.17 g/mol
Melting Point:	167-170°C

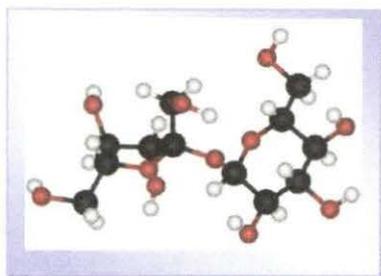
Source: S.D. Fine Chemicals Ltd., Mumbai, India

Purification: Used as purchased

Application: In plants, it is used to induce osmotic stress. It has several industrial uses, but is mainly used to produce tablets of medicine. Mannitol is used clinically in osmotherapy to reduce acutely raised intracranial pressure until more definitive treatment can be applied, e.g., after head trauma. Mannitol can also be used as a facilitating agent for the transportation of pharmaceuticals directly into the brain. Mannitol is commonly used in the circuit prime of a heart lung machine during cardiopulmonary bypass. Mannitol increases blood glucose to a

lesser extent than sucrose and is therefore used as a sweetener for people with diabetes, and in chewing gums. Although mannitol has a higher heat of solution than most sugar alcohols, its comparatively low solubility reduces the cooling effect usually found in mint candies and gums.

D-sucrose



D-sucrose is the organic compound commonly known as table sugar and sometimes called saccharose. A white, odorless, crystalline powder with a sweet taste, it is best known for its role in food. The molecule is a disaccharide composed of the

monosaccharides glucose and fructose with the molecular formula $C_{12}H_{22}O_{11}$. The word was formed in the mid-19th century from Latin *sucrum* = "sugar" and the chemical suffix *-ose*.

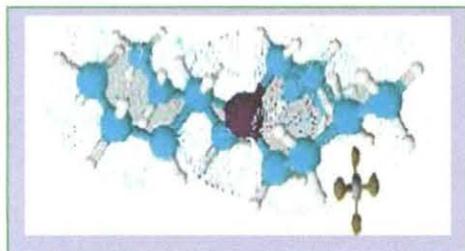
Appearance:	White crystalline powder
Molecular Formula:	$C_{12}H_{22}O_{11}$
Molecular Weight:	342.3 g/mol
Melting Point:	186°C

Source: S.D. Fine Chemicals Ltd., Mumbai, India

Purification: Used as purchased

Application: Sucrose can be used to prepare density gradients for cell/organelle separation. It is used as a supplement in plant, insect, and bacterial culture media. It can also be used in various enzymatic assays. D-sucrose is suitable for the preparation of density gradients used in purification of proteins and nucleic acids by ultracentrifugation.

Tetrabutylphosphonium tetrafluoroborate



Tetrabutylphosphonium tetrafluoroborate is an ionic liquid with molecular formula $C_{16}H_{36}BF_4P$.

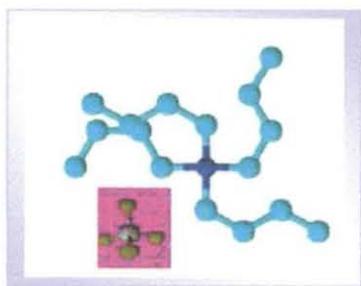
Appearance:	White powder
Molecular Formula:	$C_{16}H_{36}BF_4P$
Molecular Weight:	346.24 g/mol
Melting Point:	99°C

Source: Sigma-Aldrich, Germany

Purification: Used as purchased

Application: The ionic liquid tetrabutylphosphonium tetrafluoroborate has vast application in organic synthesis and bio-catalysis, dye sensitized-cells, batteries, electrochemical application and phase transfer catalyst, etc. It is widely used as supporting electrolytes in electrochemical measurements when control of electrode potentials is required.

Tetrabutylammonium tetrafluoroborate



Tetrabutylammonium tetrafluoroborate is a quaternary ammonium salt with a tetrafluoroborate counter ion with the molecular formula $C_{16}H_{36}BF_4N$.

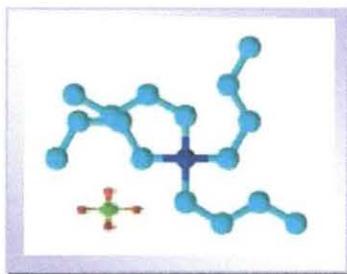
Appearance:	White powder
Molecular Formula:	C₁₆H₃₆BF₄N
Molecular Weight:	329.27 g/mol
Melting Point:	155-161^oC

Source: Sigma-Aldrich, Germany

Purification: Used as purchased

Application: It is used as reference electrolyte.

Tetrabutylammonium perchlorate



Tetrabutylammonium perchlorate is a quaternary ammonium salt with a perchlorate counter ion with the molecular formula C₁₆H₃₆ClNO₄.

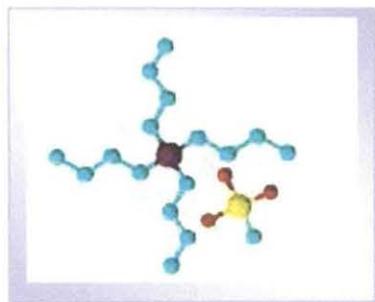
Appearance:	White powder
Molecular Formula:	C₁₆H₃₆ClNO₄
Molecular Weight:	341.91 g/mol
Melting Point:	211-215^oC

Source: Sigma-Aldrich, Germany

Purification: Used as purchased

Application: This electrolyte is used as a reference electrolyte and it is used for electrochemical analysis.

Tetrabutylphosphonium methanesulfonate



Tetrabutylphosphonium methanesulfonate is an ionic liquid with molecular formula $C_{16}H_{36}PCH_3SO_3$. Phosphonium-based ILs is less toxic, thermally more stable, and readily available in bulk quantities and less expensive.

Appearance:	White powder
Molecular Formula:	$C_{16}H_{36}PCH_3SO_3$
Molecular Weight:	354.53 g/mol
Melting Point:	59-62°C

Source: Sigma-Aldrich, Germany

Purification: Used as purchased

Application: Tetrabutylphosphonium methanesulfonate Ionic liquid is now appearing in applications as phase transfer catalysts [6], organic synthesis and electrochemical media.

3.2. EXPERIMENTAL METHODS

3.2.1. PREPARATION OF SOLVENT MIXTURES

For the preparation of solvent mixture, pure components were taken separately in glass stoppered bottles and thermostated at the desired temperature for sufficient time. When the thermal equilibrium was ensured, the required volumes of each component were transferred in a different bottle which was already cleaned and dried thoroughly. Conversion of required mass of the respective solvents to volume was accomplished by using experimental densities of the solvents at experimental temperature. It was then stoppered and the mixed contents were shaken well before use. While preparing different solvent mixtures care was taken to ensure that the same procedure was adopted throughout the entire work. The physical properties of different pure and mixed solvents have been presented in the respective chapters.

3.2.2. PREPARATION OF SOLUTIONS

A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The uncertainty of molarity of different salt solutions was evaluated to be $\pm 0.0003 \text{ mol}\cdot\text{dm}^{-3}$.

3.2.3. MASS MEASUREMENT

Mass measurements were made on digital electronic analytical balance (Mettler Toledo, AG 285, Switzerland).



It can measure mass to a very high precision and accuracy. The weighing pan of a high precision (0.0001g) is inside a transparent enclosure with doors so that dust does not collect and so any air currents in the room do not affect the balance's operation.

3.2.4. DENSITY MEASUREMENT

The density was measured with the help of Anton Paar density-meter (DMA 4500M) with a accuracy of 0.0005 g.cm⁻³.



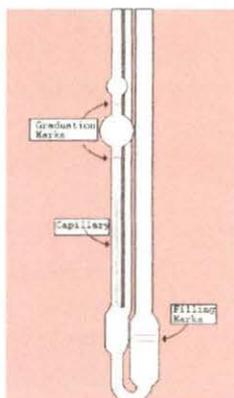
In the digital density meter, the mechanic oscillation of the U-tube is e.g. electromagnetically transformed into an alternating voltage of the same frequency. The period τ can be measured with high resolution and stands in simple relation to the density ρ of the sample in the oscillator [7]:

$$\rho = A \cdot \tau^2 - B \quad (1)$$

A and B are the respective instrument constants of each oscillator. Their values are determined by calibrating with two substances of the precisely known densities ρ_1 and ρ_2 . Modern instruments calculate and store the constants A and B after the two calibration measurements, which are mostly performed with air and water. They employ suitable measures to compensate various influences on the measuring result, e.g. the influence of the sample's viscosity and the non-linearity caused by the measuring instrument's finite mass. The instrument was calibrated by double-distilled water and dry air.

3.2.5. VISCOSITY MEASUREMENT

Solvent viscosities were measured with the help of a suspended Ubbelohde-type viscometer,



The kinematic viscosity (γ) and the absolute viscosity (η) are given by the following equations.

$$\gamma = k t - l/t \quad (2)$$

$$\eta = \gamma \cdot \rho \quad (3)$$

where, t is the time of flow, ρ is the density and k and l are the characteristic constants of the particular viscometer. The time of efflux of a constant volume of the experimental liquid through the capillary was measured with the aid of a Racer stop watch capable of measuring times accurate to ± 0.1 s. The viscometer was always kept in a vertical position in the thermostatic bath with an accuracy of ± 0.01 K of the desired temperature. The uncertainty of the viscosity measurement was ± 0.003 . In all cases, the experiments were performed in at least three replicates and the results were averaged.

Relative viscosities (η_r) were obtained using the equation:

$$\eta_r = \eta / \eta_0 = \rho t / \rho_0 t_0 \quad (4)$$

where η , η_0 , ρ , ρ_0 and t , t_0 are the absolute viscosities, densities and flow times for the solution and solvent respectively.

The viscosity was also measured with the help Brookfield DV-III Ultra Programmable Rheometer fitted to a Brookfield Digital Bath TC-500.



3.2.6. TEMPERATURE CONTROLLER

All the measurements were carried out in thermostatic water bath (Science India, Kolkata) maintained with an accuracy of ± 0.01 K of the desired temperature.



Laboratory water bath is a system in which a vessel containing the material to be heated is placed into or over the one containing water and to quickly heat it. These laboratory equipments are available in different volumes and construction with both digital and analogue controls and greater temperature uniformity, durability, heat retention and recovery. The chambers of water bath lab products are manufactured using rugged, leak proof and highly resistant stainless steel and other lab supplies.

Water Distiller (Borosil Glass Works Limited, India):

Water distillation units produce highly treated and disinfected water for laboratory usage. The distillation process removes minerals and microbiological contaminants and can reduce levels of chemical contaminants. A water distiller works by boiling water into water vapour, condensing it and then returning it to its liquid state. It is collected in a storage container.



Municipal or well water is manually or automatically fed into the distiller unit's boiling chamber. A heating element in the boiling chamber heats the water until it boils. The steam rises from the boiling chamber. Volatile contaminants (gases) are discharged through a built-in vent. Minerals and salts are retained in the boiling chamber as hard deposits or scale. The steam enters a coiled tube (condenser), which is cooled by cool water. Water droplets form as condensation occurs. The distilled water is collected in a storage tank.

Fractional Distillation Apparatus:

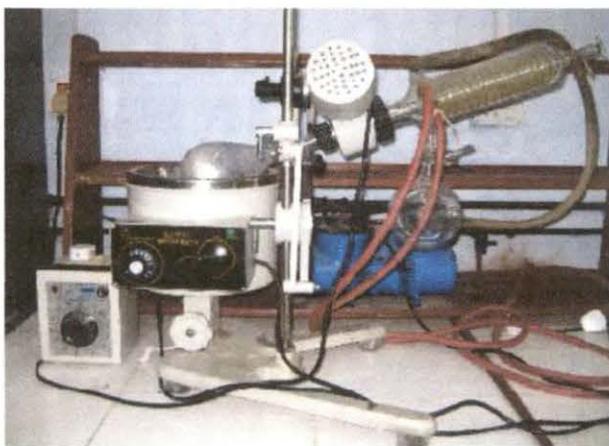
Distillation involves 2 stages and both are physical state changes. (1) The liquid or solution mixture is **boiled to vaporise** the most volatile component in the mixture (**liquid \Rightarrow gas**). The anti-bumping granules give a smoother boiling action. (2) The vapour is cooled by cold water in the condenser to **condense** (**gas \Rightarrow liquid**) it back to a liquid (the distillate) which is collected.



In the distillation flask, vaporization of a liquid and subsequent condensation of the resultant gas back to liquid form. It is used to separate liquids from non-volatile solids or solutes (e.g., water from salt and other components of sea water) or to separate two or more liquids with different boiling points (e.g., alcohol from fermented beers and wines). Many variations have been devised for industrial applications. An important one is fractional distillation, in which vapour from a heated liquid mixture is contacted by a series of trays and condensed liquid as it rises through a vertical column. The most volatile fraction of the mixture emerges from the top of the column, while less volatile fractions are withdrawn at lower points.

Rotary Vacuum Flash Evaporator (Superfit, An ISO 9001:2000 Certified Company):

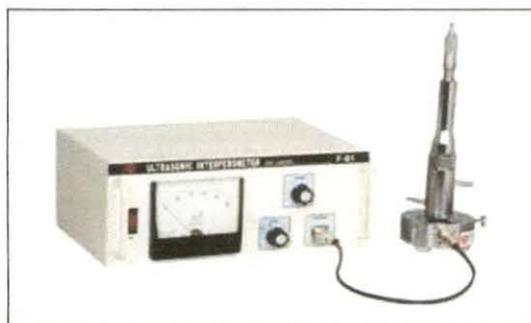
A rotary evaporator (or rotavap) is a device used in chemical laboratories for the efficient and gentle removal of solvents from samples by evaporation. When referenced in the chemistry research literature, description of the use of this technique and equipment may include the phrase "rotary evaporator", though use is often rather signaled by other language (e.g., "the sample was evaporated under reduced pressure").



Rotary evaporation is most often and conveniently applied to separate "low boiling" solvents such as n-hexane or ethyl acetate from compounds which are solid at room temperature and pressure. However, careful application also allows removal of a solvent from a sample containing a liquid compound if there is minimal co-evaporation (azeotropic behavior), and a sufficient difference in boiling points at the chosen temperature and reduced pressure.

3.2.7. ULTRASONIC SPEED MEASUREMENT

The ultrasonic speed was measured with an accuracy of 0.2% using single-crystal variable-path ultrasonic interferometer (Model M-81 Mittal Enterprises, New Delhi) operating at 4MHz which was calibrated with water, methanol and benzene at required temperature.



The principle used in the measurement of the ultrasonic speed (u) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (f) are produced by a quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes a maximum.

If the distance is now increased or decreased and the variation is exactly one half of wave length ($\lambda / 2$) or integral multiples of it, anode current becomes maximum. From the knowledge of the wave length (λ), the speed (u) can be obtained by the relation.

$$\text{Ultrasonic speed } (u) = \text{Wave Length } (\lambda) \times \text{Frequency } (f) \quad (5)$$

The ultrasonic interferometer consists of the following two parts, (i) the high frequency generator, and (ii) the measuring cell. The measuring cell is connected to the output terminal of the high frequency generator through a shielded cable. The

cell is filled with the experimental liquid before switching on the generator. The ultrasonic waves move normal from the quartz crystal till they are reflected back from the movable plate and the standing waves are formed in the liquid in between the reflector plate and the quartz crystal. The micrometer is slowly moved till the anode current on the meter on the high frequency generator shows a maximum. A number of maxima readings of anode current are passed and their number (n) is counted. The total distance (d) thus moved by the micrometer gives the value of the wavelength (λ) with the following relation.

$$d = n \times \lambda/2 \quad (6)$$

Further, the velocity is determined from which the isentropic compressibility (K_S) is calculated by the following formula:

$$K_S = 1 / (u^2 \cdot \rho) \quad (7)$$

where ρ is the density of the experimental liquid.

Figure 1(a) shows the Multifrequency Ultrasonic Interferometer i.e. (i) Cross-section of the measuring cell, (ii) Position of reflector vs. crystal current (Note : The extra peaks in between minima and maxima occurs due to a number of reasons, but these do not effect the value of $\lambda/2$) and (b) Electronic circuit diagram of the instrument)

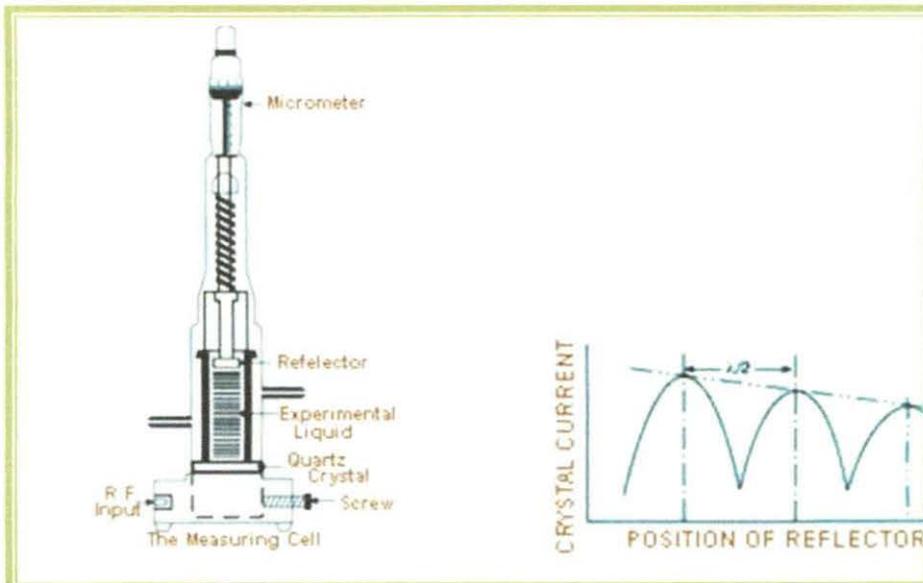


Figure 1(a): The Multifrequency Ultrasonic Interferometer

3.2.8. CONDUCTIVITY MEASUREMENT

Systronics Conductivity TDS meter-308 is used for measuring specific Conductivity of electrolytic solutions. It can provide both automatic and manual temperature compensation.



The conductance measurements were carried out on this conductivity bridge using a dip-type immersion conductivity cell of cell constant 1.11cm^{-1} . The entire conductance data were reported at 1 KHz and was found to be $\pm 0.3\%$ precise. The instrument was standardized using 0.1(M) KCl solution. The cell was calibrated by the method of Lind and co-workers [8]. The conductivity cell was sealed to the side of a 500 cm^3 conical flask closed by a ground glass fitted with a side arm through which dry and pure nitrogen gas was passed to prevent admission of air into the cell when solvent or solution was added. The measurements were made in a thermostatic water bath maintained at the required temperature with an accuracy of $\pm 0.01\text{ K}$ by means of mercury in glass thermo regulator [9].

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

3.2.9. REFRACTIVE INDEX MEASUREMENT

Refractive index was be measure with the help of Digital Refractometer (Mettler Toledo 30GS).



Calibration was performed by measuring the refractive indices of double-distilled water, toluene, cyclohexane, and carbon tetrachloride at defined temperature. The accuracy of the instrument is ± 0.0005 . 2-3 drops of the sample was put onto the measurement cell and the reading was taken. The refractive index of a sample depends on temperature. During measurement, refractometer determines the temperature and then corrects the refractive index to a temperature as desired by the user.

3.2.10. FT-IR MEASUREMENT

Infrared spectra were recorded in 8300 FT-IR spectrometer (Shimadzu, Japan)



with a resolution of $\pm 0.25 \text{ cm}^{-1}$ in the region of $400\text{-}4000 \text{ cm}^{-1}$ at room temperature ($25 \text{ }^{\circ}\text{C}$) with 49-54 % humidity. This KBr optics based instrument records data in different modes (KBr pellets, Nujol mull, non-aqueous solutions).

The intensity of light (I_0) passing through a blank is measured. The intensity is the number of photons per second. The blank is a solution that is identical to the sample solution except that the blank does not contain the solution that absorbs light. The intensity of light (I) passing through the sample solution is measured. (In practice, instrument measures the power rather than the intensity of the light. The power is the energy per second, which is the product of the intensity (photons per second) and the energy per photon. The experimental data is used to calculate two quantities: the transmittance (T) and the absorbance (A).

$$T = \frac{I}{I_0}, \quad A = -\log_{10} T \quad (10)$$

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

REFERENCES

- [1]. D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd Ed., Pergamon Press, Oxford, England (1988).
- [2]. C. Redlich, W.S. Beckett, J. Sparer, K.W. Barwick, C. A.Riely, H. Miller, S.L Sigal, S. L. Shalat, M. R. Cullen, *Annals of Internal Medicine* 108 (1988)680.
- [3]. J. Clayden, *Organic Chemistry*. Oxford: Oxford University Press (2001).
- [4]. S. Zen, E. Kaji, *Org. Synth.* 6 (1988) 503.
- [5]. J. Geiss, *The century of space science*. Kluwer Academic. (2001) p. 20.
- [6]. T. Ramnial, DD. Ino, JAC. Clyburne, *Chem Commun.*, (2005) 325.
- [7]. Oscillating U-tube. Electronic document, [http://en.wikipedia.org/wiki/Oscillating U-tube](http://en.wikipedia.org/wiki/Oscillating_U-tube), accessed January 21, (2013).
- [8]. J.E. Lind Jr., J.J. Zwolenik, R.M. Fuoss, *J. Chem. Soc. Faraday Trans I.* 81 (1959) 1557.
- [9]. B. Das, N. Saha, *J. Chem. Eng. Data.* 45 (2000) 2.

CHAPTER IV

STUDY OF SOLUTE-SOLVENT INTERACTION OF SOME BIO-ACTIVE SOLUTES PREVAILING IN AQUEOUS ASCORBIC ACID SOLUTION

4.1. INTRODUCTION

Amino acids are molecules containing an amine group, a carboxylic acid group and a side-chain that varies between different amino acids. The key elements of an amino acid are carbon, hydrogen, oxygen, and nitrogen. They are particularly important in biochemistry, where the term usually refers to *alpha-amino acids*. Amino acids are critical to life, and have many functions in metabolism. One particularly important function is to serve as the building blocks of proteins, which are linear chains of amino acids. Due to their central role in biochemistry, amino acids are important in nutrition and are commonly used in nutrition supplements, fertilizers, food technology and industry.

Importantly ascorbic acid (vitamin C) is also able to regenerate other antioxidants as vitamin E. Vitamin C is required for the synthesis of collagen, the intercellular “cement” which gives the structure of muscles, vascular tissues, bones, and tendon. Vitamin C with Zn is also important for the healing of wounds. It is also needed for the metabolism of bile acids which may have implications for blood cholesterol levels and gallstones. Ascorbic acid and its sodium, potassium, and calcium salts are commonly used as antioxidants food additives. Vitamin C plays an important role for the synthesis of several important peptide hormones, neurotransmitters and creatinine. It also enhances the eye’s ability and delay the progression of advanced age related muscular degeneration [1].

The volumetric, viscometric and interferometric behavior of solutes has been proven to be very useful in elucidating the various interactions occurring in solutions. Studies on the effect of concentration (molality), the apparent molar volumes of solutes have been extensively used to obtain information on ion-ion, ion-solvent, and solvent-solvent interactions [2-6].

In view of the above and in continuation of our studies, we have undertaken a systematic study on the density, viscosity, refractive index and ultrasonic speed of some amino acids in aqueous ascorbic acid solutions at 298.15 K and we have attempted to report the limiting apparent molar volume (ϕ_V^0), experimental slopes (S_V^*), and viscosity B -coefficients, molar refraction (R) and limiting apparent molar adiabatic compressibility (ϕ_K^0) for the cited amino acids in ascorbic acid.

4.2. EXPERIMENTAL METHODS

4.2.1. Source and purity of samples

Ascorbic acid was purchased from Sd. Fine chemicals Limited, and used as delivered. Its mass purity as supplied is 98%. The amino acids L-Glycine (S.D. Fine Chemicals, >99%), L-Alanine (S.D. Fine Chemicals, >98.5%), and L-Valine (Loba Chemie, India, >99%) were used for the present study and were used as such without further purification. Ascorbic acid was recrystallized twice from aqueous ethanol solution and dried under vacuum at $T = 348$ K for 6 h. Thereafter, it was stored over P_2O_5 in a desiccator before used [7]. Triply distilled water with a specific conductance $<10^{-6}$ S cm^{-1} was used for the preparation of different aqueous ascorbic acid solutions. The physical properties of different mass fraction of aqueous ascorbic acid mixture are listed in Table 1.

4.2.2. Apparatus and Procedure

The Density (ρ) was measured by means of vibrating-tube Anton Paar Density-Meter (DMA 4500M) with a precision of 0.00005 $g.cm^{-3}$. It was calibrated by double-distilled water and dry air [8]. The temperature was automatically kept constant within ± 0.01 K.

The viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol. A thoroughly cleaned and perfectly dried viscometer filled with experimental solution was placed

vertically in a glass-walled thermostat (Bose Panda Instruments Pvt. Ltd.) maintained to 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stop watch. The flow times were accurate to ± 0.1 s. The mixtures were prepared by mixing known volume of solutions in airtight-stopper bottles and each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of determining possible dispersion of the results obtained. Adequate precautions were taken to minimize evaporation losses during the actual measurements. Mass measurements were done on a Mettler AG-285 electronic balance with a precision of ± 0.01 mg. The precision of density measurements was $\pm 3.10^{-4}$ g·cm⁻³.

Viscosity of the solution is evaluated using the following equation [9].

$$\eta = \left(Kt - \frac{L}{t} \right) \rho \quad (1)$$

where K and L are the viscometer constants, t is the efflux time of flow in seconds and ρ is the density of the experimental liquid. The uncertainty in viscosity measurements is within ± 0.003 mPa·s.

Refractive index was measured with the help of a Digital Refractometer Mettler Toledo. The light source was LED, $\lambda=589.3$ nm. The refractometer was calibrated twice using distilled water and calibration was checked after every few measurements. The uncertainty of refractive index measurement was ± 0.0002 units.

The ultrasonic velocities, u (ms⁻¹) were measured using an ultrasonic interferometer (Model M-83) from Mittal enterprises. The interferometer working at 2 MHz is based on the same principle as was used by Freyer et al. [10] and Kiyoharo et al. [11,12]. The obtained velocities were corrected for diffraction errors as given by Subrahmayan et al. [13]. The maximum uncertainty in the velocity is ± 0.5 m s⁻¹. The temperature was controlled within ± 0.01 K using a Lauda thermostat for velocity measurements.

The solutions studied here were prepared by mass and the conversion of molarity into molality was accomplished [4] using experimental density values. The experimental values of densities (ρ), viscosities (η), refractive indices (n_D) and

ultrasonic speeds (u) of solutions are reported in Table 2 and the derived parameters are reported in Table 3 and Table 4.

4.3. RESULTS AND DISCUSSIONS

4.3.1. Density calculation

Apparent molar volumes (ϕ_v) were determined from the solution densities using the following equation [14].

$$\phi_v = M / \rho - 1000(\rho - \rho_o) / m\rho\rho_o \quad (2)$$

where M is the molar mass of the solute, m is the molality of the solution ρ_o and ρ are the densities of the mixture and the solution respectively. The limiting apparent molar volume ϕ_v^0 was calculated using a least-square treatment to the plots of ϕ_v versus \sqrt{m} using the Masson equation [15].

$$\phi_v = \phi_v^0 + S_v^* \sqrt{m} \quad (3)$$

where ϕ_v^0 is the limiting apparent molar volume at infinite dilution and S_v^* is the experimental slope. The plots of ϕ_v against square root of molal concentration (\sqrt{m}) were found to be linear with slopes. Values of ϕ_v^0 and S_v^* are reported in Table 4.

A perusal of Table 4 shows that ϕ_v^0 values for amino acids are positive and increases with the increase in the mass fractions of ascorbic acid in the mixture. This indicates the presence of strong solute-solvent interactions and these interactions are further strengthened with an increase in the mass fractions of ascorbic acid in the mixture.

L-Glycine < L-Alanine < L-Valine

This shows that with increases in the number of carbon atoms in the studied amino acids, the solute-solvent interaction also increases, similar results will be found for amino acid in methanoic acid (Formic acid) [16].

Ascorbic acid behaves as a vinylogous carboxylic acid wherein the double bond transmits electron pairs between the hydroxyl group and the carbonyl [17]. There are two resonating structures for the deprotonated form, differing in the position of double bond. The deprotonated form is an enolate which is usually strongly basic. Ascorbic acid

also converts into two unstable diketone tautomers by proton transfer, although it is the most stable in the enol form. The proton of the enol is lost, and re-acquired by electrons from the double bond to produce a diketone [18]. There are two possible forms: 1,2-diketone and 1,3-diketone (IIa and IIb). The molecule exists in equilibrium with two ketone tautomers, which are less stable than the enol form. In solutions, these forms of ascorbic acid rapidly interconvert **Scheme 1**.

It is known that the amino acids remain in zwitter ionic form in solid and in liquid. There are two acidic proton in ascorbic acid designated as H_{α} and H_{β} . On dissociation of any of this proton ascorbate ion will be formed. The stability of the conjugate base (respective ascorbate ion) will determine the acidity of the respective proton, **Scheme 2**.

Ascorbic acid (I) on dissociation of H_{α} proton gives its conjugate base structure 'X'. On the other hand enol form of ascorbic acid (I) on dissociation of H_{β} proton gives its conjugate base 'Y'. As structure 'Y' has one more equally contributing resonating structure 'Z', where as structure 'X' does not have any resonating structure. Therefore, the stability of conjugate base generated on removal of H_{β} proton is more than that of conjugate base generated on removal of H_{α} proton. Thus β proton of ascorbic acid is more acidic than the α proton as each dissociation is more facile. Therefore, the negatively charged oxygen atom in the carboxylic group of amino acids probably interacts with the most acidic hydrogen (β hydrogen) of enol form of ascorbic acid rendering higher solute-solvent interaction in comparison with solute-solute interaction as evident from ϕ_V^0 values. The order of solute-solvent interaction mentioned in Table 4 may be due to the reason, as the higher amino acids contain more alkyl groups (electron releasing group, +I effect), the caboxylate oxygen becomes more and more electron denser rendering to stronger interaction, i.e. stronger solute-solvent interaction.

A plausible mechanism of interaction between ascorbic acid and different amino acids as evident from the experimental observation explained and discussed above is given in **Scheme 3**.

The S_v^* values of the amino acid solution given in Table 4 decreases with increases in the number of carbon atoms of the studied amino acids and with increases in the mass fraction of ascorbic acid in the solvent mixture rendering minimum solute-solute interaction in the higher analogs.

The magnitude of ϕ_v^0 (Figure 1) values is much greater than those of S_v^* for all studies amino acids as well as mass fraction of ascorbic acid in the mixture suggests that solute-solvent interactions dominate over solute-solute interactions.

4.3.2. Viscosity calculation

The viscosity data has been analyzed using Jones-Dole equation [19].

$$(\eta / \eta_0 - 1) / m^{1/2} = A + Bm^{1/2} \quad (4)$$

where η_0 and η are the viscosities of the solvent and solution respectively. A and B are the viscosity co-efficient estimated by a least-squares method and are reported in Table 4. The values of the A co-efficient are found to decrease with the increase in the number of carbon atoms of amino acids (from L-Glycine to L-Valine) and with the increase in mass fraction of ascorbic acid in solvent mixture. The results indicate the presence of very weak solute-solute interactions. These results are in excellent agreement with those obtained from S_v^* values discuss earlier.

The effects of solute-solvent interactions on the solution viscosity can be inferred from the B -coefficient [20, 21]. The viscosity B -coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 4 and Figure 2 it is evident that the values of the B -coefficient are positive, thereby suggesting the presence of strong solute-solvent interactions, and strengthened with an increase the number of carbon atoms of amino acids and with the increase of mass fraction of ascorbic acid in the solvent mixture, are in agreement with the results obtained from ϕ_v^0 values discussed earlier.

4.3.3. *Refractive index calculation*

The molar refraction, R can be evaluated from the Lorentz-Lorenz relation [22].

$$R = \left\{ \frac{(n_D^2 - 1)}{(n_D^2 + 2)} \right\} (M/\rho) \quad (5)$$

where R , n_D , M and ρ are the molar refraction, the refractive index, the molar mass and the density of solution respectively. The refractive index of a substance is defined as the ratio c_0/c , where c is the speed of light in the medium and c_0 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 [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 and with the increase of mass fraction of ascorbic acid in solvent mixture refractive index value also increases. Hence a perusal of Tables 2 and 3 we found that the refractive index and the molar refraction values respectively are higher for L-Valine compare to other two amino acids, indicating the fact that the molecules are more tightly packed in the mixture. The interaction in the solution is basically solute-solvent interaction and a small amount of solute-solute interaction. This is also good agreement with the results obtained from density and viscosity parameters discussed above. The trend in the package of the studied amino acid in aqueous mixture of ascorbic acid is

L-Glycine < L-Alanine < L-Valine.

4.3.4. *Ultrasonic speed calculation*

The adiabatic compressibility (β) was evaluated from the following equation:

$$\beta = 1 / u^2 \rho \quad (6)$$

where ρ is the density of solution and u is the speed of sound in the solution. The apparent molal adiabatic compressibility (ϕ_K) of the solutions was determined from the relation [16].

$$\phi_K = M\beta / \rho + 1000(\beta \rho_o - \beta_o \rho) / m \rho \rho_o \quad (7)$$

where β_o, β are the adiabatic compressibility of the solvent and solution respectively and m is the molality of the solution. Limiting partial molal adiabatic compressibilities (ϕ_K^0) and experimental slopes (S_K^*) were obtained by fitting ϕ_K against the square root of molality of the electrolyte (\sqrt{m}) using the method of least squares.

$$\phi_K = \phi_K^0 + S_K^* \cdot \sqrt{m} \quad (8)$$

The values of β and ϕ_K are reported in Table 3. The values of ϕ_K^0 and S_K^* are presented in Table 4. Since the values of ϕ_K^0 and S_K^* are measures of solute-solvent and solute-solute interactions respectively, a perusal of Table 4 and Figure 3 shows that the ϕ_K^0 values are in good agreement with those drawn from the values of ϕ_V^0 discussed earlier.

4.4. CONCLUSION

The values of the limiting apparent molar volume (ϕ_V^0), viscosity B -coefficients and limiting partial isentropic compressibility (ϕ_K^0) indicate the presence of strong solute-solvent interactions which increases with the increase in the number of carbon atoms of the studied amino acids and with increase of mass fraction of ascorbic acid in the aqueous mixture. The refractive index and the molar refraction values suggest that L-Valine molecules are more tightly packed in the solution leading to higher solute-solvent interaction than the other studied amino acids.

REFERENCES

- [1]. M. N. Roy, R. K. Das, A. Bhattacharjee, *Russian J. Phys. Chem A*. 84 (2010) 2201.
- [2]. J. M. McDowall, C.A. Vincent, *J. Chem. Soc., Faraday Trans. 1*. 70 (1974) 1862.
- [3]. M.R. J .Deck, K.J. Bird, A.J. Parker, *Aust. J. Chem.* 28 (1975) 955.
- [4]. M.N. Roy, B. Sinha, R. Dey, A. Sinha, *Int. J. Thermophy.* 26 (2005) 1549.
- [5]. M. N. Roy, R. Dewan, P. K. Roy, D. Biswas, *J. Chem. Eng. Data*. 55 (2010) 3617.
- [6]. M. N. Roy, A. Bhattacharjee, P. Chakraborti, *Thermochim. Acta*. 507–508 (2010) 135.
- [7]. C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.* 37 (2005) 37.
- [8]. A. Bhattacharjee, M. N. Roy, *Phys. Chem. Chem. Phys.* 12 (2010) 14534.
- [9]. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data*. 49 (2004) 291.
- [10]. E. B. Freyer, J. D. Hubbard, D. H. Andrews, *J. Am. Chem. Soc.* 51 (1929) 759.
- [11]. O. Kiyohara, K. Arakawa, *Bull. Chem. Soc. Jpn.* 43 (1970) 3037.
- [12]. O. Kiyohara, J. P. E. Grolier, and G. C. Benson, *Can. J. Chem.* 52 (1974) 2287.
- [13]. N. M. Murthy, S. V. Subrahmanyam, *Bull. Chem. Soc. Jpn.* 50 (1977) 2589.
- [14]. E. Ayranci, *J. Chem. Eng. Data*. 42 (1997) 934.
- [15]. D.O. Masson, *Phil. Mag.* 8 (1929) 218.
- [16]. M. N. Roy, D. Ekka , R. Dewan, *Acta Chim. Slov.* 58 (2011) 792.
- [17]. J. Clayden, N. Greeves, S. Warren, P. Wothers, *Organic Chemistry*, Oxford University Press, Oxford: New York, (2001).
- [18]. D. Denby, Vitamin C, *Chemistry Review* 5(5) University of York, New York, May (1996).
- [19]. G. Jones, M. Dole, *J. Am. Chem. Soc.* 51 (1929) 2950.
- [20]. F. J. Millero, *Chem. Rev.* 71 (1971) 147.
- [21]. F. J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.* 82 (1978) 784.
- [22]. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press: New York, London, (1970).
- [23]. M. Born, E. Wolf, 7th ed., Cambridge University Press: London, (1999).
- [24]. M. Deetlefs, K. Seddon, M. Shara, *Phys. Chem. Chem. Phys.* 8 (2006) 642.

TABLES

Table 1. The values of density (ρ), viscosity (η), refractive index (n_D), and speed of sound (u) in different mass fraction of ascorbic acid at 298.15 K

Mass-fraction Ascorbic acid	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	n_D	u (ms^{-1})
$w_1 = 0.01$	0.99785	0.823	1.3323	1500.8
$w_1 = 0.03$	0.99936	0.835	1.3330	1504.5
$w_1 = 0.05$	1.00074	0.847	1.3338	1509.4

Table 2. Experimental values of densities (ρ), viscosities (η), refractive Index (n_D), and ultrasonic Speed (u) of L-Glycine, L-Alanine and L-Valine in different mass fraction of ascorbic acid at 298.15 K

molality (mol kg ⁻¹)	$P \times 10^{-3}$ (k m ⁻³)	η (mPas)	n_D	u (m s ⁻¹)	molality (mol kg ⁻¹)	$P \times 10^{-3}$ (kg m ⁻³)	η (mPas)	n_D	u (m s ⁻¹)
$w_1 = 0.01$					$w_1 = 0.03$				
L-Glycine					L-Glycine				
0.1001	0.99810	0.830	1.3324	1505.0	0.1001	0.99955	0.840	1.3335	1509.2
0.1584	0.99851	0.835	1.3328	1517.5	0.1583	0.99987	0.845	1.3339	1523.3
0.2004	0.99894	0.840	1.3331	1534.7	0.2003	1.00022	0.849	1.3342	1542.7
0.2351	0.99939	0.844	1.3334	1556.9	0.2349	1.00059	0.853	1.3345	1567.3
0.2653	0.99986	0.849	1.3337	1582.5	0.2651	1.00098	0.857	1.3348	1598.3
0.2924	1.00034	0.853	1.3340	1613.8	0.2923	1.00138	0.861	1.3351	1634.0
L-Alanine					L-Alanine				
0.1001	0.99806	0.832	1.3326	1504.2	0.1001	0.99949	0.843	1.3336	1508.4
0.1584	0.99842	0.842	1.3330	1515.4	0.1583	0.99974	0.853	1.3340	1521.5
0.2005	0.99881	0.851	1.3333	1531.5	0.2004	1.00004	0.861	1.3343	1540.4
0.2352	0.99922	0.860	1.3336	1552.2	0.2351	1.00037	0.870	1.3346	1564.5
0.2654	0.99966	0.870	1.3339	1578.2	0.2653	1.00074	0.879	1.3349	1593.9
0.2926	1.00011	0.878	1.3342	1609.0	0.2925	1.00112	0.889	1.3352	1629.8
L-Valine					L-Valine				
0.1002	0.99799	0.834	1.3328	1503.3	0.1001	0.99942	0.845	1.3337	1507.5
0.1585	0.99826	0.847	1.3333	1513.4	0.1584	0.99959	0.858	1.3343	1519.7

0.2006	0.99857	0.861	1.3337	1528.9	0.2005	0.99982	0.872	1.3347	1537.8
0.2354	0.99892	0.874	1.3341	1548.7	0.2353	1.00010	0.885	1.3351	1561.5
0.2658	0.99929	0.887	1.3345	1573.6	0.2656	1.00042	0.898	1.3355	1590.4
0.2931	0.99969	0.901	1.3349	1603.5	0.2929	1.00076	0.913	1.3359	1625.3
$w_1 = 0.05$									
L-Glycine									
0.1000	1.00089	0.851	1.3346	1514.6					
0.1582	1.00115	0.855	1.3350	1530.3					
0.2002	1.00144	0.859	1.3354	1552.7					
0.2348	1.00176	0.863	1.3357	1581.3					
0.2650	1.00209	0.866	1.3360	1615.3					
0.2921	1.00244	0.870	1.3363	1657.4					
L-Alanine									
0.1000	1.00078	0.854	1.3347	1513.8					
0.1582	1.00091	0.863	1.3351	1528.5					
0.2002	1.00109	0.872	1.3354	1549.4					
0.2349	1.00131	0.880	1.3357	1577.0					
0.2652	1.00157	0.889	1.3360	1610.4					
0.2924	1.00185	0.899	1.3363	1651.7					
L-Valine									
0.1000	1.00072	0.856	1.3348	1512.8					
0.1583	1.00080	0.869	1.3354	1526.0					
0.2004	1.00096	0.882	1.3358	1545.8					
0.2351	1.00117	0.896	1.3362	1571.9					
0.2655	1.00145	0.909	1.3366	1603.8					
0.2928	1.00175	0.922	1.3370	1642.6					

Table 3. Molality, apparent molar volume (ϕ_v), $(\eta/\eta_0-1)/m^{1/2}$, molar refraction (R), adiabatic compressibility (β) and apparent molal adiabatic compressibility (ϕ_K) of L-Glycine, L- Alanine, and L-Valine in ascorbic acid at 298.15 K

molality (mol kg ⁻¹)	$\phi_v \times 10^6$ (m ³ mol ⁻¹)	$(\eta/\eta_0-1)/m^{1/2}$ (kg ^{1/2} mol ^{-1/2})	R (cm ³ mol ⁻¹)	$\beta \times 10^{10}$ (Pa ⁻¹)	$\phi_K \times 10^{10}$ (m ³ mol ⁻¹ Pa ⁻¹)
$w_1 = 0.01$					
L-Glycine					
0.10001	50.1779	0.082	15.4456	4.4234	-2.3674
0.15840	48.7749	0.094	15.4562	4.3490	-3.7936
0.20040	47.9230	0.103	15.4622	4.2502	-4.7626
0.23510	47.1714	0.111	15.4678	4.1280	-5.6308
0.26530	46.4556	0.118	15.4732	3.9937	-6.3018
0.29240	45.8745	0.124	15.4784	3.8384	-6.9824
L-Alanine					
1.0010	68.2367	0.107	18.3410	4.4283	-1.7987
0.1584	66.4328	0.143	18.3544	4.3615	-3.2169
0.2005	65.2302	0.169	18.3622	4.2686	-4.2272
0.2352	64.3192	0.193	18.3697	4.1538	-5.0864
0.2654	63.3691	0.215	18.3766	4.0163	-5.9037
0.2926	62.6364	0.230	18.3833	3.8622	-6.6275
L-Valine					

0.1002	103.3723	0.132	24.1326	4.4339	-1.0809
0.1585	100.9671	0.185	24.1590	4.3737	-2.5738
0.2006	99.3636	0.229	24.1778	4.2841	-3.6863
0.2354	97.9060	0.263	24.1956	4.1738	-4.5725
0.2658	96.7867	0.293	24.2129	4.0413	-5.3977
0.2931	95.7087	0.324	24.2295	3.8904	-6.1489
<hr/> $w_1 = 0.03$ <hr/>					
L-Glycine					
0.1001	56.1059	0.061	15.4696	4.3924	-2.5846
0.1583	54.7050	0.074	15.4814	4.3101	-4.1839
0.2003	53.6043	0.084	15.4886	4.2009	-5.2589
0.2349	52.7401	0.092	15.4955	4.0685	-6.1701
0.2651	51.9604	0.100	15.5021	3.9107	-7.0559
0.2923	51.3382	0.107	15.5085	3.7402	-7.7790
L-Alanine					
0.1001	76.1387	0.094	18.3647	4.3973	-2.0036
0.1583	73.9373	0.132	18.3801	4.3208	-3.6683
0.2004	72.1362	0.157	18.3896	4.2142	-4.8442
0.2351	70.7717	0.180	18.3985	4.0840	-5.8090
0.2653	69.4201	0.200	18.4066	3.9333	-6.6564
0.2925	68.4279	0.220	18.4146	3.7605	-7.4649
L-Valine					
0.1001	111.2212	0.121	24.1572	4.4029	-1.2925
0.1584	108.0191	0.177	24.1925	4.3317	-3.0819
0.2005	105.7177	0.218	24.2132	4.2294	-4.3159
0.2353	103.7619	0.254	24.2326	4.1008	-5.3575

0.2656	102.0725	0.283	24.2511	3.9519	-6.2464
0.2929	100.7439	0.316	24.2691	3.7827	-7.0607
$w_1 = 0.05$					
L-Glycine					
0.1000	60.0256	0.043	15.4951	4.3553	-2.8085
0.1582	58.6266	0.057	15.5079	4.2653	-4.5722
0.2002	57.5274	0.067	15.5201	4.1419	-5.8505
0.2348	56.4827	0.077	15.5278	3.9922	-6.9133
0.2650	55.7430	0.084	15.5352	3.8246	-7.7756
0.2921	55.0293	0.092	15.5424	3.6315	-8.6352
L-Alanine					
0.1000	85.0271	0.078	18.3959	4.3604	-2.1905
0.1582	82.2292	0.116	18.4135	4.2764	-4.0256
0.2002	80.2806	0.144	18.4251	4.1610	-5.2728
0.2349	78.6681	0.166	18.4360	4.0158	-6.3868
0.2652	77.1757	0.185	18.4462	3.8499	-7.3201
0.2924	75.9750	0.208	18.4559	3.6588	-8.2226
L-Valine					
0.1000	119.0619	0.106	24.1980	4.3664	-1.4384
0.1583	114.6651	0.165	24.2354	4.2909	-3.3035
0.2004	111.5674	0.206	24.2577	4.1810	-4.6369
0.2351	109.2510	0.243	24.2788	4.0424	-5.7678
0.2655	106.9280	0.274	24.2982	3.8821	-6.7293
0.2928	105.1898	0.302	24.3171	3.6998	-7.6119

Table 4. Limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*), A , B coefficients, limiting partial adiabatic compressibility (ϕ_K^0), and experimental slope (S_K^*) of L-Glycine, L-Alanine, and L-Valine in aqueous ascorbic acid at 298.15 K

Salt	$\phi_V^0 \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	$S_V^* \times 10^6$ ($\text{m}^3 \text{mol}^{-3/2} \text{kg}^{1/2}$)	A (kg mol^{-1})	B ($\text{kg}^{1/2} \text{mol}^{-1/2}$)	$\phi_K^0 \times 10^{10}$ ($\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1}$)	$S_K^* \times 10^4$ ($\text{m}^3 \text{mol}^{-3/2} \text{Pa}^{-1} \text{kg}^{1/2}$)
$w_1 = 0.01$						
L-Glycine	52.366	-22.222	0.0592	0.2210	0.0143	-23.907
L-Alanine	71.083	-28.967	0.0411	0.6476	0.7418	-25.002
L-Valine	107.300	-39.660	0.0298	0.9952	1.5682	-26.222
$w_1 = 0.03$						
L-Glycine	58.625	-25.019	0.0362	0.2407	0.1121	-26.943
L-Alanine	80.256	-40.514	0.0280	0.6506	0.8187	-28.251
L-Valine	116.680	-54.719	0.0182	1.0051	1.6724	-29.846
$w_1 = 0.05$						
L-Glycine	62.716	-26.286	0.0161	0.2581	0.2131	-30.261
L-Alanine	89.716	-47.113	0.0114	0.6629	0.9370	-31.208
L-Valine	126.150	-72.078	0.0039	1.0161	1.7674	-32.021

FIGURES

Figure 1. The plots of limiting apparent molar volumes (ϕ_V^0) for L-Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of ascorbic acid in aqueous mixture at 298.15 K

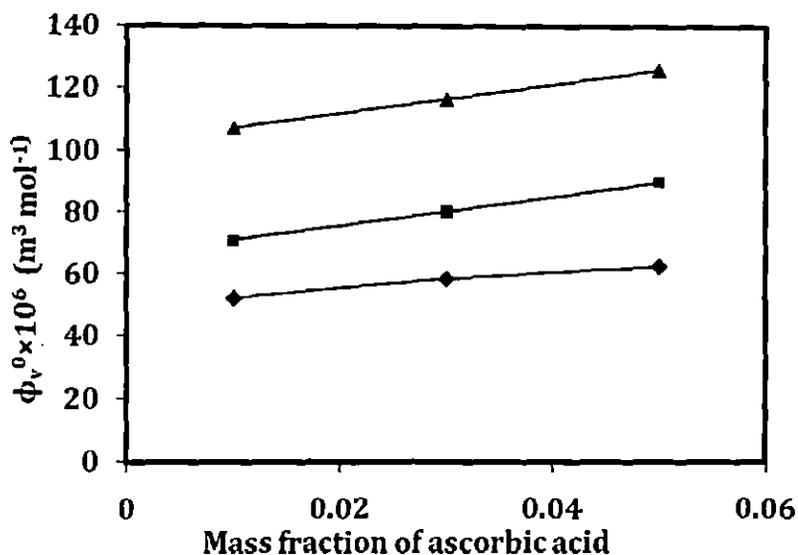


Figure 2. The plots of viscosity B -coefficient for L-Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of ascorbic acid in aqueous mixture at 298.15 K

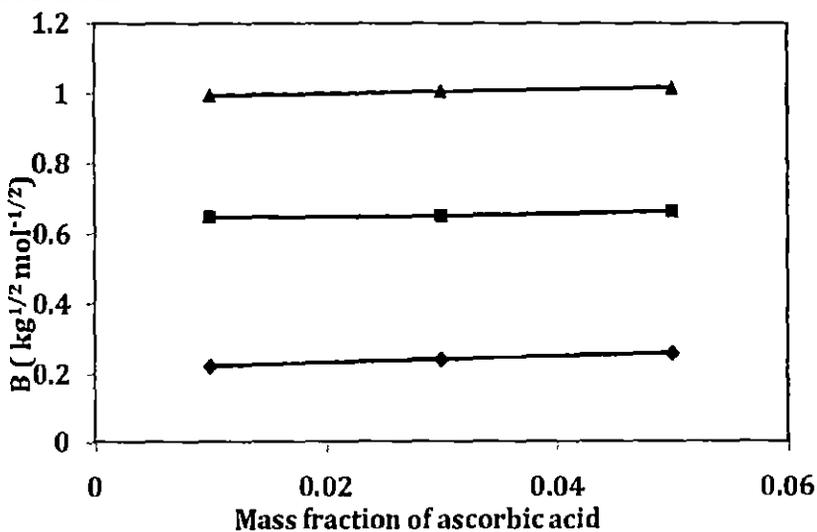
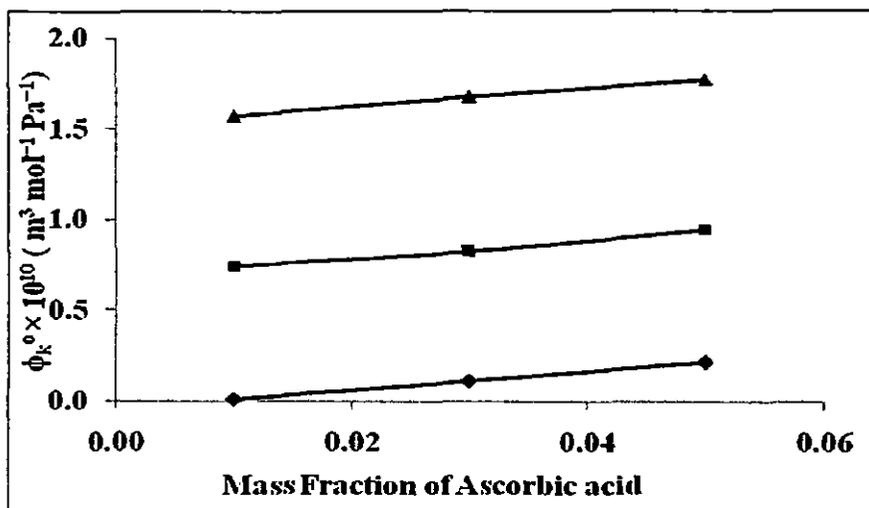
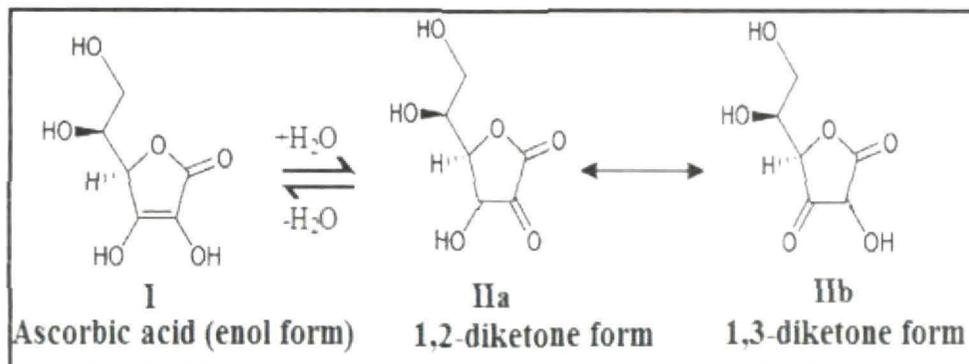


Figure 3. The plots of limiting partial adiabatic compressibility (ϕ_k^0) for L-Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of ascorbic acid in aqueous mixture at 298.15 K

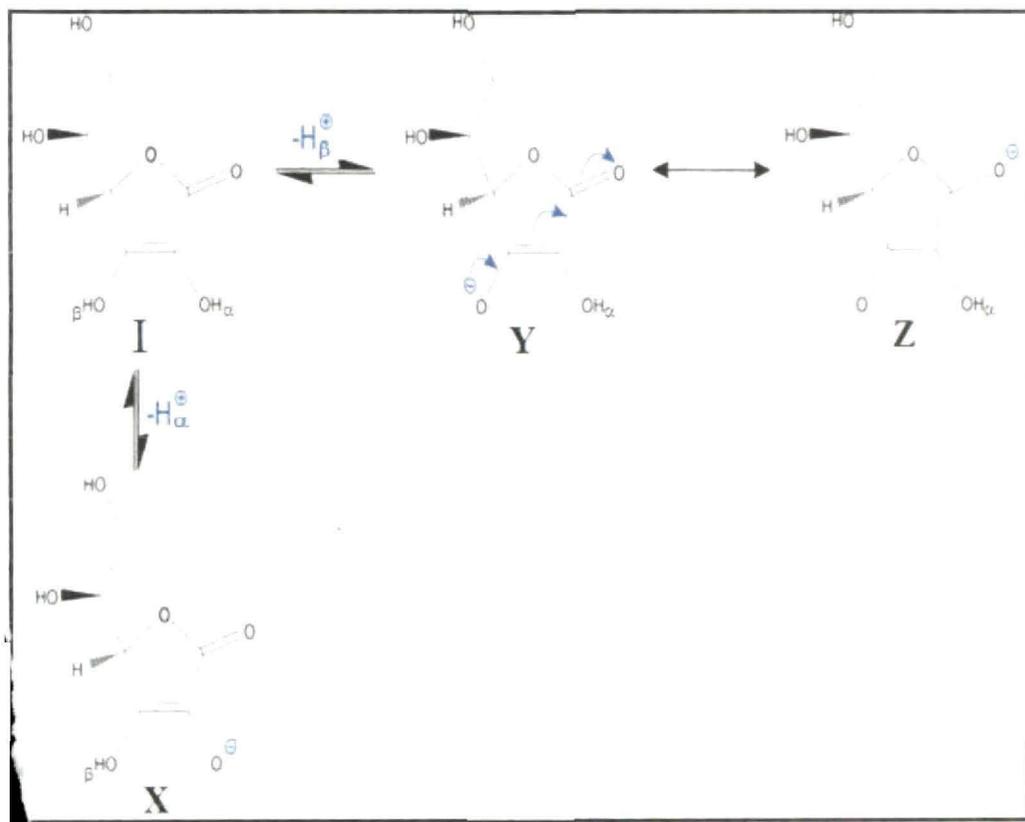


SCHEMES

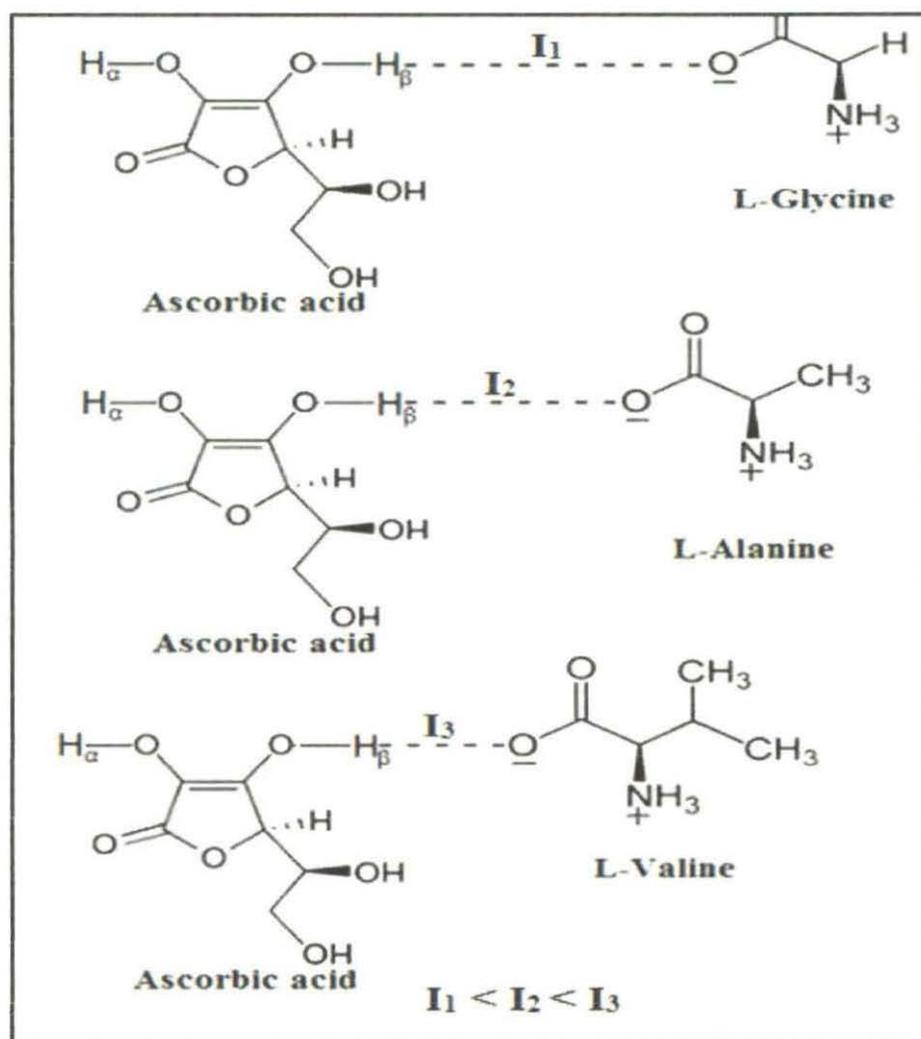
Scheme 1. Keto-enol tautomerism of ascorbic acid.



Scheme 2. The stability of the conjugate base of ascorbate ion.



Scheme 3. Interaction between ascorbic acid and different amino acids.



CHAPTER V

STRUCTURAL EFFECTS OF THREE CARBOHYDRATES IN NICOTINIC ACID/ WATER MIXED SOLVENTS

5.1. INTRODUCTION

Carbohydrates (Bio-active solutes) are the most abundant class of organic compounds found in living organism. They form numerous roles in living system for the storage and transport of energy to participation in immune-system. The study of carbohydrates in aqueous solutions has become a subject of increasing interest because of the multidimensional physical, biochemical and industrially useful properties in addition to their importance in the food pharmaceutical and chemical industries [1-7]. Understanding the behaviour of these effects in dilute solutions is of utmost importance in medicinal and biological systems. The pyridine-monocarboxylic acids are examples of amphiprotic [8] electrolytes that are of considerable biological interest. Nicotinic acid (3-pyridine carboxylic acid), also known as niacin or pellagra-preventing factor, is an important compound which play a crucial role in various physiological effects, biosynthesis, metabolic reactions, and several drug preparations [9].

The physicochemical and thermodynamic properties of nicotinic acid are of considerable interest as it is an essential nutrient for humans and certain other animal species, in which it functions as a vitamin. Studies on densities, viscosities, and refractive indices of studied solutions are of great use in characterizing the structure and properties of solutions. Various types of interactions exist between the solutes in solutions, as solute-solute and solute-solvent interactions [4, 5] provide a better understanding of the nature of the non-electrolytes in solution, which is very significant for investigate their physicochemical behaviour. Among various physical parameters, these thermodynamic parameters have been recognised as being sensitive to structural changes occurring in solutions. Moreover, model compound studies have been necessitated owing to the complex structural organisation of the biological macromolecules.

In this article, an attempt has been made to reveal the nature of various types of interactions prevailing in carbohydrates (D-glucose, D-mannitol and D-sucrose) in $w_1 = 0.005, 0.01, 0.015$ mass fraction of aqueous nicotinic acid (NA) binary mixtures at 298.15, 308.15, and 318.15 K from volumetric, viscometric and refractometric measurements. Aim of the present work is to study the molecular interactions of carbohydrates in aqueous solutions of nicotinic acid by physicochemical and thermodynamical studies, and the structural effect of carbohydrates as literature survey reveals that very scarce work has been carried out in the present ternary systems. Such study helps in better understanding of the interactions occurring between carbohydrate molecules and entities present in mixed aqueous medium in the living cells.

5.2. EXPERIMENTAL SECTION

5.2.1. Source and purity of samples

D-Glucose, D-mannitol, and D-sucrose (Sd. Fine Chemicals, India) were purified using standard methods [10] (mass fraction purity 0.98). Nicotinic acid was purchased from the Sigma Aldrich, USA; (mass fraction purity 0.99) was used as such without further purification.

5.2.2. Apparatus and Procedure

Aqueous binary solution of nicotinic acid (NA) was prepared by mass (Mettler Toledo AG-285 with uncertainty $\pm 0.0003\text{g}$), which are used as solvent. Stock solutions of the salts (carbohydrates) in different aqueous nicotinic acid solutions were also prepared by mass and the working solutions were obtained by mass dilution. The conversion of molarity into molality was accomplished using experimental density values. All solutions were prepared afresh before use. The uncertainty in molality of the solutions is evaluated to $\pm 0.0001 \text{ mol kg}^{-3}$.

A vibrating U-tube digital density meter (DMA 4500M, Anton Paar,) was used to measure the densities of the solutions (ρ) with an accuracy of $\pm 0.00005\text{g cm}^{-3}$ maintained at $\pm 0.01 \text{ K}$ of the desired temperature. It was calibrated by passing cold triply-distilled water (5-6 times), then hot (about 50-60°C) distilled water (5-6 times), after all continuous pass dry air through this U-tube to remove the water drops. The instrument has been kept about 30 mins to temperature equilibrium

with room temperature (298.15 K). After attaining the temp equilibrium the density measurement is carried on by ringing u-tube with experimental solutions. The whole experimental procedure is done in the moisture free air conditioner (AC) room at constant room temperature.

Solution viscosities (η) were measured using an Ubbelohde type viscometer thoroughly cleaned, dried and which was calibrated by measuring the flow time of double distilled water and purified methanol at 298.15, 308.15 and 318.15 K. It was filled with experimental liquid and placed vertically in a glass sided thermostat (Bose Panda Instruments Pvt. Ltd.) maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded using an electronic stop watch. The flow times were accurate to ± 0.1 s. The mixtures were prepared by mixing known volume of solutions in airtight-stopper bottles. A triplicate measurement was taken into account with sufficient precautions to minimize the evaporation loss. A Mettler AG-285 electronic balance with a precision of ± 0.01 mg was used to measure the mass. The viscosities of the solutions were calculated by using the appropriate equation [11]. The uncertainty in viscosity measurements is within ± 0.003 mPa·s.

Refractive index was measured with the help of a Digital Refractometer Mettler Toledo. The light source was LED, $\lambda=589.3$ nm. The refractometer was calibrated twice using distilled water and calibration was checked after every few measurements. The uncertainty of refractive index measurements was ± 0.0002 units.

The physical properties of different mass fractions ($w_1=0.005, 0.01, 0.015$) of aqueous NA solutions are listed in Table 1.

5.3. RESULTS AND DISCUSSION

5.3.1. Apparent molar volume

The measured experimental values of densities and viscosities, of three carbohydrates in different mass fractions ($w_1=0.005, 0.01, 0.015$) of aqueous NA mixture at 298.15, 308.15 and 318.15 K as a function of concentration (molality) are listed in Table 2. The pH value of different mass fractions ($w_1=0.005, 0.01, 0.015$) of aqueous NA mixture were measured and found to be 3.6, 3.7 and 3.8 respectively. As the aqueous solution of NA is acidic at the pH range of 3.6 to 3.8, so NA gets

dissociated into nicotinate ion and hydronium when dissolved in water. The possible interaction of nicotinate ion and water is given in Scheme 1. As the carbohydrates are added to the aqueous NA solution, the nicotinate ion present in the solution reacts with the added carbohydrate. The plausible mechanism of acid hydrolysis of the studied carbohydrates along with the nucleophilic reaction of the nicotinate ion with carbohydrates is given in Scheme 2. Plausible products I and II are obtained after the reaction of nicotinate ion with D-glucose and D-mannitol respectively. On reaction of the nicotinate ion with D-sucrose also produces the plausible product I along with fructose. Volumetric properties, such as, ϕ_V , ϕ_V^0 , are sensitive tools for the understanding of interactions in solutions. The apparent molar volume can be considered to be the sum of the geometric volume of the solute molecule and changes in the solvent volume due to its interaction with the solute. For this purpose, the apparent molar volumes ϕ_V were determined from the solution densities using the following equation and the values are presented in Table 3 [12].

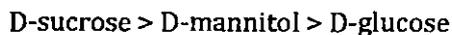
$$\phi_V = M / \rho - 1000(\rho - \rho_o) / m \rho \rho_o \quad (1)$$

Where the symbol have their usual significance. Concentration variation of apparent molar volume is very useful for understanding the interactions in a system. The variation of apparent molar volume with concentration (molality) is expressed by Masson's equation [12]

The ϕ_V^0 indicates solute-solvent interaction because at infinite dilution there is negligible solute-solute interaction. The ϕ_V^0 values have been determined by fitting the dilute data ($m < 0.1 \text{ mol}\cdot\text{kg}^{-1}$) to Masson's equation and are reported in Table 4. At infinite dilution, each monomer of solute is surrounded only by the solvent molecules, therefore, that ϕ_V^0 is unaffected by solute-solute interaction and it is a measure only of the solute-solvent interaction [13].

A perusal of Table 4 and Figure 1 shows that the ϕ_V^0 values are large and positive and increase with the rise in temperature as well as the mass of nicotinic acid in the solvent mixture. This indicates the presence of strong solute-solvent interactions [14], and these interactions are strengthened with the rise in

temperature and with an increase in the mass of NA in the solvent mixtures. As is evident from the ϕ_V^0 values, the trend in the solute-solvent interaction of the carbohydrates is as follows:



The values of ϕ_V^0 for the carbohydrates in pure water are reported in Table 5. In the Masson Eq. [12] the parameter S_V^* is the volumetric virial coefficient obtained from slope by plotting of ϕ_V vs \sqrt{m} , given in Table 4 and it characterizes the pair wise interaction of solvated species in solution [15, 16]. The S_V^* values were found to be negative and decrease further as the experimental temperature and mass of the nicotinic acid increases. This trend in S_V^* values indicates weak solute-solute interactions in the mixtures. A quantitative comparison between ϕ_V^0 and S_V^* values show that, the magnitude of ϕ_V^0 values are higher in magnitude than S_V^* , suggesting that the solute-solvent interactions dominate over the solute-solute interactions in all of the solutions at the investigated temperatures. Furthermore, S_V^* values are negative at all experimental temperatures, and the values slightly decrease with the increase of all experimental temperatures which may be attributed to less thermal aggregation at higher temperatures, resulting in diminishing the force of solute-solute interactions.

Standard Transfer Volume

The standard transfer volume for the carbohydrates, $\Delta\phi_V^0$, from pure water to aqueous NA solutions have been determined using the following relation [17]

$$\Delta\phi_V^0(\text{carbohydrate}) = \phi_V^0(\text{carbohydrate} + \text{aq. NA}) - \phi_V^0(\text{aq.}) \quad (2)$$

The $\Delta\phi_V^0$ value is, by definition, free from solute-solute interactions and therefore provides information regarding solute-solvent (co-solute) interactions [14]. Table 5 and Figures 2, 3 and 4 shows that the value of $\Delta\phi_V^0$ is positive at all the experimental temperatures and increases monotonically with the increase in mass fraction (w_1) of the nicotinic acid in solutions. The concentration dependence of the thermodynamic properties of the solutes in aqueous solutions can be explained in

terms of overlap of hydration co-spheres. According to the co-sphere model, as developed by Friedman and Krishnan, [18] the effect of overlap of the hydration co-spheres is destructive, which has been supported from the observation given in Mishra et al. [19]. Using this phenomenon it is observed that an overlap of hydration co-spheres of two ionic species results in an increase in volume but the hydration co-spheres of hydrophobic-hydrophobic groups and ion-hydrophobic groups results in a net volume decrease. However, in the present study, the positive values of $\Delta\phi_V^0$ indicates that solute-solvent interactions are predominate and the overall effect of the overlap of the hydration co-spheres of carbohydrates and nicotinic acid produce the effect of electrostriction of water by carbohydrates molecules and this effect increases with the mass fraction (w_1) of NA in the ternary mixtures. The reason behind increase in ϕ_V^0 values and the positive $\Delta\phi_V^0$ values can be attributed to the following fact. NA gets dissociated into nicotinate ion and hydronium ion when dissolved in water, and so the aq. NA solution becomes acidic. The studied carbohydrates, when dissolved in this acidic solution, get protonated and become ionic. Thus, both the species, i.e., NA and the carbohydrate, becomes ionic; and overlap of their hydration co-spheres results in the increase in the value. Therefore, the solute-solvent interaction increases with the increase in concentration of NA.

Thus the interactions between carbohydrate and nicotinic acid in water solutions can roughly be summarized as, (a) the hydrogen bonding interaction between the H atoms of water with (i) -O atom of the -OH group attached to the carbohydrate, (ii) -N atom in the heterocyclic ring of nicotinic acid, and (iii) -O atoms of the -COO group of nicotinic acid ; (b) the hydrogen bonding interaction between the O atom of water with the H atom associated with the -OH group attached to the carbohydrate. Therefore, more the number of interacting centres (-OH group) present in the carbohydrate, more is its interaction with the solvents (aq. NA). A possible interaction between the plausible products (obtained with reaction between different carbohydrates and nicotinate ion) with water is given in Scheme 3.

The overall positive values of ϕ_V^0 (Table 4) for the systems reinforce the fact that the solute-solvent interactions are predominate. Therefore the mutual overlap of the hydration spheres of solute and co-solute molecules will lead to an increase in the

magnitude of hydrogen bonding interactions between the plausible products (obtained with reaction between different carbohydrates and nicotinate ion) with water. The observation shows that with increase in the number of the interacting centres (-OH groups) present in the studied carbohydrates, the solute-solvent interaction also increases. The solute-solvent interaction in case of II is greater than I because of the presence of greater number of -OH group in II. Also I is closed chain so there is some sort of structural restriction, whereas II is open chained which favoured H-bonding to a greater extent. Therefore, the solute-solvent interaction is greater in II compared to I. Structure I and II are the plausible products obtained from the reaction between nicotinate ion in aqueous solution with D-glucose and D-mannitol respectively. So, the solute-solvent interaction is greater for D-mannitol compared to D-glucose.

The plausible products obtained from the reaction between D-sucrose with aq. NA are I and fructose respectively. The total number of the interacting centres (-OH groups) are higher in the plausible products obtained from D-sucrose compared to the plausible products of obtained from D-glucose or D-mannitol. Therefore, the solute-solvent interaction is greater for D-sucrose compared to D-mannitol or D-glucose in aqueous nicotinic acid solution. Also, the D-sucrose molecule on reacting with aq. NA breaks into two plausible products, which results into greater interactions because smaller the size greater the interaction.

Therefore, the solute-solvent interaction of the studied carbohydrates in aq.NA solution follows the trend,



At infinite dilution $\Delta\phi_V^0$ can be expressed by the following equation [20, 21]

$$\Delta\phi_V^0(\text{Water to aqueous NA solutions}) = 2 \cdot v_{AB} \cdot m_B + 3 \cdot v_{ABA} m_B^2 + \dots \quad (3)$$

where A stands for carbohydrates and B denotes NA, and m_B is the molality of NA (co-solute) and constants v_{AB} and v_{ABA} (or v_{BAB}) are pair and triplet interaction coefficient respectively. $\Delta\phi_V^0$ data have been fitted to equation (3) to obtain v_{AB} and v_{ABA} (or v_{BAB}) interaction coefficients which are given in Table 5. Both the triplet v_{ABA} (or v_{BAB}) and pair (v_{AB}) interaction coefficients are positive for all the carbohydrates in different mass fraction of (w_1) aq. NA at all studied temperatures and it suggests

that both the pair and triplet interaction are present in the studied solutions. Table 5 shows that value of v_{AB} are greater than v_{ABA} (or v_{BAB}) for all of the solutions under investigation, indicate that the contribution of paired interaction is greater than triplet interaction or in other words the paired interaction is dominant over the triplet interaction. The paired interaction coefficient increases from glucose to mannitol to sucrose, which also supports the fact that the paired (solute-solvent) interaction is strengthened with increasing number of $-OH$ group present in the studied carbohydrates. The positive values of pair interaction coefficients suggest that the interactions occur due to the overlap of hydration spheres of the solute-co-solute molecules, which again supports the conclusions drawn from the co-sphere overlap model.

Temperature dependent partial molar volume

The variation of ϕ_V^0 with the temperature of the carbohydrates in aqueous NA mixture can be expressed by the general polynomial equation [22]

$$\phi_V^0 = a_0 + a_1T + a_2T^2 \quad (4)$$

The values of a_0, a_1, a_2 coefficients for the carbohydrates in aqueous NA mixtures are reported in Table 6 (Supplementary Material).

The partial molar expansibilities, ϕ_E^0 , can be obtained by the following equation [23]

$$\phi_E^0 = \left(\delta \phi_V^0 / \delta T \right)_p = a_1 + 2a_2T \quad (5)$$

The sign of $\left(\delta \phi_E^0 / \delta T \right)_p$ is a better criterion in characterizing the long-range structure-making or breaking ability of the solutes in solution. The general thermodynamic expression used is as follows [24]

$$\left(\delta \phi_E^0 / \delta T \right)_p = \left(\delta^2 \phi_V^0 / \delta T^2 \right)_p = 2a_2 \quad (6)$$

If the sign of $\left(\delta \phi_E^0 / \delta T \right)_p$ is positive or a small negative, the molecule is a structure maker; otherwise, it is a structure breaker [24]. As is evident from Table 7 and Figure 5, the carbohydrates under investigation are predominantly structure breakers in all of the experimental solutions. When NA is dissolved in water, it gets dissociated into nicotinate ion and hydronium ion. The nicotinate ion gets solvated

by water molecule, which forms a co-sphere around it. As the carbohydrate is added to this solution, the co-sphere of nicotinate ion gets broken as it reacts with the carbohydrate to form the plausible products I or II. Thus, carbohydrates under investigation act as a structure breaker when added to aqueous NA solution.

5.3.2. Viscosity

The experimental viscosity data for the studied systems are listed in Table 2. The relative viscosity (η_r) has been analysed using the Jones-Dole equation [25]. Viscosity A - and B -coefficients, indicates solute-solute and solute-solvent interactions [13] respectively, are estimated by least-squares method by plotting $(\eta_r - 1)/\sqrt{m}$ vs \sqrt{m} , and reported in Table 3.

A -coefficients are negative for all the solutions under investigation and at all experimental temperatures. These results indicate the presence of weak solute-solute interactions. These results are in line with those obtained from S_V^* values.

The viscosity B -coefficient is a valuable tool to provide information about the solute-solvent interactions [26]. Table 4 illustrates that the values of the viscosity B -coefficient for carbohydrates in the studied aq. solutions are positive and much higher than A -coefficient, thereby suggesting the presence of strong solute-solvent interactions and these type of interactions are strengthened with a rise in temperature and also with an increase of mass fraction of NA (w_1) in the solvent mixtures. These results are in good agreement with the results obtained from ϕ_V^0 values discussed earlier.

Viscosity B -coefficients of transfer (ΔB) from water to different aqueous NA solutions have been determined using the relations [14, 17]

$$\Delta B(\text{carbohydrate}) = B(\text{carbohydrate} + \text{aqueous NA}) - B(\text{aq.}) \quad (7)$$

The ΔB values depicted graphically in Figures 2, 3, and 4 (ΔB vs mass fraction (w_1) of NA in solution) at the experimental temperatures. From Table 5 and Figures it is evident that ΔB values are positive and increases with a rise in temperature and with an increase in mass fraction of NA (w_1), thereby suggesting the presence of strong solute-solvent interactions, and the interactions are strengthened with rise in

temperature and increase of NA (w_1) in aqueous mixture. The observation supports the same results obtained from $\Delta\phi_V^0$ values discussed above.

The sign of dB/dT is another tool of structure-forming or -breaking ability of the solute [27]. It is found from Table 8 and Figure 5 that the values of the B -coefficient increase with a rise in temperature (positive dB/dT values), suggesting the structure breaking tendency of carbohydrates in the solvent systems. Moreover, it is interesting to note that the B -coefficients of the studied carbohydrates show a linear relationship with the partial molar volumes ϕ_V^0 , i.e;

$$B = A_1 + A_2\phi_V^0 \quad (8)$$

The coefficients A_1 and A_2 are included in Table 8. The positive slope (or A_2) shows the linear variation of B -coefficient with partial molar volumes ϕ_V^0 . This relationship is not unexpected, as both the viscosity B -coefficient and the partial molar volume reflect the solute-solvent interactions in the solutions.

5.3.3. Refractive index calculation

The obtained experimental values of refractive index (n_D) are given in Table 2. The molar refraction R can be evaluated from the Lorentz-Lorenz relation [28]. 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 [29]. As stated by Deetlefs et al. [30] the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser and with the increase of mass fraction of NA in solvent mixture refractive index value also increases. Hence a perusal of Table 2 and 3, we found that the refractive index and the molar refraction values respectively are higher for D-sucrose compare to other two carbohydrates, indicating the fact that the molecules are more tightly packed in the mixture at 298.15 K. It is evident from Table 3 that the molar refraction of the solutes in solution increases with increasing mass fraction of NA in the mixture leading to more solute-solvent interaction. The molar refraction is higher for D-sucrose than D-mannitol and D-glucose in solution which increases with the mass fraction of NA in solvent mixtures. The interaction in the solution is basically solute-solvent interaction and a small amount of solute-solute interaction. This is

also good agreement with the results obtained from density and viscosity parameters discussed above. The trend in the package of the studied carbohydrates in aqueous mixture of NA is



5.3.4. Other Thermodynamic Properties

According to Eyring and co-workers, [31] the free energy of activation of viscous flow per mole of solvent, $\Delta\mu_1^{0\#}$, can be calculated using the equation in ref. [22]. The viscosity data have also been analyzed on the basis of transition state theory for the viscosity of the solutions as suggested by Feakins and co-workers [32] using the relation, in ref. [22]. The values $\Delta\mu_2^{0\#}$ and $\Delta\mu_1^{0\#}$ for the carbohydrates in aqueous NA at 298.15, 308.15 and 318.15 K are listed in Table 9. The thermodynamic data, ΔH^* and $T\Delta S^*$ have proved useful in yielding structural information about solute species and solute-solvent interactions, were calculated using the following equation and are listed in Table 9.

$$\Delta\mu_2^{0\#} = \Delta H^* - T\Delta S^* \quad (9)$$

It is evident from the data in Table 9 that the $\Delta\mu_2^{0\#}$ values are positive at all experimental temperatures and solvent composition suggests that the process of viscous flow becomes difficult as the temperature and molality of nicotinic acid in solution increases. So the formation of the transition state becomes less favourable. According to Feakins and co-workers [32], $\Delta\mu_2^{0\#} > \Delta\mu_1^{0\#}$ for electrolytes having positive *B*-coefficients and indicates a stronger solute-solvent interactions, thereby suggesting that the formation of transition state is accompanied by the rupture and distortion of the intermolecular forces in solvent structure. The values of $T\Delta S_2^{0\#}$ and $\Delta H_2^{0\#}$ are found to be negative for all of the experimental solutions and all experimental temperatures suggesting that the transition state is associated with bond formation and increase in order. Although a detailed mechanism for this cannot be easily advanced, it may be suggested that the slip-plane is in the disordered state [33].

5.4. CONCLUSION

The present study reports experimental data for density, viscosity at different temperatures and refractive index at 298.15 K. From these data, several

thermodynamical parameters have been calculated and studied to explain the intermolecular interactions between mixing components. A plausible mechanism for the reaction of carbohydrates with aq. NA has been suggested, and the interaction of solute (plausible products) with solvent (water) has been shown. The observed positive values of ϕ_V^0 and inverse trends in S_V^* for all the carbohydrates studied in aqueous NA solution suggest the presence of strong solute-solvent and weak solute-solute interactions in these systems. This type of interactions gains strength with increase in concentration of NA in the solvent mixtures and with increase in temperature. The solute-solvent interaction for the studied carbohydrate in aqueous nicotinic acid solution follows the order: - D-sucrose > D-mannitol > D-glucose. The refractive index and the molar refraction value also validate the order of solute-solvent interaction of carbohydrates in aqueous nicotinic acid solution. All the carbohydrates under study were found to act as a structure breaker.

REFERENCES

- [1]. R. N. Goldberg, Y. B. Tewari, *J. Phys. Chem. Ref. Data*. 18 (1989) 809.
- [2]. J. Boerio Goates, *J. Chem. Thermodyn.* 23 (1991) 403.
- [3]. R. L. Putnam, J. Boerio-Goates, *J. Chem. Thermodyn.* 25 (1993) 607.
- [4]. R. N. Goldberg, Y. B. Tewari, *J. Biol. Chem.* 264 (1989) 9897.
- [5]. R. N. Goldberg, Y. B. Tewari, J. C. Ahluwalia, *J. Biol. Chem.* 264 (1989) 9901.
- [6]. Y. B. Tewari, R. N. Goldberg, *Biophys. Chem.* 40 (1991) 59.
- [7]. G. G. Birch, S. Shamil, *J. Chem. Soc., Faraday Trans. I.* 84 (1988) 2635.
- [8]. B. Garcia, S. Ibeas, J. M. Leal, *J. Phys. Org. Chem.* 9 (1996) 593.
- [9]. S. Budavari, The Merck Index, *An Encyclopedia of Chemicals, Drugs and Biologicals*. 12th edn, Merck, Whitehouse Station, N.J. p. 1120 (1996).
- [10]. D. D. Perrin, W. L. F. Armarego, *Purification of laboratory chemicals*, 3rd ed., Pergamon Press, Oxford, (1988).
- [11]. M.N. Roy, I. Banik, D. Ekka, *J. Chem. Thermodynamics*. 57 (2013) 230.
- [12]. A. Ali, S. Khan, F. Nabi, *J. Serb. Chem. Soc.* 72 (5) (2007) 495.
- [13]. A. K. Covington, T. Dickinson, *Physical chemistry of organic solvent systems*, Plenum, New York, (1973).
- [14]. K. Belibagli, E. Agranci, *J. Solution Chem.* 19 (1990) 867.
- [15]. R. K. Wadi, P. Ramasami, *J. Chem. Soc. Faraday Trans.* 93 (1997) 243.
- [16]. T. S. Banipal, D. Kaur, D. Banipal, *J. Chem. Eng. Data*. 49 (2004) 1236.
- [17]. C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.* 37 (2005) 37.
- [18]. H. L. Friedman, C. V. Krishnan, *Water: A comprehensive Treatise*, F. Franks, Ed., Vol. 3, Chapter 1 Plenum, New York, (1973).
- [19]. A. K. Mishra, K. P. Prasad, J. C. Ahluwalia, *Biopolymers*. 22 (1983) 2397.
- [20]. T.S. Banipal, D. Kaur, G. Singh, B. S. Lark, P.K. Banipal, *Indian J. Chem.* 41A (2002) 1131.
- [21]. T.S. Banipal, G. Singh, B. S. Lark, P. K. Banipal, *J. Sol. Chem.* 30 (2001) 657.
- [22]. M. N. Roy, R. Chanda, R. K. Das, D. Ekka, *J. Chem. Eng. Data*. 56 (2011) 3285.
- [23]. F.J. Millero, *The partial molal volumes of electrolytes in aqueous solutions*, in: R.A. Horne (Ed.), *Water and Aqueous Solutions: Structure, Thermodynamics, and Transport Processes*, Wiley Interscience, New York, p. 519 (1972).
- [24]. M. N. Roy, V. K. Dakua, B. Sinha, *Int. J. Thermophys.* 28 (2007) 1275.

- [25]. A.K. Nain, D. Chand, *J. Chem. Thermodynamics*. 41 (2009) 243.
- [26]. M. N. Roy, D. Ekka, R. Dewan, *Fluid Phase Equilibria*. 314 (2012) 113.
- [27]. A. Ali, S. Hyder, S. Sabir, D. Chand, A. K. Nain, *J. Chem. Thermodyn.* 38 (2006) 136.
- [28]. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, (1970).
- [29]. M. Born, E. Wolf, *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*, 7th ed., Cambridge University Press, London, (1999).
- [30]. M. Deetlefs, K. Seddon, M. Shara, *Phys. Chem. Chem. Phys.* 8 (2006) 642.
- [31]. S. Glasstone, K. J. Laidler, H. Eyring, *The Theory of Rate Processes*, McGraw Hill, New York, (1941).
- [32]. D. Feakins, D.J. Freemantle, K.G. Lawrence, *J. Chem. Soc. Faraday Trans. 1* 70 (1974) 795.
- [33]. U.N. Dash, B. Samantaray, S. Mishra, *J. Teach. Res. Chem.* 11 (2005) 87.

TABLES

Table 1. Values of density (ρ), viscosity (η), at 298.15, 308.15, 318.15 K and refractive index (n_D) at 298.15 K in different mass fraction (w_1) of aqueous NA

Mass fraction of aq NA (w_1)	Temp/K	$\rho \cdot 10^{-3}$ /kg m ⁻³	η /mPa s	n_D
$w_1 = 0.005$	298.15	0.99742	0.891	1.3320
	308.15	0.99431	0.720	-
	318.15	0.99047	0.584	-
$w_1 = 0.010$	298.15	0.99750	0.893	1.3323
	308.15	0.99448	0.721	-
	318.15	0.99062	0.587	-
$w_1 = 0.015$	298.15	0.99767	0.895	1.3328
	308.15	0.99465	0.722	-
	318.15	0.99081	0.589	-

Table 2. Experimental values of density (ρ) and viscosity (η) at 298.15 K, 308.15 K, 318.15 K and Refractive index (n_D) at 298.15 K of carbohydrates in different mass fraction of aqueous NA (w_1)

m /mol kg ⁻¹	$\rho \cdot 10^{-3}$ /kg cm ⁻³	η /mPa s	n_D	m /mol kg ⁻¹	$\rho \cdot 10^{-3}$ /kg cm ⁻³	η /mPa s	n_D
$w_1 = 0.005$							
D-glucose + aq. NA							
$T = 298.15$ K				$T = 298.15$ K			
0.0100	0.99801	0.893	1.3324	0.0555	1.00128	0.909	1.3343
0.0251	0.99902	0.898	1.3330	0.0707	1.00252	0.915	1.3350
0.0403	1.00012	0.904	1.3336	0.0860	1.00379	0.921	1.3357
$T = 308.15$ K				$T = 308.15$ K			
0.0101	0.99484	0.722		0.0557	0.99793	0.737	
0.0252	0.99578	0.727		0.0710	0.99912	0.742	
0.0404	0.99682	0.732		0.0863	1.00038	0.747	
$T = 318.15$ K				$T = 318.15$ K			
0.0101	0.99095	0.586		0.0559	0.99393	0.599	
0.0253	0.99183	0.590		0.0712	0.99511	0.604	
0.0406	0.99283	0.595		0.0866	0.99639	0.609	
D-mannitol+ aq. NA							
$T = 298.15$ K				$T = 298.15$ K			
0.0100	0.99803	0.894	1.3326	0.0555	1.00147	0.915	1.3346
0.0251	0.99907	0.901	1.3332	0.0707	1.00278	0.922	1.3353
0.0403	1.00023	0.908	1.3339	0.0860	1.00420	0.931	1.3361
$T = 308.15$ K				$T = 308.15$ K			
0.0101	0.99487	0.723		0.0557	0.99820	0.742	

0.0252	0.99587	0.729		0.0710	0.99949	0.748	
0.0404	0.99699	0.735		0.0863	1.00089	0.755	
T = 318.15 K				T = 318.15 K			
0.0101	0.99099	0.587		0.0559	0.99418	0.603	
0.0253	0.99194	0.592		0.0713	0.99544	0.609	
0.0406	0.99302	0.597		0.0867	0.99678	0.615	
D-sucrose+ aq. NA							
T = 298.15 K				T = 298.15 K			
0.0101	0.99870	0.896	1.3330	0.0560	1.00522	0.931	1.3365
0.0253	1.00078	0.907	1.3341	0.0714	1.00757	0.943	1.3378
0.0406	1.00296	0.919	1.3353	0.0870	1.00999	0.955	1.3391
T = 308.15 K				T = 308.15 K			
0.0101	0.99549	0.725		0.0560	1.00165	0.754	
0.0253	0.99743	0.734		0.0714	1.00390	0.765	
0.0406	0.99950	0.744		0.0870	1.00620	0.776	
T = 318.15 K				T = 318.15 K			
0.0101	0.99160	0.589		0.0562	0.99758	0.614	
0.0254	0.99347	0.597		0.0717	0.99978	0.623	
0.0407	0.99547	0.605		0.0874	1.00203	0.632	
w ₁ = 0.010							
D-glucose + aq. NA							
T = 298.15 K				T = 298.15 K			
0.0100	0.99807	0.895	1.3326	0.0555	1.00131	0.912	1.3346
0.0251	0.99906	0.900	1.3332	0.0707	1.00254	0.918	1.3353
0.0403	1.00015	0.906	1.3339	0.0860	1.00381	0.924	1.336
T = 308.15 K				T = 308.15 K			
0.0101	0.99496	0.723		0.0557	0.99796	0.738	
0.0252	0.99585	0.728		0.0710	0.99914	0.744	
0.0404	0.99686	0.733		0.0863	1.0004	0.750	
T = 318.15 K				T = 318.15 K			
0.0101	0.99104	0.588		0.0559	0.99396	0.602	
0.0253	0.99188	0.593		0.0712	0.99517	0.607	
0.0406	0.99287	0.597		0.0866	0.99644	0.612	
D-mannitol+ aq. NA							
T = 298.15 K				T = 298.15 K			
0.0100	0.99808	0.896	1.3329	0.0555	1.00152	0.918	1.3354
0.0251	0.99912	0.903	1.3338	0.0707	1.00283	0.926	1.3362
0.0403	1.00028	0.910	1.3346	0.0860	1.00423	0.934	1.337
T = 308.15 K				T = 308.15 K			
0.0101	0.99500	0.724		0.0557	0.99824	0.744	
0.0252	0.99596	0.730		0.0710	0.99950	0.752	
0.0404	0.99705	0.737		0.0863	1.00089	0.759	
T = 318.15 K				T = 318.15 K			
0.0101	0.99107	0.589		0.0559	0.99423	0.607	
0.0253	0.99197	0.595		0.0713	0.99547	0.614	
						0.620	
0.0406	0.99302	0.601		0.0867	0.99686		

D-sucrose+ aq. NA							
T = 298.15 K				T = 298.15 K			
0.0100	0.99874	0.898	1.3333	0.0558	1.00526	0.933	1.3370
0.0252	1.00079	0.910	1.3345	0.0712	1.00764	0.946	1.3383
0.0404	1.00297	0.921	1.3357	0.0866	1.01006	0.959	1.3396
T = 308.15 K				T = 308.15 K			
0.0101	0.99563	0.726		0.0560	1.00175	0.757	
0.0253	0.99754	0.736		0.0714	1.00399	0.768	
0.0406	0.99959	0.746		0.0870	1.00628	0.779	
T = 318.15 K				T = 318.15 K			
0.0101	0.99104	0.591		0.0559	0.99396	0.617	
0.0253	0.99188	0.599		0.0712	0.99517	0.627	
0.0406	0.99287	0.608		0.0866	0.99644	0.637	
w ₁ = 0.015							
D-glucose + aq. NA							
T = 298.15 K				T = 298.15 K			
0.0100	0.99823	0.896	1.3332	0.0555	1.00144	0.913	1.3355
0.0251	0.9992	0.902	1.3340	0.0707	1.00268	0.920	1.3363
0.0403	1.00028	0.907	1.3347	0.0860	1.00399	0.926	1.3371
T = 308.15 K				T = 308.15 K			
0.0101	0.99508	0.724		0.0557	0.99804	0.740	
0.0252	0.99593	0.729		0.0709	0.99925	0.747	
0.0404	0.99693	0.735		0.0863	1.00051	0.753	
T = 318.15 K				T = 318.15 K			
0.0101	0.99120	0.590		0.0559	0.99404	0.605	
0.0253	0.99200	0.594		0.0712	0.99522	0.610	
0.0406	0.99295	0.600		0.0866	0.99650	0.615	
D-mannitol+ aq. NA							
T = 298.15 K				T = 298.15 K			
0.0100	0.99824	0.897	1.3334	0.0555	1.00162	0.920	1.3357
0.0251	0.99925	0.905	1.3342	0.0707	1.00292	0.929	1.3365
0.0403	1.00038	0.912	1.3349	0.0860	1.00432	0.938	1.3373
T = 308.15 K				T = 308.15 K			
0.0101	0.99512	0.725		0.0557	0.99829	0.747	
0.0252	0.99604	0.731		0.0710	0.99957	0.755	
0.0404	0.99712	0.739		0.0863	1.00096	0.763	
T = 318.15 K				T = 318.15 K			
0.0101	0.99122	0.591		0.0559	0.99431	0.610	
0.0253	0.99207	0.597		0.0712	0.99560	0.617	
0.0406	0.99313	0.603		0.0866	0.99696	0.624	
D-sucrose+ aq. NA							
T = 298.15 K				T = 298.15 K			
0.0100	0.99888	0.900	1.3338	0.0558	1.00530	0.936	1.3375
0.0252	1.00088	0.911	1.3350	0.0712	1.00766	0.948	1.3388
0.0404	1.00303	0.923	1.3362	0.0866	1.01013	0.961	1.3402
T = 308.15 K				T = 308.15 K			
0.0101	0.99575	0.727		0.0560	1.00180	0.760	
0.0253	0.99761	0.737		0.0714	1.00403	0.772	

0.0406	0.99964	0.748	0.0870	1.00637	0.784
$T = 318.15 \text{ K}$			$T = 318.15 \text{ K}$		
0.0101	0.99183	0.593	0.0562	0.99770	0.621
0.0254	0.99361	0.601	0.0717	0.99994	0.631
0.0407	0.99558	0.611	0.0873	1.00231	0.641

Table 3. Molality (m), apparent molar volume (ϕ_v) and $(\eta_r - 1)/\sqrt{m}$ at 298.15 K, 308.15 K, 318.15 K and molar refraction (R) at 298.15 K of carbohydrates in different mass fraction of aqueous NA (w_1)

m /mol·kg ⁻¹	$\phi_v \cdot 10^6$ m ³ ·mol ⁻¹	$(\eta_r - 1)/\sqrt{m}$ kg ^{1/2} ·mol ^{-1/2}	R	m /mol·kg ⁻¹	$\phi_v \cdot 10^6$ m ³ ·mol ⁻¹	$(\eta_r - 1)/\sqrt{m}$ kg ^{1/2} ·mol ^{-1/2}	R
$w_1 = 0.005$							
D-glucose + aq. NA							
$T = 298.15$ K				$T = 298.15$ K			
0.0100	121.47	0.027	78.835	0.0555	110.26	0.088	78.866
0.0251	116.46	0.053	78.847	0.0707	107.58	0.103	78.874
0.0403	112.95	0.073	78.851	0.0860	105.49	0.116	78.879
$T = 308.15$ K				$T = 308.15$ K			
0.0101	127.89	0.031		0.0101	115.00	0.100	
0.0252	122.05	0.060		0.0252	112.08	0.115	
0.0404	118.08	0.082		0.0404	109.37	0.130	
$T = 318.15$ K				$T = 318.15$ K			
0.0101	133.43	0.032		0.0559	118.38	0.109	
0.0253	126.97	0.065		0.0712	114.97	0.126	
0.0406	122.33	0.089		0.0866	111.58	0.142	
D-mannitol+ aq. NA							
$T = 298.15$ K				$T = 298.15$ K			
0.0100	126.50	0.035	81.932	0.0555	113.83	0.115	81.966
0.0251	121.48	0.070	81.942	0.0707	110.88	0.132	81.969

Communicated in *J. Mol. Liquids*

0.0403	117.22	0.095	81.958	0.0860	107.68	0.152	81.978
	T = 308.15 K			T = 308.15 K			
0.0101	131.92	0.040		0.0557	117.11	0.128	
0.0252	125.48	0.076		0.0710	113.82	0.149	
0.0404	120.86	0.105		0.0863	110.39	0.168	
	T = 318.15 K			T = 318.15 K			
0.0101	136.47	0.040		0.0559	136.47	0.136	
0.0253	129.61	0.083		0.0713	129.61	0.156	
0.0406	124.61	0.111		0.0867	124.61	0.177	
D-sucrose + aq. NA							
	T = 298.15 K			T = 298.15 K			
							149.88
0.0100	214.85	0.061	149.855	0.0558	201.00	0.191	5
							149.90
0.0252	208.44	0.118	149.861	0.0712	197.81	0.218	5
							149.91
0.0404	204.33	0.158	149.879	0.0867	194.92	0.244	3
	T = 308.15 K			T = 308.15 K			
0.0101	225.58	0.066		0.0560	210.04	0.203	
0.0253	218.74	0.127		0.0714	206.47	0.235	
0.0406	213.77	0.168		0.0870	203.58	0.263	
	T = 318.15 K			T = 318.15 K			
0.0101	231.51	0.069		0.0562	215.08	0.212	
0.0254	224.44	0.131		0.0717	211.31	0.246	
0.0407	219.39	0.176		0.0874	208.28	0.275	

Communicated in *J. Mol. Liquids*

$w_1 = 0.010$							
D-glucose + aq. NA							
$T = 298.15 \text{ K}$				$T = 298.15 \text{ K}$			
0.0100	123.47	0.024	78.861	0.0555	111.17	0.089	78.909
0.0251	118.06	0.051	78.874	0.0707	108.43	0.104	78.918
0.0403	114.20	0.071	78.894	0.0860	106.19	0.119	78.923
$T = 308.15 \text{ K}$				$T = 308.15 \text{ K}$			
0.0101	132.89	0.027		0.0557	117.54	0.102	
0.0252	126.06	0.059		0.0710	114.22	0.120	
0.0404	121.33	0.084		0.0863	111.13	0.136	
$T = 318.15 \text{ K}$				$T = 318.15 \text{ K}$			
0.0101	139.47	0.027		0.0559	120.56	0.110	
0.0253	130.99	0.064		0.0712	116.25	0.129	
0.0406	125.08	0.088		0.0866	112.75	0.147	
D- mannitol+ aq. NA							
$T = 298.15 \text{ K}$				$T = 298.15 \text{ K}$			
0.0100	129.49	0.032	81.976	0.0555	114.37	0.120	82.088
0.0251	122.68	0.070	82.033	0.0707	111.31	0.138	82.106
0.0403	117.96	0.096	82.064	0.0860	108.26	0.155	82.116
$T = 308.15 \text{ K}$				$T = 308.15 \text{ K}$			
0.0101	135.92	0.040		0.0557	119.47	0.137	
0.0252	128.68	0.080		0.0710	116.10	0.159	
0.0404	123.60	0.112		0.0863	112.38	0.179	
$T = 318.15 \text{ K}$				$T = 318.15 \text{ K}$			

Communicated in *J. Mol. Liquids*

0.0101	143.52	0.043		0.0559	122.68	0.149	
0.0253	134.43	0.086		0.0713	119.00	0.173	
0.0406	128.37	0.120		0.0867	114.84	0.195	
D-sucrose+ aq. NA							
$T = 298.15$ K			$T = 298.15$ K				
							150.02
0.0100	218.85	0.060	149.936	0.0558	201.71	0.192	2
							150.03
0.0252	211.23	0.117	149.974	0.0712	197.94	0.223	6
							150.04
0.0404	206.07	0.157	149.993	0.0866	195.02	0.251	4
$T = 308.15$ K			$T = 308.15$ K				
0.0101	228.56	0.066		0.0560	211.28	0.211	
0.0253	221.12	0.129		0.0714	207.59	0.243	
0.0406	215.74	0.173		0.0870	204.61	0.274	
$T = 318.15$ K			$T = 318.15$ K				
0.0101	238.54	0.068		0.0562	217.25	0.221	
0.0254	229.25	0.133		0.0717	212.87	0.257	
0.0407	222.64	0.180		0.0874	208.61	0.289	
$w_1 = 0.015$							
D-glucose + aq. NA							
$T = 298.15$ K			$T = 298.15$ K				
0.0100	124.45	0.019	78.939	0.0555	111.88	0.090	79.035
0.0251	119.24	0.049	78.985	0.0707	108.84	0.106	79.058
0.0403	115.18	0.071	79.005	0.0860	106.05	0.121	79.075

Communicated in *J. Mol. Liquids*

	T = 308.15 K				T = 308.15 K		
0.0101	137.90	0.027		0.0557	119.16	0.110	
0.0252	129.65	0.063		0.0709	115.06	0.130	
0.0404	123.82	0.090		0.0863	111.82	0.147	
	T = 318.15 K				T = 318.15 K		
0.0101	142.47	0.027		0.0559	122.56	0.117	
0.0253	133.79	0.063		0.0712	118.25	0.137	
0.0406	127.83	0.093		0.0866	114.27	0.155	
D-mannitol + aq. NA							
	T = 298.15 K				T = 298.15 K		
0.0100	130.47	0.032	82.042	0.0555	115.62	0.123	82.127
0.0251	124.26	0.071	82.085	0.0707	112.43	0.144	82.145
0.0403	119.70	0.100	82.103	0.0860	109.19	0.165	82.156
	T = 308.15 K				T = 308.15 K		
0.0101	140.92	0.040		0.0557	121.64	0.149	
0.0252	132.28	0.086		0.0710	117.51	0.172	
0.0404	126.09	0.121		0.0863	113.54	0.193	
	T = 318.15 K				T = 318.15 K		
0.0101	147.53	0.039		0.0559	124.68	0.154	
0.0253	138.04	0.088		0.0712	119.84	0.179	
0.0406	130.37	0.123		0.0866	115.88	0.203	
D-sucrose + aq. NA							
	T = 298.15 K				T = 298.15 K		
0.0100	221.82	0.057	150.059	0.0558	204.05	0.196	150.15

Communicated in *J. Mol. Liquids*

							8
							150.17
0.0252	214.40	0.115	150.105	0.0712	200.05	0.226	5
							150.20
0.0404	208.79	0.159	150.127	0.0866	196.17	0.254	3
	T = 308.15 K			T = 308.15 K			
0.0101	233.55	0.069		0.0560	213.44	0.222	
0.0253	225.10	0.134		0.0714	209.42	0.259	
0.0406	218.72	0.182		0.0870	205.52	0.292	
	T = 318.15 K			T = 318.15 K			
0.0101	242.53	0.068		0.0562	219.04	0.233	
0.0254	232.44	0.137		0.0717	213.84	0.269	
0.0407	225.12	0.189		0.0873	208.93	0.303	

Table 4. Partial molar volumes (ϕ_V^0), experimental slopes (S_V^*), viscosity A - and B -coefficients of carbohydrates with their standard deviation in different mass fraction of aqueous NA (w_1) at 298.15 K, 308.15 K and 318.15 K respectively

Temp /K	$\phi_V^0 \cdot 10^6$ /m ³ ·mol ⁻¹	$S_V^* \cdot 10^6$ /m ³ ·mol ^{-3/2} ·kg ^{1/2}	B /kg·mol ⁻¹	A /kg ^{1/2} ·mol ^{-1/2}
$w_1 = 0.005$				
D-glucose + aq. NA				
298.15	129.67±0.02	-82.75±0.03	0.459±0.008	-0.0194±0.009
308.15	137.29±0.02	-94.93±0.003	0.513±0.004	-0.0212±0.006
318.15	144.81±0.03	-112.20±0.04	0.567±0.004	-0.0250±0.006
D-mannitol + aq. NA				
298.15	136.58±0.03	-97.19±0.01	0.598±0.009	-0.0250±0.004
308.15	143.04±0.02	-110.38±0.01	0.661±0.000	-0.0272±0.006
318.15	147.99±0.03	-115.27±0.02	0.702±0.006	-0.0301±0.004
D-sucrose + aq. NA				
298.15	224.85±0.02	-101.59±0.02	0.943±0.000	-0.0327±0.008
308.15	236.80±0.02	-113.24±0.01	1.011±0.010	-0.0350±0.000
318.15	243.52±0.02	-119.72±0.03	1.055±0.009	-0.0370±0.000
$w_1 = 0.010$				
D-glucose + aq. NA				
298.15	132.33±0.01	-89.69±0.02	0.490±0.006	-0.0261±0.004
308.15	143.98±0.03	-112.04±0.02	0.561±0.006	-0.0293±0.008
318.15	153.08±0.01	-137.73±0.01	0.614±0.006	-0.0345±0.010
D-mannitol + aq. NA				
298.15	140.17±0.02	-109.18±0.01	0.639±0.012	-0.0318±0.006
308.15	147.93±0.01	-120.54±0.03	0.722±0.010	-0.0330±0.000
318.15	158.1±0.02	-146.01±0.01	0.787±0.004	-0.0376±0.009
D-sucrose + aq. NA				
298.15	230.96±0.01	-123.24±0.02	0.985±0.006	-0.0398±0.013
308.15	240.86±0.03	-124.04±0.00	1.066±0.006	-0.0413±0.008
318.15	253.75±0.02	-153.20±0.01	1.132±0.004	-0.0469±0.004
$w_1 = 0.015$				
D-g + aq. NA				
298.15	134.19±0.04	-95.34±0.01	0.530±0.008	-0.0349±0.004
308.15	151.26±0.01	-135.45±0.01	0.623±0.008	-0.0360±0.000
318.15	157.03±0.04	-145.39±0.01	0.668±0.004	-0.0413±0.008
D-mannitol + aq. NA				
298.15	141.65±0.02	-110.19±0.01	0.683±0.004	-0.0371±0.004
308.15	154.76±0.02	-154.76±0.02	0.796±0.009	-0.0400±0.000
318.15	164.014±0.02	-165.04±0.02	0.849±0.013	-0.0472±0.006
D-sucrose + aq. NA				
298.15	235.23±0.01	-132.11±0.02	1.102±0.008	-0.0464±0.009
308.15	248.00±0.00	-144.69±0.04	1.149±0.010	-0.0482±0.006
318.15	259.85±0.003	-172.12±0.03	1.208±0.009	-0.0545±0.010

Table 5. Values of ϕ_V^0 (aq), $\Delta\phi_V^0$, B (aqueous), ΔB , v_{AB} , and v_{ABA}/v_{BAB} for carbohydrates in different mass fraction of aqueous NA(w_1) at 298.15 K, 308.15 K and 318.15 K respectively

Temp /K	$\phi_V^0 \cdot 10^6$ (aq) /m ³ ·mol ⁻¹	$\Delta\phi_V^0 \cdot 10^6$ /m ³ ·mol ⁻¹	B (aq) /kg·mol ⁻¹	ΔB / kg·mol ⁻¹	$v_{AB} \cdot 10^{-4}$ /m ³ kg mol ⁻²	v_{ABA} (Or v_{BAB}) · 10 ⁻⁴ /m ³ kg ² mol ⁻³
$w_1 = 0.005$						
D-glucose						
298.15	53.27	76.40	0.401	0.058	40.52	1.04
308.15	65.50	54.76	0.451	0.062	14.88	0.39
318.15	69.79	53.39	0.502	0.065	0.90	0.09
D-mannitol						
298.15	53.27	71.79	0.401	0.197	36.32	0.96
308.15	65.50	63.63	0.451	0.210	17.58	0.46
318.15	69.79	62.91	0.502	0.200	11.48	0.06
D-sucrose						
298.15	53.27	75.02	0.401	0.542	36.86	0.92
308.15	65.50	71.17	0.451	0.560	19.86	0.51
318.15	69.79	67.77	0.502	0.553	12.80	0.06
$w_1 = 0.010$						
D-glucose						
298.15	77.57	83.31	0.401	0.089	40.52	1.04

Communicated in *J. Mol. Liquids*

308.15	80.35	62.60	0.451	0.110	14.88	0.39
318.15	81.91	60.05	0.502	0.112	0.90	0.09
D-mannitol						
298.15	77.57	77.54	0.401	0.239	36.32	0.96
308.15	80.35	67.58	0.451	0.271	17.58	0.46
318.15	81.91	66.41	0.502	0.285	11.48	0.06
D-sucrose						
298.15	77.57	78.20	0.401	0.584	36.86	0.92
308.15	80.35	76.19	0.451	0.615	19.86	0.51
318.15	81.91	74.754	0.502	0.630	12.80	0.06
$w_1 = 0.015$						
D-glucose						
298.15	81.60	171.58	0.401	0.129	40.52	1.04
308.15	88.35	153.39	0.451	0.172	14.88	0.39
318.15	89.26	153.63	0.502	0.166	0.90	0.09
D-mannitol						
298.15	81.60	171.30	0.401	0.282	36.32	0.96
308.15	88.35	160.51	0.451	0.345	17.58	0.46
318.15	89.26	159.65	0.502	0.348	11.48	0.06
D-sucrose						
298.15	81.60	173.73	0.401	0.621	36.86	0.92
308.15	88.35	171.84	0.451	0.698	19.86	0.51
318.15	89.26	170.59	0.502	0.706	12.80	0.06

Communicated in *J. Mol. Liquids*

Table 6. Values of empirical coefficients (a_0 , a_1 , and a_2) of Equation 4 for carbohydrates in different mass fraction of aqueous NA (w_1)

solvent mixture	$a_0 \cdot 10^6$ /m ³ ·mol ⁻¹	$a_1 \cdot 10^6$ /m ³ ·mol ⁻¹ ·K ⁻¹	$a_2 \cdot 10^6$ /m ³ ·mol ⁻¹ ·K ⁻²
D-glucose+ aq. NA			
$w_1 = 0.005$	-143.46	1.065	-0.0050
$w_1 = 0.010$	-1386.42	8.895	-0.0128
$w_1 = 0.015$	-5173.53	33.458	-0.0525
D-mannitol+ aq. NA			
$w_1 = 0.005$	-749.68	5.224	-0.0076
$w_1 = 0.010$	1020.49	-6.560	0.0121
$w_1 = 0.015$	-2022.41	13.013	-0.0193
D-sucrose+ aq. NA			
$w_1 = 0.005$	-2533.97	17.050	-0.0262
$w_1 = 0.010$	1309.32	-8.074	0.0149
$w_1 = 0.015$	-568.13	4.066	-0.0046

Table 7. Limiting apparent molar expansibilities (ϕ_E^0) for carbohydrates in different mass fraction of aqueous NA (w_1) at 298.15 K, 308.15 K and 318.15 K respectively

Solvent mixture	$\phi_E^0 \cdot 10^6$ /m ³ ·mol ⁻¹ ·K ⁻¹			$(\partial\phi_E^0/\partial T)_P \cdot 10^6$ /m ³ ·mol ⁻¹ ·K ⁻²
D-glucose + aq. NA				
T/K	298.15	308.15	318.15	
$w_1 = 0.005$	0.767	0.757	0.747	-0.001
$w_1 = 0.010$	1.263	1.007	0.751	-0.026
$w_1 = 0.015$	2.152	1.102	0.052	-0.105
D-mannitol + aq. NA				
$w_1 = 0.005$	0.692	0.540	0.388	-0.015
$w_1 = 0.010$	0.655	0.897	1.139	0.024
$w_1 = 0.015$	1.504	1.118	0.732	-0.039
D-sucrose + aq. NA				
$w_1 = 0.005$	1.427	0.903	0.379	-0.052
$w_1 = 0.010$	0.811	1.109	1.407	0.030
$w_1 = 0.015$	1.323	1.231	1.139	-0.009

Table 8. Values of dB/dT , A_1 and A_2 coefficient of equation 8 for the carbohydrates in different mass fraction of aqueous NA (w_1)

Solvent mixture	dB/dT	A_1	A_2
D-glucose + aq. NA			
$w_1 = 0.005$	0.0054	-0.4690	0.0072
$w_1 = 0.010$	0.0062	-0.2983	0.0060
$w_1 = 0.015$	0.0069	-0.2614	0.0059
D-mannitol + aq. NA			
$w_1 = 0.005$	0.0052	-0.9187	0.0110
$w_1 = 0.010$	0.0074	-0.4933	0.0081
$w_1 = 0.015$	0.0083	-0.3812	0.0075
D-sucrose + aq. NA			
$w_1 = 0.005$	0.0056	-0.3933	0.0059
$w_1 = 0.010$	0.0074	-0.4840	0.0064
$w_1 = 0.015$	0.0093	-0.7593	0.0076

Table 9. Values of \bar{V}_1^0 , $\mu^{0\#}$, $T\Delta S^\#$, $\Delta H^\#$, for carbohydrates in different mass fraction of aqueous NA (w_1) at 298.15 K, 308.15 K and 318.15 K respectively

Parameters	$\bar{V}_1^0 \cdot 10^6$ /m ³ ·mol ⁻¹	$\Delta\mu_1^{0\#}$ / kJ·mol ⁻¹	$\Delta\mu_2^{0\#}$ / kJ·mol ⁻¹	$T\Delta S^\#$ / kJ·mol ⁻¹	$\Delta H^\#$ / kJ·mol ⁻¹
$w_1 = 0.005$					
Temp/K	D-glucose				
298.15	18.07	60.53	78.30	-242.37	-164.06
308.15	18.12	60.01	86.51	-250.49	-163.98
318.15	18.19	59.50	94.74	-258.62	-164.06
Temp/K	D-mannitol				
298.15	18.07	60.53	98.42	-223.55	-125.14
308.15	18.12	60.01	107.55	-231.05	-123.50
318.15	18.19	59.50	113.63	-238.55	-125.13
Temp/K	D-sucrose				
298.15	18.07	60.53	157.80	-248.03	-90.23
308.15	18.12	60.01	168.18	-256.35	-88.17
318.15	18.19	59.50	174.77	-264.67	-90.23
$w_1 = 0.010$					
Temp/K	D-glucose				
298.15	18.07	60.54	82.99	-284.35	-201.36
308.15	18.12	60.02	93.98	-293.88	-199.90
318.15	18.19	59.52	102.06	-303.42	-201.36
Temp/K	D-mannitol				
298.15	18.07	60.54	104.58	-324.69	-220.11
308.15	18.12	60.02	116.49	-335.58	-219.08

318.15	18.19	59.52	126.36	-346.47	-220.11
Temp/K			D-sucrose		
298.15	18.07	60.54	164.38	-327.82	-163.44
308.15	18.12	60.02	176.35	-338.81	-162.46
318.15	18.19	59.52	186.37	-349.81	-163.44
$w_1 = 0.015$					
Temp/K			D-glucose		
298.15	18.07	60.55	88.86	-314.79	-225.93
308.15	18.12	60.02	103.44	-325.35	-221.90
318.15	18.19	59.53	109.97	-335.90	-225.93
Temp/K			D-mannitol		
298.15	18.07	60.55	110.71	-372.69	-261.98
308.15	18.12	60.02	127.68	-385.19	-257.51
318.15	18.19	59.53	135.71	-397.69	-261.98
Temp/K			D-sucrose		
298.15	18.07	60.55	170.02	-411.39	-241.36
308.15	18.12	60.02	188.59	-425.19	-236.60
318.15	18.19	59.53	197.62	-438.98	-241.36

FIGURES

Figure 1. Plot of partial molar volume (ϕ_v^0) of D-glucose, D-mannitol, D-sucrose as a function of mass fraction of nicotinic acid in different binary mixtures of nicotinic acid (1)+water (2); at 298.15 K (-♦-), 308.15 K (-■-), and 318.15 K (-▲-) respectively

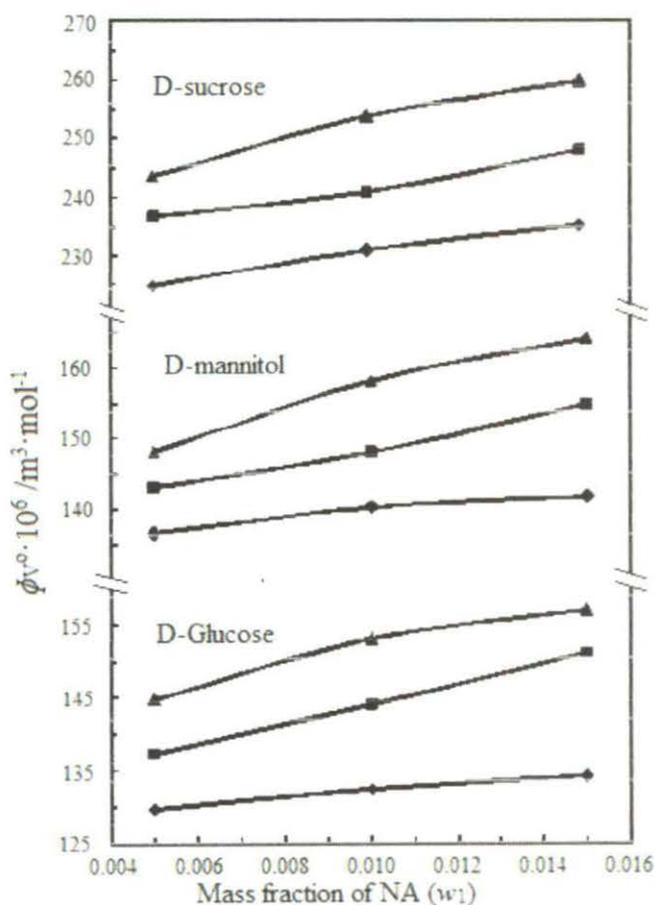


Figure 2. Plot of standard transfer volume ($\Delta\phi_V^0$), and deviation of viscosity B -coefficient (ΔB), from water to aqueous nicotinic acid solutions for D-glucose at different temperatures. Solid lines for $\Delta\phi_V^0$ at 298.15 K (-♦-), 308.15 K (-▲-), 308.15 K (-●-) and dotted lines for ΔB at 298.15 K (-◇-), 308.15 K (-△-), 318.15 K (-○-) respectively

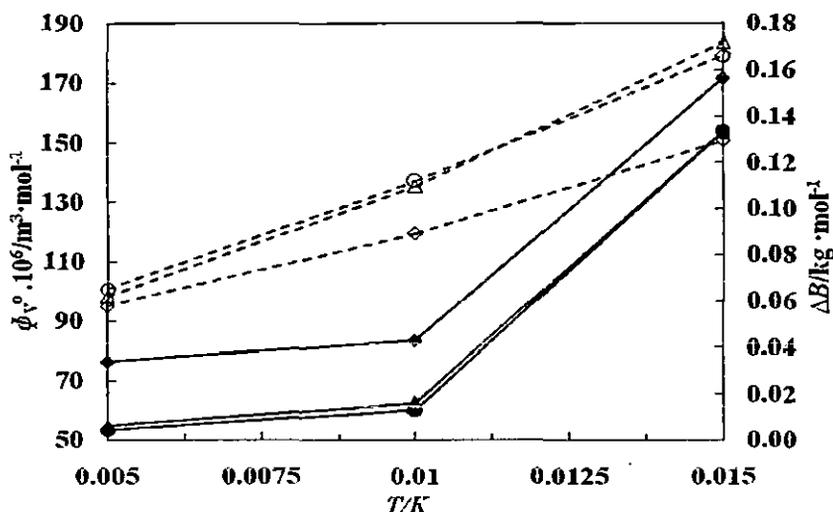


Figure 3. Plot of standard transfer volume ($\Delta\phi_V^0$), and deviation of viscosity B -coefficient (ΔB), from water to aqueous nicotinic acid solutions for D-mannitol at different temperatures. Solid lines for $\Delta\phi_V^0$ at 298.15 K (-♦-), 308.15 K (-▲-), 308.15 K (-●-) and dotted lines for ΔB at 298.15 K (-◇-), 308.15 K (-△-), 318.15 K (-○-) respectively

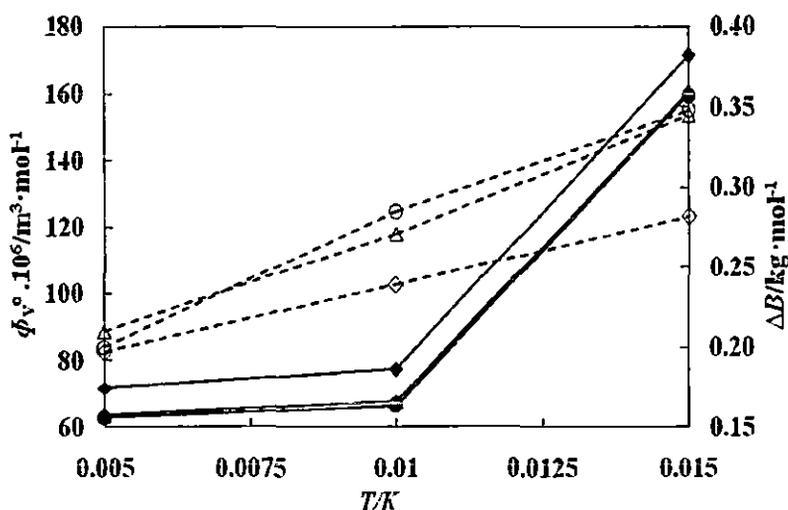


Figure 4. Plot of standard transfer volume ($\Delta\phi_v^0$), and deviation of viscosity B-coefficient (ΔB), from water to aqueous nicotinic acid solutions for D-sucrose at different temperatures. Solid lines for $\Delta\phi_v^0$ at 298.15 K (-♦-), 308.15 K (-▲-), 308.15 K (-●-) and dotted lines for ΔB at 298.15 K (-◇-), 308.15 K (-△-), 318.15 K (-○-) respectively

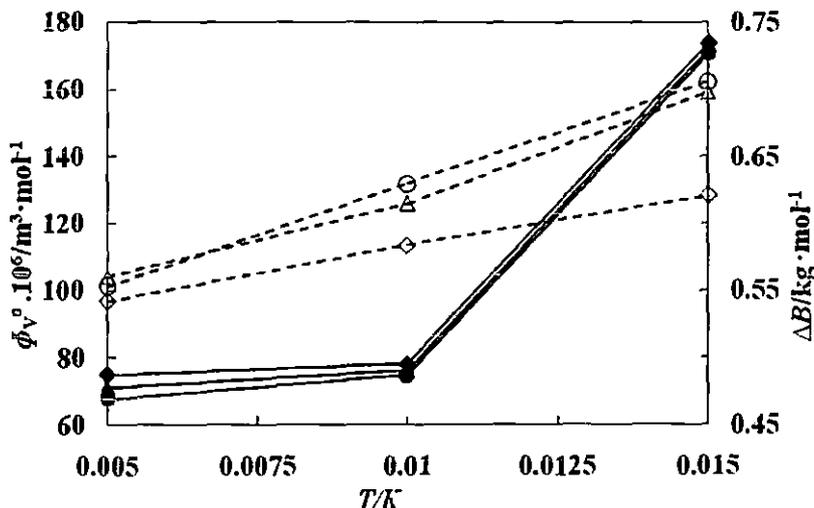
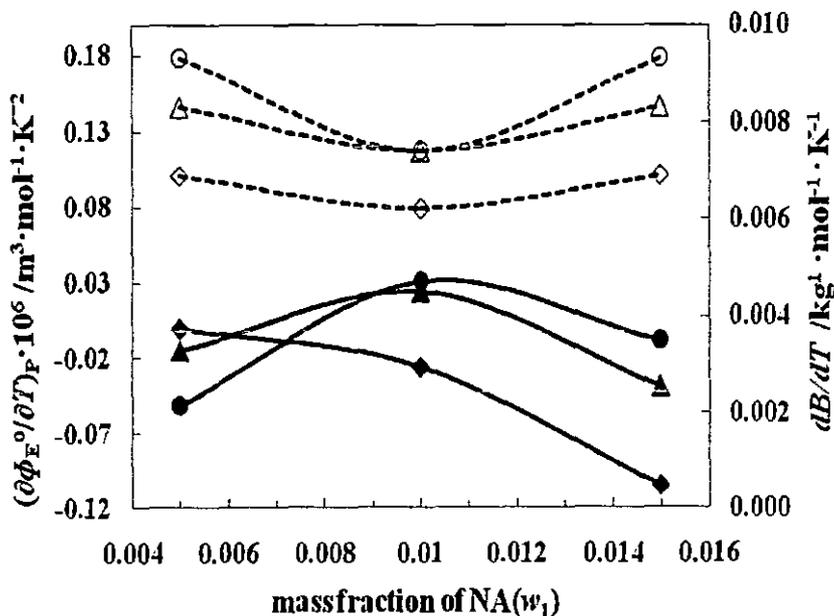
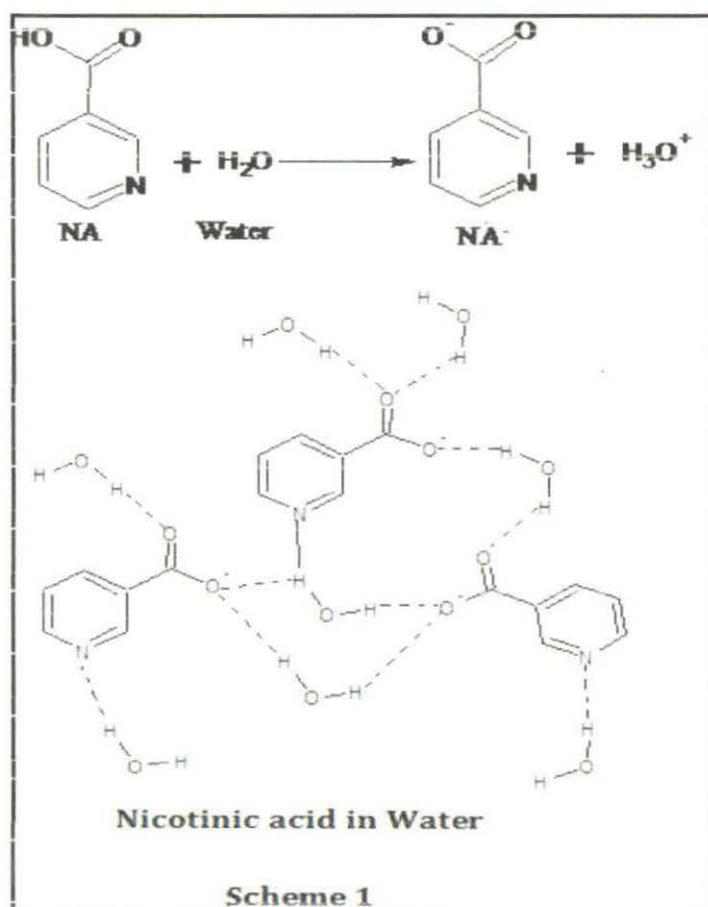


Figure 5. Plot of $(\partial\phi_E^0/\partial T)_P$ for D-glucose (-♦-), D-mannitol (-▲-), D-sucrose (-●-), and dB/dT for D-glucose (-◇-), D-mannitol (-△-), D-sucrose (-○-), against different mass fraction (w_1) of aq. NA at studied temperature (T).

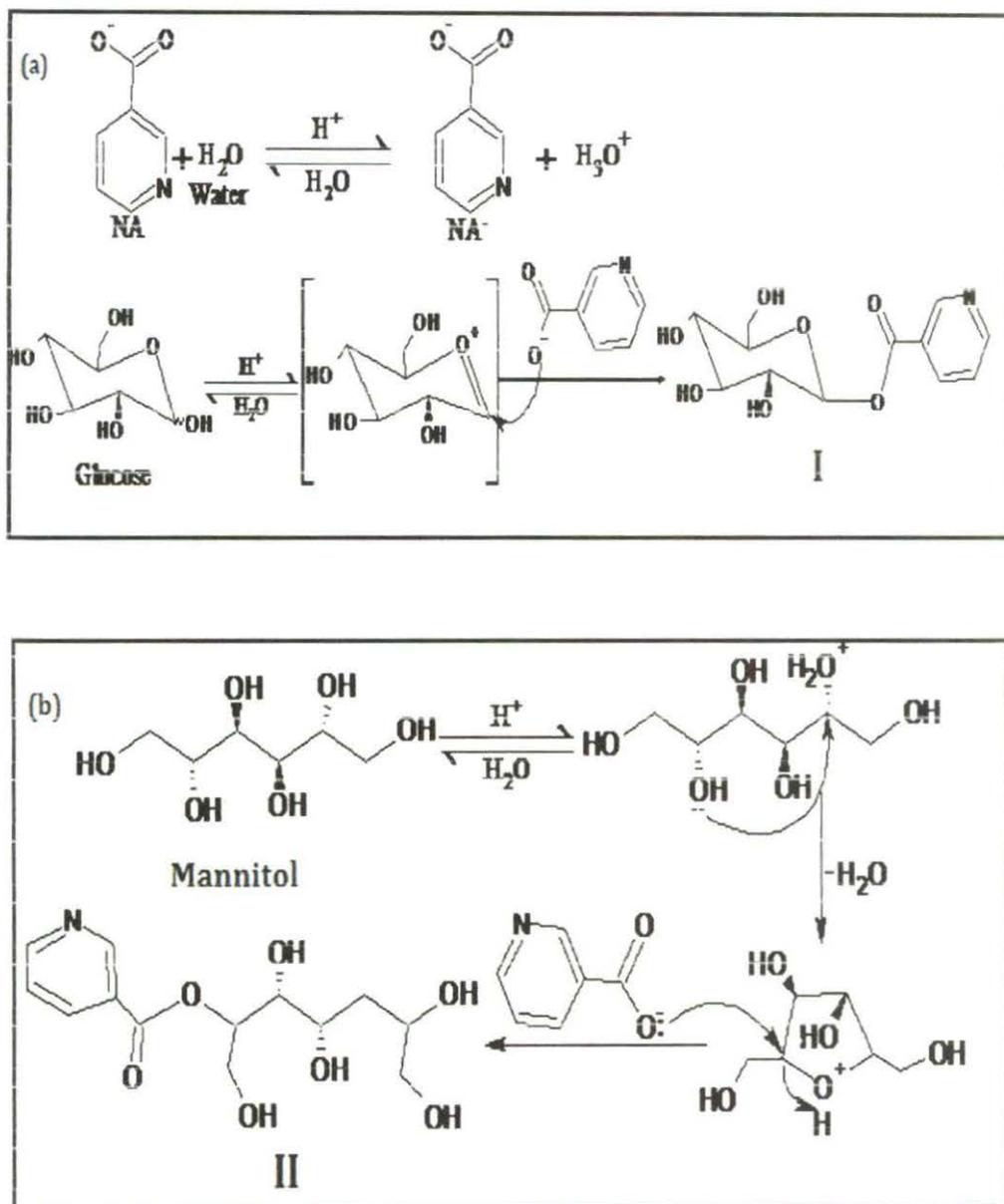


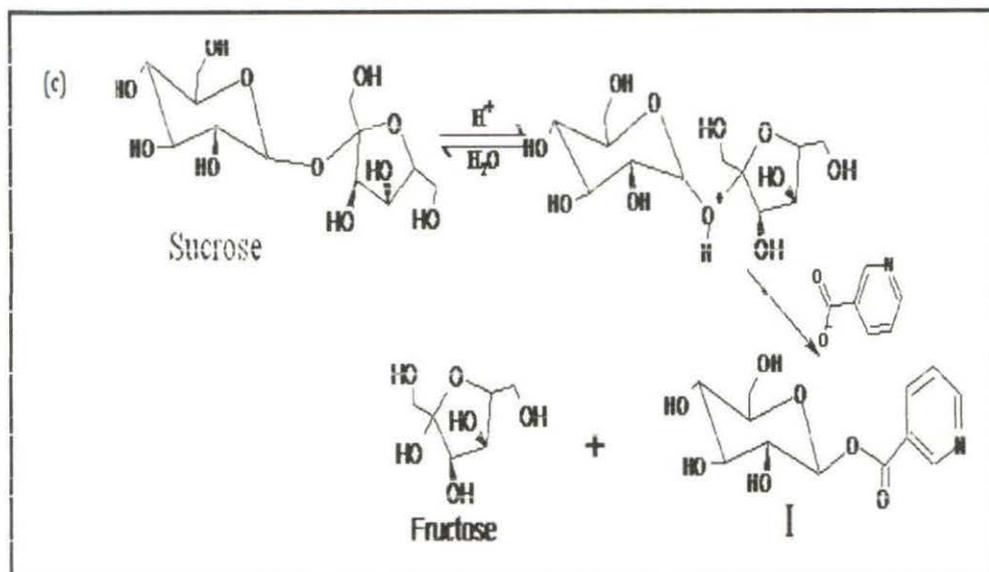
SCHEME

Scheme 1. Interaction between nicotinic acids and water.

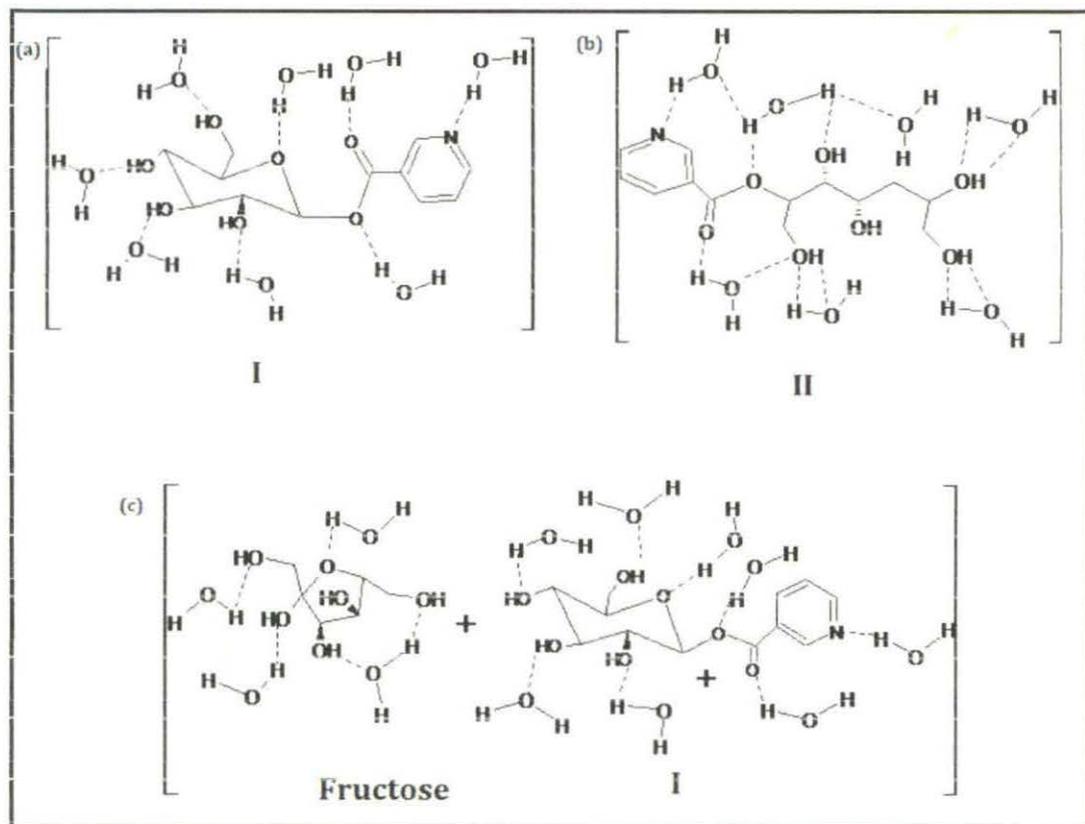


Scheme 2. A plausible mechanism of interaction between nicotinic acids and studied carbohydrates





Scheme 3. Possible interactions between solvent (water) with the plausible products [obtained with reaction between different carbohydrates {(a) glucose, (b) mannitol and (c) sucrose} and nicotinate ion]



CHAPTER VI

PHYSICS AND CHEMISTRY OF AN IONIC LIQUID IN SOME INDUSTRIALLY IMPORTANT SOLVENT MEDIA PROBED BY PHYSICOCHEMICAL TECHNIQUES

6.1. INTRODUCTION

An ionic liquid (IL) is an electrolyte in the liquid state or phase, whose melting point is below some arbitrary temperature, such as 100°C. In general, Ionic Liquids (ILs) are liquid electrolytes that consist of combinations of organic-organic or organic-inorganic cation/anions. Because of their unique physicochemical properties, such as the favorable solubility of organic and inorganic compounds, low vapor pressures, low melting points, high thermal stability, good solvent characteristics for organic, inorganic and polymeric materials, adjustable polarity, selective catalytic effects, chemical and thermal stability, non-flammability and high ionic conductivity, ionic liquids have generated significant interest for a wide range of industrial applications [1]. They are used as recyclable solvents for organic reactions and separation processes [2], lubricating fluids [3], electrolytic media in various electrochemical systems [4], pharmaceuticals, cellulose processing, food and bi-products, waste recycling, batteries among others.

It is well-known that the reaction medium plays an important role in determining reactivity reflected in thermodynamic, transport, and spectral properties [5]. Study of transport properties of electrolytes in different solvent media are of great importance to obtain information as to the solvation and association behavior of ions in solutions. Consequently, a number of conductometric [6] and related studies of electrolytes in non-aqueous solvents have been made for their optimal use in high-energy batteries [7] and for further more understanding organic reaction mechanisms [8]. The thermodynamic properties of solutions are very useful to obtain information on the intermolecular interactions and geometrical effects in the systems. Moreover,

knowledge of the thermodynamic properties is essential for the proper design of industrial processes. Accurate knowledge of thermodynamic properties of solution mixtures has great relevance in theoretical and applied areas of research. Measurements of the bulk properties, such as viscosity and density of liquids, measurements of excess molar enthalpies and measurements of isentropic compressibility provide insight into the molecular interactions prevailing in electrolyte solution systems. In general, the measurements help promote better understanding of the behaviour of the electrolyte with different solvents. Studies on the apparent and partial molar volumes of the electrolyte and the dependence of viscosity on the concentration of electrolyte have been employed as a way to study ion-ion and ion-solvent interactions [9]. The solvents used in this study find wide industrial usage. Dimethylsulfoxide (DMSO), a typical aprotic solvent having both polar and non polar groups, is an important solvent in chemistry, biotechnology, and medicine for the dissolution of various substances and as an antifreeze agent of living cells [10]. It is widely used in pharmaceutical applications, enzyme-catalyzed reactions, veterinary medicine, dermatology, experimental immunology and microbiology [11]. N,N-dimethylacetamide (DMA) is commonly used as a solvent for fibers and in the adhesive industry, in the production of pharmaceuticals and plasticizers as a reaction medium, in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings [12]. N,N-dimethylformamide (DMF), which is a versatile solvent, is used as the separation agent for saturated and unsaturated hydrocarbons, as a solvent for vinyl resins, acid gases, polyacrylic fibres, and as a catalyst in carbonylation reaction, organic electrolyte batteries, photo electrochemical cells, electro-deposition, wet electrolyte capacitors or electro-organic synthesis.

In continuation of our investigation on electrical conductances [13], an attempt has been made in the present study, to ascertain the nature of ion-solvent interactions of the ionic liquid (IL) tetrabutylphosphonium Tetrafluoroborate [Bu₄PBF₄] in dimethyl sulfoxide (DMSO), dimethylacetamide (DMA), dimethylformamide (DMF) at 298.15 K. Thermodynamic parameters are evaluated and discussed.

6.2. EXPERIMENTAL SECTION

6.2.1. Source and purity of samples

The IL [Bu₄PBF₄] of puriss grade was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of [Bu₄PBF₄] was ≥ 0.99 . The solvents DMSO, DMA and DMF were procured from Merck, India. These were further purified by standard methods [14]. The values of their mass fraction purity obtained were ≥ 0.99 . See Table 1.

6.2.2. Apparatus and Procedure

A stock solution of the electrolyte [Bu₄PBF₄] was prepared by mass (Mettler Toledo AG-285 with uncertainty ± 0.0003 g) and the working solutions were obtained by mass dilution at $T = 298.15$ K. The conductance measurements were carried out in a Systronic-308 conductivity bridge (accuracy ± 0.01 %) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 0.001) cm⁻¹. Measurements were made in a water bath maintained within $T = (298.15 \pm 0.01)$ K and the cell was calibrated by the method proposed by Lind et al.[15] The conductance data were reported at a frequency of 1 kHz and were uncertain to ± 0.3 %.

The densities of the solvents (ρ) were measured by means of vibrating-tube Anton Paar density-meter (DMA 4500M) with a precision of ± 0.00005 g. cm⁻³ maintained at ± 0.01 K of the desired temperature. It was calibrated by double-distilled water and dry air.

Solution viscosities (η) were measured by means of suspended Ubbelohde type viscometer, calibrated at $T = 298.15$ K with doubly distilled water and purified methanol. A thoroughly cleaned and perfectly dried viscometer filled with experimental solution was placed vertically in a glass-walled thermostat (Bose Panda Instruments Pvt. Ltd.) maintained to 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stop watch. The flow times were accurate to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times with the aim of determining possible dispersion of the results obtained. Adequate

precautions were taken to minimize evaporation losses during the actual measurements.

The precision of density measurements was $\pm 3.10^{-4} \text{ g} \cdot \text{cm}^{-3}$.

The viscosity of the solution is evaluated using the following equation [16]

$$\eta = \left(Kt - \frac{L}{t} \right) \rho \quad (1)$$

where K and L are the viscometer constants, t is the efflux time of flow in seconds and ρ is the density of the experimental liquid. The uncertainty in viscosity measurements is within $\pm 0.003 \text{ mPa} \cdot \text{s}$.

The ultrasonic velocities, u in $\text{m} \cdot \text{s}^{-1}$ were measured using an ultrasonic interferometer (Model M-83) from Mittal enterprises. The interferometer working at 2 MHz is based on the same principle as was used by Freyer et al. [17] and Kiyoharo et al. [18]. The velocities obtained were corrected for diffraction errors as given by Subrahmayan et al. [19]. The maximum uncertainty in the velocity is $\pm 0.5 \text{ m} \cdot \text{s}^{-1}$. The temperature was controlled within $\pm 0.01 \text{ K}$ using a Lauda thermostat for velocity measurements.

6.3. RESULTS AND DISCUSSION

6.3.1. Electrical Conductance

The physical properties of the pure solvent were in good agreement with values found in the literature, as reported in Table 2. The experimental values of equivalent conductances (Λ) of the electrolyte measured at the corresponding molar concentrations (c) in DMSO, DMA and DMF are given in Table 3. The conductance results have been analysed using the Fuoss conductance equation [20]. For a given set of conductivity values ($c_j, \Lambda_j, j=1, \dots, n$) three adjustable parameters, the limiting molar conductivity (Λ_0), the association constant (K_A), and the distance of closest approach of ions (R) are derived from the following set of equations:

$$\Lambda = P\Lambda_o[(1+R_X)+E_L] \quad (2)$$

$$P = 1 - \alpha(1 - \gamma) \quad (3)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (4)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (5)$$

$$\beta = e^2 / (\epsilon k_B T) \quad (6)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (7)$$

where R_X is the relaxation field effect, E_L is the electrophoretic counter current, k is the radius of the ion atmosphere, ϵ is the relative permittivity of the solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_S is the association constant of the contact-pairs, K_R is the association constant of the solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance. The computations were performed using a program suggested by Fuoss. The initial Λ_o values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set $(c_j, \Lambda_j, j=1, \dots, n), n, \epsilon, \eta, T$, initial values of Λ_o , and an instruction to cover a preselected range of R values.

In practice, calculations are performed by finding the values of Λ_o and R that minimize the standard deviation:

$$\delta^2 = \sum [\Lambda_j(cal) - \Lambda_j(obs)]^2 / (n-2) \quad (8)$$

or a sequence of R values and then plotting δ against R ; the best fit R corresponds to the minimum of the δ - R versus R curve. So, approximate runs are made over a fairly wide range of R values using 0.1 increments to locate the minimum, but no significant minima were found in the δ - R curves for $[\text{Bu}_4\text{PBF}_4]$ electrolytes in DMSO, DMA and DMF; thus, R values are assumed to be $R = a + d$, where a is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by

$$d (\text{\AA}) = 1.183(M / \rho)^{1/3} \quad (9)$$

where M is the molar mass of the solvent and ρ is its density. The values of Λ_o , K_A , and R obtained by this procedure are represented in Table 4. Perusal of Table 4 and Figure 1

reveals that the limiting molar conductance Λ_0 of $[\text{Bu}_4\text{PBF}_4]$ in DMF is greater than that in DMA and DMSO, which is in order DMF > DMA > DMSO. Figure 2 and the Table 4 also reveal that the association constant (K_A) of the $[\text{Bu}_4\text{PBF}_4]$ is greater in DMSO than in DMA than in DMF. Hence, this shows that there is more ion-solvent interaction in DMSO than in DMA than in DMF leading to a lower conductance of $[\text{Bu}_4\text{PBF}_4]$ in the former than the latter two. The greater viscosity of DMSO also supports the above fact because with higher viscosity the Λ_0 value should decrease.

Polar aprotic solvents, (e.g.; DMF, DMA, and DMSO) dissolve ionic compounds and solvate cations very well. They do not solvate anions to any appreciable extent because they cannot form H-bonds and having positive centers are well shielded from any interaction with anions. When the ionic compound $[\text{Bu}_4\text{PBF}_4]$ is dissolved in the above mentioned polar aprotic solvents, following interaction may be observed.

The schematic representation of ion-solvation, for the particular ion in the studied solvent is depicted in **Scheme 1**.

In case of solvent DMF, the only interaction present is between negatively charged oxygen atom of DMF and positively charged P atom of $[\text{Bu}_4\text{P}]^+$, shown in (I). Same type of interaction is present in case of solvent DMA (II). Here the interaction is more intense due to the presence of methyl ($-\text{CH}_3$) group which pushes electrons towards oxygen, making it more negative for stronger interaction. In case of DMSO as solvent, two types of interaction shown in (III) possibly occur

a) between the negatively charged oxygen atom of DMSO and positively charged P atom of $[\text{Bu}_4\text{P}]^+$ and

b) between the positively charged S atom of DMSO and negatively charged B atom of $[\text{BF}_4]$. The interaction (b) is only possible because S atom is larger than N atom and is less shielded by two methyl group compared to N atom in case of DMF and DMA. For these reason, conductance of $[\text{Bu}_4\text{PBF}_4]$ is greater in DMF than DMA and DMSO, hence, lower is the conductance, greater the interaction/association, which is in the following order



The trend in Λ_0 can be discussed through another characteristic function called the Walden product, $\Lambda_0\eta_0$. From Table 4 and Figure 1 the decreasing trend of Walden products is mainly in agreement with the concomitant decrease of solvent viscosity and increase of limiting molar conductance for the electrolyte in the solvents. This is also justified as the Walden product of an ion or solute is inversely proportional to the radius of the ion or solute in a particular solvent [21].

The starting point for most evaluations of ionic conductance is Stokes' law which states that the limiting Walden product ($\lambda_0^\pm\eta_0$), (product of the limiting ionic conductance and solvent viscosity) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions is a constant. The values of the ionic conductances λ_0^\pm (for the $[\text{Bu}_4\text{P}]^+$ cation and $[\text{BF}_4]^-$ anion) in different solvents DMSO, DMA and DMF were calculated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as a 'reference electrolyte' following the scheme as suggested by B. Das et al. [22]. The λ_0^\pm values were in turn utilized for the calculation of Stokes' radii (r_s) according to the classical expression [23]

$$r_s = \frac{F^2}{6\pi N_A \lambda_0^\pm r_c} \quad (10)$$

Ionic Walden products $\lambda_0^\pm\eta_0$, Stokes' radii r_s , and crystallographic radii r_c are presented in Table 5. The trends in Walden products $\Lambda_0\eta_0$ and ionic Walden products $\lambda_0^\pm\eta_0$ for the electrolytes in the solvent DMSO, DMA, and DMF are shown in Tables 4 and 5 and Figures 1 and 3, respectively. They indicate that both the ionic Walden products $\lambda_0^\pm\eta_0$ and Walden products $\Lambda_0\eta_0$ for the electrolyte are greater in the case of DMSO than DMA and DMF. For the Bu_4P^+ and BF_4^- ions, the Stokes' radii r_s are either lower or comparable to their crystallographic radii r_c . This suggests that the ions are comparatively less solvated than alkali metal ions due to intrinsic low surface charge density. The distance parameter R , shown in Table 4, is the least distance that two free ions can approach together before they merge into an ion pair.

The nature of the curve for the Gibbs free energy changes for ion-pair formation, ΔG° , which clearly predicts the tendency for ion-pair formation, Figure 2. The Gibbs free

energy change ΔG° is calculated by the following relationship [24] and is given in Table 4.

$$\Delta G^\circ = -RT \ln K_A \quad (11)$$

where K_A is the association constant. The negative values of ΔG° can be explained by considering the participation of specific covalent interactions in the ion-association process. The lower value of ΔG° for the $[\text{Bu}_4\text{PBF}_4]$ electrolyte in DMSO than DMA and DMF shows that greater degree of association in DMSO.

From the overall study, it is evident that the ion-solvent interaction between the ionic liquid investigated and the solvents is greater in DMSO than in DMA which is, in turn, greater than that in DMF. This is diagrammatically shown in **Scheme 2**.

6.3.2. Density calculation

The measured values of density of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF as a function of concentration at $T = 298.15$ K are listed in Table 6. Partial molar volumes are very important for the analysis of interaction of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF. For this purpose, the apparent molar volumes ϕ_V were determined from the solution densities using the following equation and the values are given in Table 6.

$$\phi_V = M / \rho_o - 1000(\rho - \rho_o) / c \rho_o \quad (12)$$

where M is the molar mass of the solute, c is the molarity of the solution ρ and ρ_o are the densities of the solution and solvent respectively. The limiting apparent molar volume ϕ_V^0 was calculated using a least-square treatment to the plots of ϕ_V versus \sqrt{c} using the Masson equation [25].

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{c} \quad (13)$$

where ϕ_V^0 is the limiting apparent molar volume at infinite dilution and S_V^* is the experimental slope. The plots of ϕ_V against square root of molar concentration (\sqrt{c}) were found to be linear with negative slopes. The values of ϕ_V^0 and S_V^* are reported in Table 6. The ϕ_V^0 value indicates the extent of ion-solvent interaction. A perusal of Table

6 reveals that the ϕ_V^0 values are positive and is highest in case of [Bu₄PBF₄] in DMSO indicating that the ion-solvent interaction is more in DMSO than in DMA than in DMF. On the other hand, S_V^* values indicate the extent of ion-ion interaction. From Table 6, the values of S_V^* is greater in the case of the DMF than DMA and DMSO. A quantitative comparison of the magnitude of ϕ_V^0 values is much greater than S_V^* values for the solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions. The values of ϕ_V^0 also support the fact that lower ion-solvent interaction in DMF leads to higher conductance of [Bu₄PBF₄] in it than DMA and DMSO obtained from the conductometric measurement.

6.3.3. Viscosity calculation

The viscosity results have been analysed using the Jones-Dole equation [26]

$$(\eta/\eta_0 - 1)/\sqrt{c} = (\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \quad (14)$$

where $\eta_r = \eta/\eta_0$, η_0 and η are the viscosities of the solvent and solution respectively, c is the molar concentration of the solution, A and B are the viscosity coefficient estimated by a least-squares method. The values of A and B coefficients are obtained from the straight line by plotting $(\eta_r - 1)/\sqrt{c}$ against \sqrt{c} reported in Table 7. A perusal of Table 7 shows that the values of the A -coefficient are lower than the value of B -coefficient for all of the solutions under investigation. The results indicate the presence of very weak ion-ion interactions. These results are in excellent agreement with those obtained from S_V^* values discussed earlier.

The effects of ion-solvent interactions on the solution viscosity can be inferred from the B -coefficient [27]. The viscosity B -coefficient is a valuable tool to provide information concerning the solvation of the ions and their effects on the structure of the solvent. From Table 7, it is evident that the values of the B -coefficient are positive and much higher than the A -coefficient, thereby suggesting the presence of strong ion-solvent interactions. The viscosity B coefficient value is lowest for [Bu₄PBF₄] in DMF supporting the fact that the conductance of [Bu₄PBF₄] in DMF is highest.

The B -coefficients as determined experimentally using the Jones-Dole equation does not give any impression regarding ion-solvent interactions unless there is some way to identify the separate contribution of cations and anions to the total ion-solvent interaction. For the division of B -values in the ionic components, Sacco *et al.* proposed the “reference electrolytic” method for the division of B -values.

The values obtained are in good agreement with those obtained by other methods. The viscosity B -coefficients for ions are given in Table 5. The criteria adopted for the separation of B -coefficients in non-aqueous solvents differ from those generally used in water. However, the methods are based on the equality of equivalent conductances of counter ions at infinite dilutions. According to Krumgalz [28] any method of resolution based on the equality of equivalent conductance, the equality of B -coefficients of these ions is likely to be solvent and ion-structure dependent. Since the electrolyte ion-structure effect is same, so the B -coefficients are dependent on the solvent. The viscosity B -value as well as the B -ionic value in DMSO is greater than DMA and DMF, which indicates ions are more solvated in DMSO.

The B -ion values can also be judged from the equations:

$$B_{Bu_4PBF_4} = B_{Bu_4P^+} + B_{BF_4^-} \quad (15)$$

The method requires knowledge of the B -values for $[Bu_4PBF_4]$ and is equally applicable to non-aqueous solvents. The B -ion values obtained by this method agree well with those reported by Sacco *et al.* in different organic solvents.

6.3.4. Ultrasonic speed calculation

The adiabatic compressibility (β) was evaluated from the following equation:

$$\beta = 1 / u^2 \rho \quad (16)$$

where ρ is the density of solution and u is the speed of sound in the solution. The apparent molar adiabatic compressibility (ϕ_K) of the solutions was determined from the relation,

$$\phi_K = M \beta / \rho + 1000(\beta \rho_o - \beta_o \rho) / c \rho \rho_o \quad (17)$$

Where β_0, β are the adiabatic compressibility of the solvent and solution respectively and c is the molarity of the solution. The values of β and ϕ_K are reported in Table 8. The limiting partial molar adiabatic compressibility (ϕ_K^0) and experimental slope (S_K^*) were obtained by fitting ϕ_K against the square root of concentration of the electrolyte (\sqrt{c}) using the least squares method.

$$\phi_K = \phi_K^0 + S_K^* \cdot \sqrt{c} \quad (18)$$

The values of ϕ_K^0 and S_K^* are also presented in Table 8. The values of ϕ_K^0 and S_K^* are measures of ion-solvent and ion-ion interactions respectively. A perusal of Table 8 shows that the ϕ_K^0 value is highest in the case of $[\text{Bu}_4\text{PBF}_4]$ in DMSO indicating that the ion-solvent interaction is greater in DMSO than in DMA than in DMF.

On the other hand, the S_K^* values indicate the extent of ion-ion interaction. From Table 8 the values of S_K^* are greater in the case of the DMF than for DMA and DMSO. A quantitative comparison of the magnitude of ϕ_K^0 values is much greater than S_K^* values, for the solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions and the values are in agreement with results drawn from the values of ϕ_V^0 and S_V^* discussed earlier.

6.4. CONCLUSIONS

The extensive conductometric study of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF leads to the conclusion that the electrolyte more associated in DMSO than in the other two solvents. The reliable value of volumetric, viscometric and interferometric studies also suggests that in solution there is more ion-solvent interaction than the ion-ion interaction.

REFERENCES

- [1]. N. H. Kim, S. V. Malhotra, M. Xanthos, *Microporous and Mesoporous Materials*. 96 (2006) 29.
- [2]. N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* 37 (2008) 123.
- [3]. R. A. Reich, P. A. Atewart, J. Bohaychick, J. A. Urbansky, *Lubr. Eng.* 59 (2003) 16.
- [4]. D. R. MacFarlane, M. Forsyth, P. C. Howlett, J. M. Pringle, J. Sun, G. Annat, W. Neil, E. I. Izgorodina, *Acc. Chem. Res.* 40 (2007) 1165.
- [5]. O. Popovych, R. P. T. Tomkins, *Nonaqueous Solution Chemistry*, Ch 4, Wiley-Interscience, New York, (1981).
- [6]. C. G. Janz, R. P. T. Tomkins, *Non-aqueous Electrolytes Handbook*, Vol. 2, Academic Press, New York, (1973).
- [7]. D. Aurbach, *Non-aqueous Electrochemistry*, Marcel Dekker, Inc., New York, (1999).
- [8]. J. A. Krom, J. T. Petty, A. Streitwieser, *J. Am. Chem. Soc.* 115 (1993) 8024.
- [9]. F. J. Millero, *In Structure and Transport Process in Water and Aqueous Solutions*, R. A. Horne, Ed., Wiley, New York, (1972).
- [10]. T. Kamiyama, M. Morita, T. Kimura, *J. Chem. Eng. Data.* 49 (2004) 1350.
- [11]. M. K. Pasha, J. R. Dimmock, M. D. Hollenberg, R. K. Sharma, *Biochem. Pharmacol.* 64 (2002) 1461.
- [12]. C. Redlich, W. S. Beckett, J. Sparer, K. W. Barwick, C. A. Riely, H. Miller, S. L. Sigal, *Ann. Intern. Med.* 108 (1988) 680.
- [13]. M. N. Roy, B. Sinha, V. K. Dakua, A. Sinha, *Pak. J. Sci. Ind. Res.* 49 (2006) 153-159.
- [14]. D. D. Perrin, W. L. F. Armarego, *Purification of laboratory chemicals*, 3rd ed., Pergamon Press, Oxford, (1988).
- [15]. J. E. Lind Jr., J. J. Zwolenik, R. M. Fuoss, *J. Am. Chem. Soc.* 81 (1959) 1557.
- [16]. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data.* 49 (2004) 291.
- [17]. E. B. Freyer, J. D. Hubbard, D. H. Andrews, *J. Am. Chem. Soc.* 51 (1929) 759.
- [18]. O. Kiyohara, J. P. E. Grolier, G. C. Benson, *Can. J. Chem.* 52 (1974) 2287.
- [19]. N. M. Murthy, S. V. Subrahmanyam, *Bull. Chem. Soc. Jpn.* 50 (1977) 2589.
- [20]. R. M. Fuoss, *J. Phys. Chem.* 82 (1978) 2427.
- [21]. J. Ishwara. Bhat, P. Bindu, *J. Ind. Chem. Soc.* 72 (1995) 783.

- [22]. J. M. Chakraborty, B. Das, *Z. Phys. Chem.* 218 (2004) 219.
- [23]. R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Ch. 6, pp. 130, Butterworth, London, (1959).
- [24]. R. M. Fuoss, C. A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 2387.
- [25]. D. O. Masson, *Phil. Mag.* 8 (1929) 218.
- [26]. G. Jones, M. Dole, *J. Am. Chem. Soc.* 51 (1929) 2950.
- [27]. F. J. Millero, *Chem. Rev.* 71 (1971) 147.
- [28]. B. S. Krumgalz, *J. Chem. Soc. Faraday I.* 76 (1980) 1275.
- [29]. T. M. Aminabhavi, B. Gopalakrishna, *J. Chem. Eng. Data.* 40(4) (1995) 856.
- [30]. A. K. Covington, T. Dickinson, *Physical chemistry of organic solvent systems*, Plenum., New York, (1973).

TABLES

Table 1.

Sample provenance and purity

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity
[Bu ₄ PBF ₄]	Sigma-Aldrich, Germany	0.99	Used as procured	0.99
DMSO	Merck, India	0.98	Purified by standard methods [14]	0.99
DMA	Merck, India	0.98	Purified by standard methods [14]	0.99
DMF	Merck, India	0.98	Purified by standard methods [14]	0.99

Table 2. Values of density (ρ), viscosity (η), refractive index (n_D), Speed of sound (u), and relative permittivity (ϵ_r) of the pure solvents studied at T = 298.15 K.

Solvent	$10^{-3}\rho^a$ (kg m ⁻³)		η^b /(mPa . s)		u^c / (m . s ⁻¹)		ϵ_r
	Expt	Lit	Expt	Lit	Expt	Lit	
DMSO	1.09602	1.09600[29]	1.946	1.948[29]	1490.8	1490.0[29]	46.70[30]
DMA	0.93680	0.93660[29]	0.923	0.920[29]	1458.5	1458.0[29]	37.78[30]
DMF	0.94450	0.94450[29]	0.794	0.796[29]	1451.7	1451.0[29]	36.71[30]

^a uncertainty in the density values: ± 0.00002 g cm⁻³.

^b uncertainty in the viscosity values: ± 0.003 mPa s.

^c uncertainty in the ultrasonic speed: ± 0.5 m s⁻¹.

Table 3. The molar conductance (Λ) and corresponding concentration (c) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K

$c^d \times 10^4$ (mol dm ⁻³)	$\Lambda^e \times 10^4$ (S m ² mol ⁻¹)	$c^d \times 10^4$ (mol dm ⁻³)	$\Lambda^e \times 10^4$ (S m ² mol ⁻¹)	$c^d \times 10^4$ (mol dm ⁻³)	$\Lambda^e \times 10^4$ (S m ² mol ⁻¹)
DMSO		DMA		DMF	
20.4903	21.28	19.8974	39.77	18.55961	55.50
37.5655	20.00	27.5503	38.47	25.69792	54.86
52.0138	19.00	34.1099	37.97	31.81648	54.37
64.3981	18.60	39.7949	37.45	37.11922	53.96
75.1311	17.97	44.7692	36.77	45.85316	53.40
84.5224	17.65	53.0598	36.35	52.74837	52.99
100.1748	17.10	59.6923	35.73	62.94129	52.46
112.6966	16.82	69.6411	34.80	70.11409	52.11
131.4794	16.28	79.5898	34.10	75.43584	51.83
150.2621	15.58	86.2223	33.72	82.05302	51.47
171.7281	15.01	92.2518	33.25	87.14948	51.19
185.1444	14.62	97.6784	32.90	92.15807	50.98

^d Uncertainty in the molarity: ± 0.0002 mol dm⁻³.^e Uncertainty in the molar conductance: ± 0.01 S m² mol⁻¹.**Table 4. Limiting molar conductivity (Λ_0), the association constant (K_A), the distance of closest approach of ions (R), Standard Deviations δ , Walden Product ($\Lambda_0 \eta_0$) and Gibbs free energy change (ΔG°) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K**

Solvents	$\Lambda_0 \times 10^4$ (S m ² mol ⁻¹)	$K_A \times 10^{-4}$ (dm ² mol ⁻¹)	R (Å)	δ	$\Lambda_0 \eta_0 \times 10^4$ (S m ² mol ⁻¹ mPa s)	ΔG° (kJ mol ⁻¹)
DMSO	35.74	23.60	12.10	0.32	69.55	-3.06
DMA	53.09	9.76	12.96	0.26	49.00	-2.84
DMF	60.84	2.37	12.64	0.08	48.31	-2.49

Table 5. Limiting Ionic Conductance (λ_o^\pm), Ionic Walden Product ($\lambda_o^\pm\eta_o$), Stokes' Radii (r_s), Crystallographic Radii (r_c), ionic viscosity B -coefficients (B_\pm) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K

Solvents	Ion	λ_o^\pm ($\text{S m}^2 \text{mol}^{-1}$)	$\lambda_o^\pm\eta_o$ ($\text{S m}^2 \text{mol}^{-1} \text{mPa s}$)	r_s (\AA)	r_c (\AA)	B_\pm ($\text{L}^{1/2} \text{mol}^{-1/2}$)
DMSO	Bu_4P^+	13.80	26.85	3.05	4.42	0.85
	BF_4^-	21.94	42.70	1.92	2.78	0.54
DMA	Bu_4P^+	20.50	18.92	4.33	4.42	0.79
	BF_4^-	32.59	30.08	2.72	2.78	0.50
DMF	Bu_4P^+	23.49	18.65	4.39	4.42	0.75
	BF_4^-	37.35	29.66	2.76	2.78	0.47

Table 6. Experimental values of Molarity (c), Densities (ρ), Apparent Molar Volume (ϕ_V), Limiting Apparent Molar Volume (ϕ_V^0) and Experimental Slope (S_V^*) of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K

c^f (mol dm^{-3})	$\rho^g \times 10^{-3}$ (kg m^{-3})	ϕ_V ($\text{m}^3 \text{mol}^{-1}$)	$\phi_V^0 \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	S_V^* ($\text{m}^3 \text{mol}^{-3/2} \text{L}^{1/2}$)
DMSO				
0.0046	1.09605	310.4323	324.21	-193.88
0.0184	1.0964	298.5712		
0.0323	1.09702	289.8383		
0.0463	1.09784	282.6956		
0.0604	1.09883	276.4632		
0.0746	1.09998	270.7432		
DMA				
0.0053	0.93722	279.9317	290.34	-146.73
0.0215	0.93869	268.7233		
0.0377	0.94034	261.6323		
0.0541	0.94213	255.8070		
0.0705	0.94401	251.1923		
0.0871	0.94594	247.6409		
DMF				
0.0053	0.94498	264.9444	275.29	-139.97
0.0213	0.94661	254.8862		
0.0374	0.9484	248.6092		
0.0536	0.95034	242.9222		

0.0699	0.9524	237.9053
0.0863	0.9545	234.2403

^fUncertainty in the molarity: $\pm 0.0002 \text{ mol dm}^{-3}$.

^gUncertainty in the density values: $\pm 0.00002 \text{ g cm}^{-3}$.

Table 7. Experimental values of Molarity (c), Viscosities (η), $(\eta_r - 1)/\sqrt{c}$, Viscosity A, B-coefficients of $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K

c^h (mol dm^{-3})	η^i (mPa s)	$(\eta_r - 1)/\sqrt{c}$ ($\text{kg}^{1/2} \text{ mol}^{-1/2}$)	A (L mol^{-1})	B ($\text{L}^{1/2} \text{ mol}^{-1/2}$)
DMSO				
0.0046	1.952	0.042		
0.0184	1.982	0.138		
0.0323	2.015	0.197	-0.05124	1.39
0.0463	2.049	0.247		
0.0604	2.085	0.290		
0.0746	2.120	0.327		
DMA				
0.0053	0.930	0.097		
0.0215	0.949	0.188		
0.0377	0.968	0.249	0.00053	1.29
0.0541	0.987	0.297		
0.0705	1.007	0.342		
0.0871	1.028	0.385		
DMF				
0.0053	0.802	0.133		
0.0213	0.820	0.218		
0.0374	0.837	0.275	0.0403	1.23
0.0536	0.854	0.322		
0.0699	0.871	0.364		
0.0729	0.889	0.406		

^h Uncertainty in the molarity: $\pm 0.0002 \text{ mol dm}^{-3}$.

ⁱ Uncertainty in the viscosity values: $\pm 0.003 \text{ mPa s}$.

Table 8. Experimental Values of Molarity (c), Speed of Sound (u), Adiabatic Compressibility (β) and Apparent Molar Adiabatic Compressibility (ϕ_K), Limiting Apparent Molar Adiabatic Compressibility (ϕ_K^0), and Experimental Slopes (S_K^*) of [Bu₄PBF₄] in DMSO, DMA and DMF at 298.15 K

c^j (mol dm ⁻³)	u^k (m s ⁻¹)	$\beta \times 10^{11}$ (Pa ⁻¹)	$\phi_K \times 10^{11}$ (m ³ mol ⁻¹ Pa ⁻¹)	$\phi_K^0 \times 10^{10}$ (m ³ mol ⁻¹ Pa ⁻¹)	$S_K^* \times 10^{10}$ (m ³ mol ^{-3/2} Pa ⁻¹ kg ^{1/2})
DMSO					
0.0046	1492.7	40.947	-8.369		
0.0184	1501.5	40.456	-17.595		
0.0323	1513.7	39.784	-24.360		
0.0463	1527.9	39.019	-29.080	0.144	-14.257
0.0604	1544.5	38.150	-33.310		
0.0746	1564.6	37.137	-37.831		
DMA					
0.0053	1461.8	49.932	-35.692		
0.0215	1473.5	49.066	-42.288		
0.0377	1486.9	48.101	-46.311		
0.0541	1501.6	47.074	-49.306	-2.958	-8.537
0.0705	1517.8	45.983	-51.986		
0.0871	1536.3	44.790	-54.958		
DMF					
0.0053	1455.6	49.945	-45.536		
0.0213	1468.7	48.974	-50.480		
0.0374	1483.2	47.930	-53.487		
0.0536	1498.6	46.854	-55.497	-4.116	-6.248
0.0699	1515.4	45.722	-57.545		
0.0863	1533.8	44.533	-59.556		

^j Uncertainty in the molarity: ± 0.0002 mol dm⁻³.

^k Uncertainty in the ultrasonic speed: ± 0.5 m s⁻¹.

FIGURES

Figure 1. Plots of values of limiting molar conductivity (Λ_0) and Walden Product ($\Lambda_0 \eta_0$) of the salt $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA, DMF at 298.15 K

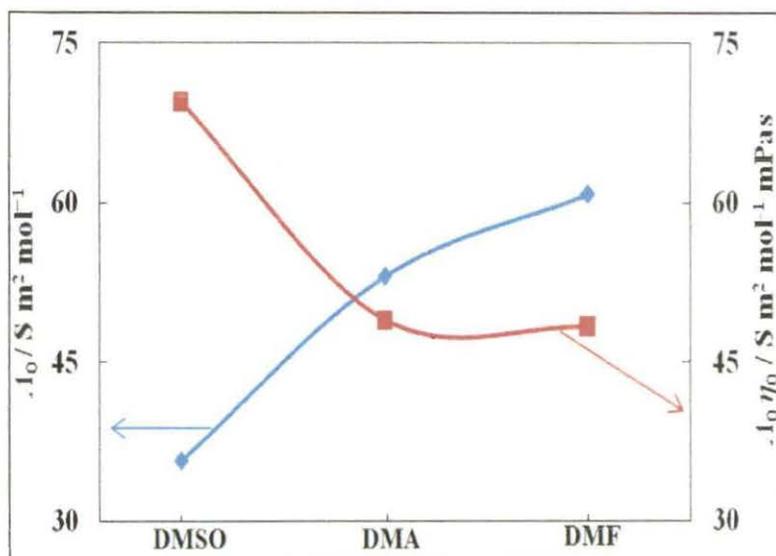


Figure 2. Plots of values of Association constant (K_A) and Gibbs free energy change (ΔG°) of the salt $[\text{Bu}_4\text{PBF}_4]$ in DMSO, DMA and DMF at 298.15 K

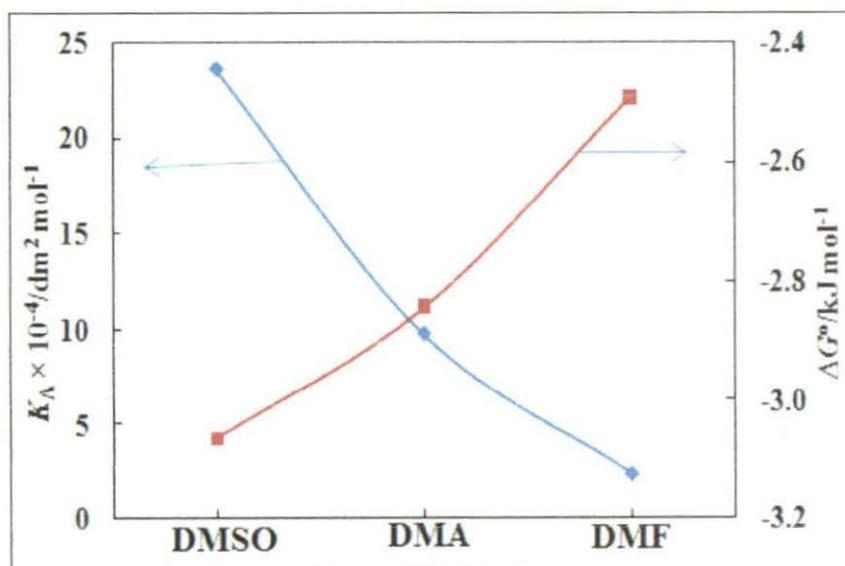
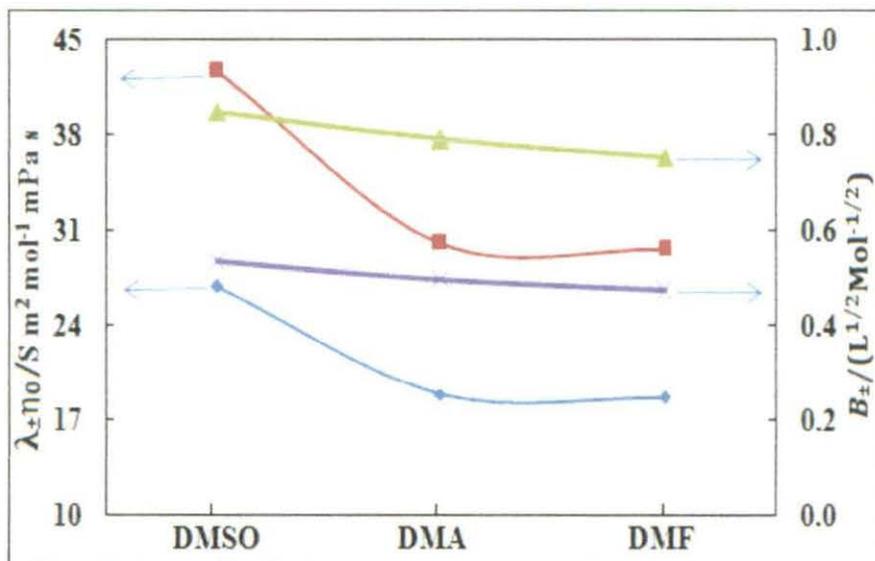
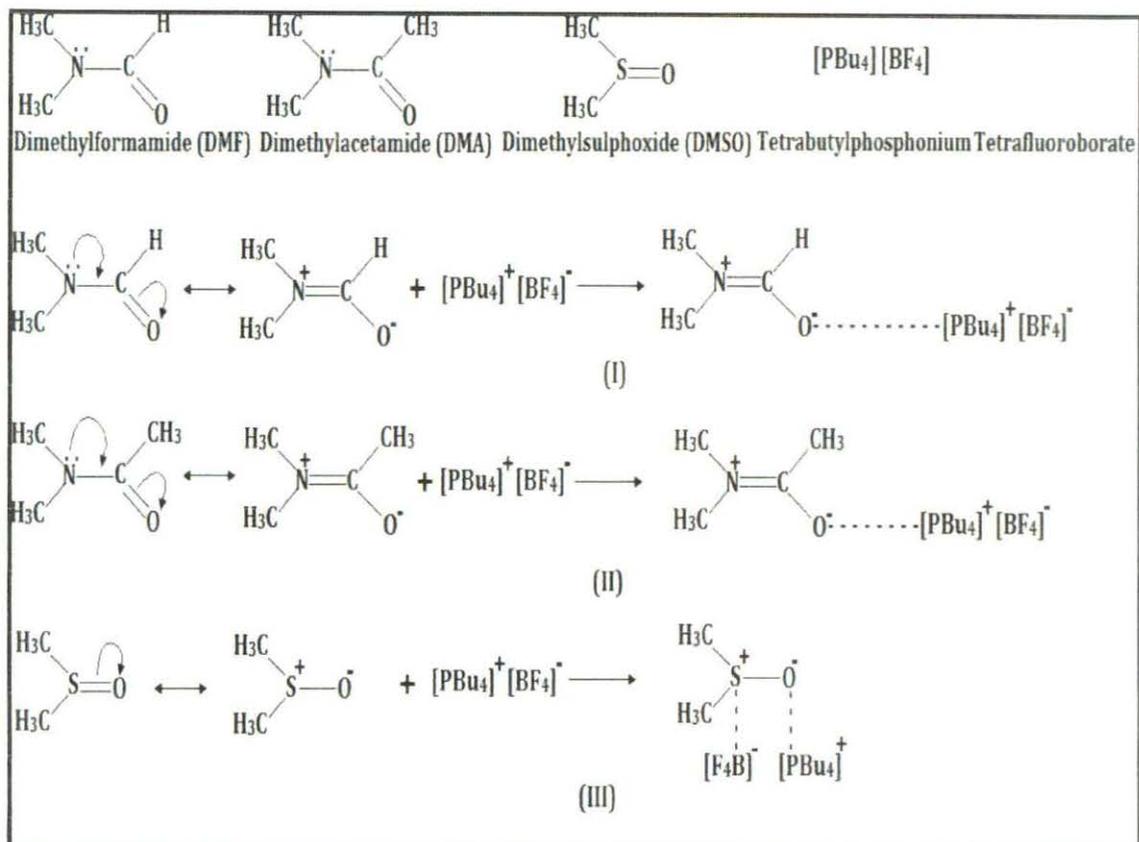


Figure 3. Plots of values of ionic Walden product ($\lambda_{\pm}^{\circ} \eta_0$) for $[\text{Bu}_4\text{P}]^+$ (■), for $[\text{BF}_4]^-$ (◆), and ionic viscosity B -coefficients (B_{\pm}) for $[\text{Bu}_4\text{P}]^+$ (▲), for $[\text{BF}_4]^-$ (×) in DMSO, DMA, DMF at 298.15 K respectively.

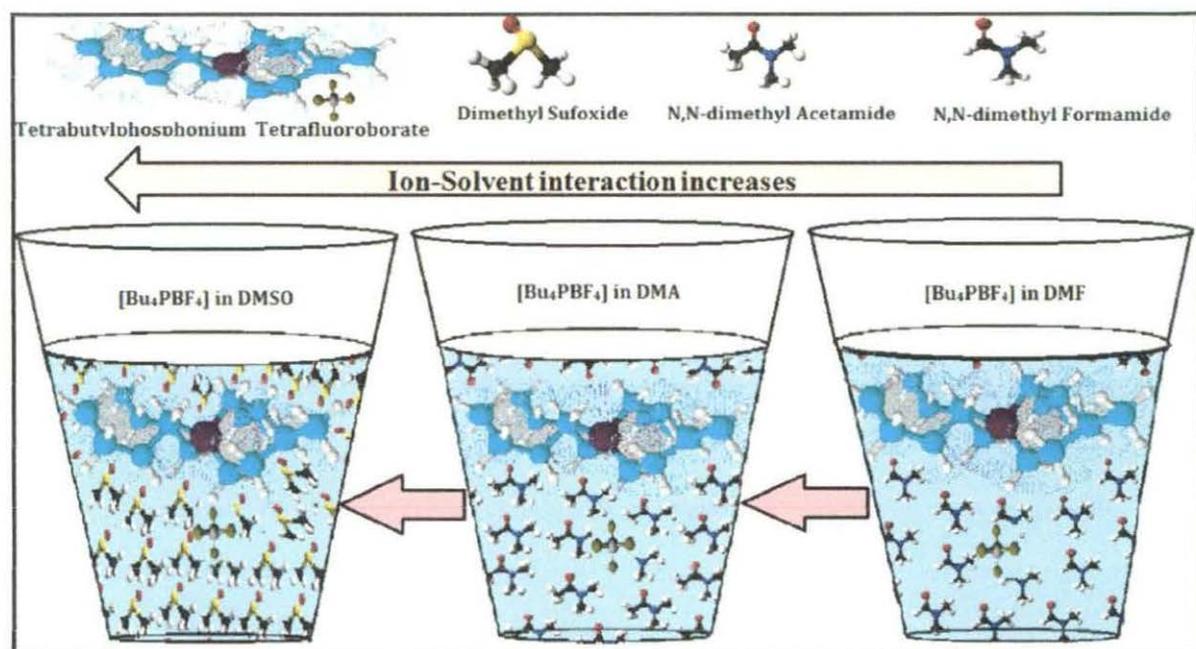


SCHEMES

Scheme 1.



Scheme 2.



CHAPTER VII

STUDY OF ASSORTED INTERACTIONS OF AN IONIC LIQUID IN SIGNIFICANT SOLVENT SYSTEMS USING COMPENSATED EQUATION OF FUOSS CONDUCTANCE AND VIBRATIONAL MODE

7.1. INTRODUCTION

In recent years, ionic liquids (ILs) have attracted considerable attention owing to their potential use in a diversified range of applications. ILs are one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering. ILs exhibit many interesting properties, such as unique permittivity, low melting point, negligible vapour pressure, a wide liquid range, high thermal stability, high electrical conductivity and wide electrochemical window. They are used as solvents or catalysts for a variety of reactions [1, 2].

The solvation of ionic liquid in various pure non-aqueous solvents has a great demand in modern battery industry [3] and, for further more understanding, organic reaction mechanisms [4]. Keeping in mind the use of ionic liquids in battery industries, here we have studied the thermodynamic and transport properties of ionic liquids in industrially important solvents. These properties provide important information about the nature and strength of intermolecular forces existing within the constituents of a solution. Fourier transform infrared (FT-IR) measurements have also been done as it is one of the most convenient methods to investigate the molecular interactions in electrolytic solutions.

There are several imidazolium-, pyridinium-, ammonium- and phosphonium-based cation ionic liquids commercially available. Compared with other ILs, the phosphonium-based ILs are less toxic, thermally more stable and readily available in bulk quantities and less expensive [5]. Phosphonium ILs have several advantages over other types of ILs, including, in specific cases and applications, higher thermal stability, lower

viscosity and higher stability in strongly basic or strongly reducing conditions. Phosphonium-based ILs is now appearing in applications as phase transfer catalysts [6], organic synthesis and electrochemical media.

The non-aqueous system has been of immense importance [7] to the technologist and theoretician as many chemical processes occur in these systems to examine the nature and magnitude of ion-ion and ion-solvent interactions. Conductance study is a very important tool in obtaining the information regarding the solvation and association behaviour of ions in solution. FT-IR spectroscopy has also been one of the most convenient methods for investigating the ion-solvent interactions in electrolytic solutions [8, 9, 10].

In this work, an attempt has been made to explore the electrolytic properties of [Bu₄PMS] (solid phase) in selected industrially important solvents. Here, we have investigated the conductance behaviour of [Bu₄PMS] in dimethyl sulphoxide (DMSO), N, N-dimethyl acetamide (DMA) and N, N-dimethyl formamide (DMF) at 298.15 K. These solvents used in the study are industrially very important. FT-IR spectroscopy of the salt in these solvents gives the information about the molecular interaction occurring in these systems.

7.2. EXPERIMENTS

7.2.1. Source and purity of samples

Ionic liquid tetrabutylphosphonium methanesulfonate [Bu₄PMS] of puriss grade was procured from Aldrich, Germany and was used as purchased. The mass fraction purity of [Bu₄PMS] was ≥ 0.98 .

All the solvents (DMSO, DMA and DMF) of spectroscopic grade were procured from Merck, India. These were further purified by standard methods [11]. The values of their mass fraction purities of the solvents were ≥ 0.99 . See Table 1.

7.2.2. Apparatus and Procedure

A stock solution of the electrolyte was prepared by mass (weighted with Mettler Toledo AG-285 with uncertainty ± 0.0003 g), and the working solutions were obtained by mass dilution at 298.15 K. Uncertainty of molarity of different salt solutions is evaluated to be ± 0.0001 mol·dm⁻³. A vibrating U-tube digital density meter (DMA 4500M, Anton Paar) with an accuracy of ± 0.00005 g cm⁻³ was used to measure the densities of the solutions (ρ) after being calibrated by triply distilled water and passing dry air. The temperature was fixed within ± 0.01 K.

The viscosity was also measured with the help Brookfield DV-III Ultra Programmable Rheometer with spindle size 42 fitted to a Brookfield Digital Bath TC-500.

The conductance measurements were carried out in a Systronic-308 conductivity meter (accuracy ± 0.01) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately 0.1 ± 0.001 cm⁻¹. Measurement was made in a water bath maintained within $T = 298.15 \pm 0.01$ K, and the cell was calibrated by the method proposed by Lind et al [12]. The conductance data were reported at a frequency of 1 kHz.

Infrared spectra were recorded on an 8300 FT-IR spectrometer (Shimadzu, Japan). The details of the instrument have already been previously described [10].

7.3. RESULTS AND DISCUSSION

7.3.1. Electrical Conductance

7.3.1.1. Ion-pair formation:

The physical properties of the pure solvent at 298.15 K are reported in Table 2. The molar conductance (Λ) has been obtained from the specific conductance (κ) value using the following equation [13]

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

where c is the molar concentration and κ is the measured specific conductance of the studied solution. The experimental values of molar conductances (Λ) of ionic liquid [Bu₄PMS] measured at the corresponding molar concentrations (c) in different studied

solvents are plotted in Figure 1. Linear conductance curves (Λ versus \sqrt{c}) were obtained (Figure 1) for the electrolyte in dimethylsulfoxide, dimethylacetamide and dimethylformamide, and extrapolation of $\sqrt{c} = 0$ evaluated the starting limiting molar conductance for the electrolytes. The conductance results for ion-pair formation have been analysed using the Fuoss conductance equation [14,15]. Thus, with a given set of conductivity values ($c_j, \Lambda_j, j=1, \dots, n$) three adjustable parameters, *i.e.* Λ_0 , K_A and R have been derived from the Fuoss equation. Here, Λ_0 is the limiting molar conductance, K_A is the observed association constant and R is the association distance, *i.e.* the maximum centre-to-centre distance between the ions in the solvent-separated ion-pairs. There is no precise method [16] for determining the R value, but in order to treat the data in our system, R value is assumed to be $R = a + d$, where $a = (r_+ + r_-)$ is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance, d , is given by [17]

$$d (\text{\AA}) = 1.183 (M / \rho)^{1/3} \quad (2)$$

where M is the molar mass and ρ is the density of the solvent.

Thus, the Fuoss conductance equation may be represented as follows:

$$\Lambda = P \Lambda_0 [(1 + R_x) + E_L] \quad (3)$$

$$P = 1 - \alpha(1 - \gamma) \quad (4)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (5)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (6)$$

$$\beta = e^2 / (\epsilon k_B T) \quad (7)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (8)$$

where R_x is the relaxation field effect, E_L is the electrophoretic counter current, κ is the radius of the ion atmosphere, ϵ is the dielectric constant of the solvents, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_A is the overall pairing constant, K_S is the association constant of the contact pairs, K_R is the association constant of the solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance.

The computations were performed using the program suggested by Fuoss. The initial Λ_0 values for the iteration procedure are obtained from Shedlovsky's extrapolation of the data [18]. Input for the program is the no. of data, n , followed by ε , η (viscosity of the solvent), initial Λ_0 value, T , ρ (density of the solvent), mole fraction of the first component, molar masses, M_1 and M_2 along with c_j , Λ_j values where $j = 1, 2, \dots, n$ and an instruction to cover preselected range of R values.

In Practice, calculations are performed by finding the values of Λ_0 and α which minimize the standard deviation, δ :

$$\delta^2 = \sum [\Lambda_j(cal) - \Lambda_j(obs)]^2 / (n - m) \quad (9)$$

where n is the number of experimental points and m is the number of fitting parameters. The conductance data have been explained and discussed by fixing the distance of closest approach R with two parameter fit ($m = 2$). For a sequence of R values and then plotting δ against R , the best-fit R corresponds to the minimum of the δ - R versus R curve. Thus, an approximated sum is made over a fairly wide range of R values using 0.1 increment to locate the minimum, but no significant minima is found in the δ - R curves; thus, R values are assumed to be $R = a + d$, with terms having usual significance. Finally, the corresponding Λ_0 and K_A values are obtained which are reported in Table 3 along with R and δ for all the solutions.

A perusal of Table 3 shows that the limiting molar conductance (Λ_0) of $[\text{Bu}_4\text{PMS}]$ is highest in the case of DMF and lowest in the case of DMSO among the studied solvents. The trend of the Λ_0 of the electrolytes in three different solvents is as follows:

$$\text{DMF} > \text{DMA} > \text{DMSO}.$$

Table 3 also implies that the association constant (K_A) of the $[\text{Bu}_4\text{PMS}]$ is greater in DMSO than in DMA than in DMF. Hence, there is greater ion-solvent interaction in DMSO than in DMA than in DMF, leading to a lower conductance of $[\text{Bu}_4\text{PMS}]$ in the former than the latter two. This shows that $[\text{Bu}_4\text{PMS}]$ is solvated more by DMSO, which has the highest viscosity value among the studied solvents. The highest ion-solvent interaction leading to very high ion-solvation is seen in case of DMSO which is evident

from the K_A values given in Table 3. The weakest ion-solvation is seen in the case of DMF. The trend in Λ_0 and ion-association can also be discussed through another characteristic function called the Walden product ($\Lambda_0\eta$, the limiting molar conductance-solvent viscosity product) is a constant under normal condition; given in Table 3. Table 3 shows that the decreasing trend of Walden's function is mainly in agreement with the concomitant decrease of solvent viscosity and increase of limiting molar conductance for the electrolyte (IL) in the solvents. This is also justified as the Walden product of an ion or solute which is inversely proportional to the effective solvated radius (r_{eff}) of the ion or solute in a particular solvent/solvent mixture [19]:

$$\Lambda_0\eta = \frac{1}{6\pi r_{\text{eff}}T} \quad (10)$$

This points out to the fact that the electrostatic ion-solvent interaction or ion-association is strong in these cases. The variation of the Walden product reflects the change of solvation [20] though the variation of the Walden product with solvent composition is difficult to interpret quantitatively, but its variation with solvent composition can still be explained by

1. *Preference to solvation of IL for solvent molecules:* Taking into consideration of the conductance and association constant value of ionic liquid in different solvents, we can say that the IL mostly prefers the dimethylsulfoxide among the other studied solvents, and the order of preference by the IL in the solvents is as follows:

dimethyl sulfoxide > N,N-dimethyl acetamide
> N,N-dimethyl formamide.

2. *Considering the structural aspect of the solvents:* Polar aprotic solvents (e.g. DMF, DMA, DMSO) dissolve ionic compounds and solvate cations very well. They do not solvate anions to any appreciable extent because they cannot form H-bonds and having positive centres are well shielded from any interaction with anions. When the ionic liquid [Bu₄PMS] is dissolved in the abovementioned polar aprotic solvents, the following interaction may be observed:

- (a) In the case of solvent DMF, the only interaction present is the between negatively charged oxygen atom of DMF and positively charged P atom of $[\text{Bu}_4\text{P}]^+$, as shown in (I).
- (b) The same type of interaction is present in the case of solvent DMA (II); here, the interaction is more intense due to the presence of methyl ($-\text{CH}_3$) group which pushes electrons towards oxygen, making it more negative for stronger interaction.
- (c) In the case of DMSO as solvent, two types of interaction shown in (III) are possible: (i) between the negatively charged oxygen atom of DMSO and positively charged P atom of $[\text{Bu}_4\text{P}]^+$, and (ii) between positively charged S atom of DMSO and negatively charged S atom of $[\text{MS}]^-$. The interaction (ii) is only possible because the S atom is larger than the N atom and is less shielded by two methyl groups compared to N atom in the case of DMF and DMA. For these reason, there is more conductance of $[\text{Bu}_4\text{PMS}]$ in DMF than DMA and DMSO. Hence, lower the conductance, the greater is the interaction/association, which is in the following order: $\text{DMSO} > \text{DMA} > \text{DMF}$

The schematic representation of ion-solvent interaction for the particular ion in the studied solvent is depicted in **Scheme 1**.

The starting point for most evaluations of ionic conductance is Stokes' law which states that the limiting Walden product ($\lambda_0^\pm \eta_0$; product of the limiting ionic conductance and solvent viscosity) for any singly charged spherical ion is a function of the ionic radius only, and thus, under normal conditions is a constant. The values of the ionic conductances λ_0^\pm (for the Bu_4P^+ cation and MS^- anion) in different solvents DMSO, DMA and DMF, were calculated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as a 'reference electrolyte' following the scheme as suggested by B. Das et al. [20].

The ionic limiting molar conductances λ_0^\pm for $[\text{Bu}_4\text{PMS}]$ in all the solvents have been calculated by interpolation of conductance data from the literature [21] using cubic spline fitting. Table 4 shows that the greater share of the conductance values comes

from the anion MS^- than the cation $[Bu_4P]^+$. The λ_o^\pm values were in turn utilised for the calculation of Stokes' radii (r_s) according to the classical expression [22]:

$$r_s = \frac{F^2}{6\pi N_A \lambda_o^\pm r_c} \quad (11)$$

Ionic Walden's function $\lambda_o^\pm \eta$, Stokes' radii r_s , and crystallographic radii r_c are presented in Table 4. The trends in Walden products $\Lambda_o \eta$ and ionic Walden products $\lambda_o^\pm \eta_o$ for the electrolytes in the solvents DMSO, DMA and DMF are depicted in Tables 3 and 4, respectively. They indicate that both the ionic Walden products $\lambda_o^\pm \eta$ and Walden products $\Lambda_o \eta$ for the electrolyte are greater in the case of DMSO than in DMA and DMF. For the Bu_4P^+ and MS^- ions, the Stokes' radii r_s are either lower or comparable to their crystallographic radii r_c ; this suggests that the ion is comparatively less solvated than alkali metal ions due to its intrinsic low surface charge density. The distance parameter R , shown in Table 3, is the least distance that two free ions can approach together before they merge into an ion pair.

The nature of the curve for the Gibbs energy changes for ion-pair formation, ΔG° , clearly predicts the tendency for ion-pair formation. The Gibbs energy change ΔG° is calculated by the following relationship [23] and is given in Table 3:

$$\Delta G^\circ = -RT \ln K_A \quad (12)$$

The negative values of ΔG° can be explained by considering the participation of specific interaction in the ion association process. It is observed from the Table 3 that the values of the Gibbs free energy are all negative, all over the solutions and the negativity increases from dimethylformamide to dimethylsulfoxide. The increasing negativity in the value of ΔG° of $[Bu_4PMS]$ leads to the increase in the ion-solvent interaction. This result indicates the extent of solvation enhanced by the following order:

$$DMSO > DMA > DMF$$

This is an excellent agreement with the observation obtained from conductance values discussed earlier in this paper.

The diffusion coefficient (D) is obtained using the Stokes-Einstein relation:

$$D = \frac{kT}{6\pi\eta r_s} \quad (13)$$

where k is the Boltzmann's constant, T is the temperature, η is the solvent viscosity and r_s is the Stoke's radii.

The ionic mobility was obtained using the following equation:

$$i = \frac{z^+ F}{RT} D \quad (14)$$

where z , F , R , T and D is the ionic charge, Faraday constant, universal gas constant, temperature, and diffusion coefficient, respectively. Table 5 shows that the diffusion coefficient of MS^- is more than Bu_4P^+ in all the solvents which indicates that MS^- ion diffuses more in the solvents. The diffusion coefficient decrease from DMF to DMSO as indicated in Table 5 for both $[Bu_4P]^+$ and MS^- ions showing greater diffusion of the ions in DMF. At the same time, the ionic mobility values given in Table 5 also shows that the mobility of MS^- is higher than that of $[Bu_4P]^+$ in all the investigated solvents because of its smaller size than that of cation. Hence, the greater share of the conductance comes from the anions than the cation.

7.3.1.2. FT-IR Spectroscopic Study

With the help of FT-IR spectroscopy, the molecular interaction existing between the solute and the solvent can be studied. The concentration of the studied solutions used in the IR study is 0.05 M, the IR spectra of the pure solvents were studied.

The stretching frequencies of the characteristic groups are given in Table 6 and Figures 2, 3, and 4. In the case of DMF, a sharp peak is obtained at $1,674.6 \text{ cm}^{-1}$ which is attributed to the C=O stretching vibration range ($1,630\text{-}1,690 \text{ cm}^{-1}$). The peak shifts to $1,700.2 \text{ cm}^{-1}$ due to the interaction of $[Bu_4P]^+ / MS^-$ ion with the C=O dipole showing ion-dipole interaction which is formed due to the disruption of H-bonding interaction in DMF molecules [24].

The IR spectra of DMA shows a sharp peak at $1,748.4 \text{ cm}^{-1}$ for C=O stretching vibration range ($1,680\text{-}1,750 \text{ cm}^{-1}$). When the IR spectra of $[Bu_4PMS]^+ + DMA$ solution was taken,

the peak shifted to $1,783.2\text{ cm}^{-1}$ leading to ion-dipole interaction between $[\text{Bu}_4\text{P}]^+ / \text{MS}^-$ and C=O dipole.

The greatest interaction is seen between $[\text{Bu}_4\text{PMS}]$ and DMSO as evidenced from the values of the K_A obtained from the conductivity studies. In the case of DMSO, a peak is obtained at $1,026.0\text{ cm}^{-1}$ since S=O stretching vibration (range $1,030\text{--}1,060\text{ cm}^{-1}$) shifts to $1,077.4\text{ cm}^{-1}$ by the addition of $[\text{Bu}_4\text{PMS}]$ to DMSO leading to the disruption of weak H-bonding interaction between the two DMSO molecules [25] and formation of ion-dipole interaction between $[\text{Bu}_4\text{P}]^+ / \text{MS}^-$ and S=O dipole.

Table 6 shows that the $\Delta\nu$ values increases from N,N-dimethyl formamide to dimethylsulfoxide, i.e. the shift in stretching frequency increases from N,N-dimethyl formamide to dimethylsulfoxide. The order of $\Delta\nu$ obtained from the FTIR spectra is



The greater the value of $\Delta\nu$, there is attraction between the electrolyte (IL) and solvent molecules. Therefore, with the increase in the value of $\Delta\nu$, the distance between the electrolyte and the solvent molecules decreases. Thus, the ion-solvent interaction increases with the increase in $\Delta\nu$ values from N,N-dimethyl formamide to dimethylsulfoxide. Thus, DMSO stabilises the electrolytes (ion-solvent interaction) to a greater extent than dimethylacetamide, which in turn stabilises the same greater than dimethylformamide. Therefore, the obtained result is in line with the conductivity study which was discussed earlier.

A schematic representation of the interaction occurring in pure solvent and $[\text{Bu}_4\text{PMS}] + \text{Solvent}$ together with the trend in the ion solvation in the studied solvents has been shown in **Scheme 2**.

7.4. CONCLUSIONS

The present work reveals an extensive study on the ion solvation behavior of the tetrabutylphosphonium methanesulfonate $[\text{Bu}_4\text{PMS}]$ in DMSO, DMA and DMF through the conductometric and FTIR measurements. From the study, it becomes clear that the salt is more associated with DMSO than the other solvents. It can also be seen that in the

conductometric studies in DMSO, DMA and DMF, the electrolyte remains as ion pairs. The ionic conductivity values suggest the fact that the anions (MS^-) conduct more than the cation $[Bu_4P]^+$. The diffusion coefficient and ionic mobility also show that in studied ionic liquid, the anions diffuses more due to high ionic mobility compared to the cation because the size of the anion is smaller than that of the cation. In all the solvents, the electrolyte forms ion-dipole interactions as evidenced from the FT- IR studies.

REFERENCES

- [1]. T. Welton, *Chem. Rev.* 99 (1999) 2071.
- [2]. J.S. Wilkes, *J. Mol. Catal A .Chem.* 214 (2004) 11-17.
- [3]. D. Aurbach, *Non-aqueous Electrochemistry*, Marcel Dekker, Inc: New York, (1999).
- [4]. J.A. Krom, J.T. Petty, A. Streitwieser, *J. Am. Chem. Soc.* 115 (1993) 8024.
- [5]. F. Atefi, M.T. Garcia, R.D. Singer, P.J. Scammells, *Green. Chem.* 11(2009) 1595.
- [6]. T. Ramnial, D.D. Ino, J.AC. Clyburne, *Chem. Commun.* (2005) 325.
- [7]. O. Popvyh, R.P.T. Tomkins, *Nonaqueous Solution Chemistry*, Chapter 4. Wiley-Interscience: New York (1981).
- [8]. R.R. Dogonadze, E. Kalman, A. A. Kornyshev, J. Ulstrup, *The Chemical Physics of Solvation, Part B, Spectroscopy Solvation*: Elsevier Amsterdam (1986).
- [9]. A. Sinha, G. Ghosh, M.N. Roy, *J. Phys. Chem. Liqs.* 48 (2010) 62-78.
- [10]. A. Sinha, A. Bhattacharjee, M.N. Roy, *J. Disp. Sc. Techn.* 30 (2009) 1003.
- [11]. D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, third ed. pp. 299. Pergamon Press: Oxford (1988).
- [12]. J.E. Jr. Lind, J.J. Zwolenik, R.M. Fuoss, *J. Am. Chem. Soc.* 81(1959) 1557.
- [13]. F.I. El-Dossoki, *J. Mol. Liq.* 151(2010) 1.
- [14]. R.M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.* 75(2010) 16.
- [15]. R.M. Fuoss, *J. Phys. Chem.* 82 (1978) 2427.
- [16]. B. Per, *Acta. Chem. Scand. A.* 31(1977) 869.
- [17]. R.M. Fuoss, F. Accascina, *Electrolytic Conductance*, Interscience: New York (1959).
- [18]. D.S. Gill, M.S. Chauhan, *Z. Phys. Chem. NF.* 140 (1984) 139.
- [19]. J. Bhat. Ishwara, P. Bindu, *J. Ind. Chem. Soc.* 72 (1995) 783.
- [20]. J.M. Chakraborty, B. Das, *Z. Phys. Chem.* 218 (2004) 219.
- [21]. R.M. Fuoss, E. Hirsch, *J. Am. Chem. Soc.* 82(1960) 1013.

- [22]. R.A. Robinson, R.H. Stokes, *Electrolyte Solutions*, Chapter 6, pp. 130. Butterworth: London (1959).
- [23]. R.M. Fuoss, C.A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 2387.
- [24]. C. Desfrancois, V. Periquet, S. Carles, J.P. Schermann, L. Adamowicz, *J. Chem. Phys.* 239 (1998) 475.
- [25]. O. Shun-Li, W. Nan-Nan, L. Jing-Yao, S. Cheng-Lin, L. Zuo-Wei, G. Shu-Qin, *Chin. Phys. B.* 19 (2010) 123101.
- [26]. T.M. Aminabhavi, B. Gopalakrishna, *J. Chem. Eng. Data.* 40(4) (1995)856. .
- [27]. A.K., Covington, T. Dickinson, *Physical chemistry of organic solvent systems*, Plenum: New York (1973).
- [28]. P.R. Philip, C. Jolicoeur, *J. Phys. Chem.* 77(1973) 3071.
- [29]. S.S. Smith, E.D. Steinle, M.E. Meyerhoff, D.C. Dawson, *J Gen Physiol.* 114 (1999) 799.

TABLES

Table 1. Sample description

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity
[Bu ₄ PMS]	Sigma-Aldrich, Germany	0.98	Used as procured	0.98
DMSO	Merck, India	0.98	Purified by standard methods [11]	0.99
DMA	Merck, India	0.98	Purified by standard methods [11]	0.99
DMF	Merck, India	0.98	Purified by standard methods [11]	0.99

Table 2. Values of Density (ρ), Viscosity (η) and Dielectric constant (ϵ_r) of pure solvents at $T = 298.15$ K

Solvents	$\rho^a \times 10^{-3} (\text{kg m}^{-3})$		$\eta^b (\text{mPa s})$		ϵ_r
	Expt	Lit	Expt	Lit	
DMSO	1.09602	1.09600 [26]	1.95	1.948 [26]	46.70 [27]
DMA	0.93680	0.93660 [26]	0.92	0.920 [26]	37.78 [27]
DMF	0.94450	0.94450 [26]	0.79	0.796 [26]	36.71 [27]

For T, uncertainty in the temperature values: ± 0.01 K

^a uncertainty in density values is ± 0.00005 g cm⁻³.

^b uncertainty in viscosity values is ± 0.03 mPa s.

Table 3. Limiting molar conductivity (Λ_0), the association constant (K_A), the distance of closest approach of ions (R), standard deviations δ of experimental Λ from equation 1, Walden product ($\Lambda_0\eta$) and Gibb's energy change (ΔG^0) of [Bu₄PMS] in studied solvent systems at $T = 298.15$ K

Solvents	$\Lambda_0 \times 10^4$ (S m ² mol ⁻¹)	K_A (dm ³ mol ⁻¹)	R (Å)	δ	$\Lambda_0\eta \times 10^4$ (S m ² mol ⁻¹ mPa s)	Log(K_A)	ΔG^0 (kJ mol ⁻¹)
DMSO	33.97	29.89	12.66	0.13	66.11	5.48	-3.12
DMA	51.31	17.36	13.11	0.12	47.36	5.24	-2.99
DMF	57.07	12.68	12.79	0.17	45.31	5.10	-2.91

Table 4. Limiting ionic conductance (λ_o^\pm), ionic Walden product ($\lambda_o^\pm\eta$), Stokes' radii (r_s) and crystallographic radii (r_c) of [Bu₄PMS] in studied at $T = 298.15$ K

Solvents	Ion	λ_o^\pm (S m ² mol ⁻¹)	$\lambda_o^\pm\eta$ (S m ² mol ⁻¹ mPa s)	r_s (Å)	r_c (Å)
DMSO	Bu ₄ P ⁺	13.26	25.80	3.18	4.42
	MS ⁻	20.71	40.30	2.03	2.83
DMA	Bu ₄ P ⁺	20.03	18.49	4.43	4.42
	MS ⁻	31.28	28.87	2.84	2.83
DMF	Bu ₄ P ⁺	22.28	17.69	4.63	4.42
	MS ⁻	34.79	27.63	2.97	2.83

^aCrystallographic radii for cation from [28] and for anion calculated and judged from Ref. [29], respectively

Table 5. Diffusion Coefficient (D) and ionic mobility (i) of [Bu₄P]⁺ and MS⁻ in studied solvents at 298.15 K

Solvents	$D \cdot 10^{10}/(\text{m}^2 \text{s}^{-1})$		$i \cdot 10^8/(\text{m}^2 \text{s}^{-1} \text{volt}^{-1})$	
	Bu ₄ P ⁺	MS ⁻	Bu ₄ P ⁺	MS ⁻
DMSO	3.53	5.52	1.38	2.15
DMA	5.34	8.33	2.08	3.24
DMF	5.94	9.27	2.31	3.61

Table 6. Stretching frequencies of the functional groups present in the pure solvent and change of frequency after addition of IL, [Bu₄PMS] in the solvents.

Solvents	Functional Group	Range (ν cm ⁻¹)	Stretching frequencies		$\Delta\nu$ (cm ⁻¹)
			Pure Solvent (ν_o cm ⁻¹)	[Bu ₄ PMS]+Solvent (ν_s cm ⁻¹)	
DMF	(aldehydic) C=O	1630-1690	1674.6	1700.2	25.6
DMA	(carbonyl) C=O	1680-1750	1748.4	1783.2	34.8
DMSO	S=O	1030-1060	1026.0	1077.4	51.4

FIGURES

Figure 1. Plot of molar conductance (Λ) and the square root of molar concentration (\sqrt{c}) of $[\text{Bu}_4\text{PMS}]$ in DMSO (*black diamond*), DMA (*black triangle*), and DMF (*black circle*), respectively, at $T = 298.15 \text{ K}$

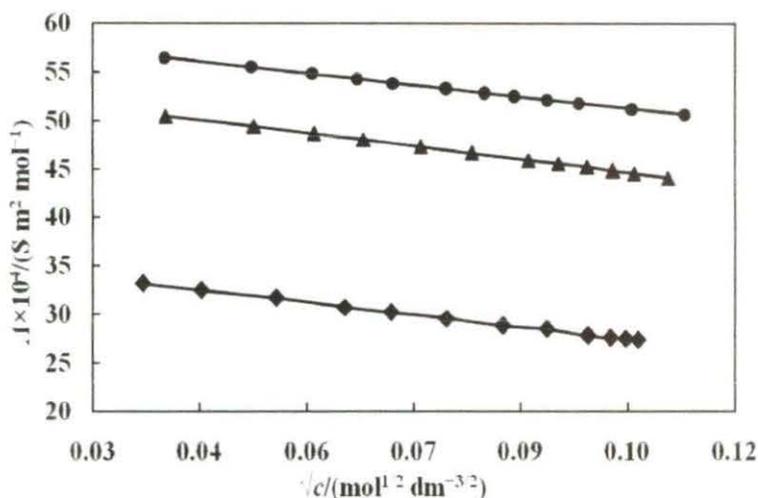


Figure 2. Stretching frequency of C-O in DMF (*black solid line*) and $[\text{Bu}_4\text{PMS}] + \text{DMF}$ (*red solid line*).

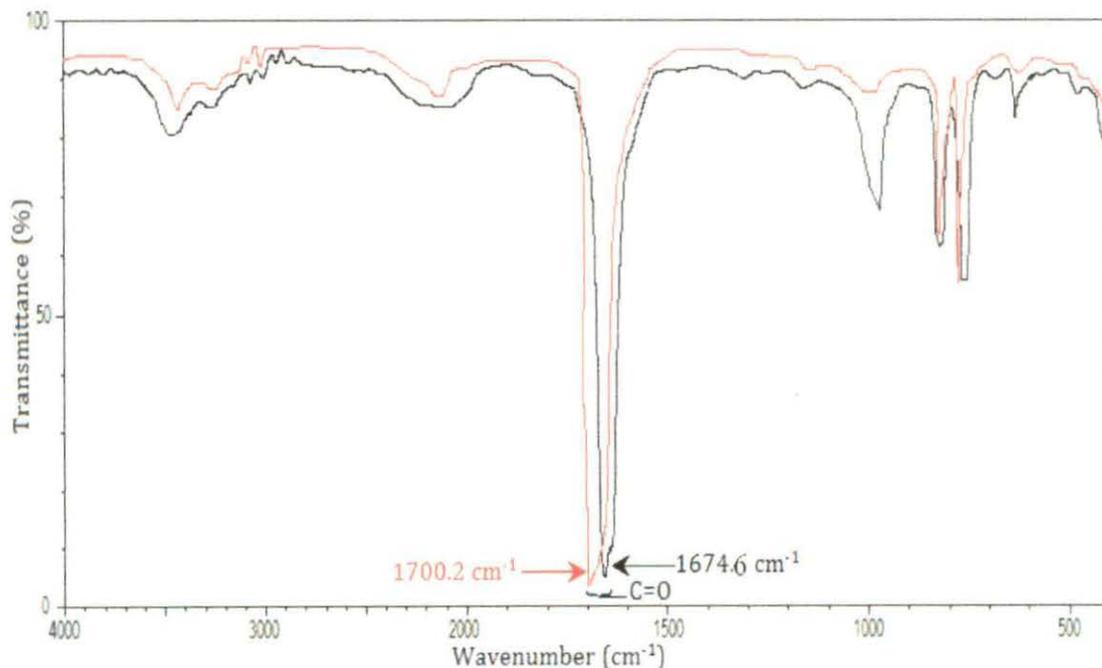


Figure 3. Stretching frequency of C-O in DMA (black solid line) and [Bu₄PMS] + DMA (red solid line).

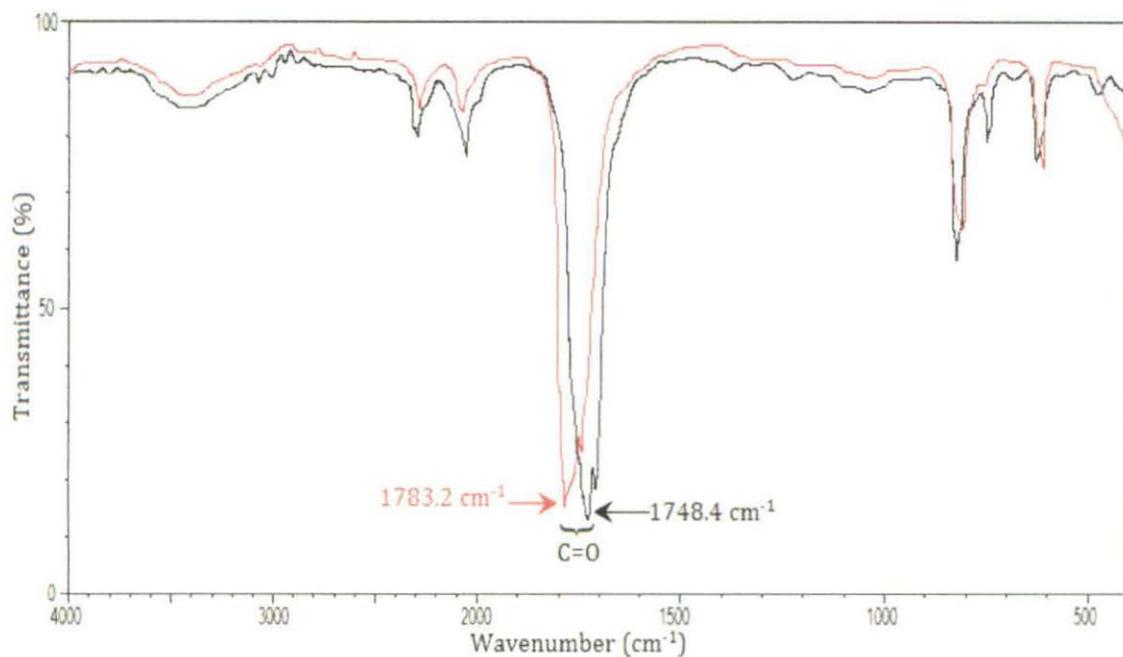
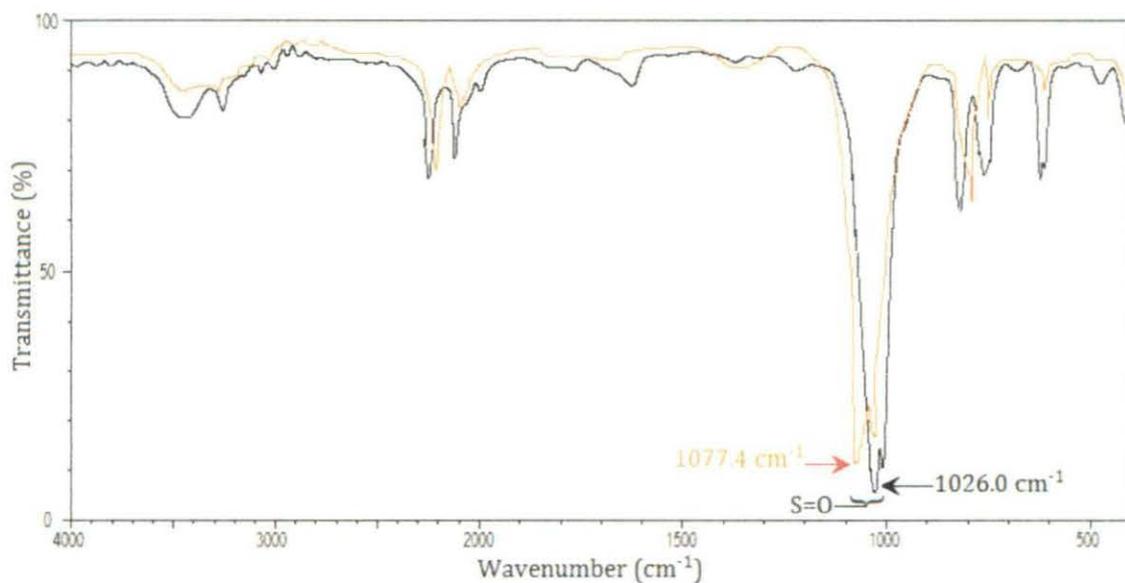
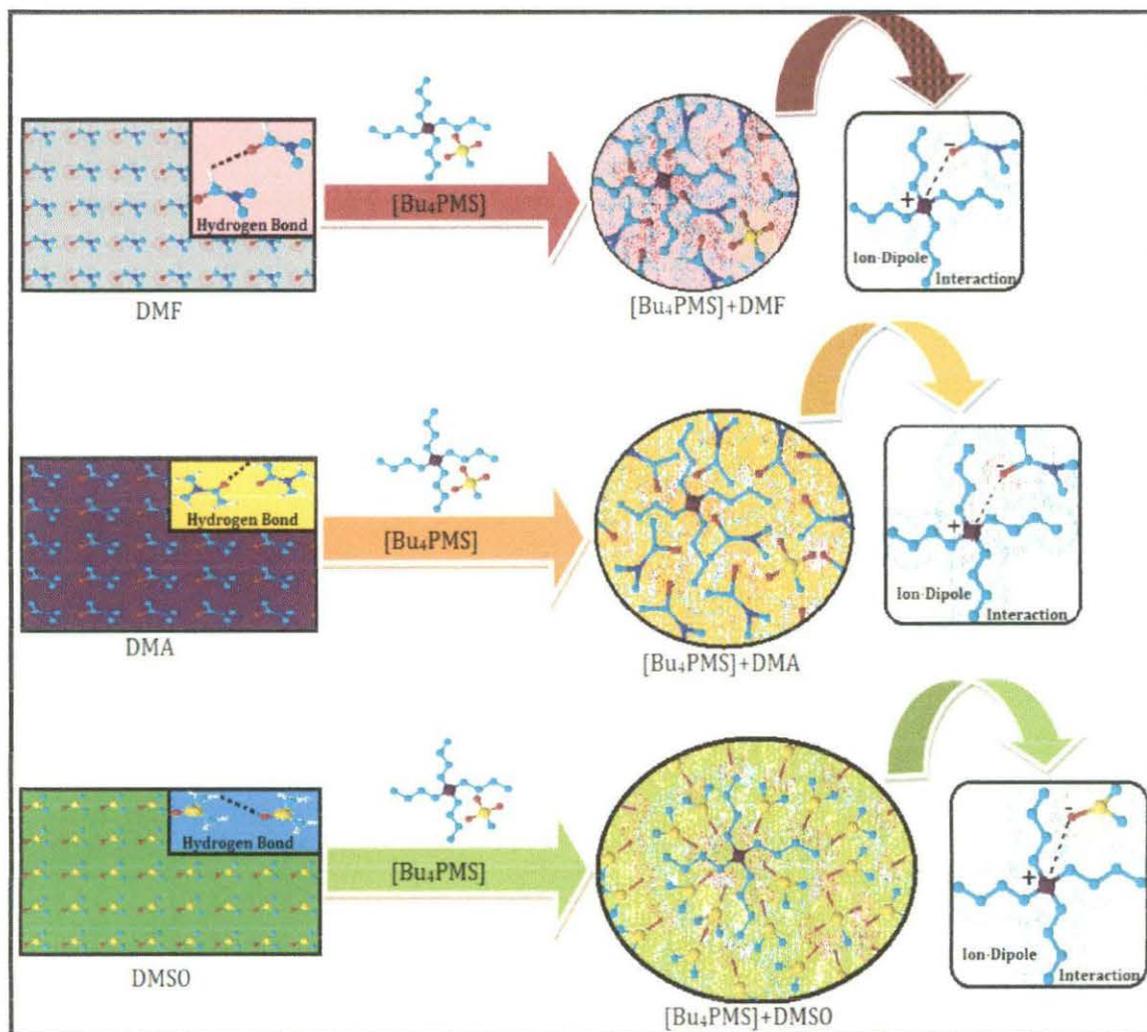


Figure 4. Stretching frequency of S=O in DMSO (black solid line) and [Bu₄PMS] + DMSO (red solid line).



Scheme 2. Schematic representation of the interaction occurring in pure solvent and {[Bu₄PMS] +solvents} together with the trend in the ion solvation in the studied solvent which is as follows: DMF < DMA < DMSO



CHAPTER VIII

PROBING SUBSISTENCE OF ION-PAIR AND TRIPLE-ION OF AN IONIC SALT IN LIQUID ENVIRONMENTS BY MEANS OF CONDUCTOMETRIC CONTRIVANCE

8.1. INTRODUCTION

The exploration of molecular interaction existing in solution is always of interest to chemists. Molecular interaction can be studied in the solution phase by studying its thermodynamic and transport properties. These properties provide important information about the nature and strength of intermolecular forces operating among mixed components. Study on the transport properties of electrolytes in different solvent media is of great importance to obtain information as to the solvation and association behavior of ions in solutions. In the modern technology the application of the salt is well understood by studying the ion solvation. A number of conductometric [1] and related studies of electrolytes in non-aqueous solvents have been done in relation to the use of these types of electrolytes in high-energy batteries [2] and for further understanding of organic reaction mechanisms [3]. Tetraalkylammonium salts are very suitable due to the excellent solubility characteristics in aqueous/non-aqueous solvents. Tetraalkylammonium salts have a broad range of applications that includes trace analysis (of metals and organic compounds), environmental analytic chemistry pharmaceutical and medicinal.

The solvents chosen for the study are all polar aprotic except methanol (CH_3OH) which is polar protic. The solvents used in this study find wide industrial usage. Industrially important acetonitrile (CH_3CN) is predominantly used in the manufacture of pharmaceutical and in battery industries.

Alcohols have varied applications in chemical and cosmetic industries. Methanol (CH_3OH) is used as solvent for paints and varnishes, antifreeze for automobile radiators, motor fuel, denaturant for ethanol, etc.

Dimethylsulfoxide (DMSO), a typical aprotic solvent having both polar and non polar groups is used in veterinary medicine, in organic synthesis and as an antifreeze agent of living cells [4]. It is widely used in pharmaceutical applications, enzyme-catalyzed reactions, veterinary medicine, dermatology, experimental immunology and microbiology [5].

1, 3-Dioxolane is cyclic diether and it figures prominently in the high energy battery technology [6] and has also found application in organic synthesis as manifested from the physico-chemical studies in this media. The knowledge of the type and structure of the complex species in solution is essential for the optimal choice of solvents. Even though these solvents have drawn much focus in recent years as solvents for physico-chemical investigations, still a lot remains to be explored.

In continuation of our investigation on electrical conductances [7,8] an attempt has been made in the present study, to ascertain the nature of ion-solvent interactions of tetrabutylammonium tetrafluoroborate [Bu_4NBF_4] in acetonitrile (CH_3CN), methanol (CH_3OH), dimethyl sulfoxide (DMSO) and 1,3-dioxolane(1,3-DO) at 298.15 K. The conductometric studies have been done for the electrolyte in the studied solvents and the obtained results have been discussed for the formation of ion-pairs and triple-ions. In the solvents, viz. CH_3CN , CH_3OH and DMSO; ion-pairs are formed due to the high/moderate dielectric constant of the solvents. However, in case of 1, 3-DO triple-ions are formed due to its low dielectric constant ($\epsilon < 10$). Different thermodynamic parameters such as association constant (K_A), and Gibbs energy change of solvation (ΔG°), have been evaluated and discussed.

8.2. EXPERIMENTAL

8.2.1. Source and purity of samples

$[\text{Bu}_4\text{NBF}_4]$ of puriss grade was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of $[\text{Bu}_4\text{NBF}_4]$ was ≥ 0.99 .

The solvents CH₃CN, CH₃OH, DMSO and 1,3-DO were procured from Merck, India. These were further purified by standard methods [9]. The values of purity obtained were ≥ 0.99 . See Table 1.

8.2.2. Apparatus and Procedure

A stock solution of the electrolyte [Bu₄NBF₄] was prepared by mass (Mettler Toledo AG-285 with uncertainty ± 0.0003 g) and the working solutions were obtained by mass dilution at 298.15 K and atmospheric pressure.

The densities of the solvents (ρ) were measured by means of vibrating-tube Anton Paar density-meter (DMA 4500 M) with a precision of ± 0.00005 g·cm⁻³ maintained at ± 0.01 K of the desired temperature. Adequate precautions were taken to minimize evaporation loses during the actual measurements. The precision of density measurements was $\pm 3.10^{-5}$ g·cm⁻³. It was calibrated by double-distilled water and dry air. Measurement of solvent viscosities was carried out by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature [10-12]. A thoroughly cleaned and perfectly dried viscometer filled with experimental solution was placed vertically in a glass-walled thermostat (Bose Panda Instruments Pvt, Ltd.) and maintained the temperature to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stop watch. The flow times were accurate to ± 0.1 s. At least three repetitions of each datum reproducible to ± 0.1 s were taken to average the flow times.

Viscosity of the solution is evaluated using the following equation [13];

$$\eta = \left(Kt - \frac{L}{t} \right) \rho \quad (1)$$

where K and L are the viscometer constants, t is the efflux time of flow in seconds and ρ is the density of the experimental liquid. The uncertainty in viscosity measurements is within ± 0.003 mPa·s.

The conductance measurements were carried out in a Systronics-308 conductivity bridge of accuracy $\pm 0.01\%$, using a dip-type immersion conductivity cell, CD-10 having a cell constant of approximately $(0.1 \pm 0.001) \text{ cm}^{-1}$. Measurements were carried out in a thermostat water bath maintained at $T = (298.15 \pm 0.01) \text{ K}$. The cell was calibrated by the method proposed by Lind et al. [14]. During the conductance measurements, cell constant was maintained within the range 1.10 to 1.12 cm^{-1} . The conductance data were reported at a frequency of 1 kHz and the accuracy was $\pm 0.3\%$. During the measurements, uncertainty of temperatures was $\pm 0.01 \text{ K}$.

8.3. RESULTS AND DISCUSSION

8.3.1. Electrical Conductance

8.3.1.1. Ion-pair formation

The electrolyte was freely soluble in all proportions of the solvent. The physical properties of the pure solvents were in good agreement with values found in the literature, as reported in Table 2, where appropriate corrections were made by the specific conductance of the solvents at that temperature.

The molar conductance (Λ) for all studied system was calculated using following equation. [15]

$$\Lambda = 1000 \kappa / c \quad (2)$$

where c is the molar concentration and κ is the measured specific conductance of the studied solution. The experimental values of molar conductances (Λ) of electrolyte $[\text{Bu}_4\text{NBF}_4]$ measured at the corresponding molar concentrations (c) in CH_3CN , CH_3OH , DMSO and $1,3\text{-DO}$ are given in Table 3. The conductance data for $[\text{Bu}_4\text{NBF}_4]$ in the studied solvents have been analyzed using the Fuoss conductance equation [16]. So with a given set of conductivity values ($c_j, \Lambda_j, j=1, \dots, n$) three adjustable parameters, i.e. Λ_0 , K_A and R have been derived from the Fuoss equation. Here, Λ_0 is the limiting molar conductance, K_A is the observed association constant and R is the association

distance, i.e., the maximum centre to centre distance between the ions in the solvent separated ion-pairs. There is no precise method [17] for determining the R value but in order to treat the data in our system, R value is assumed to be, $R = a + d$, where $a = (r_+ + r_-)$ is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance, d is given by [18]:

$$d (\text{\AA}) = 1.183 (M / \rho)^{1/3} \quad (3)$$

where M is the molar mass and ρ is the density of the solvent.

Thus, the Fuoss conductance equation may be represented as follows:

$$\Lambda = P \Lambda_o [(1 + R_x) + E_L] \quad (4)$$

$$P = 1 - \alpha(1 - \gamma) \quad (5)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (6)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (7)$$

$$\beta = e^2 / (\epsilon k_B T) \quad (8)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (9)$$

where R_x is the relaxation field effect, E_L is the electrophoretic counter current, k^{-1} is the radius of the ion atmosphere, ϵ is the relative permittivity of the solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_A is the overall pairing constant, K_S is the association constant of the contact-pairs, K_R is the association constant of the solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance.

The computations were performed using the program suggested by Fuoss. The initial Λ_o values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [19]. Input for the program is the set $(c_j, \Lambda_j, j = 1, \dots, n), n, \epsilon, \eta, T$, initial values of Λ_o , and an instruction to cover a pre-selected range of R values.

The best value of a parameter is the one when equations is best fitted to the experimental data corresponding to minimum standard deviation δ for a sequence of predetermined R values, and standard deviation δ was calculated by the following equation

$$\delta^2 = \sum [A_j(cal) - A_j(obs)]^2 / (n - m) \quad (10)$$

where n is the number of experimental points and m is the number of fitting parameters. The conductance data were analyzed by fixing the distance of closest approach R with two parameter fit ($m = 2$). For a sequence of R values and then plotting δ against R , the best-fit R corresponds to the minimum of the δ - R versus R curve. So, approximate runs are made over a fairly wide range of R values using 0.1 increments to locate the minimum, but no significant minima were found in the δ - R curves for the electrolyte in CH_3CN , CH_3OH and DMSO.

The values of Λ_0 , K_A , and R obtained by this procedure are represented in Table 4. Perusal of Table 4 and Figure 1 reveals that the limiting molar conductance Λ_0 of $[\text{Bu}_4\text{NBF}_4]$ in CH_3CN is greater than that in CH_3OH and DMSO which is in the order $\text{CH}_3\text{CN} > \text{CH}_3\text{OH} > \text{DMSO}$. Table 3 and Figure 2 also imply that the association constant (K_A) of the $[\text{Bu}_4\text{NBF}_4]$ is more in DMSO, than in CH_3OH and CH_3CN . Hence, there is more ion-solvent interaction in DMSO than in CH_3OH and CH_3CN ; leading to a lower conductance of $[\text{Bu}_4\text{NBF}_4]$ in the former than in the latter two. The higher viscosity of DMSO also supports the above fact because with higher viscosity the Λ_0 value should decrease.

Solvent polarity and dielectric constant play a very important role in determining the physico-chemical properties of solution. As all the solvents used are polar, dielectric constant becomes more important here because it is the ability of the solvent to stabilize the charges or dipoles. So, more the dielectric constant of the solvent more will be its ability to stabilize the charges or dipoles. Dielectric constant of DMSO, CH_3CN and CH_3OH is about 46.7, 35.94 and 32.7 respectively at 298.15 K. Therefore ion-solvent

interaction should have been in the following order $\text{DMSO} > \text{CH}_3\text{CN} > \text{CH}_3\text{OH}$. But our finding tells the order of ion-solvent interaction of $[\text{Bu}_4\text{NBF}_4]$ to be $\text{DMSO} > \text{CH}_3\text{OH} > \text{CH}_3\text{CN}$.

Out of the three solvents used, DMSO and CH_3CN are polar aprotic solvents whereas CH_3OH is a polar protic solvent. Polar aprotic solvents, (*e.g.*, DMSO and CH_3CN) dissolve ionic compounds and stabilize cations very well, but do not stabilize anions to any appreciable extent because they cannot form H-bonds and having positive centers are well shielded from any interaction with anions. On the other hand polar protic solvent (*e.g.*; CH_3OH) dissolves ionic compounds by forming H-bonds [20], because they have an H atom attached to an atom of strong electronegative element. When the ionic compound $[\text{Bu}_4\text{NBF}_4]$ is dissolved in the above mentioned polar aprotic and polar protic solvents, the following interaction may be observed.

The schematic representation of ion-solvation, for the particular ion in the studied solvent is depicted in Scheme 1.

In case of solvent CH_3CN , the only interaction present is between negatively charged N atom of CH_3CN and positively charged N atom of $[\text{Bu}_4\text{N}]^+$, shown in (i). In case of DMSO as solvent, two types of interaction shown in (iii) are possible –

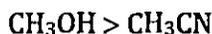
a) Between the negatively charged O atom of DMSO and positively charged N atom of $[\text{Bu}_4\text{N}]^+$.

b) Between positively charged S atom of DMSO and negatively charged species $[\text{BF}_4]^-$.

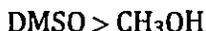
The interaction (b) is only possible because S atom is larger than C atom and is more electropositive than C atom present in CH_3CN . For this reason conductance of $[\text{Bu}_4\text{NBF}_4]$ is more in CH_3CN than DMSO. Also higher dielectric constant of DMSO than CH_3CN complies with the results. Hence, lower the conductance, more the interaction/association, which is in the following order-



In case of solvent CH_3OH , the H-bond interaction is present between F atom of negatively charged species $[\text{BF}_4]^-$ and H atom of CH_3OH . Also the free electron pairs present in O atom of CH_3OH can stabilize positively charged N atom of $[\text{Bu}_4\text{N}]^+$ as shown in (ii). Though dielectric constant of CH_3CN is greater than CH_3OH , ion-solvent interaction of CH_3OH is more than CH_3CN because it can stabilize both the charged species. Moreover CH_3CN has the tendency to form anti-parallel dimer [21] shown in Scheme 2. The formation of anti-parallel dimer reduces the degree of ion-solvent interaction. So conductance of $[\text{Bu}_4\text{NBF}_4]$ is more in CH_3CN than in CH_3OH . Hence, lower the conductance, more the interaction/association, which is in the following order-



As dielectric constant of DMSO is much higher than CH_3OH , and it can stabilize both the positively charged species $[\text{Bu}_4\text{N}]^+$ and negatively charged species $[\text{BF}_4]^-$ as CH_3OH does. So ion-solvent interaction is more in DMSO compared to CH_3OH . Hence, lower the conductance, more the interaction/association, which is in the following order-



Thus, the overall ion-solvent interaction of electrolyte $[\text{Bu}_4\text{NBF}_4]$ in the three solvents DMSO, CH_3CN and CH_3OH is of the order



The results are in accordance with the obtained data.

The above trend in Λ_0 values can be verified through another characteristic function called the Walden product, $\Lambda_0\eta_0$ given in Table 4. From Table 4 and Figure 3 the increasing trend of Walden product is mainly in agreement with the concomitant increase of solvent viscosity and decrease of limiting molar conductance for the electrolyte in the studied solvents. This is also justified as the Walden product of an ion or solute is inversely proportional to the radius of the ion or solute in a particular solvent. [22]

The starting point for most evaluations of ionic conductance is Stokes' law which states that the limiting ionic Walden product ($\lambda_0^\pm \eta_0$), (product of the limiting ionic conductance and solvent viscosity) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions is a constant. The ionic conductances λ_0^\pm (for $[\text{Bu}_4\text{N}]^+$ cation and $[\text{BF}_4]^-$ anion) in different solvents CH_3CN , CH_3OH and DMSO , were calculated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as a 'reference electrolyte' following the scheme as suggested by B. Das et al.[23] The λ_0^\pm values were in turn utilized for the calculation of Stokes' radii (r_s) according to the classical expression [24]

$$r_s = \frac{F^2}{6\pi N_A \lambda_0^\pm r_c} \quad (11)$$

Ionic Walden products $\lambda_0^\pm \eta_0$, Stokes' radii r_s , and crystallographic radii r_c are presented in Table 5. The trends in Walden products $\lambda_0 \eta_0$ and ionic Walden products $\lambda_0^\pm \eta_0$ for the electrolytes in the solvents CH_3CN , CH_3OH and DMSO , are depicted in Tables 4 and 5 and Figures 3 and 5 respectively. It shows that both the ionic Walden products $\lambda_0^\pm \eta_0$ and Walden products $\lambda_0 \eta_0$ for the electrolyte are higher in the case of DMSO than CH_3OH and CH_3CN . For Bu_4N^+ and BF_4^- ion, the Stokes' radii r_s are either lower or comparable to their crystallographic radii r_c , this suggests that the ion is comparatively less solvated than alkali metal ions due to its intrinsic low surface charge density. The distance parameter R , shown in Table 3, is the least distance that two free ions can approach together before they merge into an ion pair. R values have been found to be greater in case of DMSO than other two solvents.

The nature of the curve for the Gibbs energy changes for ion-pair formation, ΔG° , which clearly predicts the tendency for ion-pair formation. The Gibbs energy change ΔG° is calculated by the following relationship [25] and is given in Table 3.

$$\Delta G^\circ = -RT \ln K_A \quad (12)$$

where K_A is the association constant. The negative values of ΔG° can be explained by considering the participation of specific covalent interaction in the ion-association process. The lower value of ΔG° for $[\text{Bu}_4\text{NBF}_4]$ electrolyte in DMSO than CH_3OH and CH_3CN indicates the highest degree of association in DMSO. This result indicates the extent of solvation enhanced by the following order:



This is an excellent agreement with the observation obtained from conductance values discussed earlier in this paper.

There are marked characteristic behaviors in the K_A values, which are highest in case of DMSO than CH_3OH and CH_3CN . So, ion-association for the electrolyte increases in case of DMSO.

8.3.1.2. Triple-ion formation

Figure 4 present the graphical representation of Λ vs. \sqrt{c} , which shows that, the electrolyte follows the same trend, *i.e.* decreases with increasing concentration, reaches a minimum and then increases. Due to the deviation of the conductometric curves (Λ vs \sqrt{c}) from linearity in case of $[\text{Bu}_4\text{NBF}_4]$ in 1, 3- DO, the conductance data have been analyzed by using the classical Fuoss-Kraus theory of triple-ion formation in the form [18, 25]

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_p}} + \frac{\Lambda_0^T K_T}{\sqrt{K_p}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \quad (13)$$

where $g(c)$ is a factor that lumps together all the intrinsic interaction terms and is defined by:

$$g(c) = \frac{\exp\{-2.303 \beta' (c\Lambda)^{0.5} / \Lambda_0^{0.5}\}}{\{1 - S(c\Lambda)^{0.5} / \Lambda_0^{1.5}\} (1 - \Lambda / \Lambda_0)^{0.5}} \quad (14)$$

$$\beta' = 1.8247 \times 10^6 / (\epsilon T)^{1.5} \quad (15)$$

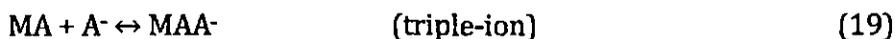
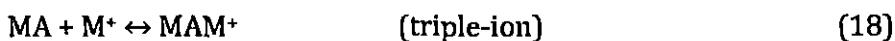
$$S = \alpha \Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\epsilon T)^{1.5}} \Lambda_0 + \frac{82.501}{\eta (\epsilon T)^{0.5}} \quad (16)$$

In the above equations, Λ_0 is the sum of the molar conductance of the simple ions at infinite dilution, Λ_0^T is the sum of the conductance value of the two triple-ions $[(\text{Bu}_4\text{N})_2]^+\text{BF}_4$ and $\text{Bu}_4\text{N}[(\text{BF}_4)_2]^-$ for $[\text{Bu}_4\text{NBF}_4]$ salt; $K_P \approx K_A$ and K_T are the ion-pair and triple-ion formation constants respectively and S is the limiting Onsager coefficient. To make equation (13) applicable, the symmetrical approximation of the two possible formation constants of triple-ions, $K_{T1} = [(\text{Bu}_4\text{N})_2]^+\text{BF}_4 / \{[\text{Bu}_4\text{N}^+][\text{Bu}_4\text{NBF}_4]\}$ and $K_{T2} = \text{Bu}_4\text{N}[(\text{BF}_4)_2]^- / \{[\text{BF}_4^-][\text{Bu}_4\text{NBF}_4]\}$ equal to each other has been adopted, *i.e.* $K_{T1} = K_{T2} = K_T$ [26] and Λ_0 values for the studied electrolyte in 1,3-DO have been calculated following the scheme as suggested by Krumgalz [27] [1983]. The calculated values are listed in Table 5. Λ_0^T has been calculated by setting the triple-ion conductance equal to $2/3 \Lambda_0$ [28]

The ratio Λ_0^T / Λ_0 was thus set equal to 0.667 during linear regression analysis of equation (13). Table 5 shows the calculated limiting molar conductance of simple ion (Λ_0), limiting molar conductance of triple-ion (Λ_0^T), slope and intercept of equation (13) for $[\text{Bu}_4\text{NBF}_4]$ in 1, 3-DO at 298.15 K. The linear regression analysis of equation (13) for the electrolytes with an average regression constant, $R^2 = 0.9889$, gives intercepts and slopes. These values permit the calculation of other derived parameters such as K_P and K_T listed in Table 6. The value of $\log (K_T/K_P)$ has also been reported. A perusal of Table 7 shows that the major portion of the electrolytes exists as ion-pairs with a minor portion as triple ions. The tendency of triple ion formation can be judged from the K_T/K_P ratios and $\log (K_T/K_P)$. These ratios suggest that strong association between the ions is due to the coulombic interactions as well as to covalent forces in the solution. These results are in good agreement with those of Roy et al. [21]

At very low dielectric constant of the solvent, *i.e.*, $\epsilon < 10$, electrostatic ionic interactions are very large. So the ion-pairs attract the free cations or anions present in the solution medium as the distance of the closest approach of the ions becomes minimum. These

result in the formation of triple-ions, which acquires the charge of the respective ions, attracted from the bulk solution [25, 29] i.e;



where M^+ and A^- are Bu_4N^+ and BF_4^- respectively. The effect of ternary association [30] thus removes some non-conducting species, MA, from solution, and replaces them with triple-ions which increase the conductance manifested by non-linearity observed in conductance curves for the electrolyte in 1,3-DO. The Scheme 3 depicts the pictorial representation of triple-ion formations for the electrolyte, in 1,3-DO.

Furthermore, the ion-pair and triple-ion concentrations, C_P and C_T , respectively of the $[Bu_4NBF_4]$ in 1,3-DO have also been calculated using the following equations [21]

$$\alpha = 1 / (K_P^{1/2} \cdot C^{1/2}) \quad (20)$$

$$\alpha_T = (K_T / K_P^{1/2}) C^{1/2} \quad (21)$$

$$C_P = C(1 - \alpha - 3\alpha_T) \quad (22)$$

$$C_T = (K_T / K_P^{1/2}) C^{3/2} \quad (23)$$

Here α and α_T are the fractions of ion-pairs and triple-ions present in the salt-solutions respectively and are given in Table 8. Thus, the values of C_P and C_T also given in Table 8, indicate that the ions are mainly present as ion-pairs even at high concentration and a small fraction existing as triple-ions. The ion-pair fraction (α), triple-ion fraction (α_T), ion-pair concentration (C_P) and triple-ion concentration (C_T) have also been calculated over the whole concentration range of $[Bu_4NBF_4]$ in 1, 3- DO and the data are provided in Table 8. It is observed that the amount of the triple-ions in the solution increases with the increase in concentration. (see Table 9)

The schematic representation of ion-solvation, for the particular ion in the studied solvent in view of various derived parameters is depicted in Scheme 4.

8.4. CONCLUSIONS

The present work reveals an extensive study on the ion-solvation behavior of the tetrabutylammonium tetrafluoroborate [Bu₄NBF₄] in CH₃CN, CH₃OH, DMSO and 1,3-DO through the conductometric measurements. From the study it becomes clear that the salt is more associated with DMSO than the other three solvents. It can also be seen that in the conductometric studies in CH₃CN, CH₃OH and DMSO, the electrolyte remains as ion-pairs but in 1,3-DO it remains as triple-ions. The tendency of the ion-pair and triple-ion formation depends on the size and the charge distribution of the ions.

REFERENCES

- [1]. G.J. Janz, R.P.T. Tomkins, *Non-aqueous Electrolytes Handbook*, Academic Press: New York, Vol. 1, (1972).
- [2]. M. Salomon, *J. Sol. Chem.* 22 (1993) 715.
- [3]. J. A. Krom, J. T. Petty, A. J. Streitwieser, *J. Am. Chem. Soc.* 115 (1993) 8024.
- [4]. T. Kamiyama, M. Morita, T. Kimura, *J. Chem. Eng. Data.* 49 (2004) 1350.
- [5]. M. K. Pasha, J. R. Dimmock, M. D. Hollenberg, R. K. Sharma, *Biochem. Pharmacol.* 64 (2002) 1461.
- [6]. C. G. Janz, R. P. T. Tomkins, *Non-Aqueous Electrolytes Handbook*, Academic Press: New York, Vol. 4 (1975).
- [7]. M. N. Roy, B. Sinha, V. K. Dakua, A. Sinha, *Pak. J. Sci. Ind. Res.* 49 (2006) 153.
- [8]. M. N. Roy, P. Pradhan, R. K. Das, P. G. Guha, B. Sinha, *J. Chem. Eng. Data.* 53 (2008) 1417.
- [9]. D. D. Perrin, W. L. F. Armarego, *Purification of laboratory chemicals*, 3rd ed., Pergamon Press: Oxford, (1988).
- [10]. B. Sinha, V. K. Dakua, M. N. Roy, *J. Chem. Eng. Data.* 52 (2007) 1768.
- [11]. J.A. Dean, *Lange's handbook of chemistry*, 11th ed., McGraw-Hill Book Company New York, (1973).
- [12]. A. Chatterjee, B. Das, *J. Chem. Eng. Data.* 51 (2006) 1352.
- [13]. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data.* 49 (2004) 291.
- [14]. J. E. Lind Jr, J. J. Zwolenik, R. M. Fuoss, *J. Am. Chem. Soc.* 81 (1959) 1557.
- [15]. El-Dossoki, Farid I, *J. Mol. Liquids.* 151 (2010) 1.
- [16]. R. M. Fuoss, *J. Phys. Chem.* 82 (1978) 2427.
- [17]. B. Per, *Acta Chem. Scand. A.* 31 (1977) 869.
- [18]. R. M. Fuoss, F. Accascina, *Electrolytic Conductance*, Interscience, New York, (1959).
- [19]. D. S. Gill, M. S. Chauhan, *Z. Phys. Chem. NF.* 140 (1984) 139.

- [20]. Marco Pagliai, *J. Chem. Phys.* 119 (2003) 6655.
- [21]. M. N. Roy; D. Ekka, I. Banik, A. Majumder, *Thermochimica Acta.* 547 (2012) 89.
- [22]. J. I. Bhat, P. Bindu, *J. Ind. Chem. Soc.* 72 (1995)783.
- [23]. J. M. Chakraborty, B. Das, *Z. Phys. Chem.* 218 (2004) 219-230.
- [24]. R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Butterworth: London, Ch. 6, pp. 130. (1959).
- [25]. R. M. Fuoss, C. A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 2387.
- [26]. Y. Harada, M. Salamon, S. Petrucci, *J. Phys. Chem.* 89 (1985) 2006.
- [27]. B. S. Krungalz, *J. Chem. Soc, Faraday Trans. I.* 79 (1983) 571.
- [28]. M. Delsignore, H. Farber, *J. Phys. Chem.* 89 (1985) 4968.
- [29]. R. M. Fuoss, E. Hirsch, *J. Am. Chem. Soc.* 82 (1960) 1013.
- [30]. A. Sinha, M. N. Roy, *Phys. Chem. Liq.* 45 (2007) 67.
- [31]. G.P. Cunningham, G.A. Vidulich, R.L. Kay, *J. Chem. Eng. Data.* 12 (1967) 336.
- [32]. A. K. Covington, T. Dickinson, *Physical chemistry of organic solvent systems*, Plenum, New York, 1973.
- [33]. M.N. Roy, L. Sarkar, R. Dewan, *Bull. Chem. Soc. Ethiop.* 24 (2010) 1.
- [34]. W. Libus, B. Chachulski and L. Fraczyk, *J. Sol. Chem.* 9(5) (1980) 355.

TABLES

Table 1. Sample description

Chemical name	Source	Initial mass fraction	mass purity	Purification method	Final mass fraction	purity
[Bu ₄ NBF ₄]	Sigma-Aldrich, Germany	0.99		Used as procured	0.99	
CH ₃ CN	Merck, India	0.98		Purified by standard methods [9]	0.99	
CH ₃ OH	Merck, India	0.98		Purified by standard methods [9]	0.99	
DMSO	Merck, India	0.98		Purified by standard methods [9]	0.99	
1,3-DO	Merck, India	0.98		Purified by standard methods [9]	0.99	

Table 2. Values of density (ρ), viscosity (η) and dielectric constant (ϵ) of CH₃CN, CH₃OH, DMSO, and 1,3-DO at $T = 298.15$ K and atmospheric pressure

Solvents	^a ρ (kg m ⁻³)		^b η (mPa s)		ϵ
	Expt	Lit	Expt	Lit	
CH ₃ CN	776.74	776.70[31]	0.343	0.344[33]	35.94[21]
CH ₃ OH	786.60	786.60[32]	0.545	0.545[32]	32.70[32]
DMSO	1096.00	1095.80[32]	1.948	1.960[32]	46.70[32]
1,3-DO	1058.70	1058.72[21]	0.592	0.597[21]	7.34[21]

^a uncertainty in the density values: ± 0.00003 g. cm⁻³.

^b uncertainty in the viscosity values: ± 0.003 mPa. s.

Table 3. Molar conductance (Λ) and the corresponding concentration (c) of $[\text{Bu}_4\text{NBF}_4]$ in CH_3CN , CH_3OH , DMSO and 1, 3-DO at $T = 298.15$ K and atmospheric pressure

$C^c \times 10^4$ ($\text{mol} \cdot \text{dm}^{-3}$)	$\Lambda^d \times 10^4$ ($\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$)	$C^c \times 10^4$ ($\text{mol} \cdot \text{dm}^{-3}$)	$\Lambda^d \times 10^4$ ($\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$)
Acetonitrile		Methanol	
9.35	156.35	13.31	104.08
16.33	153.33	18.19	101.99
23.09	151.21	26.00	99.56
28.10	149.63	35.53	97.08
33.82	148.14	44.58	94.84
38.57	147.03	53.20	93.14
42.42	145.97	60.93	91.65
47.22	144.91	69.24	90.20
53.88	143.56	75.00	88.99
60.00	142.39	81.21	87.99
65.48	141.34	88.89	86.91
70.91	140.34	94.56	85.88
75.31	139.59	102.01	84.85
79.30	138.86	110.24	83.86
83.08	138.22	118.82	82.69
Dimethylsulfoxide		1,3-Dioxolane	
20.63	32.94	0.17	59.60
37.83	30.01	0.23	53.97
52.38	28.18	0.29	50.15
64.85	27.04	0.33	47.40
75.66	26.03	0.38	45.27
93.46q	24.24	0.44	42.25
107.52	23.05	0.50	39.80
118.89	21.96	0.57	37.95
132.40	20.99	0.63	35.88
142.91	20.31	0.69	34.05
151.32	19.80	0.77	33.26
158.19	19.29	0.84	32.68
168.78	18.59	0.93	33.09
176.54	17.99	1.00	34.63
187.85	17.12	1.05	35.71

^c Uncertainty in the molarity: $\pm 0.0002 \text{ mol} \cdot \text{dm}^{-3}$.^d Uncertainty in the molar conductance: $\pm 0.01 \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$

Table 4. Limiting molar conductivity (Λ_0), the association constant (K_A), the distance of closest approach of ions (R), standard deviations δ of experimental Λ from Equation (2), Walden product ($\Lambda_0\eta_0$) and Gibbs energy change (ΔG°) of $[\text{Bu}_4\text{NBF}_4]$ in CH_3CN , CH_3OH and DMSO at $T = 298.15$ K and atmospheric pressure

Solvents	$\Lambda_0 \times 10^4$ ($\text{S m}^2 \text{mol}^{-1}$) ^a	K_A	R (\AA)	Δ	$\Lambda_0\eta_0$ ($\text{S m}^2 \text{mol}^{-1} \text{mPa s}$)	ΔG° (kJ mol^{-1})
CH_3CN	162.01	12.07	11.84	0.08	55.37	-0.62
CH_3OH	112.70	29.77	11.87	0.18	61.27	-0.84
DMSO	45.75	112.19	12.71	1.27	89.11	-1.17

Table 5. Limiting ionic conductance (λ_o^\pm), ionic Walden product ($\lambda_o^\pm\eta_0$), Stokes' radii (r_s) and crystallographic radii (r_c) of $[\text{Bu}_4\text{NBF}_4]$ in CH_3CN , CH_3OH , and DMSO at $T = 298.15$ K and atmospheric pressure

Solvents	Ion	λ_o^\pm ($\text{S m}^2 \text{mol}^{-1}$)	$\lambda_o^\pm\eta_0$ ($\text{S m}^2 \text{mol}^{-1} \text{mPa s}$)	r_s (\AA)	r_c (\AA)
CH_3CN	Bu_4N^+	58.34	20.01	4.09	4.94
	BF_4^-	103.67	35.56	2.30	2.78
CH_3OH	Bu_4N^+	40.58	22.10	3.71	4.94
	BF_4^-	72.12	39.27	2.09	2.78
DMSO	Bu_4N^+	16.47	32.09	2.55	4.94
	BF_4^-	29.27	57.02	1.44	2.78

^a Crystallographic radii of cation and anion from ref. [32, 34] respectively.

Table 6. The calculated limiting molar conductance of ion-pair (Λ_0), limiting molar conductance of triple-ion (Λ_0^T), slope and intercept of Equation (13) of $[\text{Bu}_4\text{NBF}_4]$ in 1, 3-DO at $T = 298.15$ K and atmospheric pressure

Solvents	$\Lambda_0 \times 10^4$ ($\text{S m}^2 \text{mol}^{-1}$)	$\Lambda_0^T \times 10^4$ ($\text{S m}^2 \text{mol}^{-1}$)	Slope	Intercept
1,3-DO	100.49	67.03	1.58	0.33

Table 7. Salt concentration at the minimum conductivity (c_{\min}) along with the ion-pair formation constant (K_P), triple-ion formation constant (K_T) of $[\text{Bu}_4\text{NBF}_4]$ in 1, 3-DO at $T = 298.15$ K and atmospheric pressure

Solvent	$c_{\min} \times 10^4$ (mol dm^{-3})	$\log c_{\min}$	$K_P \times 10^{-4}$	K_T	$(K_T/K_P) \times 10^{-5}$	$\log(K_T/K_P)$
1,3-DO	0.84	-4.08	9.51	7.25	7.62	-4.12

Table 8. Salt concentration (c_{\min}) at the minimum conductivity (Λ_{\min}), the ion-pair fraction (α), triple-ion fraction (α_T), ion-pair concentration (C_P) and triple-ion concentration (C_T) of $[\text{Bu}_4\text{NBF}_4]$ in 1,3-DO at $T = 298.15$ K and atmospheric pressure

Solvent	$c_{\min} \times 10^4$ (mol dm^{-3})	$\Lambda_{\min} \times 10^4$	α	$\alpha_T \times 10^4$	$C_P \times 10^5$ (mol dm^{-3})	$C_T \times 10^8$ (mol dm^{-3})
1,3-DO	0.84	32.68	0.35	2.16	5.44	1.81

Table 9. Salt concentration (c), the ion-pair fraction (α), triple-ion fraction (α_T), ion-pair concentration (C_P) and triple-ion concentration (C_T) of $[\text{Bu}_4\text{NBF}_4]$ in 1, 3-DO at 298.15 K and atmospheric pressure

$c \times 10^4$ (mol dm ⁻³)	α	$\alpha_T \times 10^4$	$C_P \times 10^5$ (mol dm ⁻³)	$C_T \times 10^8$ (mol dm ⁻³)
0.17	0.79	0.96	0.34	0.16
0.23	0.67	1.13	0.75	0.26
0.29	0.61	1.26	1.13	0.36
0.33	0.56	1.36	1.46	0.45
0.38	0.53	1.44	1.77	0.54
0.44	0.49	1.57	2.29	0.70
0.50	0.46	1.66	2.71	0.83
0.57	0.43	1.77	3.22	1.00
0.63	0.41	1.87	3.73	1.17
0.69	0.39	1.96	4.27	1.37
0.77	0.37	2.06	4.84	1.58
0.84	0.35	2.16	5.44	1.81
0.93	0.34	2.27	6.19	2.11
1.00	0.32	2.35	6.78	2.36
1.05	0.31	2.41	7.18	2.53

FIGURES

Figure 1. Plots of molar conductance, Λ , and the square root of concentration (\sqrt{c}), of $[\text{Bu}_4\text{NBF}_4]$ in CH_3CN ($-\blacktriangle-$), CH_3OH ($-\blacksquare-$), DMSO ($-\blacklozenge-$) at $T = 298.15$ K

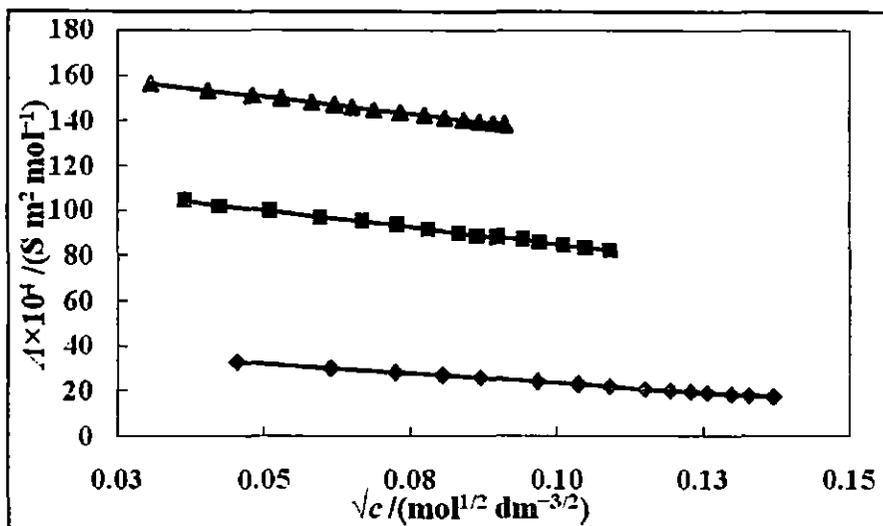


Figure 2. Plots of values of Gibbs energy change, ΔG° , ($-\blacklozenge-$) and Association constant, K_A , ($-\blacktriangle-$) of $[\text{Bu}_4\text{NBF}_4]$ in CH_3CN , CH_3OH and DMSO 298.15 K

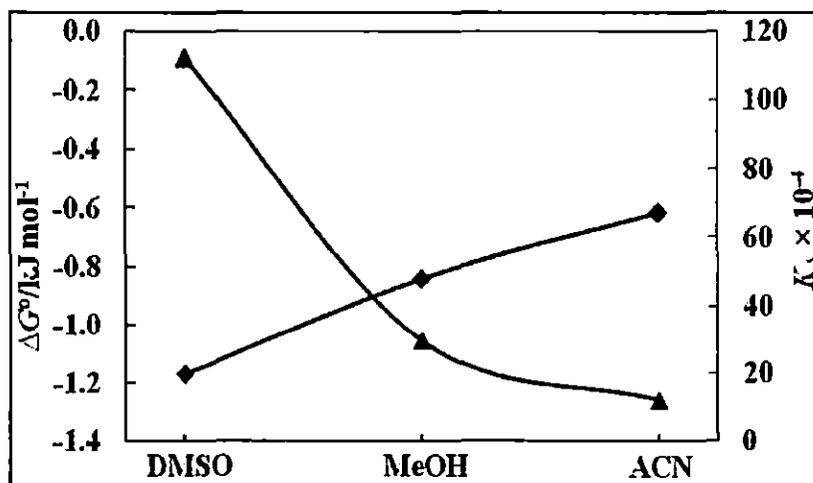


Figure 3. Plots of values of limiting molar conductivity, Λ_0 , (—■—) and Walden Product, $\Lambda_0\eta_0$, (—▲—) of $[\text{Bu}_4\text{NBF}_4]$ in CH_3CN , CH_3OH and DMSO at 298.15 K

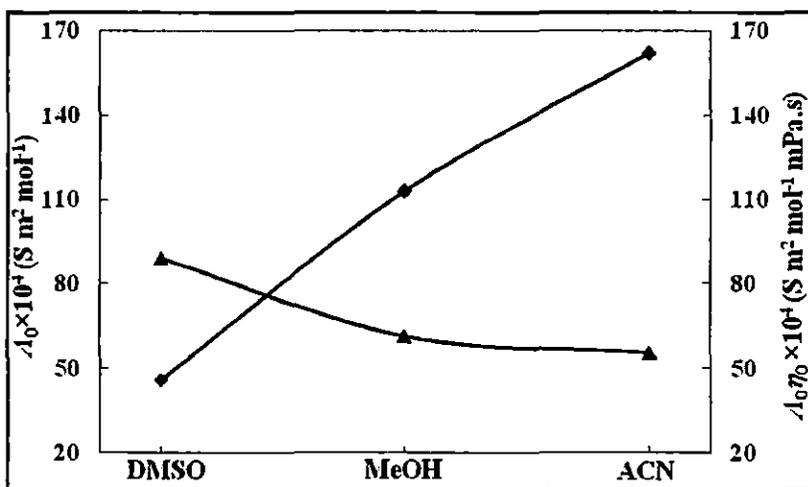


Figure 4. Plot of values of Molar conductance (Λ) and the square root of concentrations (\sqrt{c}) of $[\text{Bu}_4\text{NBF}_4]$ in 1,3- DO at 298.15 K

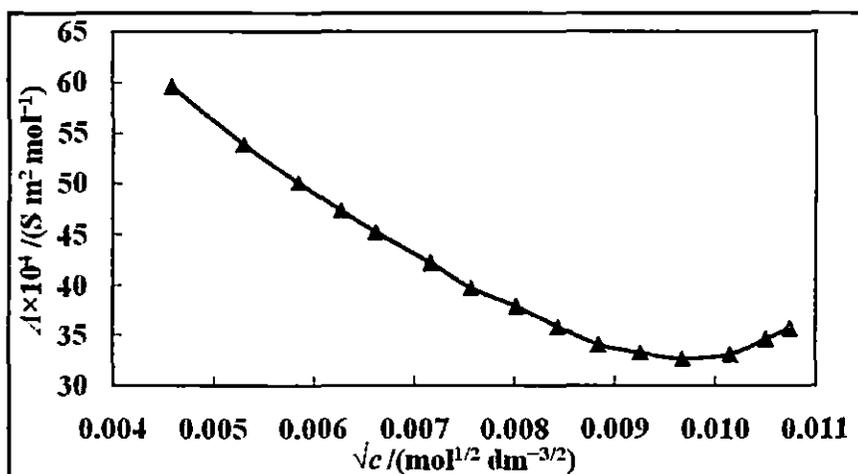
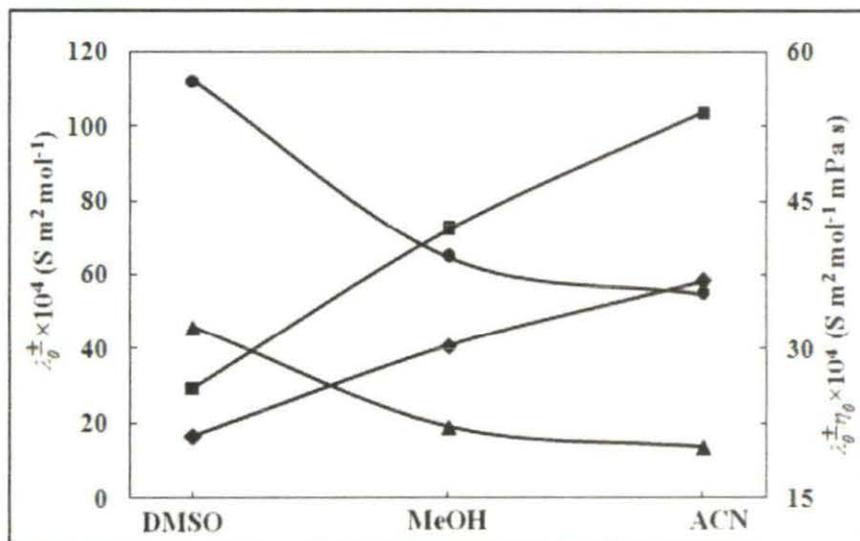
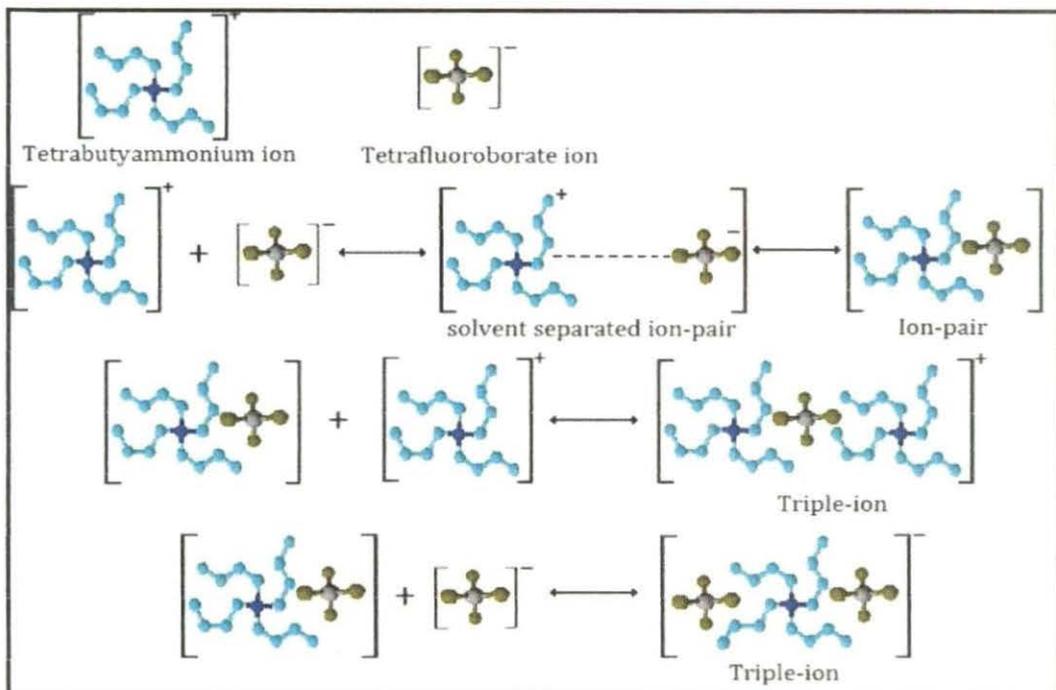


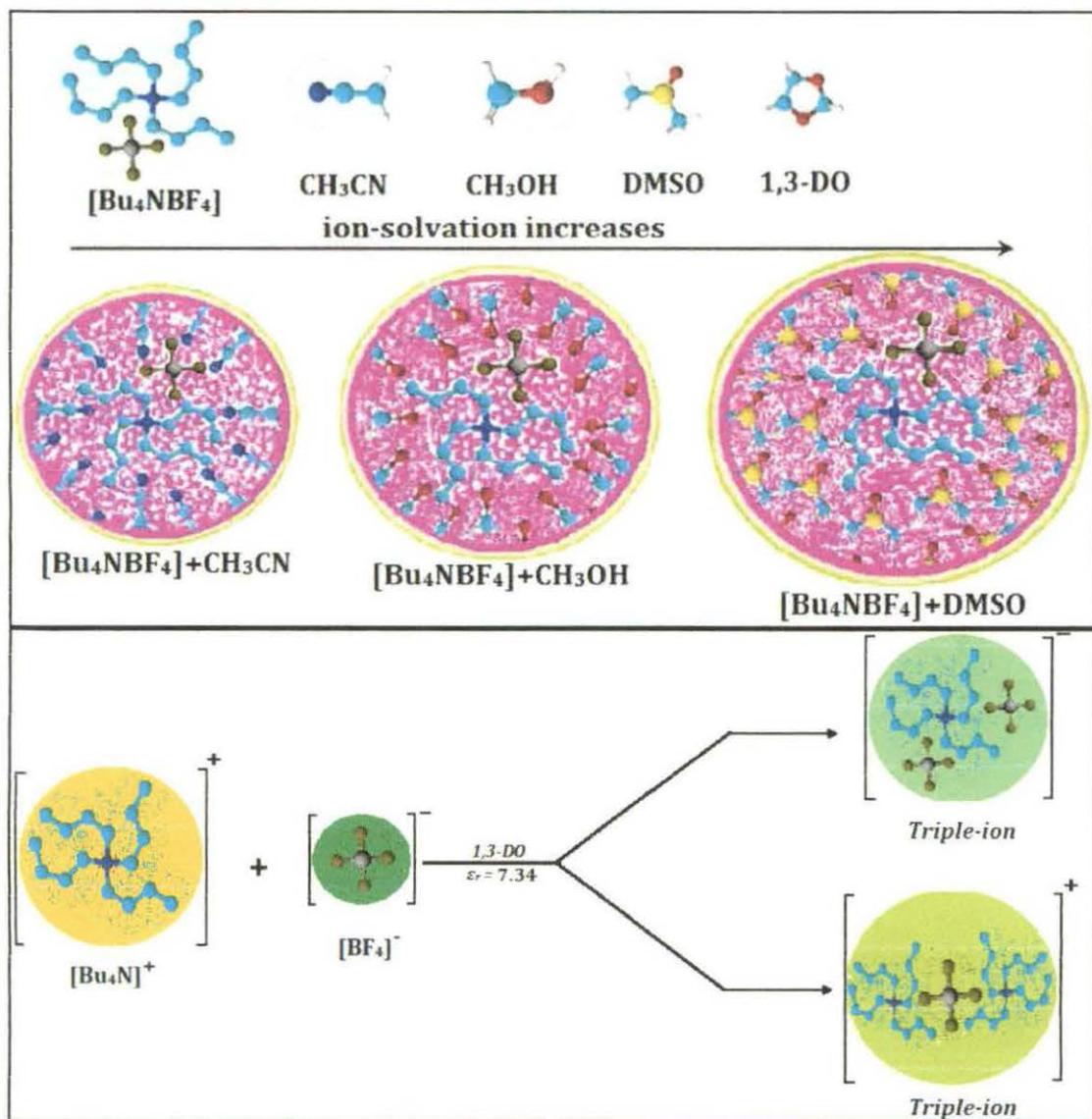
Figure 5. Plots of values of limiting ionic conductance, λ_o^\pm , for $[\text{Bu}_4\text{N}]^+$ (—◆—), for $[\text{BF}_4]^-$ (—■—) and ionic Walden product, $\lambda_o^\pm \eta_o$, for $[\text{Bu}_4\text{N}]^+$ (—▲—), for $[\text{BF}_4]^-$ (—●—), in CH_3CN , CH_3OH and DMSO at 298.15 K respectively.



Scheme 3. The pictorial representation of triple-ion formations for the electrolyte in 1,3-DO.



Scheme 4. The schematic representation of ion-solvation, for the particular ion in the studied solvent in view of various derived parameters.



CHAPTER IX

ROLE OF ANIONS (TETRAFLUOROBORATE, PERCHLORATE) OF TETRABUTYLAMMONIUM SALTS IN DETERMINING SOLVATION EFFECTS PREVAILING IN INDUSTRIALLY ESSENTIAL SOLVENTS PROBED BY CONDUCTANCE AND FT-IR SPECTRA

9.1. INTRODUCTION

Studies of the transport properties of electrolytes in different solvent media are very useful to gain information on the behavior of ions in solution. In the modern technology, the study of ion solvation is very helpful in knowing any salt's application. Therefore, a number of conductometric [1] and related studies of electrolytes in nonaqueous common solvents have been done for their optimal use in high-energy batteries [2] and understanding organic reaction mechanisms [3]. The nature of the solvent/solvent mixtures plays an important role in the mode of solvation of the electrolyte in solution, which in turn dictates its ionic association. Solvent properties such as viscosity and the relative permittivity have been taken into consideration in order to determine the extent of ion association and the ion-solvent interactions. Technologist and theoretician find the nonaqueous solution systems [4] very useful, as many chemical processes occur in these systems, whose nature and magnitude of ion-ion and ion-solvent interactions can be examined.

The excellent solubility characteristic of tetraalkylammonium salts in aqueous as well as non-aqueous solvents makes it very suitable. These salts find its application in trace analysis (of metals and organic compounds), environmental analytical chemistry, pharmaceutical and medicinal chemistry. Both the thermodynamics and kinetics of reactions carried out in electrolytes are different from those in conventional molecular solvents, which make it very interesting for the chemist. The usage of aqueous solutions of symmetrical tetraalkylammonium ions, particularly those with large alkyl groups, has played a significant role in revealing hydrophobic interaction and hydration behavior through various experimental approaches, because of the high solubility of the salts and the simple geometrical structures [5]. Another benefit for their use is the possibility of systematically changing the ionic

size by the proper choice of an alkyl group without a nonuniform charge in the distribution on the ionic surface.

Keeping in mind the use of electrolytes in battery industries we have here studied the thermodynamic and the transport properties of electrolytes in industrially important solvents, which will provide significant information about the nature and strength of intermolecular forces operating between components of mixture. As Fourier transform infrared (FT-IR) measurements is one of the most convenient methods for investigating the molecular interactions in electrolytic solutions, so it has also been done [6-8].

In continuation with our investigation on understanding the behaviour of electrolytes in organic solvents by physicochemical techniques, we have studied the conductance and FT-IR measurements of tetrabutylammonium tetrafluoroborate $[\text{Bu}_4\text{NBF}_4]$ and tetrabutylammonium perchlorate $[\text{Bu}_4\text{NClO}_4]$ in nitromethane (NM), N-methylformamide (NMF), and formamide (FA) at 298.15 K.

9.2. EXPERIMENTAL SECTION

9.2.1. Source and purity of samples

Tetrabutylammonium tetrafluoroborate $[\text{Bu}_4\text{NBF}_4]$ and Tetrabutylammonium perchlorate $[\text{Bu}_4\text{NClO}_4]$ of puriss grade were obtained from Aldrich, Germany and was used as purchased. The mass fraction purity for $[\text{Bu}_4\text{NBF}_4]$ was 0.99 and for $[\text{Bu}_4\text{NClO}_4]$ was ≥ 0.98 .

All the solvents of spectroscopic grade were procured from Thomas Baker, India, and were rid of impurities using standard methods [9]. The mass fraction of purity found was ≥ 0.99 .

9.2.2. Apparatus and Procedure

Stock solutions for the two electrolytes in three different solvents were made by mass (Mettler Toledo AG285 with uncertainty ± 0.0003 g), and mass dilution was employed to obtain the working solutions at 298.15 K. The uncertainty of molality of different solutions was estimated to ± 0.0001 mol.kg⁻¹. The density (ρ) was determined using vibrating-tube Anton Paar density-meter (DMA 4500M) with an accuracy of ± 0.00005 g.cm³. The calibration was carrying out by triply-distilled water and passing dry air.

The viscosity was also measured with the help Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 fitted to a Brookfield Digital Bath TC-500. The viscosities were determined using the following equation:

$$h = (100 / \text{RPM}) \times \text{TK} \times \text{torque} \times \text{SMC}$$

where RPM, TK (0.09373) and SMC (0.327) indicates the speed, viscometer torque constant, and spindle multiplier constant, respectively. The calibration of instrument was done using the standard viscosity samples supplied with the instrument, water, and aqueous CaCl₂ solution [10]. Temperature of the solution was kept within ± 0.01 °C with the help of Brookfield Digital TC-500 temperature thermostat bath. The viscosities were calculated with an accuracy of ± 1 %. Each measurement given here is an average of triplicate reading with a precision of 0.3 %.

All the conductance measurements were carried out in a Systronic-308 conductivity bridge (accuracy ± 0.01) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 0.001) cm⁻¹. A water bath maintained within $T = (298.15 \pm 0.01)$ K was used, and the method proposed by Lind et al. [11] was used to calibrate the cell and cell constant was calculated based on 0.01 M aqueous KCl solution. The conductance data was obtained at a frequency of 1 kHz. Throughout each and every one measurement, uncertainty of temperatures was ± 0.01 K.

Infrared spectra were recorded in 8300 FT-IR spectrometer (Shimadzu, Japan). The details of the instrument have already been previously described [8].

9.3. RESULTS AND DISCUSSION

9.3.1. *Electrical Conductance*

The selected electrolytes were freely soluble in all proportion of the solvents. The experimental values of physical properties of the pure solvents obtained were almost same as the values found in the literature, given in Table 1.

The molar conductances (Λ) for all studied solution systems have been calculated with the help of the following equation [12]:

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

where c and κ denote the molar concentration and specific conductance of the studied solutions respectively. The molar conductances (Λ) of the solutions of studied electrolytes with the corresponding molar concentrations (c) in different solvents (nitromethane, N-methylformamide, and formamide) are represented in Table 2. Linear conductance curves (Λ versus \sqrt{c}) were obtained, and with the extrapolation of $\sqrt{c} = 0$, the starting limiting molar conductances for the electrolytes were evaluated. Fuoss conductance equation [13, 14] was used to analyze the ion-pair formation from conductance data.

The following set of equations were used to derive the three adjustable parameters, namely, the limiting molar conductance (Λ_0), the association constant (K_A), and the distance of closest approach of ions (R) from a given set of conductivity values ($c_j, \Lambda_j; j = 1, \dots, n$)

$$\Lambda = P\Lambda_0[(1+R_x)+E_L] \quad (2)$$

$$P = 1 - \alpha(1 - \gamma) \quad (3)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (4)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (5)$$

$$\beta = e^2 / (\epsilon_r k_B T) \quad (6)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (7)$$

Where R_x denotes the relaxation field effect, E_L denotes the electrophoretic counter current, k is the radius of an ionic atmosphere, and e is the electron charge, ϵ is the relative permittivity of the solvent mixture, c is the molarity of the solution, k_B is the Boltzmann constant, K_A is the overall pairing constant, K_S is the association constant of the contact-pairs, K_R is the association constant of the solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature, and β is twice the Bjerrum distance.

The computations were performed analyzed by Fuoss program. The initial Λ_0 values for the iteration procedure are obtained from the Shedlovsky extrapolation of the data. Input for the program is the no. of data, n , followed by ϵ, η, T , initial values of Λ_0 , along with c_j, Λ_j values, where $j = 1, 2, \dots, n$ and an instruction to cover a pre-selected range of R values.

The computations along with calculations have been determined supplemented with the values of Λ_0 and α which minimization the standard deviation, δ , whereby

$$\delta^2 = \sum [A_j(\text{cal}) - A_j(\text{obs})]^2 / (n - m) \quad (8)$$

where n is the number of experimental points and m is the number of fitting parameters. The conductance data have been explained and discussed by fixing the distance of closest approach R with two parameter fit ($m = 2$). From a graphical representation of δ against R the minimum of the δ - R versus R curve predicts the best-fit R . Through the iteration and running of the computer program with small

increments of the data of the studied electrolytes in nitromethane, N-methylformamide and formamide, the R values assumed to be as follows:

$$R = a + d \quad (9)$$

Where $a = (r_+ + r_-)$ represents the sum of the crystallographic radii of the ions and the average distance corresponding to the side of a cell occupied by a solvent molecule is denoted by d . The distance, d is given by [15]

$$d (\text{\AA}) = 1.183 (M / \rho)^{1/3} \quad (10)$$

where M and ρ are molar mass and density of the solvents, respectively. The values of Λ_0 , K_A and R obtained by this procedure are given in Table 3 along with δ for the all the solutions.

Inspection of Table 3 and Figure 1 shows that the limiting molar conductance (Λ_0) of the electrolytes among the studied solvents is highest in the case of nitromethane (NM) and lowest in case of formamide (FA). The trend of the Λ_0 value of the electrolytes in the studied solvents is as follows:

Nitromethane > N-methylformamide > formamide

This illustrates that the electrolytes are solvated more by formamide, due to its highest viscosity value among the studied solvents. It is also seen that with an increase in the size of the anion, the extent of solvation also increase.

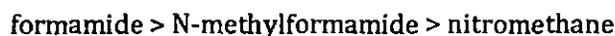
Table 3 and Figure 4 also show that the association constant (K_A) of the electrolytes is greater in FA than in NMF and NM. Hence, the ion-solvent interaction is greater in FA than in NMF and NM, which results in lower conductance of the electrolytes in the former than in the latter two. The above observation is also supported by the higher viscosity of FA because with the increase in viscosity the Λ_0 value decreases. The maximum ion-solvent interaction leading to very high solvation is observed in the case of $[\text{Bu}_4\text{NBF}_4]$ and FA, which is evident from the K_A values given in Table 3 and Figure 4. The weakest ion-solvent interaction is between $[\text{Bu}_4\text{NClO}_4]$ and the lowest viscous solvent NM.

The observed order of Λ_0 values can be confirmed through another characteristic function called the Walden product, $\Lambda_0\eta$ (Product of the limiting molar conductance and solvent viscosity), given in Table 3. Figure 2 demonstrates that the increasing order of Walden product is mainly in agreement with the associated increase of solvent viscosity and decrease of limiting molar conductance for the electrolytes in the studied solvents. This same observation is also justified as the Walden product of an ion or solute is inversely proportional to the radius of the ion or solute in a particular solvent [16]

$$\Lambda_0\eta = \frac{1}{6\pi r_{eff}T} \quad (11)$$

This shows that the electrostatic ion-solvent interaction or ion-association is strong in these cases. The deviation of the Walden product reflects the change of solvation [17] though the deviation of the Walden product with solvent composition is difficult to understand quantitatively, but its deviation with solvent composition can still be explained by

- (i) Preferential solvation [18] of the electrolyte by solvent molecules. Considering the conductance and association constant values of electrolytes in different solvents, we can say that the studied electrolytes mostly prefer the formamide among the solvents and the order of preferential solvation by the electrolytes is as follows:



- (ii) With considering the structural aspect of the solvents,
- (a) In case of nitromethane, where the two electronegative oxygen atoms are present with nitrogen, resulting in more ion-solvent interaction, shown in (I). Thus in the solution of electrolytes and nitromethane, the nitromethane interact with the electrolytes through ion-dipole interaction. The interaction is between negatively charged O atom (single bonded with N) in NM with

positive species of electrolyte, positively charged N atom in NM and negative species of electrolyte, and between lone pair of electron of O atom (doubly bonded with N) in NM and positive species of electrolyte.

- (b) From the structure of N-methylformamide, there are three possibilities of interaction of solvent with solute: ion-dipole interaction of lone pair(s) of electron present in O atom and N atom, and H-bonding with H atom attached with electronegative N atom shown in (II) of Scheme 1. Thus in the solution of electrolytes and N-methylformamide, the N-methylformamide strongly interact with the electrolytes with H-bond/ion-dipole interactions. The lone pairs of electron in electronegative carbonyl oxygen stabilizes the positive species of the electrolytes through ion-dipole interaction; the lone pair of electron in N also stabilizes the positive species of the electrolytes, whereas the H-atom attached to nitrogen forms hydrogen bonds with negative species of the electrolyte. As N-methylformamide is the derivative of formamide, where an H-atom attached to nitrogen in formamide is replaced by a methyl group, the hydrogen bonding ability of N-methylformamide is less than that of formamide.
- (c) From the structure of formamide, there are three possibilities of interaction of solvent with solute: ion-dipole interaction of lone pair(s) of electron present in O atom and N atom, and H-bonding with H atom attached with electronegative N atom shown in (III) of Scheme 1. Thus in the solution of electrolytes and formamide, the formamide strongly interact with the electrolytes with H-bond/ion-dipole interactions. The lone pair of electron in electronegative carbonyl oxygen stabilizes the positive species of the electrolyte through ion-dipole interaction; the lone pair of electron in N also stabilizes the positive species of the electrolytes, whereas H-atom attached to nitrogen forms H bonds with negative species of the electrolyte. Also the respective average number of hydrogen-bonds was found to be higher in the

case of formamide as compared to N-methylformamide, as one H atom in formaldehyde is replaced by methyl group in N-methylformamide.

The values of conductance shows that the solution of electrolytes ([Bu₄NBF₄] and [Bu₄NClO₄]) in solvents is in the following order:

formamide (FA) < N-methylformamide (NMF) < nitromethane (NM)

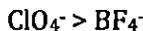
The electrolytic solution of nitromethane is more conducting than N-methylformamide, which in turn is greater than formamide. As we know, the greater the conductance, the lesser is the ion-solvent interaction in the solution. Therefore the interaction between the electrolytes and solvents will follow the reverse trend

formamide (FA) > N-methylformamide (NMF) > nitromethane (NM)

This observation implies that the degree of interaction (ion-dipole) also obeys the above order. Therefore, formamide stabilizes the electrolytes ([Bu₄NBF₄] and [Bu₄NClO₄]) to a greater degree than N-methylformamide, which in turn that stabilizes same to a greater degree than nitromethane.

The schematic representation of plausible ion-solvent interaction, for the particular ion in the studied solvents (i.e; electrolytes in solvents), in view of various derived parameters is represented in Scheme 1.

Stokes' law is considered to be the starting point for most evaluations of ionic conductance, and it states that the limiting ionic Walden product ($\lambda_0^{\pm}\eta$), (the product of the limiting ionic conductance and solvent viscosity) for any singly charged spherical ion is a function only of the ionic radius (crystallographic radius) and thus, under normal conditions, is a constant. The ionic conductances λ_0^{\pm} for the [Bu₄N]⁺ cation and BF₄⁻, ClO₄⁻ anion in different solvent arrangements, were computed as described in the literature values [19] The ionic limiting molar conductances λ_0^{\pm} , in investigated solvents were determined by interpolation of conductance data from the literature [20] using cubic spline fitting. A perusal of Table 4 and Figure 3 shows that the anion (BF₄⁻, ClO₄⁻) holds the greater share of the conductance value than the common cation [Bu₄N]⁺. For a particular solvent, the order of limiting ionic conductance of anion is as follow:



The λ_o^\pm values were utilized for the calculation of Stokes' radii (r_s) according to the classical expression.²¹

$$r_s = \frac{F^2}{6\pi N_A \lambda_o^\pm r_c} \quad (12)$$

where, r_s and r_c are the Stokes' radii and crystallographic radii respectively, N_A is the Avogadro's no., λ_o^\pm is the limiting ionic conductance and F is the Faraday Constant.

Ionic Walden products $\lambda_o^\pm \eta$, Stokes' radii r_s , and crystallographic radii r_c are represented in Table 4. The Walden products ($\Lambda_o \eta$) and ionic Walden products ($\lambda_o^\pm \eta$) for the electrolytes in different solvents are reported in Tables 3 and 4 and Figures 2 and 3, respectively, indicating that both the ionic Walden products $\lambda_o^\pm \eta$ and Walden products $\Lambda_o \eta$ for the electrolytes are higher in the case of FA than NMF and NM. For Bu_4N^+ , BF_4^- and ClO_4^- ion, the Stokes' radii r_s are either lower or comparable to their crystallographic radii r_c ; this implies that the ion is relatively less solvated due to its intrinsic low surface charge density. The distance parameter R , is the least distance that two free ions can move towards together before they merge into an ion pair which was shown in Table 3.

The graphical representation of the 'Gibbs free energy' for ion-pair formation, ΔG° , categorically interprets the tendency for ion-pair formation where 'Gibbs free energy' ΔG° , is derived by analyzing the following equation [22] and given in Table 3.

$$\Delta G^\circ = -RT \ln K_A \quad (13)$$

The negative values of ΔG° can give explanation of considering the participation of specific covalent interaction in the ion-association process. It is evident from the Table 3 and Figure 4 that the values of the 'Gibbs free energy' are all negative entirely all over the solutions and the negativity increases from nitromethane to formamide. The negative value of ΔG° is highest for electrolytes in FA than NFM and NM, shows that the highest degree of association in FA. This result indicates that the extent of solvation is in the following order:

formamide (FA) > N-methylformamide (NMF) > nitromethane (NM)

The same type of observation was established from the conductance data elaborated and explained earlier in this paper.

The significance of the term (*A*-coefficient) has since then been realized due to the development Debye-Hückel theory [23] of inter-ionic attractions in 1923. The *A*-coefficient depends on the ion-ion interactions and can be determined from interionic attraction theory and analyzed by the Falkenhagen and Vernon [24] equation:

$$A_{Theo} = \frac{0.2577 A_o}{\eta_o (\epsilon T)^{0.5} \lambda_+^o \lambda_-^o} \left[1 - 0.6863 \left(\frac{\lambda_+^o \lambda_-^o}{A_o} \right)^2 \right] \quad (13a)$$

where the symbols have their usual significance. *A*-coefficient should be calculated from conductivity measurements and given in the Table 3. Table 3 shows that *A*-coefficient is negative and very small, shows that the existence of the ion-ion interaction is negligible, as compared to the ion-solvent interaction for all the chosen electrolytes in the studied solvents.

Stokes-Einstein Relation was used to obtain the diffusion coefficient (*D*):

$$D = \frac{k_B T}{6\pi\eta_o r_s} \quad (14)$$

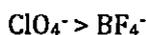
where k_B is the Boltzmann's constant, *T* is the temperature, η is the solvent viscosity and r_s denotes Stoke's radii.

The ionic mobility was obtained using the following equation:

$$i = \frac{z^+ F}{RT} D \quad (15)$$

where z_+ , *F*, *R*, *T* and *D* is the ionic charge, Faraday constant, universal gas constant, temperature, and diffusion co-efficient respectively. Table 5 depicts that the contribution of diffusion coefficient of the anions (BF_4^- , ClO_4^-) is greater than the cation $[\text{Bu}_4\text{N}]^+$ in all the investigated solvents, which indicates that (BF_4^- , ClO_4^-)

diffuses greater in the solvents. The diffusion coefficient decrease from nitromethane to formamide as indicated in Table 5 for both $[\text{Bu}_4\text{N}]^+$ and $(\text{BF}_4^-, \text{ClO}_4^-)$ ions showing larger diffusion of the ions in nitromethane. Table 5 also illustrates that the mobility of anions $(\text{BF}_4^-, \text{ClO}_4^-)$ are higher than that of cation $[\text{Bu}_4\text{N}]^+$ in all the studied solvents, which indicates that greater share of conductance by $(\text{BF}_4^-, \text{ClO}_4^-)$ mentioned earlier i.e; the diffusion coefficient is directly proportional to the ionic mobility, and these are the driving force to conduct electricity by electrolyte or ions in solutions. The trend of the anions is enhanced by the following order, which was derived from the same observation.



This is because of the increase in solvent's viscosity and the increase in the ion-solvent interaction or ion-solvation, which is evident from the association constant values, given in Table 3. A graphical comparison of diffusion coefficient (D_{\pm}) and ionic mobility (i_{\pm}), for anions $(\text{BF}_4^-$ and $\text{ClO}_4^-)$ is given in Figure 5.

9.3.2. FT-IR Spectroscopic Study

FT-IR spectroscopy was used to present the molecular interaction existing between the electrolytes and the solvents qualitatively and also used as supportive evidence to study the bond formation due to the ion-solvent and solvent-solvent interactions. The IR spectra of the pure solvents as well as the solutions of $\{[\text{Bu}_4\text{N}][\text{Y}]$ and Solvents $\}$ have been studied, and the stretching frequencies of the functional groups and mixed with electrolytes are given in Table 6 and Figure 6-8 within the range of wavenumber 400-4000 cm^{-1} .

Table 6 shows that presence of strong bands at 1564.8 cm^{-1} and 1363.3 cm^{-1} attributed to asymmetric stretching vibration (ν_{as}) of N-O (1500-1570 cm^{-1}), and symmetric stretching vibration (ν_s) of N-O (1300-1370 cm^{-1}), respectively, in nitromethane. When the IR spectra of $\{[\text{Bu}_4\text{N}][\text{Y}]$ and nitromethane $\}$ solution was taken, the asymmetric stretching vibration (ν_{as}) of N-O got shifted to 1601.7 cm^{-1} and 1614.7 cm^{-1} for the electrolytes $[\text{Bu}_4\text{NClO}_4]$ and $[\text{Bu}_4\text{NBF}_4]$ respectively. The

symmetric stretching vibration (ν_s) got shifted to 1388.8 cm^{-1} and 1402.3 cm^{-1} for the electrolytes $[\text{Bu}_4\text{NClO}_4]$ and $[\text{Bu}_4\text{NBF}_4]$, respectively. The shift resulted due to the strengthening of N-O bond [25] because of the reduction in the resonance effect in NM. The reduction in resonance is due to the presence of ionic interaction between negatively charged oxygen atom of NM and positive part of $\{[\text{Bu}_4\text{N}][\text{Y}]\}$. Because of the reduction in the resonance effect, the negative charge in oxygen atom gets somewhat localized, therefore, the other oxygen atom has more double bond characteristic with nitrogen atom than in the NM in idle case. Therefore, due to the increase in double bond characteristic in N-O bond, the IR spectra of N-O got shifted to increased wavenumber.

In case of N-methylformamide, the IR spectra shows a sharp peak at 1679.8 cm^{-1} for C=O stretching vibration. The peak got shifted to 1721.9 cm^{-1} and 1734.5 cm^{-1} in the solution of N-methylformamide with $[\text{Bu}_4\text{NClO}_4]$ and $[\text{Bu}_4\text{NBF}_4]$ respectively, due to the reduction in resonance effect in N- methylformamide, which results in strengthening of C=O bond. As the lone pair of electron-present N atom of N-methylformamide is involved in ion-dipole interaction with the positive part of $\{[\text{Bu}_4\text{N}][\text{Y}]\}$, the delocalization of electron pair from N atom to O atom is reduced; thus the double bond characteristic of C=O bond is somewhat increased. This results in the shift of IR spectra of C=O bond in N- methylformamide to higher wavenumber, when $\{[\text{Bu}_4\text{N}][\text{Y}]\}$ is added to it.

Greatest interaction is seen between $[\text{Bu}_4\text{N}][\text{Y}]$ ($\text{Y} = \text{BF}_4^-$ and ClO_4^-) and formamide, as obvious from the values of the K_A obtained from the conductivity study as described earlier. The IR spectra of formamide shows a sharp peak at 1692.9 cm^{-1} for C=O stretching vibration. When the IR spectra of $[\text{Bu}_4\text{NY}]$ and formamide solution were taken, the peak moved to 1740.6 cm^{-1} (ν_1) and 1754.1 cm^{-1} (ν_2) for $[\text{Bu}_4\text{NClO}_4]$ and $[\text{Bu}_4\text{NBF}_4]$ respectively showing the presence of ion-dipole interaction. The shift is the result of the strengthening of C=O in formamide²⁶ due to reduction in the resonance effect in it. The reason for reduction in resonance effect in formamide is same as that in the case of N-methylformamide. The greater

reduction in resonance effect in formamide than that of N-methylformamide is because of the presence of H atom in place of methyl group. The ion-dipole interaction between the lone pair of electron-present N atom and the positive part of $\{[Bu_4N][Y]\}$ is somewhat hindered because of the presence of methyl group in N-methylformamide, but this hindrance is not present in the case of formamide because of the absence of methyl group. Therefore, because of the greater reduction in resonance effect, the ion-dipole interaction is more in the case of formamide than that of N-methylformamide. Thus, the shift in IR spectra of C=O bond in formamide is greater than N- methylformamide.

From Table 6 we can see that shift in IR vibration data of C-H bond in nitromethane; and N-H and C-N bond in N-methylformamide and formamide is negligible when the electrolytes are added to it.

The shift in IR vibration is caused due to the weakening of solvent-solvent interaction. Therefore, more the shift toward higher frequency, better the interaction. The order of magnitude of shift in case of both $[Bu_4NBF_4]$ and $[Bu_4NClO_4]$ is in the following order

formamide (FA) > N-methylformamide (NMF) > nitromethane (NM)

This implies that the degree of interaction (ion-dipole) also obeys the same order. Therefore formamide stabilizes the electrolytes (ion-solvent association) to a greater extent than N-methylformamide, which in turn stabilizes the same greater than nitromethane.

9.4. CONCLUSION

Precise electrical conductivity study of $[Bu_4NBF_4]$ and $[Bu_4NClO_4]$ in nitromethane, N-methylformamide, and formamide confirms that the conductance for the electrolytes is highest in the case of nitromethane and lowest in the case of formamide. Among the two electrolytes, $[Bu_4NBF_4]$ is associated most with the studied solvents, and the highest association is seen between $[Bu_4NBF_4]$ and

formamide. The greater share of the conductance holds the $[Y]^-$ ion than the $[Bu_4N]^+$ as clear from their ionic conductance values. In all of the investigated solvents, the electrolytes shows ion-dipole interactions observed from the FT- IR and conductance studies. The derived parameters obtained by analyzing various equations supplemented with experimental data predict the same conclusion as discussed and described in this manuscript, demanding the individuality of the work.

REFERENCES

- [1].G.J. Janz, R.P.T. Tomkins, *Non-aqueous Electrolytes Handbook*, Vol. 1 Academic Press: New York, (1972).
- [2].D. Aurbach, *Non-aqueous Electrochemistry*, Marcel Dekker, Inc: New York, (1999).
- [3].J. A. Krom, J. T. Petty, A. J. Streitwieser, *J. Am. Chem. Soc.* 115 (1993) 8024.
- [4].O. Popvyh, R. P. T. Tomkins, *Nonaqueous Solution Chemistry*, Chapter 4, Wiley-Interscience: New York, (1981).
- [5].W.Y. Wen, *Water and Aqueous Solutions. Structure, Thermodynamics, and Transport Process*, R. A. Horne, ed. Chapter 15, Wiley-Interscience: New York, (1971).
- [6].R. R. Dogonadze, E. Kalman, A. A. Kornyshev, J. Ulstrup, *The Chemical Physics of Solvation, Part B, Spectroscopy Solvation*, Elsevier: Amsterdam, (1986).
- [7].A. Sinha, G. Ghosh, M. N. Roy, *J. Phys. Chem. Liqs.* 48 (2010) 62.
- [8].A. Sinha, A. Bhattacharjee, M. N. Roy, *J. Disp. Sc. and Techn.* 30 (2009) 1003.
- [9].D. D. Perrin, W. L. F. Armarego, *Purification of laboratory chemicals*, 3rd ed., Pergamon Press: Oxford, (1988).
- [10]. I. M. Abdulagatov, N. D. Azizov, *Fluid Phase Equilibria.* 240 (2006) 204.
- [11]. J. E. Lind Jr, J. J. Zwolenik, R. M. Fuoss, *J. Am. Chem. Soc.* 81 (1959) 1557.
- [12]. F. I. El-Dossoki, *J. Mol. Liquids.* 151 (2010) 1.
- [13]. R. M. Fuoss, *Proc. Natl. Acad. Sci., U.S.A.* 75 (1978) 16,
- [14]. R. M. Fuoss, *J. Phys. Chem.* 82 (1978) 2427.
- [15]. R. M. Fuoss, F. Accascina, *Electrolytic Conductance*, Interscience: New York, (1959).
- [16]. J. I. Bhat, P. Bindu, *J. Ind. Chem. Soc.* 72 (1995) 783.
- [17]. C. G. Janz, R. P. T. Tomkins, *Non-aqueous Electrolytes Handbook*, Vol. 2, Academic Press: New York, (1973).

- [18]. R. Yamdagni, P. Kebarle, *J. Am. Chem. Soc.* 94(9) (1972) 2940.
- [19]. J. M. Chakraborty, B. Das, *Z. Phys. Chem.* 218 (2004) 219.
- [20]. R. M. Fuoss, E. Hirsch, *J. Am. Chem. Soc.* 82 (1960) 1013.
- [21]. R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Chapter 6, p 130, Butterworth: London, (1959).
- [22]. R. M. Fuoss, C. A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 2387.
- [23]. P. Debye, E. Hückel, *Phys. Z.* 24 (1923) 185.
- [24]. H. Falkenhagen, E.L. Vernon, *Phil. Mag.* 14 (1932) 537.
- [25]. J. Li, F. Zhao, F. Jing, *J. Comp. Chem.* 24 (2003) 345.
- [26]. P. G. Jasien, W. J. Stevens, *J. Chem. Phys.* 84 (1986) 3271.
- [27]. M. N. Roy, D. Ekka, R. Dewan, *Fluid Phase Equilibria.* 314 (2012) 113.
- [28]. A. K. Covington, T. Dickinson, *Physical chemistry of organic solvent systems*, Plenum: New York, (1973).
- [29]. W. Libus, B. Chachulski, L. Fraczyk, *J. Sol. Chem.* 9 (5) (1980) 355.
- [30]. O. N. Kalugin, S.M. Gubsky, I.N. Vyunnik, *J. Chem. Soc. Faraday Trans.* 87 (1991) 63.

TABLES

Table 1. Values of Density (ρ), Viscosity (η) and Relative Permittivity (ϵ_r) of Studied Pure Solvents at $T = 298.15$ K and $P = 0.1$ MPa^a

solvents	$\rho^b \cdot 10^{-3} (\text{kg} \cdot \text{m}^{-3})$		$\eta^c (\text{mPa} \cdot \text{s})$		ϵ_r
	expt	lit	expt	lit	
nitromethane	1.13015	1.13015 [27]	0.62	0.614 [27]	35.87 [27]
N-methylformamide	0.99761	0.99760 [28]	1.65	1.650 [28]	182.40 [28]
formamide	1.12922	1.12920 [28]	3.30	3.302 [28]	109.50 [28]

^a Standard uncertainties u are $u(T) = 0.01$ K, $u(P) = 0.1$ MPa, ^b $u(\rho) = 0.00005$ g. cm⁻³.
^c $u(\eta) = 0.03$ mPa.s

Table 2. Molar Conductance (Λ) and the Corresponding Concentration (c) of the Studied Electrolytes in Different Solvents at $T = 298.15$ K and $T = 0.1$ MPa^a

$m^d \cdot 10^4 /$ $\text{mol} \cdot \text{kg}^{-1}$	$\Lambda^e \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$m^d \cdot 10^4 /$ $\text{mol} \cdot \text{kg}^{-1}$	$\Lambda^e \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$m^d \cdot 10^4 /$ $\text{mol} \cdot \text{kg}^{-1}$	$\Lambda^e \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$
[Bu₄NBF₄] in Nitromethane		[Bu₄NBF₄] in N-Methylformamide		[Bu₄NBF₄] in Formamide	
7.73	83.32	7.95	35.23	8.29	21.50
13.03	79.43	15.13	33.07	14.52	20.30
17.31	76.51	20.25	31.43	20.25	19.20
23.72	73.50	27.35	29.93	26.32	18.30
29.27	70.93	32.95	28.64	31.81	17.50
35.76	68.40	39.56	27.52	37.82	16.70
41.34	65.96	48.02	26.15	45.70	15.80
49.14	63.97	53.88	25.28	52.91	15.02
56.55	61.75	60.53	23.97	61.31	14.30
65.77	59.35	73.27	22.34	70.56	13.44
75.69	56.84	78.32	21.59	79.21	12.49
85.56	54.33	87.98	20.45	84.82	11.90
[Bu₄NClO₄] in Nitromethane		[Bu₄NClO₄] in N-Methylformamide		[Bu₄NClO₄] in Formamide	

8.64	100.53	7.95	44.93	8.07	31.23
13.47	98.03	15.13	42.34	14.98	29.01
18.06	95.45	20.25	40.73	20.61	27.83
24.30	92.71	27.35	38.88	26.73	26.43
29.92	89.94	32.95	37.14	32.38	25.54
35.28	87.93	39.56	35.77	38.56	24.44
41.86	85.42	48.02	34.24	46.65	23.12
49.98	83.08	53.88	33.34	52.42	22.39
57.15	80.89	60.53	32.27	62.09	21.17
66.42	77.67	68.23	30.86	71.57	20.24
76.39	75.26	78.32	29.26	80.10	19.59
86.68	73.06	87.98	27.94	86.12	18.95

^a Standard uncertainties u are $u(T) = 0.01$ K, $u(P) = 0.1$ MPa, ^d $u(m) = 0.0001$ mol.kg⁻¹. ^e The relative standard uncertainty u_r is $u_r(A) = 0.01$.

Table 3. Limiting Molar Conductivity (Λ_0), the Association Constant (K_A), the Distance of Closest Approach of Ions (R), Standard Deviations δ of Experimental Λ from Eq 1, Walden Product ($\Lambda_0\eta$), Gibb's energy change (ΔG°) and A -coefficient of Electrolytes in Different Studied Solvents at $T = 298.15$ K

Solvents	$\Lambda_0 \cdot 10^4$ ($\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$)	K_A ($\text{dm}^3 \cdot \text{mol}^{-1}$)	R (\AA)	δ	$\Lambda_0\eta \cdot 10^4$ ($\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \cdot \text{mPa} \cdot \text{s}$)	$\text{Log}(K_A)$	ΔG° ($\text{kJ} \cdot \text{mol}^{-1}$)	$A \cdot 10^4$ ($\text{mPa} \cdot \text{K}^{1/2} \cdot \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$)
[Bu₄NBF₄]								
NM	94.60±0.12	182.09±0.01	12.69	0.58	58.08	2.26	-1.29	-3.93
NMF	41.04±0.14	203.76±0.01	12.83	0.57	67.72	2.31	-1.32	-1.72
FA	26.18±0.06	265.96±0.01	12.26	0.47	86.44	2.42	-1.38	-2.17
[Bu₄NClO₄]								
NM	111.42±0.07	114.15±0.02	12.31	0.67	68.41	2.06	-1.17	-3.75
NMF	50.55±0.04	154.56±0.01	12.45	0.45	83.41	2.19	-1.25	-0.73
FA	35.94±0.08	195.88±0.01	11.88	0.27	118.67	2.29	-1.31	-1.20

Table 4. Limiting Ionic Conductance (λ_o^\pm), Ionic Walden Product ($\lambda_o^\pm \eta$), Stokes' Radii (r_s) and Crystallographic Radii (r_c) of Ammonium Based Electrolytes in Different Studied Solvents at $T = 298.15$ K

solvents	$\lambda_o^\pm \cdot 10^4$ (S . m ² . mol ⁻¹)		$\lambda_o^\pm \eta \cdot 10^4$ (S . m ² . mol ⁻¹ mPa. s)		r_s (Å)		r_c (Å)	
	[Bu ₄ N] ⁺	BF ₄ ⁻	[Bu ₄ N] ⁺	BF ₄ ⁻	[Bu ₄ N] ⁺	BF ₄ ⁻	[Bu ₄ N] ⁺	BF ₄ ⁻
NM	34.07	60.53	20.92	37.17	3.92	2.20	4.94	2.78
NMF	14.78	26.26	24.38	43.33	3.36	1.89	4.94	2.78
FA	9.43	16.75	31.13	55.31	2.63	1.48	4.94	2.78
	[Bu ₄ N] ⁺	ClO ₄ ⁻	[Bu ₄ N] ⁺	ClO ₄ ⁻	[Bu ₄ N] ⁺	ClO ₄ ⁻	[Bu ₄ N] ⁺	ClO ₄ ⁻
NM	36.43	74.99	22.37	46.04	3.66	1.78	4.94	2.40
NMF	16.53	34.02	27.27	56.14	3.00	1.46	4.94	2.40
FA	11.75	24.19	38.80	79.87	2.11	1.03	4.94	2.40

^a Crystallographic radii for cation from ref [28] and for anion calculated and judged from refs [29] and [30] respectively.

Table 5. Diffusion Coefficient (D_\pm) and Ionic Mobility (i_\pm) of Electrolytes in Different Studied Solvents at 298.15 K

solvents	$D_\pm \cdot 10^9 / (\text{m}^2 \cdot \text{s}^{-1})$		$i_\pm \cdot 10^8 / (\text{m}^2 \cdot \text{s}^{-1} \cdot \text{volt}^{-1})$	
	[Bu ₄ N] ⁺	BF ₄ ⁻	[Bu ₄ N] ⁺	BF ₄ ⁻
NM	0.91	1.62	3.53	6.29
NMF	0.39	0.70	1.53	2.72
FA	0.25	0.45	0.98	1.74
	[Bu ₄ N] ⁺	ClO ₄ ⁻	[Bu ₄ N] ⁺	ClO ₄ ⁻
NM	0.97	1.99	3.78	7.78
NMF	0.44	0.91	1.72	3.53
FA	0.31	0.64	1.22	2.50

Table 6. IR Vibration Data of the Functional Groups Present in the Pure Solvent and Change of Frequency after Addition of Electrolytes [Bu₄NClO₄] and [Bu₄NBF₄] in the Solvents.

IR vibration data				
solvents	functional group	pure solvent (ν_0 cm ⁻¹)	[Bu ₄ N]ClO ₄ (ν_1 cm ⁻¹)	[Bu ₄ N]BF ₄ (ν_2 cm ⁻¹)
NM	N-O	1564.8 (ν_{as})	1601.7 (ν_{as})	1614.7 (ν_{as})
		1363.3 (ν_s)	1388.8 (ν_s)	1402.3 (ν_s)
	C-H	2960.9 (ν_{as})	2963.1 (ν_{as})	2964.5 (ν_{as})
		2872.5 (ν_s)	2873.9 (ν_s)	2874.1 (ν_s)
NMF	C=O	1679.8	1721.9	1734.5
	N-H	1543.3	1545.5	1546.2
	C-N	1400.1	1401.6	1403.9
FA	C=O	1692.9	1740.6	1754.1
	N-H	1578.2	1579.5	1582.9
	C-N	1401.8	1403.0	1404.2

FIGURES

Figure 1. Plot of molar conductance (Λ) and the square root of molar concentration (\sqrt{c}) for $[\text{Bu}_4\text{NBF}_4]$ in nitromethane (\blacklozenge), N-methylformamide (\blacksquare), formamide (\blacktriangle), for $[\text{Bu}_4\text{NClO}_4]$ in nitromethane (\diamond), N-methylformamide (\square), and formamide (\triangle) respectively, at $T = 298.15$ K.

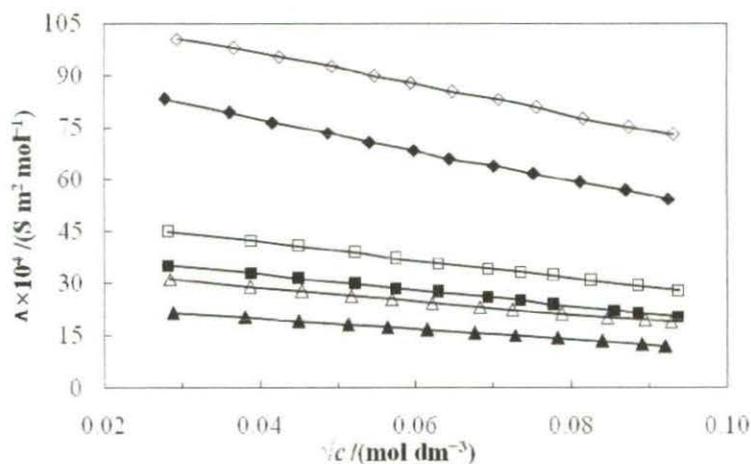


Figure 2. Plot of limiting molar conductance (Λ_0) for $[\text{Bu}_4\text{NBF}_4]$ (\blacklozenge), $[\text{Bu}_4\text{NClO}_4]$ (\blacktriangle), and Walden Product ($\Lambda_0\eta$) for $[\text{Bu}_4\text{NBF}_4]$ (\diamond), $[\text{Bu}_4\text{NClO}_4]$ (\triangle), in nitromethane, N-methylformamide and formamide respectively at $T = 298.15$ K

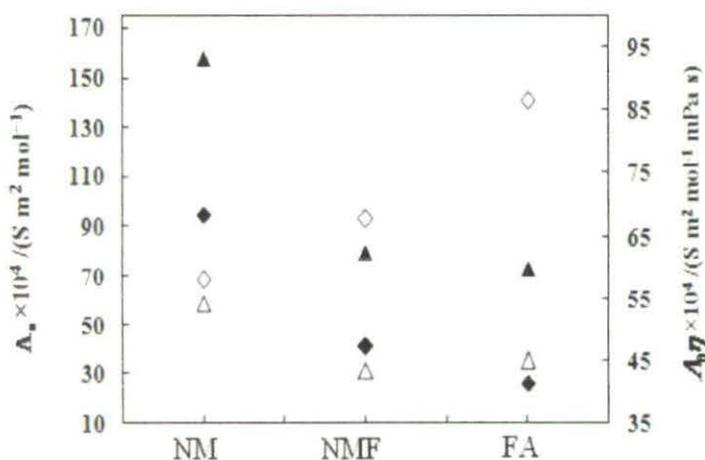


Figure 3. Plot of limiting ionic conductance (λ_o^\pm) for BF_4^- (\blacksquare), ClO_4^- (\blacktriangle) and ionic Walden Product ($\lambda_o^\pm \eta$) for BF_4^- (\square), ClO_4^- (\triangle) in nitromethane, N-methylformamide and formamide respectively at $T = 298.15$ K.

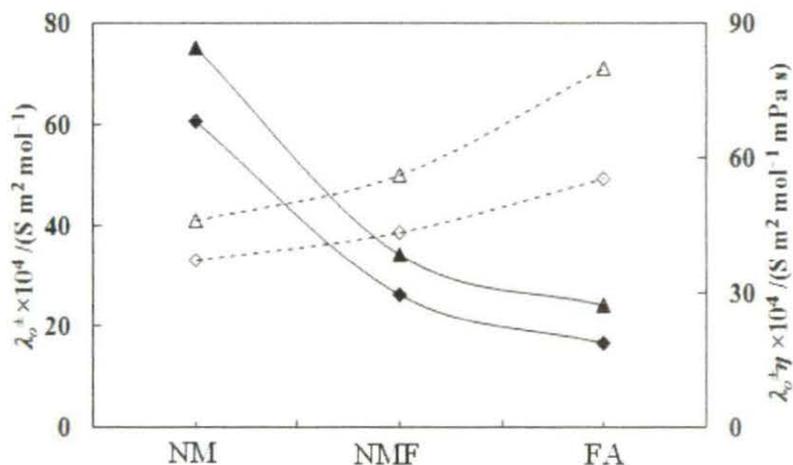


Figure 4. Plot of association constant (K_A) for $[\text{Bu}_4\text{NBF}_4]$ (\blacklozenge), $[\text{Bu}_4\text{NClO}_4]$ (\blacktriangle), and Gibb's energy change (ΔG°) for $[\text{Bu}_4\text{NBF}_4]$ (\diamond) and $[\text{Bu}_4\text{NClO}_4]$ (\triangle), in nitromethane, N-methylformamide, and formamide respectively at $T = 298.15$ K.

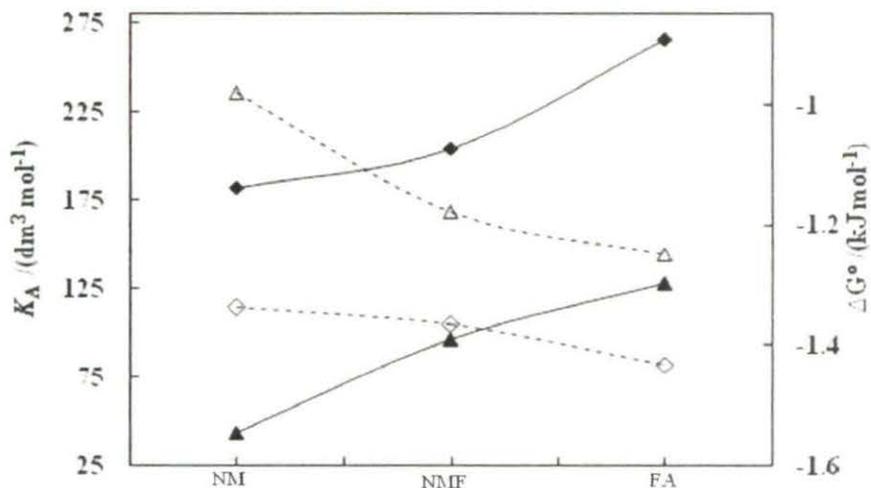


Figure 5. Plot of diffusion coefficient (D_{\pm}) for BF_4^- (■), ClO_4^- (▲) and ionic mobility (i_{\pm}) for BF_4^- (□), ClO_4^- (Δ), in nitromethane, N-methylformamide, and formamide, respectively, at $T = 298.15$ K.

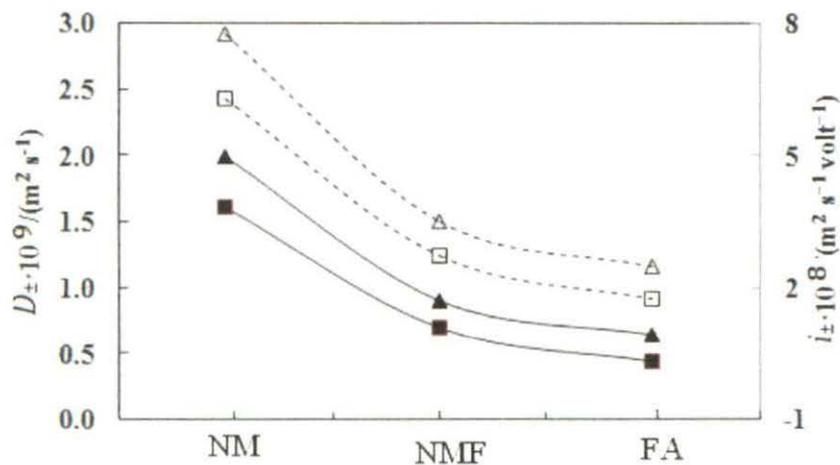


Figure 6. IR vibration data of -N-O in nitromethane (black solid line) and in {[Bu₄NClO₄] and nitromethane} (red solid line), {[Bu₄NBF₄] and nitromethane} (blue solid line)

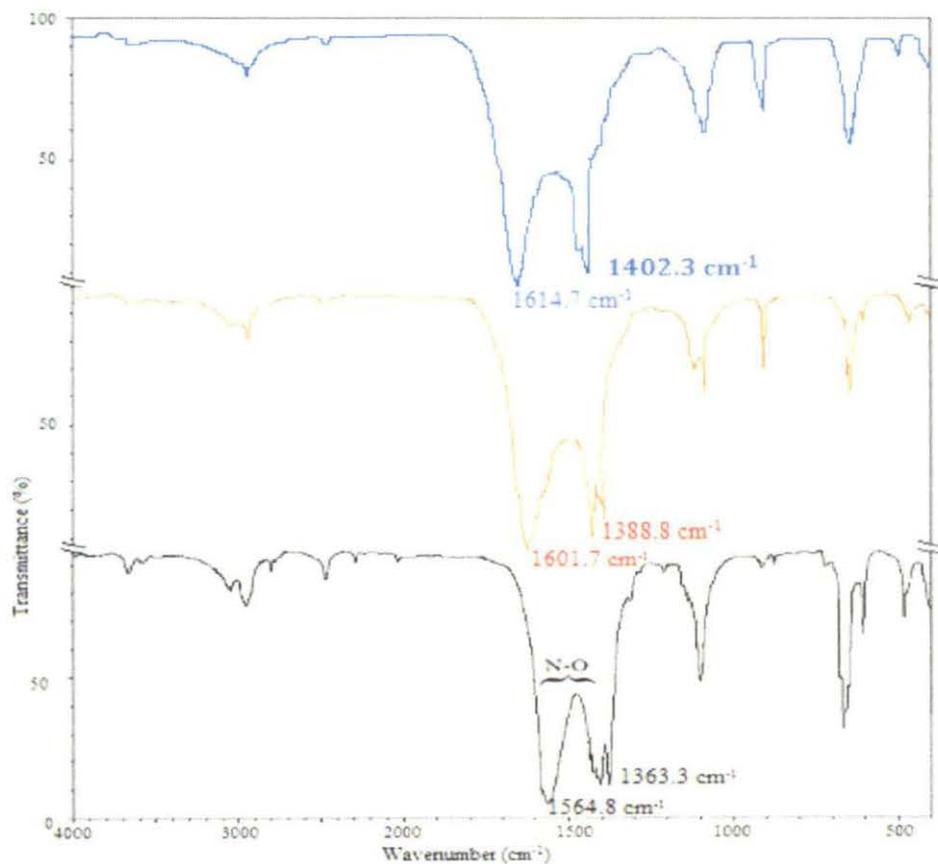


Figure 7. IR vibration data of C=O in N-methylformamide (black solid line) and in {[Bu₄NClO₄] and N-methylformamide} (red solid line) and {[Bu₄NBF₄] and N-methylformamide } (blue solid line).

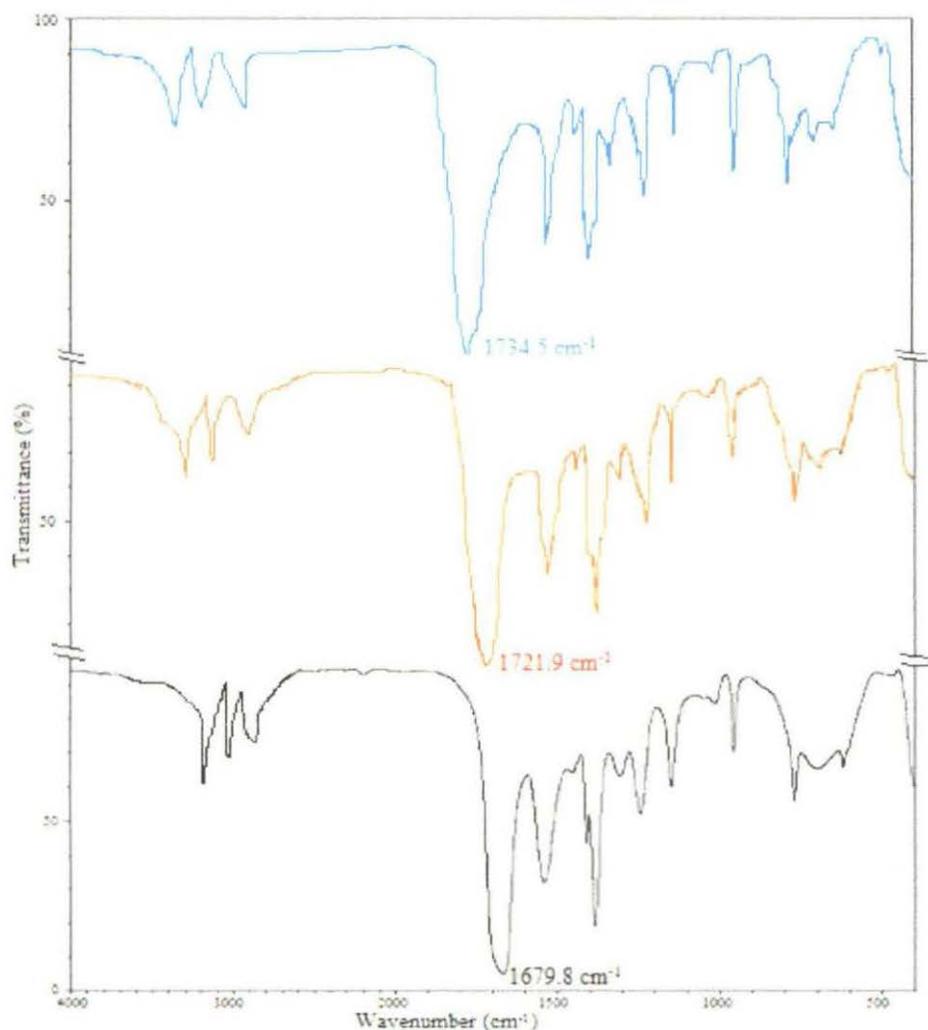
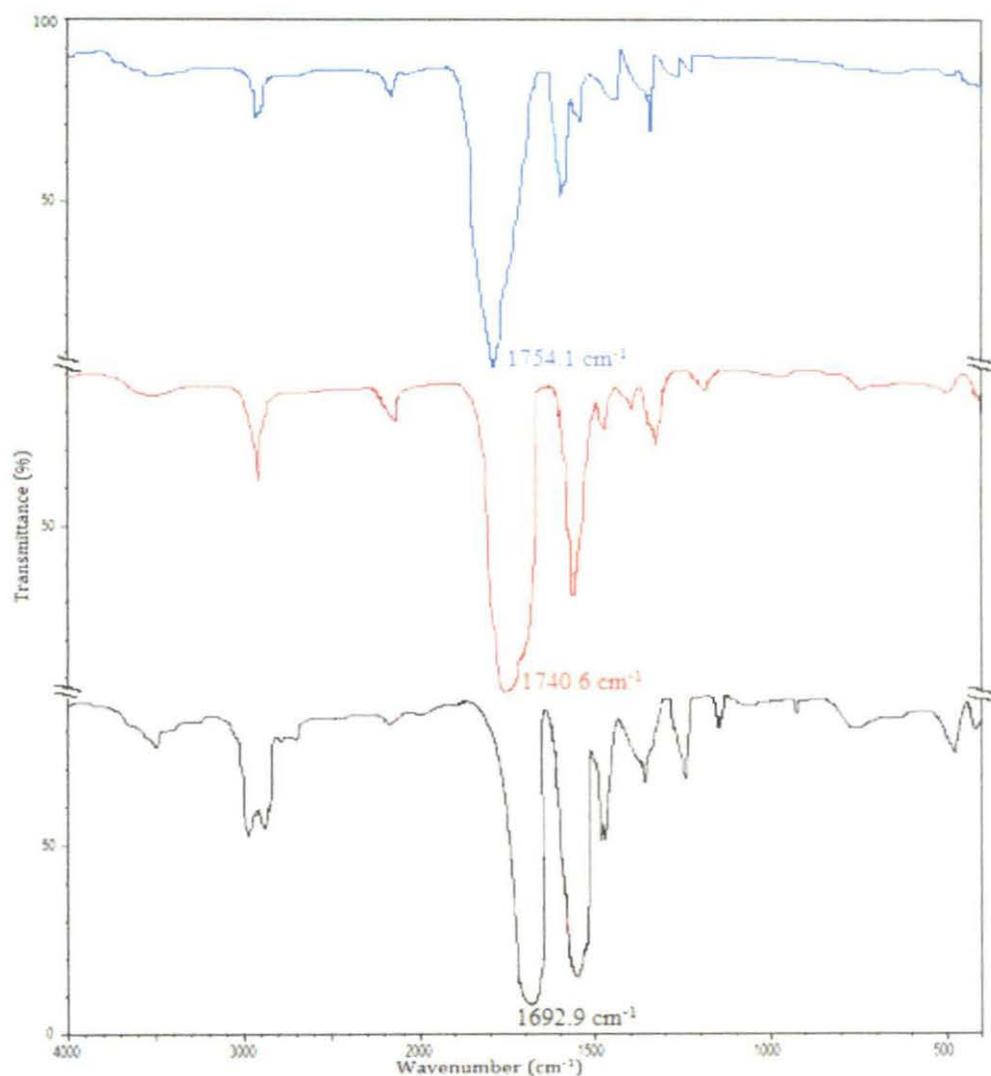
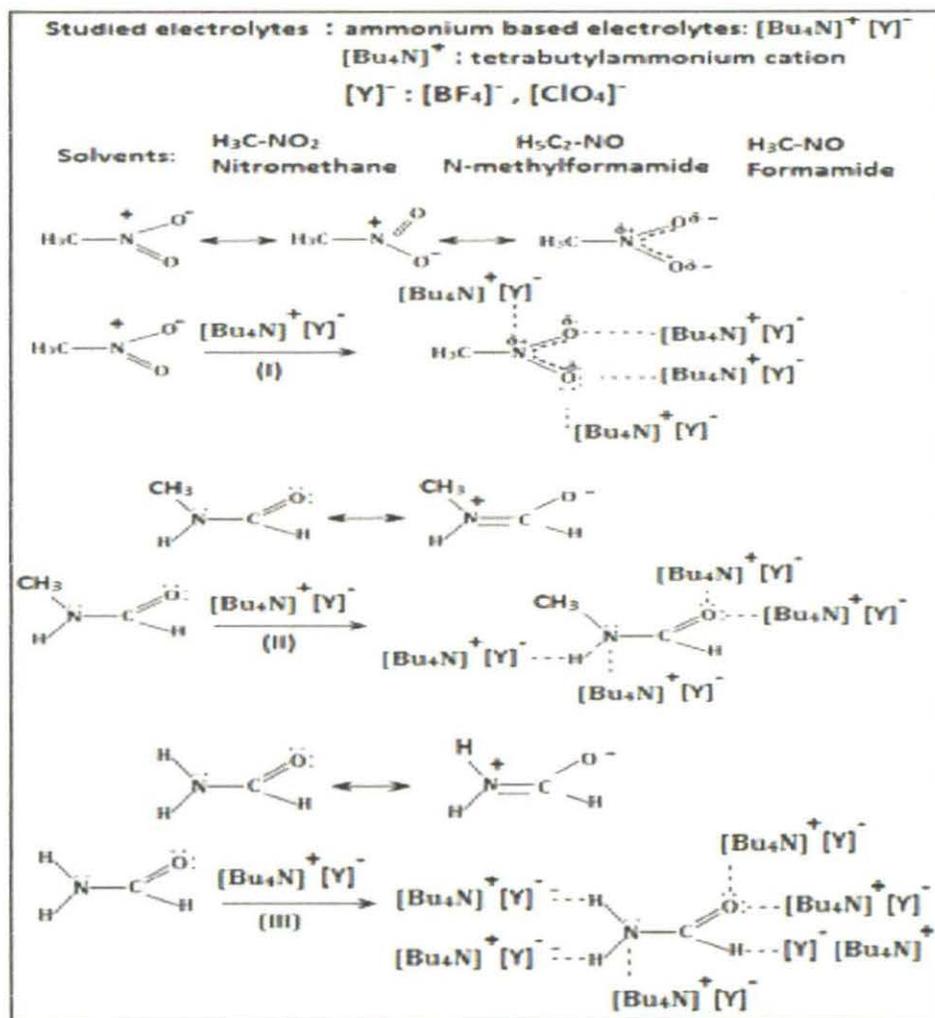


Figure 8. IR vibration data of C=O in formamide (black solid line) and in {[Bu₄NClO₄] and formamide} (red solid line) and {[Bu₄NBF₄] and formamide} (blue solid line).



SCHEMES

Scheme 1. Two Dimensional Representation of the Plausible Interaction Occurring in $\{[Bu_4N][Y]$ and Solvent $\}$ Together with the Trend in the Ion-Solvation in the Studied Solvents, Which Is Given Below: $I < II < III$



CHAPTER- X

CONCLUDING REMARKS

In my research work, described in this thesis, I have tried to investigate the solution properties of some biologically-active solutes and ionic salts in some aqueous and non-aqueous industrially important liquid systems respectively in terms of various interactions such as solute-solute/ion-ion, solute-solvent/ion-solvent and solvent-solvent of some compounds. Molecular interactions have been examined with the help of thermodynamic and transport properties of solutions. Systematic study made on these properties has great importance in gaining a better knowledge of these interactions. Such study will find importance in chemical engineering areas especially to understand the mixing behaviour of different components in the mixture.

The volumetric, viscometric, interferometric, conductometric and refractive index studies helped us to evaluate the extent of molecular interaction in a particular solution quantitatively whereas the FT-IR measurements gave an insight into the type of molecular interaction occurring in any given systems. Various types of interactions exist between the ions in solutions, and of these, ion-ion and ion-solvent interactions are of current interest in all branches of chemistry. These interactions help in better understanding the nature of solute and solvent, that is, whether the solute modifies or distorts the structure of the solvent.

Different quantities strongly influenced by solvent properties could be derived from concentration dependence of the electrolyte conductivity. Consequently, a number of conductometric and related studies of different electrolytes in non-aqueous solvents, have been made for their optimal use in high-energy batteries and for understanding organic reaction mechanisms. Ionic association of electrolytes in solution depends upon the mode of solvation of its ions, which in turn depends on the nature of the solvent or solvent mixtures. Such solvent properties as viscosity and the relative permittivity have

been taken into consideration as these properties help in determining the extent of ion association and the solvent-solvent interactions.

In Chapter IV, after a thorough investigation of apparent molar volume, viscosities, limiting partial isentropic compressibility, viscosity *B*-coefficient and molar refraction of some amino acids (biologically-active solutes) like glycine, L-alanine and L-valine in different concentration of aqueous ascorbic acid solution (vitamin-C) at 298.15 K, reveals the fact that the presence of strong solute-solvent interactions which increases with the increase of the mass fractions of ascorbic acid in aqueous mixture. The size and number of carbon atoms of the alkyl chain groups of the amino acids also play a pivotal role in determining the nature and strength of the interactions in these solvent media.

In Chapter V, the behaviour of carbohydrates (D-glucose, D-mannitol and D-sucrose) in aqueous binary solutions of nicotinic acid (NA) was observed at 298.15, 308.15, and 318.15 K temperature from volumetric, viscometric and refractometric measurements. Nicotinic acid is an important compound which plays a crucial role in various physiological effects, biosynthesis, metabolic reactions, and several drug preparations. This study indicates the presence of strong solute-solvent and weak solute-solute interactions and these interactions are further strengthened at higher temperatures and higher concentration of nicotinic acid in the ternary solutions. Here carbohydrates under investigation act as a structure breaker when added to aqueous NA solution.

In chapter VI, the extensive study of Tetrabutylphosphonium tetrafluoroborate [Bu₄PBF₄] in dimethyl sulfoxide (DMSO), N,N-dimethyl acetamide (DMA) and N,N-dimethyl formamide (DMF) at 298.15 K through conductometric measurements. From the experimental measurements we have seen that the limiting molar conductance of [Bu₄PBF₄] in DMF is greater than that in DMA and DMSO, and the association constant (K_A) of the electrolyte is greater in DMSO than in DMA than in DMF. Hence, this shows that there is more ion-solvent interaction in DMSO than that in the other two solvents. The reliable value of volumetric, viscometric and interferometric studies also suggests that in solution there is more ion-solvent interaction than the ion-ion interaction.

Qualitative and quantitative analyses of molecular interaction prevailing in ionic liquid [Bu₄PMS] in dimethyl sulfoxide (DMSO), N,N-dimethyl acetamide (DMA) and N,N-dimethyl formamide (DMF), probed by electrical conductance and FT-IR measurements have been reported in chapter VII. In this chapter the extent of interaction is expressed in terms of the association constant (K_A) and shows the ion-dipole interaction to be a function of viscosity and the FT-IR measurements were supplemented to explain the ion-dipole interaction in the solution. It was seen that the conductance of [Bu₄PMS] was highest in case of dimethylformamide (DMF) in comparison to the other solvents. Greater ion-solvent interaction of the salt was seen in dimethylsulfoxide (DMSO). It can also be seen that in the conductometric studies in DMSO, DMA and DMF, the electrolyte remains as ion-pairs. The ionic conductivity value suggests the fact that the anions (MS^-) conduct more than the cation [Bu₄P⁺]. The diffusion coefficient and ionic mobility also show that in studied ionic liquid, the anions diffuse more due to high ionic mobility compared to cation because the size of the anion is smaller than that of the cation. In all the solvents, the electrolyte forms ion-dipole interactions as evidenced by the FT-IR studies.

Chapter VIII dealt with solvation behaviour of tetrabutylammonium tetrafluoroborate [Bu₄NBF₄] in acetonitrile (CH₃CN), methanol (CH₃OH), dimethyl sulfoxide (DMSO) and 1,3-dioxolane(1,3-DO) at 298.15 K which was realised by conductometric study. The observed molar conductivities were explained by the formation of ion-pairs ($M^+X^- \leftrightarrow MX$) and triple-ions ($2M^+ + X^- \leftrightarrow M_2X^+$; $M^+ + 2X^- \leftrightarrow MX_2^-$). From the study we get a clear idea that the electrolyte was more solvated by DMSO than other three solvents. During the conductometric studies triple-ion formation was seen in case of 1,3-dioxolane and the major portion of electrolyte was exists as ion-pairs in CH₃CN, CH₃OH and DMSO. The classical Fuoss-Kraus theory of triple-ion formation which occurs in low dielectric solvent was found to be valid in the study. The tendency of the ion-pair and triple-ion formation of electrolyte depends on the size and charge distribution of the ions.

Chapter IX quantifies the precise measurements on electrical conductance of tetrabutylammonium tetrafluoroborate [Bu₄NBF₄] and tetrabutylammonium

perchlorate $[\text{Bu}_4\text{NClO}_4]$ in nitromethane, N-methylformamide, and formamide at 298.15 K. From the experimental data it is evident that the conductance for the electrolytes is highest in the case of nitromethane and lowest in the case of formamide. Among the two electrolytes, $[\text{Bu}_4\text{NBF}_4]$ is associated most with the studied solvents, and the highest association is seen between $[\text{Bu}_4\text{NBF}_4]$ and formamide. This illustrates that the electrolytes are solvated more by formamide, due to its highest viscosity value among the studied solvents. It is also seen that, with an increase in the size of the anion, the extent of solvation also increases. The present study also reveals that the greater share of the conductance holds the $[\text{Y}]^-$ ion than the $[\text{Bu}_4\text{N}]^+$ as clear from their ionic conductance values. In all of the investigated solvents, the electrolytes shows ion-dipole interactions observed from the FT-IR and conductance studies.

The volumetric behaviour of solutes has been proven to be very useful in elucidating the various interactions occurring in aqueous and nonaqueous solutions. Studies on the apparent and partial molar volumes of electrolytes and the dependence of viscosity on concentration of solutes and temperature of solutions have been employed as a function of studying ion-ion and ion-solvent interactions. It has been found that the addition of electrolyte could either break or make the structure of a liquid. Because a liquid's viscosity depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at different concentrations and temperatures.

More extensive studies of the different thermodynamic and transport properties of the electrolytes will be of sufficient help in understanding the nature of the ion-solvent interactions and the role of solvents in different chemical processes.

The proper understanding of the ion-ion and ion-solvent interactions may form the basis of explaining quantitatively the influence of the solvents and ions in solution and thus pave the way for real understanding of different phenomena associated with solution chemistry. However, it is necessary to remember that molecular interactions are very complex in nature. There are strong forces existing in the molecule and it is not really possible to separate them all. Nevertheless, if careful judgement is used, valid

conclusions can be drawn in many cases relating to degree of structure and order of the system.

To conclude it may be stated that extensive studies of the different physico-chemical, biological or pharmaceutical activity between different components of a given mixture will be of immense help in understanding the nature of the different interactions prevailing in mixed systems. The proper understanding of the ion-ion and ion-solvent interactions may form the basis of explaining quantitatively the influence of the solvents and ions in solution and thus pave the way for real understanding of different phenomena associated with solution chemistry.

BIBLIOGRAPHY

CHAPTER I:

- [1]. M. N. Roy, R. K. Das, A. Bhattacharjee, *Russian J. Phys.Chem A*. 84 (2010) 2201.
- [2]. R. N. Goldberg, Y. B. Tewari, *J. Phys. Chem. Ref. Data*. 18 (1989) 809.
- [3]. J. Boerio Goates, *J. Chem. Thermodyn*. 23 (1991) 403.
- [4]. S. Budavari, The Merck Index, An Encyclopedia of Chemicals, *Drugs and Biologicals*. 12th edn, p. 1120. Merck, Whitehouse Station, N.J. (1996).
- [5]. Joan F. Brennecke, Edward J. Maginn, *AIChE Journal*. 47 (2001) 2384.
- [6]. N. H. Kim, S. V. Malhotra, M. Xanthos, *Microporous and Mesoporous Materials* 96 (2006) 29.
- [7]. A. J. Queimade, I. M. Marrucho, J. A. P. Coutinho, E. H. Stenby, *Int. J. Thermophys*. 26 (2005) 47.
- [8]. N. N. Wankhede, M. K. Lande, B. R. Arbad, *J. Chem. Eng. Data*. 55 (2005) 969.
- [9]. A. Sinha, M. N. Roy, *J. Chem. Eng. Data*. 51 (2006) 1415.
- [10]. L. H. Blanco, E. F. Vargas, *J. Soln. Chem*. 35 (2006) 21.
- [11]. D. K. Meck, *The Chemistry of Non-Aqueous Solvents*, Ed. J. J. Lagowski, Vol-10, Chapter 1, Academic, New York, (1976).
- [12]. F. Franks, *Physico-Chemical Processes in Mixed Aqueous Solvents*, Heinemann Educational Books Ltd. (1967).
- [13]. O. Popovych, *Crit. Rev. Anal. Chem.*, 1 (1970) 73.
- [14]. R. G. Bates, *Solute-Solvent Interactions*, Eds. J. J. Coetzee, C.D. Ritchie, Marcel Dekker, New York, (1999).
- [15]. A. J. Parker, *Electrochim. Acta*. 21(1976) 671.
- [16]. C. M. Criss, M. Salomon, *J. Chem. Edu*. 53 (1976) 763.
- [17]. Y. Marcus, *Ion Solvation*, Wiley, Chinchester, (1986).
- [18]. R. R. Dogonadze, E. Kalman, A. A. Kornyshev, J. Ulstrup, *The Chemical Physics of Solvation*, Elsevier, Amsterdam, (1988).
- [19]. A. K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, (1973).
- [20]. Y. Marcus, *Ion Properties*, Dekker, New York, (1998),
- [21]. A. F. D. Namor, M. A. L. Tanco, M. Solomon, J. C. Y. Ng, *J. Phys. Chem*. 98 (1994) 11796.

- [22]. E.L. Heric, J.G. Brewer, *J. Chem. Eng. Data.* 14 (1969) 55.
- [23]. P.K. Gessner, M.P. Shakarjian, *J. Pharm. Exptal. Therap.* 235 (1988) 32.
- [24]. P. Pradhan, R.S. Sah, M.N. Roy, *J. Mol. Liq.* 144 (2009) 149.

CHAPTER II:

- [1]. (a) J. D. Pandey and A. Yasmin, *Proc. Ind. Acad. Sci.* 109 (1997) 289.
(b) J. D. Pandey, Y. Akhtar and A. K. Sharma, *Ind. J. Chem.* 37A (1998) 1094.
- [2]. J. I. Kim, *J. Phys. Chem.* 82 (1978) 191.
- [3]. W. Kemp, *Organic spectroscopy*, 3rd (ELBS) Ed., Macmillan Press, Hampshire, U.K., (1993).
- [4]. H.S. Harned, B.B. Owen, *The physical chemistry of Electrolytes Solutions*, 3rd ed., Reinhold Publishing Co., New work, (1958).
- [5]. J.E. Gordon, *The Organic Chemistry of Electrolyte Solutions*, Wiley Interscience, (1975).
- [6]. B.E. Conway, R.G. Barradas, *Chemical Physics of Ionic Solutions*, Wiley, New York (1966).
- [7]. D.T. Richens, *The Chemistry of Aqua Ions*; Wiley, New York (1997).
- [8]. K. Ibuki, M. Nakahara, *J. Phys. Chem.* 94 (1990) 8370.
- [9]. A. Henni, J.H. Jonathan, T. Paitoon, A. Chakma, *J. Chem. Eng. Data.* 48 (2003) 1062.
- [10]. J. Burgess, *Metal Ions in Solutions*; Ellis Horwood, New York (1978).
- [11]. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York (1958).
- [12]. J. J. Lagowski, *The Chemistry of Non-Aqueous Solvents*, Academic, New York (1966).
- [13]. B.E. Conway, R.G. Barradas, *Chemical Physics of Ionic Solutions*, Wiley, New York (1966).
- [14]. J.S. Muishead-Gould, K.J. Laidler, *Chemical Physics of Ionic Solutions*, Wiley, New York (1966).
- [15]. J.F. Coetzee, C.D. Ritchie, *Solute-Solvent Interactions*, Marcel Dekker, New York (1969).
- [16]. R.G. Bates, *J. Electroanal. Chem.* 29 (1972) 1.
- [17]. G.S. Kell, C.M. Daries, J. Jarynski, *Water and Aqueous Solutions, Structure, Thermodynamics and Transport process*, Wiley, New York (1972).
- [18]. E.S. Amis, J.F. Hinton, *Solvent effects on Chemical Phenomena*, Academic, New York (1973).

- [19]. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York (1973).
- [20]. J.E. Gordon, *The Organic Chemistry of Electrolyte Solutions*, Wiley- Interscience, New York (1975).
- [21]. F. Franks, *Physico-Chemical processes in Mixed Aqueous Solvents*, Heinemann, London (1967).
- [22]. F. Franks, *Water—A Comprehensive Treatise*, Plenum Press, New York (1973).
- [23]. V. Gutmann, *Electrochim. Acta.* 21 (1967) 661.
- [24]. U. Mayer, V. Gutmann, *Adv. Inorg.Chem. Radiochem.* 17 (1975) 189.
- [25]. R.G. Pearson, *Hard and Soft Acids and Bases*, Strondburgh (1973).
- [26]. G.R. Behbehani, M. Dillon, J. Symth, W.E. Waghorne, *J. Solution Chem.* 31 (2002) 811.
- [27]. C. Guha, J.M. Chakraborty, S. Karanjai, B. Das, *J. Phys. Chem. B.* 107 (2003) 12814.
- [28]. L. Jones, J.F. Devonshire, *A. F. Proc. Royal Soc.* (1937).
- [29]. I. Prigogine, S. Garikian, *Physica.* 16 (1950) 239.
- [30]. I. Prigogine, A. Belleman, *J. Phys. Chem.* 21 (1953) 561.
- [31]. A.J. Treszczanowicz, G.C. Benson, *Fluid Phase Equilib.* 23 (1985) 117.
- [32]. Wen-Lu Weng, *J. Chem. Eng. Data.* 45 (2000) 606.
- [33]. P.S. Nikam, S.J. Kharat, *J. Chem. Eng. Data.* 50 (2005) 455.
- [34]. R.P. Rastogi, J. Nath, J. Mishra, *J. Phys. Chem.* 71 (1967) 1277.
- [35]. K.S. Pitzer, G. Mayora, *J. Phys. Chem.* 77 (1973) 2300.
- [36]. D. Cook, L-Higgins, *H. C. Proc. Royal. Soc.* A209 (1951) 28.
- [37]. J.S. Rowlinson, *Liquid and Liquid Mixtures*, Scientific Publications, London (1959).
- [38]. J.S. Rowlinson, *Proc. Royal. Soc.* A214 (1952) 192.
- [39]. J.L. Lebowitz, J. S. Rowlinson, *J. Chem. Phys.* 41 (1964) 133.
- [40]. J.A. Barker, D.J. Henderson, *J. Phys. Chem.* 47 (1967) 4714.
- [41]. P.J. Flory, R.A. Orwoll, A. Vrij, *J. Am. Chem. Soc.* 86 (1964) 3507.
- [42]. P.J. Flory, A. Abe, *J. Am. Chem. Soc.* 86 (1964) 3563.
- [43]. P.J. Flory, *J. Am. Chem. Soc.* 87 (1965) 1833.
- [44]. D. Patterson, G. Delmas, *Discuss. Faraday Soc.* 49 (1970) 98.
- [45]. A. Heintz, *Ber. Bunsenges. J. Phys.chem.* 89 (1985) 172.
- [46]. H. Funke, M. Wetzal, A. Heintz, *J. Pure. Appl. Chem.* 61 (1989) 1429.
- [47]. A. Heintz, D. Papaioannou, *Thermochimica Acta.* 310 (1998) 69.

- [48]. A. Heintz, P.K. Naicker, S.P. Verevkin, R. Pfestrof, B. Bunsenges, *Phys. Chem.* 102 (1998) 953.
- [49]. S. Villa, N. Riesco, I. Garcia de la Fuente, J.A. Gonzalaz, J.C. Cobos, *Fluid Phase Equilib.* 216 (2004) 123.
- [50]. S.L. Oswal, *J. Thermochim. Acta.* 425 (2005) 59.
- [51]. A. Pineiro, A. Amigo, R. Bravo, P. Brocos, *Fluid Phase Equilib.* 173 (2000) 211.
- [52]. A. Pineiro, *Fluid Phase Equilib.* 216 (2004) 245.
- [53]. M. Gepert, B. Stachowska, *J. Sol. Chem.* 35 (2006) 425.
- [54]. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolyte Solutions*, Reinhold Publishing Corporation, New York (1943).
- [55]. C. Tanford, *Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Wiley-Interscience, New York (1980).
- [56]. E. Vikingstad, *Aggregation Process in Solutions*, Elsevier, Amsterdam (1983).
- [57]. J.E. Desnoyers, M. Arel, H. Perron, C. Jolicoenn, *J. Phys. Chem.* 73 (1969) 3346.
- [58]. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York (1973).
- [59]. D.K. Hazra, B. Das, *J. Chem. Eng. Data.* 36 (1991) 403.
- [60]. D.O. Masson, *Phil. Mag.* 8 (1929) 218.
- [61]. O. Redlich, D.M. Meyer, *Chem. Rev.* 64 (1964) 221.
- [62]. B.B. Owen, S.R. Brinkley, *J. Ann. N. Y. Acad. Sci.* 51 (1949) 753.
- [63]. F.J. Millero, *Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes*, Wiley- Interscience, New York (1972).
- [64]. R. Gopal, M.A. Siddiqi, *J. Phys. Chem.* 73 (1969) 3390.
- [65]. J. Padova, I. Abrahamen, *J. Phys. Chem.* 71 (1967) 2112.
- [66]. R. Gopal, D.K. Agarwal, R. Kumar, *Bull. Chem. Soc. Jpn.* 46 (1973) 1973.
- [67]. R. Gopal, P.P. Rastogi, *Z. Phys. Chem. (N.F.)* 69 (1970) 1.
- [68]. B. Das, D.K. Hazra, *J. Chem. Eng. Data.* 36 (1991) 403.
- [69]. L. G. Hepler, *Can. J. Chem.* 47 (1969) 4617.
- [70]. L.G. Hepler, J.M. Stokes, R.H. Stokes, *Trans. Faraday Soc.* 61 (1965) 20.
- [71]. F.H. Spedding, M.J. Pikal, B.O. Ayres, *J. Phys. Chem.* 70 (1966) 2440.
- [72]. L.A. Dunn, *Trans. Faraday Soc.* 64 (1968) 2951.
- [73]. R. Pogue, G. Atkinson, *J. Chem. Eng. Data.* 33 (1988) 370.
- [74]. B.E. Conway, R.E. Verral, J.E. Desnoyers, *Trans. Faraday Soc.* 62 (1966) 2738.

- [75]. K. Uosaki, Y. Koudo, N. Tokura, *Bull. Chem. Soc. Jpn.* 45 (1972) 871.
- [76]. B.S. Krumgalz, *J. Chem. Soc. Faraday Trans. I.* 76 (1980) 1887.
- [77]. A.W. Quin, D.F. Hoffmann, P. Munk, *J. Chem. Eng. Data.* 37 (1992) 55.
- [78]. Z. Atik, *J. Sol. Chem.* 33 (2004) 1447.
- [79]. R.H. Stokes, R. Mills, *Viscosity of Electrolytes and Related Properties*, Pergamon, Great Britain (1965).
- [80]. F. Vaslow, *Water and Aqueous Solutions*, Wiley- Interscience, New York (1972).
- [81]. E.N.da C. Andrade, *Phil. Mag.* 17 (1934) 698.
- [82]. J. Frankel, *Kinetic Theory of Liquids*, Dover Publications, New York (1955).
- [83]. R. Furth, *Proc. Camb. Phil. Soc.* 37 (1941) 281.
- [84]. R. Furth, *Proc. Camb. Phil. Soc.* 37 (1941) 252.
- [85]. R.H. Ewell, H. Eyring, *J. Chem. Phys.* 5 (1937) 726.
- [86]. F.C. Auluck, S.C. De, D.S. Kothari, *Proc. Natl. Inst. Sci.* 10(4) (1944) 397.
- [87]. R. Eisenschitz, *Proc. Roy. Soc.* 215A (1952) 29.
- [88]. J.E. Lennard-Jones, A.F. Devonshire, *Proc. Roy. Soc.* 163A (1937) 53.
- [89]. J.E. Lennard-Jones, A.F. Devonshire, *Proc. Roy. Soc.* 165A (1938) 1.
- [90]. J.A. Pople, *Proc. Roy. Soc.* 215A (1952) 67.
- [91]. R. Eisenchitz, *Proc. Phys. Soc.* 62A (1949) 41.
- [92]. J.G. Kirkwood, *J. Chem. Phys.* 14 (1946) 180.
- [93]. J.G. Kirkwood, *Theory of Liquids*, Science Publishers, New York (1968).
- [94]. J.E. Mayer, E. Montroll, *J. Chem. Phys.* 9 (1941) 2.
- [95]. J.E. Mayer, *J. Chem. Phys.* 15 (1947) 187.
- [96]. M. Born, H.S. Green, *Proc. Roy. Soc.* 188A (1946) 10.
- [97]. M. Born, H.S. Green, *Proc. Roy. Soc.* 190A (1947) 455.
- [98]. J.G. Kirkwood, F.P. Buff, M.S. Green, *J. Chem. Phys.* 17 (1949) 988.
- [99]. J.G. Kirkwood, *J. Chem. Phys.* 3 (1935) 300.
- [100]. J.G. Kirkwood, *J. Chem. Phys.* 7 (1939) 919.
- [101]. J.G. Kirkwood, Z.W. Salsburg, *Faraday Soc. Discuss.* 15 (1953) 25.
- [102]. J.G. Kirkwood, E.M. Boggs, *J. Chem. Phys.* 10 (1942) 394.
- [103]. J.G. Kirkwood, E.K. Maun, B.J. Alder, *J. Chem. Phys.* 18 (1950) 1040.
- [104]. J.G. Kirkwood, V.A. Lewinson, B.J. Alder, *J. Chem. Phys.* 20 (1952) 929.

- [105]. R.W. Zwanzig, J.G. Kirkwood, K.F. Stripp, I. Oppenheim, *J. Chem. Phys.* 21 (1953) 2050.
- [106]. S.A. Rice, P. Gray, *The Statistical Mechanics of Simple Liquids. An introduction to the theory of equilibrium and Non-equilibrium Phenomena*, Interscience Publishers, New York (1965).
- [107]. S.A. Rice, *The Kinetic Theory of Dense Fluids, Colloquium Lecturers in Pure and Applied Science*, No. 9 Mobil Oil Corp. Research Lab., Dallas, Texas (1964).
- [108]. S.A. Rice, A.R. Allnatt, *J. Chem. Phys.* 34 (1961) 2144.
- [109]. A.R. Allnatt, S.A. Rice, *J. Chem. Phys.* 34 (1961) 2156.
- [110]. H.C. Longuet-Higgins, J.P. Valteau, *Mol. Phys.* 1 (1958) 284.
- [111]. H.T. Davis, S.A. Rice, J.V. Sengers, *J. Chem. Phys.* 35 (1961) 2210.
- [112]. H.T. Davis, K.D. Luks, *J. Phys. Chem.* 69 (1965) 869.
- [113]. J.O. Hirschfelder, C.F. Curtis, R.B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley and Sons, New York, (1954), reprinted with notes added (1964).
- [114]. J.D. Rogers, F.G. Brickwedde, *Physica*. 32 (1966) 100.
- [115]. J.P. Boon, G. Thomaes, *Physica*. 29 (1963) 208.
- [116]. J.P. Boon, G. Thomaes, *Physica*. 28 (1962) 1074.
- [117]. J.P. Boon, G. Thomaes, *Physica*. 29 (1963) 123.
- [118]. J.P. Boon, J. C. Legros, G. Thomaes, *Physica*. 33 (1967) 547.
- [119]. T.H. Holleman, J. Hijmans, *Physica*. 28 (1962) 604.
- [120]. H. Eyring, *J. Chem. Phys.* 4 (1936) 283.
- [121]. H. Eyring, J.O. Hirschfelder, *J. Phys. Chem.* 41 (1937) 249.
- [122]. J.F. Kincaid, H. Eyring, A.E. Stearn, *Chem. Rev.* 28 (1941) 301.
- [123]. H. Eyring, T. Ree, N. Hirai, *Proc. Natl. Acad. Sci.* 44 (1958) 683.
- [124]. E.J. Fuller, T. Ree, H. Eyring, *Proc. Natl. Acad. Sci.* 45 (1959) 1594.
- [125]. C.M. Carlson, H. Eyring, *Proc. Natl. Acad. Sci.* 46 (1960) 333.
- [126]. T.R. Thomson, H. Eyring, T. Ree, *Proc. Natl. Acad. Sci.* 46 (1960) 336.
- [127]. J. Walter, H. Eyring, *J. Chem. Phys.* 9 (1941) 393.
- [128]. T. Ree, H. Eyring, *Ind. Eng. Chem.* 50 (1958) 1036.
- [129]. C.M. Carlson, H. Eyring, T. Ree, *Proc. Natl. Acad. Sci.* 46 (1960) 649.
- [130]. H. Eyring, T. Ree, *Proc. Natl. Acad. Sci.* 47 (1961) 526.
- [131]. H. Eyring, M.S. John, *Significant Liquid Structures*, John Willey & Sons, New York (1969).

- [132]. Gruneisen, Wiss, Abhaudl, *Physik-tech. Reich-austatt.* 4 (1905) 239.
- [133]. G. Jones, M. Dole, *J. Am. Chem. Soc.* 51 (1929) 2950.
- [134]. P. Debye, E. Hückel, *Z. Phys. Chem.* 24 (1923) 185.
- [135]. H. Falkenhagen, M. Dole, *Phys. Z.* 30 (1929) 611.
- [136]. H. Falkenhagen, E.L. Vernon, *Phys. Z.* 33 (1932) 140.
- [137]. H. Falkenhagen, E.L. Vernon, *Phil. Mag.* 14 (1983) 537.
- [138]. M. Kaminsky, *Discuss Faraday Soc.* 24 (1957) 171.
- [139]. D. Feakins, D.J. Freemantle, K.G. Lawrence, *J. Chem. Soc. Faraday Trans. I.* 70 (1974) 795.
- [140]. J. Crudden, G.M. Delancy, D. Feakins, P.J. O'Reilly, W. E. Waghorne, K. G. Lawrence, *J. Chem. Soc. Faraday Trans I.* 82 (1986) 2195.
- [141]. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York (1973).
- [142]. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York (1958).
- [143]. M. Kaminsky, *Z. Phys. Chem.* 12 (1957) 206.
- [144]. J. Desnoyers, G. Perron, *J. Solution Chem.* 1 (1972) 199.
- [145]. R.J.M. Bicknell, K.G. Lawrence, D. Feakins, *J. Chem. Soc. Faraday I.* 76 (1980) 637.
- [146]. R.L. Kay, T. Vituccio, C. Zawoyski, D.F. Evans, *J. Phys. Chem.* 70 (1966) 2336.
- [147]. N.P. Yao, D.N. Bennion, *J. Phys. Chem.* 75 (1971) 1727.
- [148]. M. Kaminsky, *Discussions Faraday Soc.* 24 (1957) 171.
- [149]. D. Feakins, K.G. Lawrence, *J. Chem. Soc. A* (1966) 212.
- [150]. V. Vand, *J. Phys. Chem.* 52 (1948) 277.
- [151]. D.G. Thomas, *J. Colloid Sci.* 20 (1965) 267.
- [152]. S.P. Moulik, *J. Ind. Chem. Soc.* 49 (1972) 483.
- [153]. D. England, G. Pilling, *J. Phys. Chem.* 76 (1972) 1902.
- [154]. D.E. Goldsack, R.C. Franchetto, *Can. J. Chem.* 55 (1977) 1062.
- [155]. D.E. Goldsack, R.C. Franchetto, *Can. J. Chem.* 56 (1978) 1442.
- [156]. C.A. Angell, *J. Phys. Chem.* 70 (1966) 2793.
- [157]. C.A. Angell, *J. Chem. Phys.* 46 (1967) 4673.
- [158]. K.R. Chowdhury, D.K. Majumdar, *Electrochim. Acta.* 28 (1983) 23.
- [159]. K.R. Chowdhury, D.K. Majumdar, *Electrochim. Acta.* 28 (1983) 597.

- [160]. K.R. Chowdhury, D.K. Majumdar, *Electrochim. Acta.* 29 (1984) 1371.
- [161]. P.P. Rastogi, *Bull. Chem. Soc. Japan.* 43 (1970) 2442.
- [162]. R. Gopal, P.P. Rastogi, *Z. Phys. Chem. (N.F.)* 69 (1970) 1.
- [163]. C.M. Criss, M.J. Mostroiani, *J. Phys. Chem.* 75 (1971) 2532.
- [164]. K. Tamaski, Y. Ohara, Y. Isomura, *Bull. Chem. Soc. Japan.* 46 (1973) 951.
- [165]. P.P. Deluca, T.V. Rabagay, *J. Phys. Chem.* 79 (1975) 2493.
- [166]. B.N. Prasad, N.P. Singh, M.M. Singh, *Ind. J. Chem.* 14A (1976) 322.
- [167]. B.N. Prasad, M.M. Agarwal, *Ind. J. Chem.* 14A (1976) 343.
- [168]. R.T.M. Bicknell, K.G. Lawrence, M.A. Scelay, D. Feakins, L. Werblan, *J. Chem. Soc. Faraday I.* 72 (1976) 307.
- [169]. J.M. McDowall, N. Martinus, C.A. Vincent, *J. Chem. Soc. Faraday I.* 72 (1976) 654.
- [170]. A. Sacco, G. Petrella, M. Castagnola, *J. Phys. Chem.* 80 (1976) 749.
- [171]. R.L. Blokhra, Y.P. Segal, *Ind. J. Chem.* 15A (1977) 36.
- [172]. N.C. Das, P.B. Das, *Ind. J. Chem.* 15A (1977) 826.
- [173]. A. Sacco, G. Petrella, M. Della Monica, M. Castagnola, *J. Chem. Soc. Faraday I.* 73 (1977) 1936.
- [174]. P.K. Mandal, B.K. Seal, A.S. Basu, *Z. Phys. Chem.* 258 (1977) 809.
- [175]. J.I. Kim, *J. Phys. Chem.* 82 (1978) 191.
- [176]. S.K. Vijaylakshamna, *Indian J. Chem.* 17A (1979) 511.
- [177]. A. Sacco, G. Petrella, M.D. Monica, *J. Chem. Soc. Faraday I.* 75 (1979) 2325.
- [178]. P.T. Thomson, M. Durbana, J.L. Turner, R.H. Wood, *J. Sol. Chem.* 9 (1980) 955.
- [179]. K. Kurotaki, S. Kawamura, *J. Chem. Soc. Faraday I.* 77 (1981) 217.
- [180]. N. Martinus, C.A. Vincent, *J. Chem. Soc. Faraday Trans I.* 77 (1981) 141.
- [181]. A. Sacco, A. D. Giglio, A. D. Atti, *J. Chem. Soc. Faraday I.* 77 (1981) 2693.
- [182]. D.S. Gill, A.N. Sharma, *J. Chem. Soc. Faraday I.* 78 (1982) 78475.
- [183]. A. Sacco, G. Petrella, A.D. Atti, M. Castagnolo, *J. Chem. Soc. Faraday I.* 78 (1980) 955.
- [184]. A. Sacco, A.D. Giglio, A.D. Atti, M. Castagnolo, *J. Chem. Soc. Faraday I.* 79 (1983) 431.
- [185]. K.G. Lawrence, A. Sacco, *J. Chem. Soc. Faraday I.* 79 (1983) 615.
- [186]. K. Miyajima, M. Sawada, M. Nakagaki, *Bull. Chem. Soc. Jpn.* 56 (1983) 827.
- [187]. J. Doenech, S. Rivera, *J. Chem. Soc. Faraday I.* 80 (1984) 1249.

- [188]. D. Dasgupta, S. Das, D.K. Hazra, *Bull. Chem. Soc. Jpn.* 62 (1989) 1246.
- [189]. S. Taniewska-Osinska, M. Jozwaik, *J. Chem. Soc. Faraday Trans I.* 85 (1989) 2147.
- [190]. D. Nandi, D.K. Hazra, *J. Chem. Soc. Faraday Trans I.* 85 (1989) 4227.
- [191]. I. Ibulci, M. Nakahara, *J. Phys. Chem.* 94 (1990) 8370.
- [192]. W.M. Cox, J. H. Wolfenden, *Proc. Roy. Soc. London.* 145A (1934) 475.
- [193]. R.W. Gurney, *Ionic Processes in Solution*, Mc Graw Hill, New York (1953).
- [194]. E.R. Nightingale, *J. Phys. Chem.* 63 (1959) 1381.
- [195]. A. Einstein, *Ann. Phys.* 19 (1906) 289.
- [196]. G.S. Benson, A.R. Gordon, *J. Chem. Phys.* 13 (1945) 473.
- [197]. [D.F.T. Tuan, R.M. Fuoss, *J. Phys. Chem.* 67 (1963) 1343.
- [198]. C.H. Springer, J.F. Coetzee, R.L. Key, *J. Phys. Chem.* 78 (1969) 471.
- [199]. G. Petrella, A. Sacco, *J. Chem. Soc. Faraday I.* 74 (1978) 2070.
- [200]. B.S. Krumgalz, *J. Chem. Soc. Faraday I.* 76 (1980) 1275.
- [201]. B.S. Krumgalz, *Russ. J. Phys. Chem.* 46 (1972) 858.
- [202]. B.S. Krumgalz, *Russ. J. Phys. Chem.* 47 (1973) 956.
- [203]. B.S. Krumgalz, *Russ. J. Phys. Chem.* 48 (1974) 1163.
- [204]. B.S. Krumgalz, *Russ. J. Phys. Chem.* 45 (1971) 1448.
- [205]. H.D.B. Jenkins, M.S.F. Pritchett, *J. Chem. Soc. Faraday I.* 80 (1984) 721.
- [206]. K. Fajan, *Naturwissenschaften.* 9 (1921) 729.
- [207]. D.F.C. Morris, *Struct. Bonding.* 6 (1969) 157.
- [208]. R.W. Gurney, *Ionic Processes in Solutions*, Doves, New York (1962).
- [209]. H.S. Frank, W.Y. Wen, *Disc. Farad. Soc.* 24 (1957) 133.
- [210]. Z. Asmus, *Naturforsch.* 4A (1949) 589.
- [211]. M.H. Abraham, J. Liszi, E. Papp, *J. Chem. Soc. Faraday I.* 78 (1982) 197.
- [212]. M.H. Abraham, J. Liszi, L. Meszaros, *J. Chem. Phys.* 70 (1979) 249.
- [213]. M.H. Abraham, J. Liszi, *J. Chem. Soc. Faraday I.* 76 (1980) 1219.
- [214]. S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw Hill, New York (1941).
- [215]. E.R. Nightingale, R.F. Benck, *J. Phys. Chem.* 63 (1959) 1777.
- [216]. D. Feakins, D.J. Freemantle, K.G. Lawrence, *J. Chem. Soc. Faraday I.* 70 (1974) 795.
- [217]. R. Sinha, *J. Phys. Chem.* 44 (1940) 25.

- [218]. V. Vand, *J. Phys. Chem.* 52 (1948) 277.
- [219]. D.G. Thomas, *J. Colloid Sci.* 20 (1965) 267.
- [220]. S.P. Moulik, *J. Phys. Chem.* 72 (1968) 4688.
- [221]. S.P. Moulik, *Electrochim. Acta.* 17 (1972) 1491.
- [222]. S.P. Moulik, *J. Indian Chem. Soc.* 49 (1972) 483.
- [223]. R.J. Fort, W.R. Moore, *Trans. Faraday Soc.* 62 (1966) 1112.
- [224]. G.R. Naidu, P.R. Naidu, *Ind. J. Chem.* 22A (1983) 324.
- [225]. O. Redlich, A.T. Kister, *Ind. Eng. Chem.* 40 (1948) 345.
- [226]. L. Pikkarainen, *J. Chem. Eng. Data.* 28 (1983) 344.
- [227]. L. Pikkarainen, *J. Chem. Eng. Data.* 28 (1983) 381.
- [228]. L.S. Manjeshwar, T. Aminabhavi, *J. Chem. Eng. Data.* 33 (1988) 184.
- [229]. K.P. Rao, K.S. Reddy, *J. Chem. Eng. Data.* 33 (1988) 130.
- [230]. S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw Hill, New York (1941).
- [231]. D.S. Gill, T.S. Kaur, H. Kaur, I.M. Joshi, J. Singh, *J. Chem. Soc. Faraday Trans.* 89 (1993) 1737.
- [232]. J.V. Herraiez, R. Belda, *J. Soln. Chem.* 33 (2004) 117.
- [233]. J. Ferguson, Z. Kemblonski, *Applied Fluid Rheology*, Elsevier, Cambridge (1991).
- [234]. H.A. Barnes, J.F. Hutton, K. Walters, *An Introduction to Rheology*, Elsevier, Amsterdam (1993).
- [235]. C.W. Macosk, *Rheology. Principles, Measurements and Applications* (VCH), New York (1994).
- [236]. M. Garcia-Velarde, *Revista Esp. Fisica.* 9 (1995) 12.
- [237]. R. Shukla, M. Cheryan, *J. Membrane Sci.* 198 (2002) 104.
- [238]. J.M. Resa, C. Gonzalez, J. Lanz, *J. Food Eng.* 51 (2002) 113.
- [239]. M.J. Assael, N.K. Dalaouti, I. Metaxa, *Fluid Phase Equilibria.* 199 (2002) 237.
- [240]. A. Darr, *Technología Farmacéutica*, S.A. Acribia, Zaragoza (1979).
- [241]. R. Voight, S.A. Acribia, *Tratado de Tecnología Farmacéutica*, Zaragoza (1982).
- [242]. C.K. Z'eborg-Mikkelsen, S.E. Quiñones-Cisneros, S.H. Stenby, *Fluid Phase Equilibria.* 1191 (2002) 194.
- [243]. C. Fauli-Trillo, *Tratado de Farmacia Galénica*, S.A. Lujan, Madrid (1993).

- [244]. J. Swarbrik, J.C. Boyland, *Encyclopedia of Pharmaceutical Technology*, Marcel Dekker, NewYork (1993).
- [245]. J. Pellicer, *Sinergia Viscosa*, Valencia, Spain (1997).
- [246]. G. Copetti, R. Lapasin, E.R. Morris, *Proceedings of the Fourth European Rheology Conference*, Seville, Spain (1994).
- [247]. G. Kalentunc-Gencer, M. Peleg, *J. Texture Studies*. 17 (1986) 61.
- [248]. D.D. Christianson, *Hydrocolloidal Interactions with Starches*, Wesport. Conn. (1982).
- [249]. N.K. Howell, *Proceedings of the Seventh International Conference*, Wales (1993)
- [250]. J.G. Mathieson, B.E. Conway, *J. Sol. Chem.* 3 (1974) 455.
- [251]. S. Bhowmik, R.K. Mohanty, *Ind. J. Chem.* 25A (1986) 416.
- [252]. M.V. Kaulgud, K.S. Mohan Rao, *Ind. J. Chem.* 27A (1988) 12.
- [253]. K.J. Patil, A.B. Wazalwar, G.R. Mehta, *Ind. J. Chem.* 27A (1988) 799.
- [254]. M. Iqbal, R.E. Verral, *Can. J. Chem.* 67 (1989) 727.
- [255]. M. Kikuchi, M. Sakurai, K. Nitta, *J. Chem. Eng. Data*. 41 (1996) 1439.
- [256]. B.E. Conway, R.E. Verral, *J. Phys. Chem.* 70 (1966) 3952.
- [257]. K. Gekko, H. Noguchi, *J. Phys. Chem.* 83 (1979) 2706.
- [258]. W.L. Masterson, *J. Chem. Phys.* 22 (1954) 1830.
- [259]. L.G. Hepler, *Can. J. Chem.* 47 (1969) 4613.
- [260]. M.V. Kaulgud, K.J. Patil, *J. Phys. Chem.* 80 (1976) 138.
- [261]. K.J. Patil, G.R. Mehta, R.K. Chandewar, *Ind. J. Chem.* 25A (1986) 1147.
- [262]. C. Lafuente, B. Ginar, A. Villares, I. Gascon, P. Cea, *Int. J. Thermophys.* 25 (2004)1735.
- [263]. G. Douheret, A. Pal, M.I. Davis, *J. Chem. Thermodyn.* 22 (1990) 99.
- [264]. I. Gascon, S. Martin, P. Cea, M.C. Lopez, F.M. Royo, *J. Sol. Chem.* 31 (2002) 905.
- [265]. R. Mehra, M. Pancholi, *J. Ind. Chem. Soc.* 82 (2005) 791.
- [266]. S.L. Oswal, K.D. Prajapati, *J. Chem. Eng. Data*. 43 (1998) 367.
- [267]. K. Hsu-Chen, T. Chein-Hsium, *J. Chem. Eng. Data*. 50 (2005) 608.
- [268]. D.W. Marquardt, *J. Soc. Ind. Appl. Math.* 11 (1963) 431.
- [269]. L. Onsager, *Z. Phys. Chem.* 28 (1927) 277.
- [270]. R.M. Fuoss, *Rev. Pure Appl. Chem.* 18 (1968) 125.
- [271]. E. Pitts, *Proc. Roy. Soc.* 217A (1953) 43.

- [272]. R.M. Fuoss, L. Onsager, *J. Phys. Chem.* 61 (1957) 668.
- [273]. R.M. Fuoss, *Chemical Physics of Ionic Solutions*, Wiley, New York (1966).
- [274]. E. Pitts, R.E. Tabor, J. Daly, *Trans. Faraday Soc.* 65 (1969) 849.
- [275]. (a) R.M. Fuoss, K.L. Hsia, *Proc. Natl. Acad. Sci.* 57 (1967) 1550.
(b) R.M. Fuoss, K.L. Hsia, *J. Am. Chem. Soc.* 90 (1968) 3055.
- [276]. R. Fernandez-Prini, *J.E. Prue. Z. Phys. Chem.* 228 (1965) 373.
- [277]. R. Fernandez-Prini, *J.E. Prue. Z. Phys. Chem.* 228 (1965) 473.
- [278]. D.F. Evans, R.L. Kay, *J. Phys. Chem.* 70 (1966) 366.
- [279]. D. F. Arrington, E. Griswold, *J. Phys. Chem.* 74 (1970) 123.
- [280]. R.M. Fuoss, C.A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 476.
- [281]. T. Shedlovsky, J. Franklin, *Instt.* 225 (1938) 739.
- [282]. (a) J.C. Justice, *J. Chem. Phys.* 65 (1968) 353.
(b) J.C. Justice, R. Bury, C. Treiner, *J. Chem. Phys.* 65 (1968) 1708.
- [283]. R.M. Fuoss, F. Accascina, *Electrolytic Conductance*, Wiley, New York (1959)
- [284]. N.K. Bjerrum, *Dan. Vidensk. Selek. Mat.Fys.Medd.* 7 (1926) 9.
- [285]. M. Tissier, G. Douheret, *J. Soln. Chem.* 7 (1978) 87.
- [286]. R. Fernandez-Prini, *J. Prue, Trans. Faraday Soc.* 62 (1966) 1257.
- [287]. (a) R.M. Fuoss, L. Onsager, *J. Phys. Chem.* 66 (1962) 1722.
(b) R.M. Fuoss, L. Onsager, *J. Phys. Chem.* 67 (1963) 621.
- [288]. R.M. Fuoss, *J. Phys. Chem.* 49 (1975) 525.
- [289]. P.C. Carman, D.P. Laurie, *J. Sol. Chem.* 5 (1976) 457.
- [290]. R.M. Fuoss, *J. Phys. Chem.* 81 (1977) 1829.
- [291]. R.M. Fuoss, *Proc. Nat. Acad. Sci.* 75 (1978) 16.
- [292]. R.M. Fuoss, *J. Phys. Chem.* 82 (1978) 2427.
- [293]. (a) W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday II.* 74 (1978) 743.
(b) W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday II.* 74 (1978) 1456.
- [294]. W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday Trans. I.* 75 (1979) 1128.
- [295]. W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday Trans II.* 74 (1978) 1456.
- [296]. A.D. Pethybridge, S.S. Tara, *J. Chem. Soc. Faraday I.* 76 (1980) 368.
- [297]. M. Bester-Rogac, R. Neueder, J. Barthel, *J. Solution Chem.* 28 (1999) 1071.
- [298]. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York (1964).

- [299]. E. Balaguruswami, *Numerical Methods*, Tata McGraw-Hill Publishing Company, New Delhi (2007).
- [300]. M.N. Roy, B. Sinha, V.K. Dakua, *Pak. J. Sci. Ind. Res.* 49 (2006) 153.
- [301]. (a) B.S. Krumgalz, *J. Chem. Soc. Faraday I.* 79 (1983) 571.
(b) B.S. Krumgalz, *J. Chem. Soc. Faraday I.* 81 (1985) 241.
- [302]. P. Walden, H. Ulich, D. Bush, *Z. Phys. Chem.* 123 (1926) 429.
- [303]. R.M. Fuoss, E. Hirsch, *J. Am. Chem. Soc.* 82 (1960) 1018.
- [304]. S. Takezawa, Y. Kondo, N. Tokura, *J. Phys. Chem.* 77 (1973) 2133.
- [305]. (a) D.S. Gill, *J. Chem. Soc. Faraday I.* 77 (1981) 751.
(b) D.S. Gill, N. Kumari, M.S. Chauhan, *J. Chem. Soc. Farada Trans I.* 81 (1985) 687.
- [306]. M.A. Coplan, R.M. Fuoss, *J. Phys. Chem.* 68 (1964) 1177.
- [307]. J.F. Coetzee, G.P. Cunningham, *J. Am. Chem. Soc.* 87 (1965) 2529.
- [308]. R.H. Stokes, R.A. Robinson, *Trans. Faraday Soc.* 53 (1957) 301.
- [309]. M. Born, *Z. Phys. Chem.* 1 (1920) 221.
- [310]. R.H. Boyd, *J. Chem. Phys.* 35 (1961) 1281.
- [311]. R. Zwanzig, *J. Chem. Phys.* 38 (1963) 1603.
- [312]. E.J. Passeron, *J. Phys. Chem.* 68 (1964) 2728.
- [313]. (a) P. Walden, *Z. Phys. Chem.* 55 (1906) 207.
(b) P. Walden, *Z. Phys. Chem.* 78 (1912) 257.
- [314]. R.A. Robinson, R.H. Stokes, *Electrolyte Solutions*, Butterworths, London (1959)
- [315]. R. Gopal, M.M. Hussain, *J. Ind. Chem. Soc.* 40 (1963) 981.
- [316]. L.G. Longworth, *J. Phys. Chem.* 67 (1963) 689.
- [317]. M. Della Monica, U. Lamauna, L. Seutatore, *J. Phys. Chem.* 72 (1968) 2124.
- [318]. S. Brocus, *J. Chem. Phys.* 28 (1958) 1158.
- [319]. D.G. Miller, *J. Phys. Chem.* 64 (1960) 1598.
- [320]. G.J. Hills, *Chemical Physics of Ionic Solutions*, Wiley, New York (1966).
- [321]. R.H. Stokes, I.A. Weeks, *Aust. J. Chem.* 17 (1964) 304.
- [322]. R.H. Stokes, *The Structure of Electrolytic Solutions*, Wiley, New York (1959).
- [323]. D.S. Gill, *J. Chem. Soc. Faraday Trans .I.* 77 (1981) 751.
- [324]. R. Zwanzig, *J. Chem. Phys.* 52 (1970) 3625.
- [325]. H.S. Franks, *Chemical Physics of Ionic Solutions*, Wiley, New York (1966).

- [326]. G. Atkinson, S.K. Koz, *J. Phys. Chem.* 69 (1965) 128.
- [327]. R.L. Kay, G.P. Cunningham, D.F. Evans, *Hydrogen bonded Solvent Systems*, Taylor and Francis, London (1968).
- [328]. R.L. Kay, B.J. Hales, G.P. Cunningham, *J. Phys. Chem.* 71 (1967) 3925.
- [329]. R.L. Kay, C. Zawoyski, D.F. Evans, *J. Phys. Chem.* 69 (1965) 4208.
- [330]. D. F. Evans, J. L. Broadwater, *J. Phys. Chem.* 72 (1968) 1037.
- [331]. M. Spiro, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York (1973).
- [332]. R. Fernandez-Prini, G. Atkinson, *J. Phys. Chem.* 75 (1971) 239.
- [333]. L. Bahadur, M.V. Ramanamurti, *J. Chem. Soc. Faraday I.* 76 (1980) 1409.
- [334]. L. Bahadur, M.V. Ramanamurti, *J. Electrochem. Soc.* 128 (1981) 339.
- [335]. L. Bahadur, M.V. Ramanamurti, *Can. J. Chem.* 62 (1984) 1051.
- [336]. J.L. Broadwater, R.L. Kay, *J. Phys. Chem.* 74 (1970) 3803.
- [337]. S. Das, D.K. Hazra, *Indian J. Chem.* 274 (1988) 1073.
- [338]. S. Das, D.K. Hazra, *J. Ind. Chem. Soc.* LXV (1988) 100.
- [339]. (a) R.L. Kay, J.L. Broadwater, *Electrochim. Acta.* 16 (1971) 667.
(b) R.L. Kay, J.L. Broadwater, *J. Sol. Chem.* 5 (1976) 57.
- [340]. A.D. Aprano, R.M. Fuoss, *J. Phys. Chem.* 67 (1963) 1704.
- [341]. P. Hemmes, *J. Phys. Chem.*, 78 (1974) 907.
- [342]. J. Hubbard, L. Onsager, *J. Chem. Phys.* 53 (1977) 4850.
- [343]. N. Islam, M.R. Islam, M. Ahmed, *Z. Phys. Chem.* 262 (1981) 129.
- [344]. D.S. Gill, A.N. Sharma, H. Schneider, *J. Chem. Soc. Faraday I.* 78 (1982) 465.
- [345]. C.J. Cramer, D.G. Truhlar, *J. Am. Chem. Soc.* 113 (1991) 8305.
- [346]. D.J. Giesen, J.W. Stores, C.J. Cramer, D.G. Truhlar, *J. Am. Chem. Soc.* 117 (1995) 1057.
- [347]. (a) C.J. Cramer, D.G. Truhlar, *J. Org. Chem.* 61 (1996) 8720.
(b) C.J. Cramer, D.G. Truhlar, *Erratum.* 101 (1999) 309.
- [348]. G.D. Hawkins, C.J. Cramer, D.G. Truhlar, *J. Phys. Chem. B.* 101 (1997) 7147.
- [349]. G.D. Hawkins, C.J. Cramer, D.G. Truhlar, *J. Phys. Chem. B.* 102 (1998) 3257.
- [350]. A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burgess, *J. Chem. Phys.* 106 (1997) 4168.
- [351]. A. Galindo, L.A. Davies, A. Gil-Villegas, G. Jackson, *Mol. Phys.* 93 (1998) 241.

- [352]. M. Roses, C. Rafols, J. Ortega, E. Bosch, *J. Chem. Soc. Perkin Trans. 2* (1995) 1607.
- [353]. O. Bernard, W. Kunz, P. Turq, L. Blum, *J. Phys. Chem.* 96 (1992) 3833.
- [354]. S. Durand-Vidal, P. Turq, O. Bernard, *J. Phys. Chem.* 100 (1996) 17345.
- [355]. H.L. Bianchi, I. Dujovne, R. Fernandez-Prini, *J. Sol. Chem.* 29 (2000) 237.
- [356]. A. Chandra, B. Bagchi, *J. Phys. Chem. B.* 104 (2000) 9067
- [357]. W. Heller, *J. Phys. Chem.* 69 (1965) 1123.
- [358]. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York (1970).
- [359]. O. Redlich, A. Kister, *Ind. Eng. Chem.* 40 (1948) 345.
- [360]. J.F. Comesaña, J.J. Otero, E. Gamesella, A. Correa, *J. Chem. Eng. Data.* 46 (2001) 1153.

CHAPTER III:

- [1]. D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd Ed., Pergamon Press, Oxford, England (1988).
- [2]. C. Redlich, W.S. Beckett, J. Sparer, K.W. Barwick, C. A.Riely, H. Miller, S.L. Sigal, S. L. Shalat, M. R. Cullen, *Annals of Internal Medicine* 108 (1988)680.
- [3]. J. Clayden, *Organic Chemistry*. Oxford: Oxford University Press (2001).
- [4]. S. Zen, E. Kaji, *Org. Synth.* 6 (1988) 503.
- [5]. J. Geiss, *The century of space science*. Kluwer Academic. (2001) p. 20.
- [6]. T. Ramnial, DD. Ino, JAC. Clyburne, *Chem Commun.*, (2005) 325.
- [7]. Oscillating U-tube. Electronic document, [http://en.wikipedia.org/wiki/Oscillating U-tube](http://en.wikipedia.org/wiki/Oscillating_U-tube), accessed January 21, (2013).
- [8]. J.E. Lind Jr., J.J. Zwolenik, R.M. Fuoss, *J. Chem. Soc. Faraday Trans I.* 81 (1959) 1557.
- [9]. B. Das, N. Saha, *J. Chem. Eng. Data.* 45 (2000) 2.

CHAPTER IV:

- [1]. M. N. Roy, R. K. Das, A. Bhattacharjee, *Russian J. Phys. Chem A.* 84 (2010) 2201.
- [2]. J. M. McDowall, C.A. Vincent, *J. Chem. Soc., Faraday Trans. 1.* 70 (1974) 1862.
- [3]. M.R. J .Deck, K.J. Bird, A.J. Parker, *Aust. J. Chem.* 28 (1975) 955.
- [4]. M.N. Roy, B. Sinha, R. Dey, A. Sinha, *Int. J. Thermophy.* 26 (2005) 1549.

- [5]. M. N. Roy, R. Dewan, P. K. Roy, D. Biswas, *J. Chem. Eng. Data*, 55 (2010) 3617.
- [6]. M. N. Roy, A. Bhattacharjee, P. Chakraborti, *Thermochim. Acta*, 507–508 (2010) 135.
- [7]. C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.* 37 (2005) 37.
- [8]. A. Bhattacharjee, M. N. Roy, *Phys. Chem. Chem. Phys.* 12 (2010) 14534.
- [9]. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data*, 49 (2004) 291.
- [10]. E. B. Freyer, J. D. Hubbard, D. H. Andrews, *J. Am. Chem. Soc.* 51 (1929) 759.
- [11]. O. Kiyohara, K. Arakawa, *Bull. Chem. Soc. Jpn.* 43 (1970) 3037.
- [12]. O. Kiyohara, J. P. E. Grolier, and G. C. Benson, *Can. J. Chem.* 52 (1974) 2287.
- [13]. N. M. Murthy, S. V. Subrahmanyam, *Bull. Chem. Soc. Jpn.* 50 (1977) 2589.
- [14]. E. Ayranci, *J. Chem. Eng. Data*, 42 (1997) 934.
- [15]. D. O. Masson, *Phil. Mag.* 8 (1929) 218.
- [16]. M. N. Roy, D. Ekka, R. Dewan, *Acta Chim. Slov.* 58 (2011) 792.
- [17]. J. Clayden, N. Greeves, S. Warren, P. Wothers, *Organic Chemistry*, Oxford University Press, Oxford: New York, (2001).
- [18]. D. Denby, Vitamin C, *Chemistry Review* 5(5) University of York, New York, May (1996).
- [19]. G. Jones, M. Dole, *J. Am. Chem. Soc.* 51 (1929) 2950.
- [20]. F. J. Millero, *Chem. Rev.* 71 (1971) 147.
- [21]. F. J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.* 82 (1978) 784.
- [22]. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press: New York, London, (1970).
- [23]. M. Born, E. Wolf, 7th ed., Cambridge University Press: London, (1999).
- [24]. M. Deetlefs, K. Seddon, M. Shara, *Phys. Chem. Chem. Phys.* 8 (2006) 642.

CHAPTER V:

- [1]. R. N. Goldberg, Y. B. Tewari, *J. Phys. Chem. Ref. Data*, 18 (1989) 809.
- [2]. J. Boerio Goates, *J. Chem. Thermodyn.* 23 (1991) 403.
- [3]. R. L. Putnam, J. Boerio-Goates, *J. Chem. Thermodyn.* 25 (1993) 607.
- [4]. R. N. Goldberg, Y. B. Tewari, *J. Biol. Chem.* 264 (1989) 9897.
- [5]. R. N. Goldberg, Y. B. Tewari, J. C. Ahluwalia, *J. Biol. Chem.* 264 (1989) 9901.
- [6]. Y. B. Tewari, R. N. Goldberg, *Biophys. Chem.* 40 (1991) 59.
- [7]. G. G. Birch, S. Shamil, *J. Chem. Soc., Faraday Trans. I.* 84 (1988) 2635.

- [8]. B. Garcia, S. Ibeas, J. M. Leal, *J. Phys. Org. Chem.* 9 (1996) 593.
- [9]. S. Budavari, *The Merck Index, An Encyclopedia of Chemicals, Drugs and Biologicals*. 12th edn, Merck, Whitehouse Station, N.J. p. 1120 (1996).
- [10]. D. D. Perrin, W. L. F. Armarego, *Purification of laboratory chemicals*, 3rd ed., Pergamon Press, Oxford, (1988).
- [11]. M.N. Roy, I. Banik, D. Ekka, *J.Chem.Thermodynamics*. 57 (2013) 230.
- [12]. A. Ali, S. Khan, F. Nabi, *J. Serb. Chem. Soc.* 72 (5) (2007) 495.
- [13]. A. K. Covington, T. Dickinson, *Physical chemistry of organic solvent systems*, Plenum, New York, (1973).
- [14]. K. Belibagli, E. Agranci, *J. Solution Chem.* 19 (1990) 867.
- [15]. R. K. Wadi, P. Ramasami, *J. Chem. Soc. Faraday Trans.* 93 (1997) 243.
- [16]. T. S. Banipal, D. Kaur, D. Banipal, *J. Chem. Eng. Data.* 49 (2004) 1236.
- [17]. C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.* 37 (2005) 37.
- [18]. H. L. Friedman, C. V. Krishnan, *Water: A comprehensive Treatise*, F. Franks, Ed., Vol. 3, Chapter 1 Plenum, New York, (1973).
- [19]. A. K. Mishra, K. P. Prasad, J. C. Ahluwalia, *Biopolymers*. 22 (1983) 2397.
- [20]. T.S. Banipal, D. Kaur, G.Singh, B. S. Lark, P.K. Banipal, *Indian J. Chem.* 41A (2002) 1131.
- [21]. T.S. Banipal, G. Singh, B. S. Lark, P. K. Banipal, *J. Sol. Chem.* 30 (2001) 657.
- [22]. M. N. Roy, R. Chanda, R. K. Das, D. Ekka, *J. Chem. Eng. Data.* 56 (2011) 3285.
- [23]. F.J. Millero, *The partial molal volumes of electrolytes in aqueous solutions*, in: R.A. Horne (Ed.), *Water and Aqueous Solutions: Structure, Thermodynamics, and Transport Processes*, Wiley Interscience, New York, p. 519 (1972).
- [24]. M. N. Roy, V. K. Dakua, B. Sinha, *Int. J. Thermophys.* 28 (2007) 1275.
- [25]. A.K. Nain, D. Chand, *J. Chem. Thermodynamics*. 41 (2009) 243.
- [26]. M. N. Roy, D. Ekka, R. Dewan, *Fluid Phase Equilibria*. 314 (2012) 113.
- [27]. A. Ali, S. Hyder, S. Sabir, D. Chand, A. K. Nain, *J. Chem. Thermodyn.* 38 (2006) 136.
- [28]. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, (1970).
- [29]. M. Born, E. Wolf, *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*, 7th ed., Cambridge University Press, London, (1999).
- [30]. M. Deetlefs, K. Seddon, M. Shara, *Phys. Chem. Chem. Phys.* 8 (2006) 642.
- [31]. S. Glasstone, K. J. Laidler, H. Eyring, *The Theory of Rate Processes*, McGraw Hill, New York, (1941).

- [32]. D. Feakins, D.J. Freemantle, K.G. Lawrence, *J. Chem. Soc. Faraday Trans. 1* 70 (1974) 795.
[33]. U.N. Dash, B. Samantaray, S. Mishra, *J. Teach. Res. Chem.* 11 (2005) 87.

CHAPTER VI:

- [1]. N. H. Kim, S. V. Malhotra, M. Xanthos, *Microporous and Mesoporous Materials*. 96 (2006) 29.
[2]. N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* 37 (2008) 123.
[3]. R. A. Reich, P. A. Atewart, J. Bohaychick, J. A. Urbansky, *Lubr. Eng.* 59 (2003) 16.
[4]. D. R. MacFarlane, M. Forsyth, P. C. Howlett, J. M. Pringle, J. Sun, G. Annat, W. Neil, E. I. Izgorodina, *Acc. Chem. Res.* 40 (2007) 1165.
[5]. O. Popovych, R. P. T. Tomkins, *Nonaqueous Solution Chemistry*, Ch 4, Wiley-Interscience, New York, (1981).
[6]. C. G. Janz, R. P. T. Tomkins, *Non-aqueous Electrolytes Handbook*, Vol. 2, Academic Press, New York, (1973).
[7]. D. Aurbach, *Non-aqueous Electrochemistry*, Marcel Dekker, Inc., New York, (1999).
[8]. J. A. Krom, J. T. Petty, A. Streitwieser, *J. Am. Chem. Soc.* 115 (1993) 8024.
[9]. F. J. Millero, *In Structure and Transport Process in Water and Aqueous Solutions*, R. A. Horne, Ed., Wiley, New York, (1972).
[10]. T. Kamiyama, M. Morita, T. Kimura, *J. Chem. Eng. Data.* 49 (2004) 1350.
[11]. M. K. Pasha, J. R. Dimmock, M. D. Hollenberg, R. K. Sharma, *Biochem. Pharmacol.* 64 (2002) 1461.
[12]. C. Redlich, W. S. Beckett, J. Sparer, K. W. Barwick, C. A. Riely, H. Miller, S. L. Sigal, *Ann. Intern. Med.* 108 (1988) 680.
[13]. M. N. Roy, B. Sinha, V. K. Dakua, A. Sinha, *Pak. J. Sci. Ind. Res.* 49 (2006) 153-159.
[14]. D. D. Perrin, W. L. F. Armarego, *Purification of laboratory chemicals*, 3rd ed., Pergamon Press, Oxford, (1988).
[15]. J. E. Lind Jr., J. J. Zwolenik, R. M. Fuoss, *J. Am. Chem. Soc.* 81 (1959) 1557.
[16]. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data.* 49 (2004) 291.
[17]. E. B. Freyer, J. D. Hubbard, D. H. Andrews, *J. Am. Chem. Soc.* 51 (1929) 759.
[18]. O. Kiyohara, J. P. E. Grolier, G. C. Benson, *Can. J. Chem.* 52 (1974) 2287.
[19]. N. M. Murthy, S. V. Subrahmanyam, *Bull. Chem. Soc. Jpn.* 50 (1977) 2589.

- [20]. R. M. Fuoss, *J. Phys. Chem.* 82 (1978) 2427.
- [21]. J. Ishwara. Bhat, P. Bindu, *J. Ind. Chem. Soc.* 72 (1995) 783.
- [22]. J. M. Chakraborty, B. Das, *Z. Phys. Chem.* 218 (2004) 219.
- [23]. R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Ch. 6, pp. 130, Butterworth, London, (1959).
- [24]. R. M. Fuoss, C. A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 2387.
- [25]. D. O. Masson, *Phil. Mag.* 8 (1929) 218.
- [26]. G. Jones, M. Dole, *J. Am. Chem. Soc.* 51 (1929) 2950.
- [27]. F. J. Millero, *Chem. Rev.* 71 (1971) 147.
- [28]. B. S. Krumgalz, *J. Chem. Soc. Faraday I.* 76 (1980) 1275.
- [29]. T. M. Aminabhavi, B. Gopalakrishna, *J. Chem. Eng. Data.* 40(4) (1995) 856.
- [30]. A. K. Covington, T. Dickinson, *Physical chemistry of organic solvent systems*, Plenum., New York, (1973).

CHAPTER VII:

- [1]. T. Welton, *Chem. Rev.* 99 (1999) 2071.
- [2]. J.S. Wilkes, *J. Mol. Catal A .Chem.* 214 (2004) 11-17.
- [3]. D. Aurbach, *Non-aqueous Electrochemistry*, Marcel Dekker, Inc: New York, (1999).
- [4]. J.A. Krom, J.T. Petty, A. Streitwieser, *J. Am. Chem. Soc.* 115 (1993) 8024.
- [5]. F. Atefi, M.T. Garcia, R.D. Singer, P.J. Scammells, *Green. Chem.* 11(2009) 1595.
- [6]. T. Ramnial, D.D. Ino, J.AC. Clyburne, *Chem. Commun.* (2005) 325.
- [7]. O. Popvyh, R.P.T. Tomkins, *Nonaqueous Solution Chemistry*, Chapter 4. Wiley-Interscience: New York (1981).
- [8]. R.R. Dogonadze, E. Kalman, A. A. Kornyshev, J. Ulstrup, *The Chemical Physics of Solvation, Part B, Spectroscopy Solvation*: Elsevier Amsterdam (1986).
- [9]. A. Sinha, G. Ghosh, M.N. Roy, *J. Phys. Chem. Liqs.* 48 (2010) 62-78.
- [10]. A. Sinha, A. Bhattacharjee, M.N. Roy, *J. Disp. Sc. Techn.* 30 (2009) 1003.
- [11]. D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, third ed. pp. 299. Pergamon Press: Oxford (1988).
- [12]. J.E. Jr. Lind, J.J. Zwolenik, R.M. Fuoss, *J. Am. Chem. Soc.* 81(1959) 1557.
- [13]. F.I. El-Dossoki, *J. Mol. Liq.* 151(2010) 1.
- [14]. R.M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.* 75(2010) 16.

- [15]. R.M. Fuoss, *J. Phys. Chem.* 82 (1978) 2427.
- [16]. B. Per, *Acta. Chem. Scand. A.* 31(1977) 869.
- [17]. R.M. Fuoss, F. Accascina, *Electrolytic Conductance*, Interscience: New York (1959).
- [18]. D.S. Gill, M.S. Chauhan, *Z. Phys. Chem. NF.* 140 (1984) 139.
- [19]. J. Bhat. Ishwara, P. Bindu, *J. Ind. Chem. Soc.* 72 (1995) 783.
- [20]. J.M. Chakraborty, B. Das, *Z. Phys. Chem.* 218 (2004) 219.
- [21]. R.M. Fuoss, E. Hirsch, *J. Am. Chem. Soc.* 82(1960) 1013.
- [22]. R.A. Robinson, R.H. Stokes, *Electrolyte Solutions*, Chapter 6, pp. 130. Butterworth: London (1959).
- [23]. R.M. Fuoss, C.A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 2387.
- [24]. C. Desfrancois, V. Periquet, S. Carles, J.P. Schermann, L. Adamowicz, *J. Chem. Phys.* 239 (1998) 475.
- [25]. O. Shun-Li, W. Nan-Nan, L. Jing-Yao, S. Cheng-Lin, L. Zuo-Wei, G. Shu-Qin, *Chin. Phys. B.* 19 (2010) 123101.
- [26]. T.M. Aminabhavi, B. Gopalakrishna, *J. Chem. Eng. Data.* 40(4) (1995)856. .
- [27]. A.K., Covington, T. Dickinson, *Physical chemistry of organic solvent systems*, Plenum: New York (1973).
- [28]. P.R. Philip, C. Jolicoeur, *J. Phys. Chem.* 77(1973) 3071.
- [29]. S.S. Smith, E.D. Steinle, M.E. Meyerhoff, D.C. Dawson, *J Gen Physiol.* 114 (1999) 799.

CHAPTER VIII:

- [1]. G.J. Janz, R.P.T. Tomkins, *Non-aqueous Electrolytes Handbook*, Academic Press: New York, Vol. 1, (1972).
- [2]. M. Salomon, *J. Sol. Chem.* 22 (1993) 715.
- [3]. J. A. Krom, J. T. Petty, A. J. Streitwieser, *J. Am. Chem. Soc.* 115 (1993) 8024.
- [4]. T. Kamiyama, M. Morita, T. Kimura, *J. Chem. Eng. Data.* 49 (2004) 1350.
- [5]. M. K. Pasha, J. R. Dimmock, M. D. Hollenberg, R. K. Sharma, *Biochem. Pharmacol.* 64 (2002) 1461.
- [6]. C. G. Janz, R. P. T. Tomkins, *Non-Aqueous Electrolytes Handbook*, Academic Press: New York, Vol. 4 (1975).
- [7]. M. N. Roy, B. Sinha, V. K. Dakua, A. Sinha, *Pak. J. Sci. Ind. Res.* 49 (2006) 153.
- [8]. M. N. Roy, P. Pradhan, R. K. Das, P. G. Guha, B. Sinha, *J. Chem. Eng. Data.* 53 (2008) 1417.

- [9]. D. D. Perrin, W. L. F. Armarego, *Purification of laboratory chemicals*, 3rd ed., Pergamon Press: Oxford, (1988).
- [10]. B. Sinha, V. K. Dakua, M. N. Roy, *J. Chem. Eng. Data*. 52 (2007) 1768.
- [11]. J.A. Dean, *Lange's handbook of chemistry*, 11th ed., McGraw-Hill Book Company New York, (1973).
- [12]. A. Chatterjee, B. Das, *J. Chem. Eng. Data*. 51 (2006) 1352.
- [13]. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data*. 49 (2004) 291.
- [14]. J. E. Lind Jr, J. J. Zwolenik, R. M. Fuoss, *J. Am. Chem. Soc.* 81 (1959) 1557.
- [15]. El-Dossoki, Farid I, *J. Mol. Liquids*. 151 (2010) 1.
- [16]. R. M. Fuoss, *J. Phys. Chem.* 82 (1978) 2427.
- [17]. B. Per, *Acta Chem. Scand.* A. 31 (1977) 869.
- [18]. R. M. Fuoss, F. Accascina, *Electrolytic Conductance*, Interscience, New York, (1959).
- [19]. D. S. Gill, M. S. Chauhan, *Z. Phys. Chem. NF*. 140 (1984) 139.
- [20]. Marco Pagliai, *J. Chem. Phys.* 119 (2003) 6655.
- [21]. M. N. Roy; D. Ekka, I. Banik, A. Majumder, *Thermochimica Acta*. 547 (2012) 89.
- [22]. J. I. Bhat, P. Bindu, *J. Ind. Chem. Soc.* 72 (1995) 783.
- [23]. J. M. Chakraborty, B. Das, *Z. Phys. Chem.* 218 (2004) 219-230.
- [24]. R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Butterworth: London, Ch. 6, pp. 130. (1959).
- [25]. R. M. Fuoss, C. A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 2387.
- [26]. Y. Harada, M. Salamon, S. Petrucci, *J. Phys. Chem.* 89 (1985) 2006.
- [27]. B. S. Krumgalz, *J. Chem. Soc, Faraday Trans. I*. 79 (1983) 571.
- [28]. M. Delsignore, H. Farber, *J. Phys. Chem.* 89 (1985) 4968.
- [29]. R. M. Fuoss, E. Hirsch, *J. Am. Chem. Soc.* 82 (1960) 1013.
- [30]. A. Sinha, M. N. Roy, *Phys. Chem. Liq.* 45 (2007) 67.
- [31]. G.P. Cunningham, G.A. Vidulich, R.L. Kay, *J. Chem. Eng. Data*. 12 (1967) 336.
- [32]. A. K. Covington, T. Dickinson, *Physical chemistry of organic solvent systems*, Plenum, New York, 1973.
- [33]. M.N. Roy, L. Sarkar, R. Dewan, *Bull. Chem. Soc. Ethiop.* 24 (2010) 1.
- [34]. W. Libus, B. Chachulski and L. Fraczyk, *J. Sol. Chem.* 9(5) (1980) 355.

CHAPTER IX:

- [1]. G.J. Janz, R.P.T. Tomkins, *Non-aqueous Electrolytes Handbook*, Vol. 1 Academic Press: New York, (1972).
- [2]. D. Aurbach, *Non-aqueous Electrochemistry*, Marcel Dekker, Inc: New York, (1999).
- [3]. J. A. Krom, J. T. Petty, A. J. Streitwieser, *J. Am. Chem. Soc.* 115 (1993) 8024.
- [4]. O. Popvysh, R. P. T. Tomkins, *Nonaqueous Solution Chemistry*, Chapter 4, Wiley-Interscience: New York, (1981).
- [5]. W.Y. Wen, *Water and Aqueous Solutions. Structure, Thermodynamics, and Transport Process*, R. A. Horne, ed. Chapter 15, Wiley-Interscience: New York, (1971).
- [6]. R. R. Dogonadze, E. Kalman, A. A. Kornyshev, J. Ulstrup, *The Chemical Physics of Solvation, Part B, Spectroscopy Solvation*, Elsevier: Amsterdam, (1986).
- [7]. A. Sinha, G. Ghosh, M. N. Roy, *J. Phys. Chem. Liqs.* 48 (2010) 62.
- [8]. A. Sinha, A. Bhattacharjee, M. N. Roy, *J. Disp. Sc. and Techn.* 30 (2009) 1003.
- [9]. D. D. Perrin, W. L. F. Armarego, *Purification of laboratory chemicals*, 3rd ed., Pergamon Press: Oxford, (1988).
- [10]. I. M. Abdulagatov, N. D. Azizov, *Fluid Phase Equilibria.* 240 (2006) 204.
- [11]. J. E. Lind Jr, J. J. Zwolenik, R. M. Fuoss, *J. Am. Chem. Soc.* 81 (1959) 1557.
- [12]. F. I. El-Dossoki, *J. Mol. Liquids.* 151 (2010) 1.
- [13]. R. M. Fuoss, *Proc. Natl. Acad. Sci., U.S.A.* 75 (1978) 16,
- [14]. R. M. Fuoss, *J. Phys. Chem.* 82 (1978) 2427.
- [15]. R. M. Fuoss, F. Accascina, *Electrolytic Conductance*, Interscience: New York, (1959).
- [16]. J. I. Bhat, P. Bindu, *J. Ind. Chem. Soc.* 72 (1995) 783.
- [17]. C. G. Janz, R. P. T. Tomkins, *Non-aqueous Electrolytes Handbook*, Vol. 2, Academic Press: New York, (1973).
- [18]. R. Yamdagni, P. Kebarle, *J. Am. Chem. Soc.* 94(9) (1972) 2940.
- [19]. J. M. Chakraborty, B. Das, *Z. Phys. Chem.* 218 (2004) 219.
- [20]. R. M. Fuoss, E. Hirsch, *J. Am. Chem. Soc.* 82 (1960) 1013.

- [21]. R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Chapter 6, p 130, Butterworth: London, (1959).
- [22]. R. M. Fuoss, C. A. Kraus, *J. Am. Chem. Soc.* 55 (1933) 2387.
- [23]. P. Debye, E. Hückel, *Phys. Z.* 24 (1923) 185.
- [24]. H. Falkenhagen, E.L. Vernon, *Phil. Mag.* 14 (1932) 537.
- [25]. J. Li, F. Zhao, F. Jing, *J. Comp. Chem.* 24 (2003) 345.
- [26]. P. G. Jasien, W. J. Stevens, *J. Chem. Phys.* 84 (1986) 3271.
- [27]. M. N. Roy, D. Ekka, R. Dewan, *Fluid Phase Equilibria.* 314 (2012) 113.
- [28]. A. K. Covington, T. Dickinson, *Physical chemistry of organic solvent systems*, Plenum: New York, (1973).
- [29]. W. Libus, B. Chachulski, L. Fraczyk, *J. Sol. Chem.* 9 (5) (1980) 355.
- [30]. O. N. Kalugin, S.M. Gubsky, I.N. Vyunnik, *J. Chem. Soc. Faraday Trans.* 87 (1991) 63.

INDEX

Subject	Page no.
A	
Acetonitrile	123, 250
Apparent molal isentropic compressibility	77
Apparent molar volume	49, 155
Ascorbic acid	132
L-alanine	130
C	
Conductance	80
Covalent bonding	35
D	
N, N-dimethyl acetamide	126, 209, 231
N, N-dimethyl formamide	124, 209, 231
Dimethyl sulphoxide	127, 209, 231
Densitometry	30
Density	48
1, 3-Dioxolane	124, 251
Dipole-dipole forces	32
F	
Formamide	120, 277
Fuoss-Kraus equation	82
G	
Gibbs energy	98
D-glucose	133, 173
Glycine	129

H	
Hydrogen bond	34
I	
Interferrometry	30
Ionic association	82
Ionic attraction	31
Ion-ion interaction	45
Ion-pair formation	98
Ion-solvent interaction	42
J	
Jones-Dole equation	59
L	
Limiting equivalent conductance	89
London dispersion forces	33
Lorentz-Lorenz equation	102
M	
D-Mannitol	134
Masson equation	50
Metallic bonding	36
Methanol	122, 251
Molar refractivity	102
N	
Nicotinic acid	132
Nitromethane	119, 277
N-methylformamide	121
P	
Partial molar volumes	49

R

Refractive index	101
Refractometry	30

S

Solute – solute interactions	38
Solute – solvent interactions	38
Solution	30
Solution chemistry	30
Solvation	92
Solvent – solvent interactions	46
Stokes' law	93
D-Sucrose	135

T

Tetrabutylammonium perchlorate	137, 277
Tetrabutylammonium tetrafluoroborate	136, 277
Tetrabutylphosphonium tetrafluoroborate	136, 209
Tetrabutylphosphonium methanesulfonate	138, 231

U

Ultrasonic speed	77
------------------	----

V

Viscosity	54
L-valine	131

W

Walden's rule	93
---------------	----