

**STUDIES ON INTERACTIONS OF SOME
BIOMOLECULES AND SIMPLE
MOLECULES BY PHYSICO-CHEMICAL
PROCESSES IN LIQUID MEDIA**

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By

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MAY 2015



*Dedicated to
my mother for her
ongoing love, support
& countless prayers
and to my father who
could not see the
thesis completed*

DECLARATION

I declare that the thesis entitled "**STUDIES ON INTERACTIONS OF SOME BIOMOLECULES AND SIMPLE MOLECULES BY PHYSICO-CHEMICAL PROCESSES IN LIQUID MEDIA**" has been prepared by me under the guidance of Dr. Mahendra Nath Roy, Professor of Chemistry, University of North Bengal. No part of the thesis has formed the basis for the award of any degree or fellowship previously.

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CERTIFICATE

I certify that Mr.Pritam De has prepared the thesis entitled “**STUDIES ON INTERACTIONS OF SOME BIOMOLECULES AND SIMPLE MOLECULES BY PHYSICO-CHEMICAL PROCESSES IN LIQUID MEDIA**” for the award of Ph. D. Degree of the University of North Bengal under my guidance. He has carried out the work at the Department of Chemistry, University of North Bengal.

Mr. De holds a good academic career with excellent scores. I am very happy to mention that he was the **1st class 1st in M. Sc.(Chemistry)** of the **University of North Bengal** in **2009**. He has also shown immense caliber in qualifying **GATE -2009,2010,NET-2010(L.S.)** and **SET-2010**.

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ABSTRACT

The branch of physical chemistry involving the change in properties in the course of dissolution of one substance in another is termed as 'Solution Chemistry'. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. Solution Chemistry broadly deals with two types of approaches to estimate the extent of solvation by physico-chemical processes in liquid media. Those approaches include the studies of density, viscosity, refractive index and conductance, etc., of electrolytes 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.

Studies on interactions of molecules in solutions are very useful to acquire information on the geometrical effects and intermolecular interactions taking place in the liquid media. 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.

The exact structure of the solvent molecule is not known with certainty. The addition of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The introduction of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The interactions between solute and solute, solute and solvent, and solvent and solvent molecules and the resulting ion-solvation become predominant. The assessment of ion pairing in these systems is important because of its effect on the ionic conductivity and hence the mobility of the ions in solution. The extent of ion-solvation is dependent upon the interactions taking place between solute-solute, solute-solvent, solvent-solvent species. This explains the spurt in research in solution chemistry to elucidate the exact nature of these interactions through experimental investigations involving

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densitometry, viscometry, interferrometry, refractometry and other suitable methods and to interpret the experimental data collected.

The behaviour of electrolytes in solution depends mainly on ion-ion and ion-solvent interactions. The former interaction, in general, is stronger than the latter. Ion-ion interaction in dilute electrolytic solutions is now theoretically well understood, but the ion-solvent interaction or ion-solvation still remains a complex process

Studies on transport properties of electrolytes, along with thermodynamic and compressibility studies, give very valuable information about ion-ion and ion-solvent interactions in solutions. The influence of these ion-solvent interactions is 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.

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become increasingly clear that the majority of the solutes are significantly modified by all solvents. Conversely, the nature of strongly structured solvents, like water, is substantially modified by the presence of solutes.

Barium nitrate, Barium chloride, Lithium perchlorate, Sodium perchlorate and Potassium perchlorate, Potassium acetate, Nicotinic acid, Glycine, L-Alanine, L-Valine, 1-methyl-3-octylimidazoliumtetrafluoroborate, Tetrabutylphosphonium tetrafluoroborate, Potassium chloride, Potassium bromide and potassium iodide are used as solutes. On the other hand, Formamide, N,N-Dimethyl formamide, n-Propanol, n-Butanol, n-Pentanol, 1,3-dioxolane, Nitromethane, Dimethyl sulfoxide are considered as solvents.

The study of these solutes and solvents, in general, are of interest because of their wide range of applications in many industries ranging from pharmaceutical to cosmetic products.

In this research work additional emphasis has been given to Biomolecules being the organic molecules produced by a living organism. Amino acid is the

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monomeric unit of the Polypeptide (protein) belonging to the class of Biomolecules. Amino acids combine into peptide chains to form the building blocks of linear array of proteins. Because of the key role in biochemistry, amino acids are commonly used in nutrition supplements, fertilizers, food technology and also in the manufacture of biodegradable plastic and drugs in industry.

In order to evaluate the potential health benefits of Biomolecules information about regarding the knowledge of their absorption, metabolism and biological effects, is necessary. Pharmacological activity is often considered to describe beneficial effects of biomolecules. This translates towards recommending a diet rich in a variety of vegetables, fruits, whole grains, legumes, oils, and nuts. Many vital functions are regulated by pulsed or transient release of bioactive substances at a specific time and site in the body under physiological conditions. In drug delivery research, they have been notably used as therapeutic agents to a patient in a palatine or staggered release profile over the last two decades.

Glycine is used as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, and toiletries. Glycine serves as intermediate in the synthesis of a number of products. Glycine is also used for the treatment of schizophrenia, stroke, benign prostatic hyperplasia (BPH), and some rare inherited metabolic disorders. It is also used to protect kidneys from the harmful side effects of certain drugs used after organ transplantation as well as the liver from harmful effects of alcohol. Other uses include cancer prevention and memory enhancement.

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. Alanine 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.

Valine is used to treat amyotrophic lateral sclerosis (ALS, Lou Gehrig's disease), brain conditions due to liver disease (chronic hepatic encephalopathy,

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latent hepatic encephalopathy), a movement disorder called tardive dyskinesia, a genetic disease called McArdle's disease, a disease called spino-cerebellar degeneration, and poor appetite in elderly kidney failure patients and cancer patients.

Nicotinic acid is the vitamin B₃, plays a very important role to maintain the normal function of the digestive systems and cholesterol levels in the human body. Nicotinic acid and nicotinamide combinedly act as precursor of the coenzymes nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP). The combination of nicotinic acid and nicotinamide is clinically referred to as niacin. Insufficient niacin in the diet can cause nausea, skin and mouth lesions, anemia, headaches, and tiredness. Chronic niacin deficiency leads to a disease called pellagra.

In summary many biomolecules appear to have beneficial health effects. Much scientific research needs to be conducted before we can set in in motion to make science-based nutritional recommendations.

On the other hand, some naturally-occurring simple compounds are needed by the body for its vital activities. Each compound, with its own specific task, even in the small and often minute quantities necessary, is indispensable for important life functions.

Potassium levels can be low as a result of a disease or from taking certain medicines, or after a prolonged illness with diarrhea or vomiting. Potassium chloride is used to prevent or to treat low blood levels of potassium (hypokalemia). Potassium bromide finds uses in human and veterinary medicine as an anti-seizure medication. Potassium iodide is also used along with antithyroid medicines to prepare the thyroid gland for surgical removal, to treat certain overactive thyroid conditions (hyperthyroidism), and to protect the thyroid in a radiation exposure emergency. Potassium Acetate being a simple compound is widely used as an additive to dialysis fluids, in the manufacture of fire extinguishers and in the petroleum industry. Besides it is used as a food additive as well as a preservative and acidity regulator. Barium nitrate is a strong oxidizer which burns and

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explodes with organics. It is used in explosives, fireworks, matches, and fertilizers.

Alkali metal perchlorates are extensively used to block iodine uptake for the patients with subclinical hyperthyroidism. They are also used in the manufacture of chemical sources of energy.

Ionic liquids have potential uses as 'designer solvents' and 'green' replacements for volatile organic solvents used in reactions involving inorganic and bio-catalysis. They are also utilized as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells).

Summary of the Works Done

CHAPTER I

This chapter entails the object and utility of the research work. This mainly comprises of the choice of the main solvents and solutes used and their applications in various fields, methods of investigation and summary of the work done associated with the thesis.

CHAPTER-II

This chapter deals with the general introduction (Review of the Earlier Work) of the thesis and the background of the present work. After presenting a brief review of notable works in the field of solute-solute, solute-solvent and solvent-solvent interactions, the discussion centers on the conductance, density, viscosity, refractive index and adiabatic compressibility of different electrolytes in various liquid systems at different temperatures. The solution properties of the various electrolytes in different solvents are then elaborated and discussed, stressing the importance of the work associated with the thesis.

CHAPTER-III

This chapter states and explains the experimental section consisting of the sources, structure, purification and application of the solutes and solvents

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under investigation along with the studied electrolytes and various experimental methods employed for measurement of the transport, thermodynamic, optical and acoustic properties.

CHAPTER-IV

This chapter involves the study of solvation consequences of α -Amino Acids in aqueous ionic liquid solution probed by physico-chemical approach. The apparent molar volume (ϕ_v), viscosity B -coefficient, molar refraction (R) and adiabatic compressibility (ϕ_k) of Glycine, L-Alanine, and L-Valine have been studied in 0.001, 0.003, 0.005 mol-dm⁻³ aqueous Tetrabutylphosphonium Tetrafluoroborate (Bu₄PBF₄) solutions at 298.15 K from the values of density (ρ), viscosity (η), refractive index (n_D) and speed of sound (u) respectively. The limiting apparent molar volumes (ϕ_v^0), experimental slopes (S_V^*) are obtained from the Masson equation and have been interpreted in terms of solute-solvent and solute-solute interactions respectively. Jones-Dole equation were employed to analyse the viscosity data and the interpretation of the derived parameters A and B have also been carried out in terms of solute-solute and solute-solvent interactions in the solutions respectively. Molar refractions (R) have been determined with the help of Lorentz-Lorenz equation. Limiting apparent molar adiabatic compressibilities (ϕ_k^0) of three amino acids at infinite dilution were evaluated and discussed.

CHAPTER-V

This chapter deals with the physico-chemical study of solution behaviour of alkali metal perchlorates prevailing in N, N- Dimethyl Formamide with the manifestation of ion solvation consequences. Physico-chemical analysis on densities (ρ), viscosities (η) and speed of sound (u) and electrolytic conductivities (Λ) of Lithium Perchlorate, Sodium Perchlorate and Potassium Perchlorate in pure N,N-Dimethyl Formamide have been performed at 298.15K. Limiting molar conductance (Λ_0), Association constant (K_A) and co-sphere diameter (R) for ion-pair formation have been obtained from Fuoss conductance

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equation. Masson equation is used to determine the limiting apparent molar volume (ϕ_V^0) and experimental slope (S_V^*) to study the ion-solvent and ion-ion interactions respectively. The derived parameters A and B obtained from Jones-Dole equation represent ion-ion and ion-solvent interactions respectively. The u -values have been used to determine adiabatic compressibility (β_s) and limiting apparent molar adiabatic compressibility (ϕ_K^0).

CHAPTER-VI

This chapter describes physico-chemical study of some Bio-active solutes in aqueous Potassium Acetate Solution. The apparent molar volume (ϕ_V), viscosity B -coefficient, molar refraction (R) and adiabatic compressibility (ϕ_K) of Glycine, L-Alanine, and L-Valine have been determined in 0.01, 0.03, 0.05 mol·dm⁻³ aqueous Potassium Acetate solutions at 298.15 K from the measurement of density (ρ), viscosity (η), refractive index (n_D) and speed of sound (u) respectively. Masson equation was employed for the limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) to interpret the solute-solvent and solute-solute interactions respectively. The calculations of Molar refractions (R) have been done using the Lorentz-Lorenz equation. 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. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) of these amino acids at infinite dilution were examined from the u values.

CHAPTER-VII

This chapter includes probing solute-solvent interactions of some bio-active solutes in aqueous Barium Nitrate solution on the basis of physico-chemical contrivances. Apparent molar volume (ϕ_V), molar refraction (R), viscosity B -coefficient and adiabatic compressibility (ϕ_K) of some Bio-active solutes such as Glycine, L-Alanine, and L-Valine have been measured in 0.01,

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0.03, 0.05 mol·dm⁻³ aqueous Barium Nitrate solutions at 298.15 K. Masson equation was employed for the experimental slopes (S_V^*) and limiting apparent molar volumes (ϕ_V^0) to interpret the solute-solvent and solute-solute interactions respectively. Molar refractions (R) have been calculated using the Lorentz-Lorenz equation. Jones-Dole equation was used to derive parameters A and B to interpret the interactions. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) at infinite dilution were examined from the sound speed values.

CHAPTER-VIII

This chapter represents an exploration of solution behaviour of potassium halides in mixtures of nicotinic acid and water at 298.15, 308.15 and 318.15 K by physico-chemical approach. Apparent molar volume (ϕ_V) and viscosity B-coefficients were estimated for potassium chloride, potassium bromide and potassium iodide in aqueous mixture of nicotinic acid from measured solution density (ρ) and viscosity (η) at 298.15, 308.15 and 318.15 K at various electrolyte concentrations. The experimental density data were evaluated by Masson equation and the derived data were interpreted in terms of ion-solvent and ion-ion interactions. The viscosity data has been investigated using Jones-Dole equation and the derived parameters, B and A , have also been interpreted in terms of ion-solvent and ion-ion interactions respectively. The structure-making or breaking capacity of the electrolyte under investigation has been discussed in terms of $\text{sign}(\partial\phi_V^0/\partial T)_p$.

CHAPTER-IX

This chapter corresponds to a study on interactions of some Metal Perchlorates prevailing in Formamide by physico-chemical approach. The physico-chemical properties, electrolytic conductivities (Λ), densities (ρ), viscosities (η) and speed of sound (u) of Lithium Perchlorate, Sodium Perchlorate and Potassium Perchlorate have been evaluated in pure Formamide at 298.15 K. Association constants (K_A), Limiting molar conductances (Λ_0), and

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co-sphere diameter (R) for ion-pair formation have been obtained from Fuoss conductance equation. Viscosity B-coefficient, apparent molar volume (ϕ_v) and apparent molar adiabatic compressibility (ϕ_k) have been calculated from the measurement of viscosity (η), density (ρ) and speed of sound (u) respectively. Masson Equation has been employed to inspect the ion-solvent and ion-ion interactions from the values of limiting apparent molar volume (ϕ_v^0) and experimental slope (S_v^*) respectively. Ion-ion and ion-solvent interactions have been interpreted with the help of the derived parameters A and B obtained from Jones-Dole equations respectively. The limiting apparent molar adiabatic compressibility (ϕ_k^0) and adiabatic compressibility (β_s) have been assessed using the u values.

CHAPTER-X

This chapter includes the concluding remarks on the works associated with the thesis.

PREFACE

This dissertation is submitted for the degree of Doctor of Philosophy at the University of North Bengal. The work in this thesis entitled "**STUDIES ON INTERACTIONS OF SOME BIOMOLECULES AND SIMPLE MOLECULES BY PHYSICO-CHEMICAL PROCESSES IN LIQUID MEDIA**" was conducted under the supervision of Prof. M. N. Roy in the Department of Chemistry, University of North Bengal after being initiated in September 2011.

The atmosphere and environment here were far above my expectations. Aside from learning new skills and applications, the whole research period has been a great opportunity for me to meet and interact with renowned scientists from different parts of the world. From a chemistry perspective, I have had the chance to broaden my horizons whilst participating in the seminar and convention across the country. I was fortunate enough to publish my works in International Journals of repute.

The work is a serious attempt to explore molecular interactions prevailing in liquid media from the studies based on volumetric, viscometric, conductometric, refractometric and acoustic measurements. 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 sole responsibility of any unpremeditated oversights and errors, which might have crept in spite of serious precautions.

The knowledge that I have acquired is practical, rather than theoretical. I feel that the experience I am having will definitely be helpful for my future career in the chemistry domains. I hope that I will be given more challenges in my life so that the knowledge that I have earned during my work can be put into action in the future.

It is not only my privilege whilst writing this Ph.D. thesis containing the result of my research work, but also a great life experience for me.

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Pursuing a Ph.D. degree is a both painful and enjoyable experience. It is just like climbing a high peak, step by step, accompanied with bitterness, hardships, frustration, encouragement and trust and with kind help of so many people. When I found myself at the top enjoying the beautiful scenery, I realized that it was, in fact, the teamwork that got me there. Though it will not be enough to express my gratitude in words to all those people who helped me, I would still like to give my thanks to all these people.

At the outset, I feel extremely excited and privileged enough whilst expressing my inner sentiments and utmost gratitude to my favourite teacher of all times and my honorific supervisor, Dr. Mahendra Nath Roy, Professor of Physical Chemistry, University of North Bengal, Darjeeling. I am profoundly indebted to him for his constant guidance, priceless suggestions, inspirations, constructive criticism, strong motivation, constant encouragement and sympathetic consideration. His subtle guidance, advices have always helped me to think positively and remain optimistic. The fruitful scientific discussions with him furthered my keen interest as well as the freedom to pursue an interesting research. His presence in my life is very significant at times and will remain so throughout my life. I have learned a lot from him, without his help I could not have finished my dissertation successfully.

I also express my profound sense of gratitude to the respected faculty members and thanks to the non-teaching staff, Department of Chemistry, University of North Bengal for their helpful assistance and continual inspiration during the course of my research work. I am grateful to the University authority for providing library and laboratory amenities, especially Computer Centre and University Scientific Instrumentation Centre (USIC) for helping me in my research.

My thanks are extended to several labmates at the Department of Chemistry, with whom I have had longer or shorter enlightening discussions about the various topics of this work. I am thankful to Mr. Partha Sarathi Sikdar, Mrs. Rajani Dewan and Mr. Deepak Ekka for their whole-hearted co-operation during my research work.

It is impossible for me to express my gratitude to those authors of monographs, articles etc. from which I have collected information related to my research work. I can only hope that some measure of my gratitude is expressed by the references I have cited to their works.

I would also like to record my thankfulness to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi [F. 540/12 DRS/2013 (SAP-I)] for financial and instrumental assistance in connection with my research work.

I owe a lot to my parents, who encouraged and helped me at every stage of my personal and academic life and longed to see this achievement come true. I deeply miss my father Late Pijush Kanti De, who is not with me anymore in this world to share this joy. My mother, Mrs. Sandhya Dey, being a teacher by profession, has been a resource person for me and a great support at every stage of my work for her ceaseless inspiration, sincere help, constructive suggestion and whole-hearted cooperation in order to complete the work associated with my thesis and keeping me aloof from the family responsibilities. I am also thankful to my beloved sister Mrs. Poulomi Dey for enough encouragements and supports for me throughout this experience.

Finally, I thank my God, for letting me through all the difficulties. I have experienced Your guidance day by day. You are the one who let me finish my degree. I will keep on trusting You for my future. Thank you, Lord.

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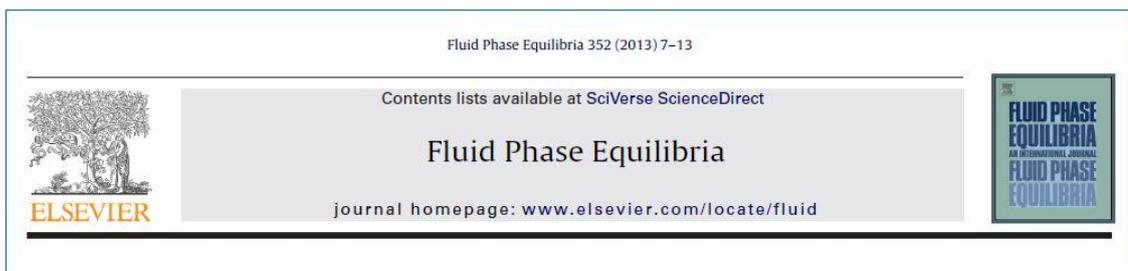
ATTENDED

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LIST OF PUBLICATION(S) /COMMUNICATION (S)

1. **Study of Solvation Consequences of α -Amino Acids in Aqueous Ionic Liquid Solution Probed by Physico-chemical Approach**

Fluid Phase Equilibria **2013**, 43, 7.

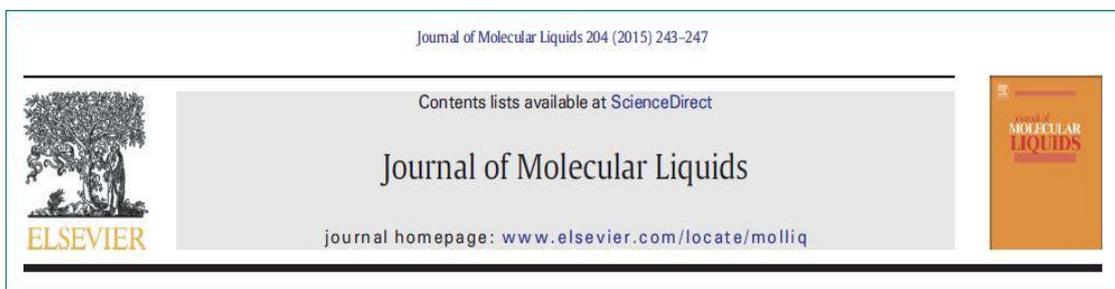
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2. **Physico-chemical Study of Solution Behaviour of Alkali Metal Perchlorates Prevailing in N, N- Dimethyl Formamide with the Manifestation of Ion Solvation Consequences**

Journal of Molecular Liquids **2015**, 204, 243.

(INCLUDED IN THESIS)



3. **Physico-chemical Study of Some Bio-active Solutes in Aqueous Potassium Acetate Solution**

Journal of Teaching and Research in Chemistry **2012**, 19(2), 65.

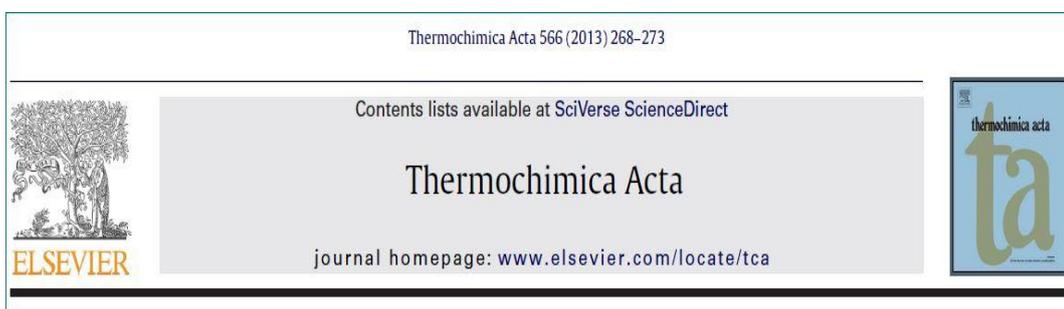
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4. **Probing Solute-solvent Interactions of Some Bio-active Solutes in Aqueous Barium Nitrate Solution on the Basis of Physico-chemical Contrivances**

Thermochimica Acta **2013**, 566, 268.

(INCLUDED IN THESIS)



5. **Study on Interactions of Potassium Halides Prevailing in Aqueous Nicotinic Acid solution by Physico-chemical Approach**

Communicated.

(INCLUDED IN THESIS)

6. **Study on Interactions of Some Metal Perchlorates Prevailing in Formamide by Physico-chemical Approach**

Indian Journal of Advances in Chemical Science, **2015**, 3(2), 147.

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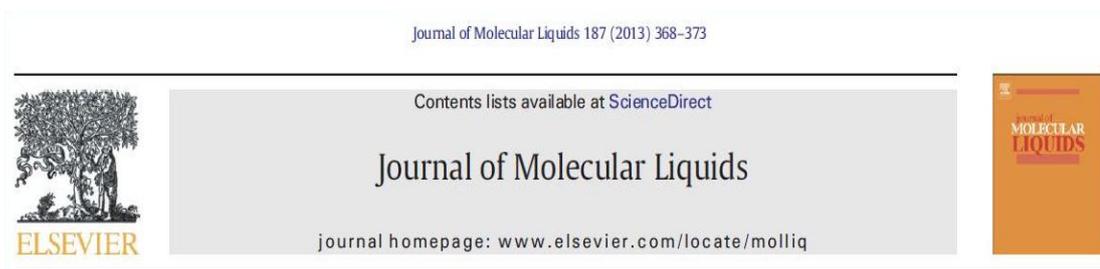
7. **Study of Solvation Behavior of Some Biologically Active Compounds in Aqueous Barium Chloride Solution**

J. Chem. Eng. Data **2013**, 58, 1662.



8. **Physico-chemical study of lithium perchlorate in alkanols (C3–C5) with the manifestation of solvation consequences**

Journal of Molecular Liquids **2013**, 187, 368.



9. **Probing Subsistence of Diverse Interplay of an Imidazolium Based Ionic Liquid Insight into Industrially Significant Solvent Environments**

Indian Journal of Advances in Chemical Science **2014**, 3, 64.



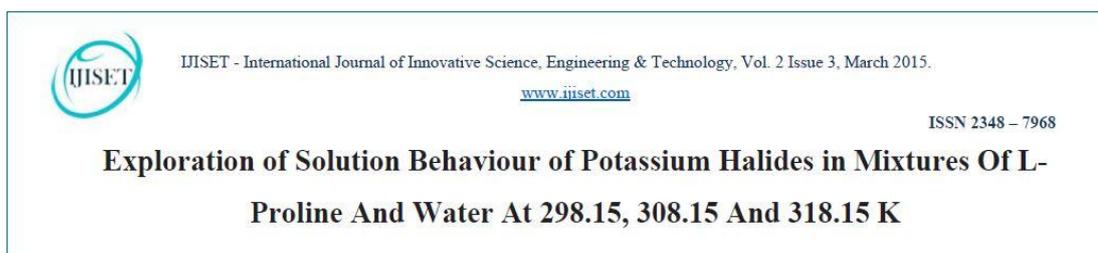
Available online at
www.ijacskros.com

**Indian
Journal of Advances in
Chemical Science**

Indian Journal of Advances in Chemical Science 3 (2014) 64-76

10. **Exploration of Solution Behaviour of Potassium Halides in Mixtures of L-Proline and Water At 298.15, 308.15 And 318.15 K**

International Journal of Innovative Science, Engineering & Technology Advances in Chemical Science **2015**, 2(3), 763.



APPENDIX B

LIST OF SEMINARS/SYMPOSIUMS/CONFERENCES ATTENDED

1. Science Academies' Lecture Workshop on "Recent Trends in Chemistry" organized by the Department of Chemistry, University of North Bengal on November 11-12, 2011.
2. Science Academies' Lecture Workshop on "Modern Trends in Chemistry and Chemistry Education" organized by the Department of Chemistry, University of North Bengal on November 22-23, 2012.
3. Workshop on Diversities and Frontiers in Chemistry jointly organized by the Department of Chemistry, Jadavpur University, Kolkata and Department of Chemistry, University of North Bengal on August 7-8, 2013.
4. 50th Annual Convention of Chemist 2013 organized by Indian Chemical Society held at the Department of Chemistry & Centre for Advanced Studies in Chemistry, Panjab University, Chandigarh on December 4-7, 2013.
5. Frontiers in Chemistry-2015 organized by the Department of Chemistry, University of North Bengal on February 17-18, 2015.

CHAPTER-I

FUNDAMENTAL OF THE RESEARCH WORK

1.1. Object and Utility of The Research Work

Life set in around 4 million years ago. Small cells or so called microorganisms could strap up the energy from inorganic source or sunlight to construct small biomolecules. They gave the impression to obey the laws of Physics and Chemistry yet constitute the diverse living biota. They actually comprised the dynamic and vibrant living world. Thus it becomes very intriguing to be acquainted with these seemingly lifeless molecules, their structure in order to make out how they formed and contribute to the functioning of the living world.

A biomolecule is an organic molecule produced by a living organism, primarily consisting of carbon, hydrogen and oxygen and to lesser extent phosphorus and sulfur. Therefore all living organisms are essentially made up carbon, hydrogen and oxygen. Other elements sometimes are incorporated but are much less common. All these biomolecules work together in an interrelated fashion to form an organism. They include large macromolecules such as proteins, polysaccharides, lipids and nucleic acids, as well as small molecules such as primary metabolites, secondary metabolites and natural products.

Amino acid is the monomeric unit of the Polypeptide (protein). They are molecules that contain an amine group, a carboxylic acid group and a side-chain varying between different amino acids. Since the carboxylic acid group has a proton available for binding with the electrons of another atom, and the amino group has electrons available for binding with a proton from another atom, the amino acid behaves as an acid and a base simultaneously. Carbon, hydrogen, oxygen, and nitrogen are the key elements of an amino acid. In biochemistry the term usually refers to *alpha-amino acids* being important in metabolism. Amino acids combine into peptide chains to form the building blocks of linear array of proteins. Because of the key role in biochemistry, amino acids are commonly

used in nutrition supplements, fertilizers, food technology and also in the manufacture of biodegradable plastic and drugs in industry.

Glycine is used as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, and toiletries. Glycine becomes intermediate in the synthesis of a number of products. Glycine is used for the treatment of schizophrenia, stroke, benign prostatic hyperplasia (BPH), and some rare inherited metabolic disorders. It is also used to protect kidneys from the harmful side effects of certain drugs used after organ transplantation as well as the liver from harmful effects of alcohol. Other uses include cancer prevention and memory enhancement.

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. Alanine 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.

Valine is used to treat amyotrophic lateral sclerosis (ALS, Lou Gehrig's disease), brain conditions due to liver disease (chronic hepatic encephalopathy, latent hepatic encephalopathy), a movement disorder called Tardive dyskinesia, a genetic disease called McArdle's disease, a disease called Spino-cerebellar degeneration, and poor appetite in elderly kidney failure patients and cancer patients.

Nicotinic acid is the vitamin B₃, plays a very important role to maintain the normal function of the digestive systems and cholesterol levels in the human body. Nicotinic acid and nicotinamide combinedly act as precursor of the coenzymes nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP). The combination of nicotinic acid and nicotinamide is clinically referred to as niacin. Insufficient niacin in the diet can cause nausea, skin and mouth lesions, anemia, headaches, and tiredness. Chronic niacin deficiency leads to a disease called pellagra.

In summary numerous biomolecules appear to have beneficial health effects. Much scientific research needs to be conducted before we can set in motion to make science-based nutritional recommendations.

On the other hand, some naturally-occurring simple compounds are needed by the body for its vital activities. Each compound, with its own specific task, even in the small and often minute quantities necessary, is indispensable for important life functions.

Potassium levels can be low as a result of a disease or from taking certain medicines, or after a prolonged illness with diarrhea or vomiting. Potassium chloride is used to prevent or to treat low blood levels of potassium (hypokalemia). Potassium bromide finds uses in human and veterinary medicine as an anti-seizure medication. Potassium iodide is also used along with antithyroid medicines to prepare the thyroid gland for surgical removal, to treat certain overactive thyroid conditions (hyperthyroidism) and to protect the thyroid in a radiation exposure emergency. Potassium Acetate being a simple compound is widely used as an additive to dialysis fluids, in the manufacture of fire extinguishers and in the petroleum industry. Besides it is used as a food additive as a preservative and acidity regulator. Barium nitrate is a strong oxidizer which burns and explodes with organics. It is used in explosives, fireworks, matches, and fertilizers.

Alkali metal perchlorates are extensively used to block iodine uptake for the patients with subclinical hyperthyroidism. They are also used in the manufacture of chemical sources of energy.

Ionic liquids have potential uses as 'designer solvents' and 'green' replacements for volatile organic solvents used in reactions involving inorganic and bio-catalysis. They are also utilized as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells).

Physico-chemical investigation of density and viscosity of liquids, measurements of refractive index and adiabatic compressibility offer insight into the molecular arrangement in liquids to make out the thermodynamic properties in liquid media. Physico-chemical processes help us to be aware of many

practical problems regarding mass transport, energy transport, heat transport and fluid flow. Acoustic properties have been the subject of widespread research activity to study the intermolecular interactions in ion-solvent systems. The non-aqueous systems have been of enormous importance to the technologist owing to the occurrence of chemical processes occur in these systems.

Study on interactions by physico-chemical processes play a crucial role to interpret the intermolecular interactions among mixed components at microscopic and macroscopic levels. Such interactions thermodynamic, transport, acoustic and optical studies on binary and ternary solvent systems are highly useful.

The refractive index is a thermodynamic property for a pure fluid depends upon temperature and pressure. The refractive index, n_D , is defined as the ratio of velocity of light in the vacuum to the velocity of light in the medium and, therefore, for a fluid it is greater than unity. For liquids, it is greater than 1 but for gases, the refractive index is very close to unity. The refractive index or refractivity (n_D) can be easily measured by the sodium D line of a simple refractometer at a temperature of interest. The refractive index is used to estimate the physico-chemical properties of solvent/solution mixtures. Properties such as heat capacity, critical constants and transport properties are related to the refractive index.

Rheology is the branch of Science [1] that studies material flow and deformation, and is implicated in the mixing and flow of medicinal formulations and cosmetics and is increasingly applied to the analysis of the viscous behaviour of many pharmaceutical products, [2-6] and to set up their stability and even bio-availability.

The molecular and rheological behaviour of a formulation [7] can effect aspects such as patient acceptability, since it has been well established that density and viscosity both influence the rate of absorption of such products in the body [8, 9]. The study of viscous synergy and antagonism is important in connection with the rheological perspective, since many products are formulated with more than one component in order to yield the desired physical structure and properties [10]. Synergy and antagonism provide the mutual decrement or

enhancement of the biological, pharmaceutical activity of different components of a given mixture.

The inspection of the viscous behaviour of pharmaceuticals, foodstuffs, cosmetics or industrial products, etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the products. The system [11, 12] is said to lack interaction if the total viscosity of the system is equal to the sum of the viscosities of each component considered separately.

In solution chemistry, the assessment of ion-solvent interactions can be known thermodynamically and also from the measurement of viscosity B – coefficient, partial molar volumes, and limiting ionic conductivity studies. Suitable values of ion-solvent interactions help the chemists to choose solvents that will enhance (i) the solubility of minerals in leaching operations (ii) the rates of chemical reactions, or (iii) reverse the direction of equilibrium reactions.

The implications of the investigation of reaction in non-aqueous and mixed liquid media have been summarized by Popovych, [13] Bates, [14] Meck, [15] Franks, [16] Parker, [17] Criss and Salomon, [18] Marcus [19] and others [20-22]. The studies on interactive properties of aqueous solutions have provided sufficient information on the thermodynamic aspects 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 [23].

On the other hand, 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 the organic solvents transcends the traditional boundaries of organic, inorganic, physical, analytical and electrochemistry [24].

Studies of transport properties of electrolytes with thermodynamic and acoustic studies, give very valuable information about molecular interactions in solutions [25, 26]. The changes in ionic solvation have important applications in diverse areas such as studies of reaction mechanisms, organic and inorganic synthesis, non-aqueous battery technology and extraction [27].

Fundamental research on non-aqueous electrolyte solutions has catalysed their wide technical applications in many fields. 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 successes [28-30].

Knowledge of ion-solvent interactions in non-aqueous solutions is extremely important in several practical problems concerning energy transport, heat transport, mass transport and fluid flow. Conversely, the nature of strongly structured solvents like water is substantially modified by the presence of solutes [31].

Exploration of a series of investigations have been performed on the conductometric, volumetric, viscometric, refractometric and interferometric behaviour to investigate the chemical nature and the structure of solutes and solvents and their specific and mutual interactions in the liquid media.

1.2. Scope and Importance of Physico-Chemical Parameters:

The study on interactions by physico-chemical processes involves the departure from ideal behaviour of some physical properties such as viscosity, density, volume, speeds of sound, refractive index etc [32, 33] in liquid media. Density of liquid mixtures and volumetric properties like excess molar volume are indispensable for practical as well as theoretical aspects. The positive values of excess molar volume (V^E) imply the dominance of dispersion forces [34, 35] while the negative values hint specific interactions [35, 36] between the mixing components in the mixture. The negative (V^E) values may arise due to the difference in the dielectric constants of the components of the liquid mixtures. The negative (V^E) values point towards explicit interactions such as intermolecular hydrogen bonding between the mixing components and also the interstitial accommodation of the mixing components owing to the difference in molar volumes.

Viscosity data has become a valuable tool to obtain information regarding the nature and strength of interactions operating within and between the unlike molecules. Recently the enhancement of computer simulation of molecular dynamics has led to noteworthy improvement towards a successful molecular theory of transport properties in fluids and a proper consideration of molecular

motions and interaction patterns in non electrolyte solvent mixtures involving both hydrogen bonding and non hydrogen bonding solvents [36, 37].

Deviations in molar refractivity and refractive index also provide important information about molecular interactions prevailing in solution. Positive and negative values of either ΔR or Δn_D have enormous implication to make out the molecular interactions in liquid media.

Physico-chemical processes like dissociation or association can be employed to explore structure and interactions of molecules from the values of adiabatic compressibility with the help of acoustic measurements. It can also be used for the test of a variety of solvent theories and statistical models being quite sensitive to changes in ionic concentrations as well as useful in illuminating the solute-solvent interactions.

The study on interactions of bio-molecules plays a pivotal role in the elucidation of thermodynamic properties of physico-chemical processes taking place in living cells. The noteworthy illustrations of interaction between drug and bio-macromolecules are namely the process of protein binding, drug transport, anaesthesia etc. Physico-chemical properties of drugs control the transport in biological cells and membranes. One of the well-premeditated attempts is the study of molecular interactions in fluids by thermodynamic methods as because the thermodynamic parameters are convenient for the elucidation of intermolecular interactions in liquid media. Moreover, the study of thermodynamic properties of drug in a suitable medium can be synchronized to its therapeutic effects [38, 39].

These facts therefore encouraged to embark on the study of different binary or ternary systems. Besides, the excess properties derived from experimental density, viscosity, refractive index and speeds of sound data alongside the interpretation of the nature and strength of intermolecular interactions facilitate the testing and development of several conjectures and surmises in liquid media.

1.3. Solutes and Solvents Used

During the course of research work the study was made on Barium nitrate, Barium chloride, Lithium perchlorate, Sodium perchlorate and Potassium perchlorate, Potassium acetate, Nicotinic acid, Glycine, L-Alanine, L-Valine, 1-methyl-3-octylimidazolium tetrafluoroborate, Tetrabutyl phosphonium tetrafluoroborate, Potassium chloride, Potassium bromide and Potassium iodide as solutes and Formamide, N,N-Dimethyl formamide, n-Propanol, n-Butanol, n-Pentanol, 1,3-dioxolane, Nitromethane, Dimethyl sulfoxide as solvents.

1.4. Methods of Investigations

The interactions and equilibria of ions in aqueous and non-aqueous media in different concentration ranges are of enormous importance to the theoretician and technologist as most of the chemical processes occur in these systems. The structures and existence of free ions, solvated ions, and ion pairs depend on concentration regions.

The occurrence of ion-solvent, ion-ion, antagonism, synergy, solvent-solvent interactions is intriguing. It is desirable to attack this problem using different experimental techniques. We have, therefore, employed five important methods, namely, conductometry, densitometry, viscometry, refractometry and ultrasonic interferometry and to probe the problem of solvation phenomena. Various techniques [40] have been employed to study the solvation structure, ion-solvent interactions and dynamics of ions by physico-chemical processes in aqueous and non-aqueous liquid media.

The transport properties are investigated using the conductance data, specially the conductance at infinite dilution. Conductance data obtained as a function of concentration are used to explore the ion-association with the help of appropriate equations.

Thermodynamic properties, like apparent molar volumes, partial molar expansibility, etc. obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution. The compressibility, a second derivative of Gibbs energy, is also a

susceptible indicator of molecular interactions and provides useful information in such cases where partial molar volume data alone cannot provide an unambiguous interpretation of these interactions.

The change in solvent viscosity by the addition of electrolyte solutions is accredited to interionic and non-solvent effects. The viscosity B -coefficients gives an agreeable interpretation of ion-solvent interactions such as the effects of solvation and structure-breaking or structure-making capacity of the solutes [41].

To investigate thermodynamic properties refractive index, molar refractivity and deviation in both have been computed. Various acoustical parameters have been derived in carrying out the investigation.

References

1. J.V. Herraiez, R. Belda, *J. Solution Chem.* **2004**, *33*, 117.
2. C.K. Zeberg-Mikkelsen, S.E. Quinones-Cisneros, S.H. Stenby, *Fluid Phase Equil.* **2002**, *194*, 1191.
3. R. Shukla, M. Cheryan, *Journal of Membrane Science* **2002**, *198*, 104.
4. M.J. Assael, N.K. Dalaouti, I. Metaxa, *Fluid Phase Equil.* **2002**, *199*, 237.
5. J.M. Resa, C. Gonzalez, J. Lanz, *Journal of Food Engineering* **2002**, *51*, 113.
6. M. Garcia-Velarde, *Revista Espanola de Fisica* **1995**, *9*, 12.
7. S.T. Young, *Phil. Mag.* **1882**, *33*, 153.
8. C. Fauli-Trillo, *Tratado de Farmacia Galencia*, Ed. S.A. Lujan, Madrid, **1993**.
9. J. Swarbrik, J.C. Boyland, *Encyclopedia of Pharmaceutical Technology*, Marcel Dekker, New York, **1993**.
10. E.R. Morris, *Food Gels - Applied Science*, Elsevier, London, **1984**.
11. J. Pellicer, *Sinergia Viscosa*, Valencia, Spain, October **1997**.
12. G. Copetti, R. Lapasin, E.R. Morris, *Proceedings of the 4th European Rheology Conference*, Seville, Spain, **1994**, 215.
13. O. Popovych, *Crit. Rev. Anal. Che.* **1973**, *1*, 73.
14. R.G. Bates, *Solute-Solvent Interactions*, Eds. J.J. Coetzee, C.D. Ritchie, Marcel Dekker, New York, **1969**.
15. D.K. Meck, *The Chemistry of Non-Aqueous Solvents*, Ed. J.J. Lagowski, Academic, New York, Vol-1, **1966**, Ch. 1.
16. F. Franks, *Physico-Chemical Processes in Mixed Aqueous Solvents*, Heinemann Educational Books Ltd., **1967**.
17. A.J. Parker, *Electrochim. Acta* **1976**, *21*, 671.
18. C.M. Criss, M. Salomon, *J. Chem. Edu.* **1976**, *53*, 763.
19. Y. Marcus, *Ion Solvation*, Wiley, Chinchester, **1986**.
20. R.R. Dogonadze, E. Kalman, A.A. Kornyshev, J. Ulstrup, *The Chemical Physics of Solvation*, Elsevier, Amsterdam, **1988**.
21. O. Popovych, R.P.T. Tomkins, *Non-Aqueous Solution Chemistry*, John Wiley and Sons, New York, **1981**.
22. E.J. King, *Acid-Base Equilibria*, Pergamon, Oxford, **1965**.

23. G.S. Kell, C.M. Daries, J. Jarynski, *Water and Aqueous Solutions, Structure, Thermodynamics and Transport Process*, Ed. R.A. Horne, Wiley, **1972**, Ch. 9 & 10.
24. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, **1973**.
25. A. Chandra, B. Bagchi, *J. Phys. Chem. B.* **2000**, *104*, 9067.
26. G. Atkinson, R. Garney, M.J. Taft, *Hydrogen Bonded Solvent Systems*, Eds. A.K. Covington, P. Jones, Taylor and Francis, London, **1968**.
27. W.E. Waghorne, *Chem. Soc. Rev.* **1993**, *22*, 285.
28. Y. Marcus, *Ion Properties*, Dekker, New York, **1997**.
29. A. Masquez, A Vargas, P.B. Balbuena, *J. Electron. Soc.* **1998**, *45*, 3328.
30. A.F.D. Namor, M.A.L. Tanco, M. Solomon, *J. Phys. Chem.* **1994**, *98*, 11796.
31. K. Gunaseelau, S. Dev, K. Ismail, *Indian. J. Chem.* **2000**, *39A*, 761.
32. M. Iqbal, R.E. Verral, *Can. J. Chem.* **1989**, *67*, 727.
33. E.P. Georgios, I.Z. Ioannis, *J. Chem. Eng. Data* **1992**, *37*, 167.
34. J.N. Nayak, M.I. Aralaguppi, T.J. Aminabhavi, *J. Chem. Eng. Data* **2003**, *48*, 1489.
35. K. Hsu-Chen, T. Chein-Hsiun, *J. Chem. Eng. Data* **2005**, *50*, 608.
36. A. Ali, A.K. Nain, *J. Pure. Appl. Ultrasonics* **2000**, *22*, 10.
37. J.H. Dymond, *Chem. Soc. Rev.* **1985**, *14*, 317.
38. E.L. Herric, J.G. Brewer, *J. Chem. Eng. Data* **1969**, *14*, 55.
39. P.K. Gessner, M.P. Shakarjian, *J. Pharm. Exptal. Therap.* **1985**, *32*, 235.
40. H. Ohtaki and T. Radnai, *Chem.Rev.* **1993**, *93*, 1157.
41. W.M. Cox and J.H. Wolfenden, *Proc. Roy, Soc., London*, **1934**, *145A*, 475.

CHAPTER-II

GENERAL INTRODUCTION (REVIEW OF THE EARLIER WORKS)

2.1. Solution Chemistry

Solution chemistry is the branch of physical chemistry dealing with the change in properties arising out of course of dissolution of one substance in another. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent.

Solution Chemistry broadly deals with different types of approaches to estimate the extent 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, 2]. Another approach 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 [3].

Study on interaction of chemico-physical properties of solutions is very useful to attain information on the geometrical effects and intermolecular interactions in the liquid media. The knowledge of the thermodynamic properties is indispensable for the proper scheming of industrial processes involved in the theoretical and applied areas of research.

The mixing of different solute or solvent with another solvent/solvent mixtures brings about the deviation from ideality. This deviation from ideality is expressed in terms of several thermodynamic parameters, by excess properties in case of liquid-liquid mixtures and apparent molar properties in case of solid-liquid mixtures. These thermodynamic properties of solvent mixtures corresponds to the difference between the actual property and the property if the system behaves ideally and thus are useful in the study of molecular interactions and arrangements.

Thermodynamic properties reflect the interaction that take place between solute-solute, solute-solvent and solvent-solvent species. The addition of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. Ion-solvation is dependent upon the interactions

taking place between solute-solvent, solute-solute and solvent-solvent species. The extent of ion-pairing in these systems is significant owing to its effect on the ionic mobility and hence on the ionic conductivity of the ions in liquid medium. These phenomenon thus covers the path for research in solution chemistry to explicate the nature of interaction through experimental studies involving densitometry, viscometry, refractometry interferometry and other suitable methods and to interpret the experimental data obtained.

2.2. Several Types of Forces of Attraction

Intermolecular forces play important roles in solutions. The forces holding molecules together are generally called intermolecular forces. Intermolecular forces of attraction operate between neighbouring particles (atoms, molecules or ions). In a molecule the forces binding atoms are attributable to chemical bonding. The bond-energy is the energy required to break a bond. For example the average bond-energy for O-H bonds in water is 463 kJ/mol. The energy required to break molecules apart is much smaller than a typical bond-energy; but intermolecular forces play vital 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.

In general, intermolecular forces can be divided into several categories. The prominent types are as follows.

a. **Covalent Bonding:** Covalent bonding entails the sharing of electrons between two atoms. These solids are hard, brittle, and have high melting points. Covalent bonding holds atoms tighter than ionic attraction. Covalent is really intramolecular force rather than intermolecular force.

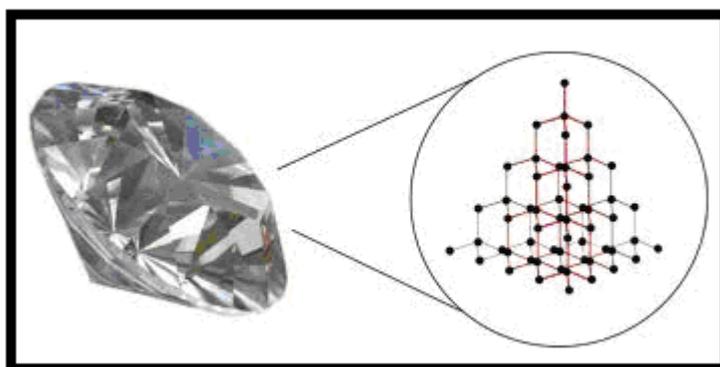


Figure 1. Covalent Bonding in Diamond

b. **Hydrogen Bond:** Hydrogen bond is the electrostatic attraction between polar molecules occurring when a hydrogen atom is bound to a highly electronegative atom such as F, O, N or experiences attraction to some other nearby highly electronegative atom. Certain substances such as H_2O , HF , NH_3 form hydrogen bonds, and the formation of which affects properties such as MP, BP, solubility.

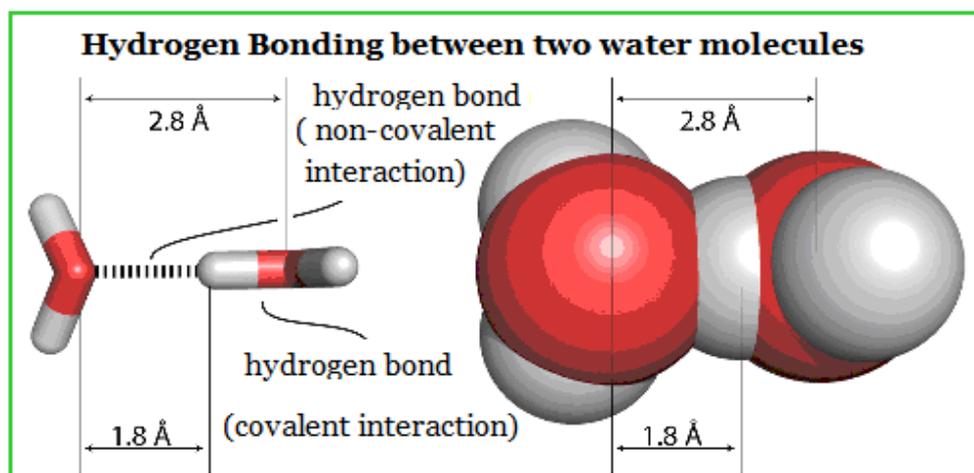


Figure 2. Hydrogen Bond between Two Water Molecules

c. **Strong Ionic Attraction:** Ionic bonding is a type of chemical bond involving transfer of electrons originating from the electrostatic attraction between oppositely charged ions. 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.

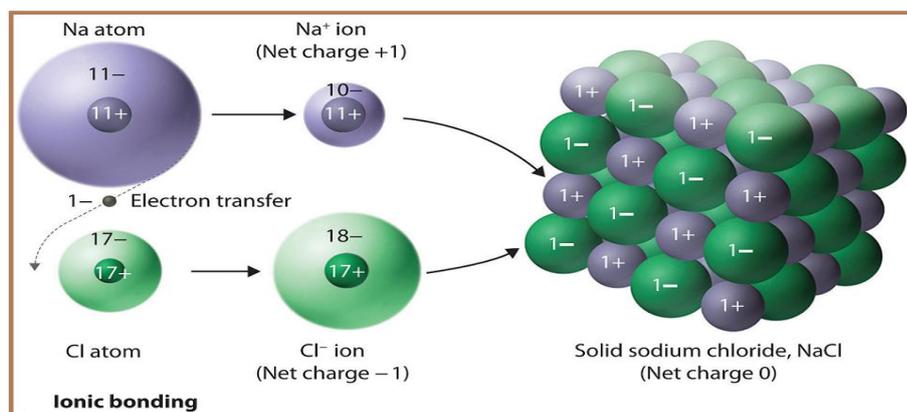


Figure 3. Ionic Bonding in Sodium Chloride

d. **Intermediate Dipole-Dipole Forces:** Dipole-dipole interactions result when two polar molecules approach each other in space. When this occurs, the partially negative portion of one of the polar molecules is attracted to the partially positive portion of the second molecule.

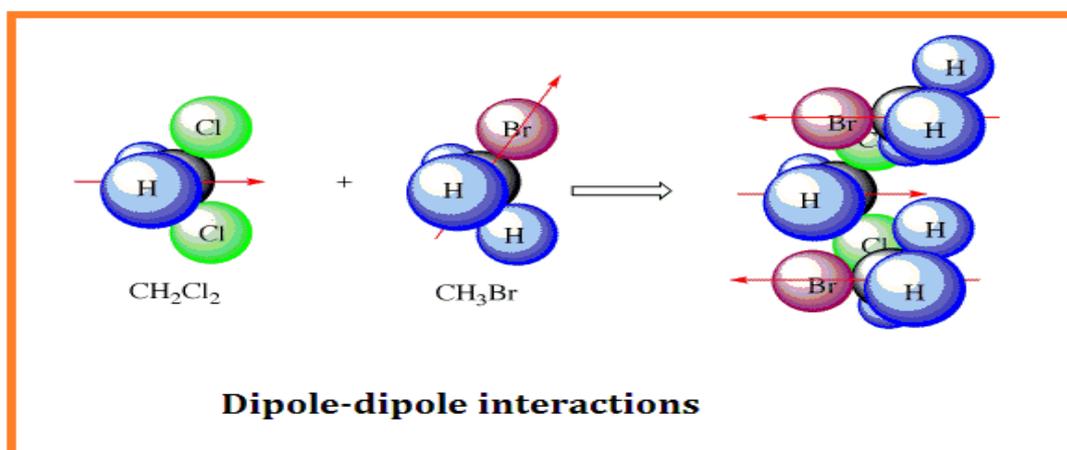


Figure 4. Dipole-dipole Interactions

e. **Weak London Dispersion Forces or Van der Waal's Force:** These forces operate in any substance, arise from induced dipole and the interaction is weaker than the dipole-dipole interaction. In general, the heavier the molecule, the stronger the van der Waal's force of interaction. Owing to stronger London dispersion interactions, the boiling points of inert gases increase with the increase in atomic mass.

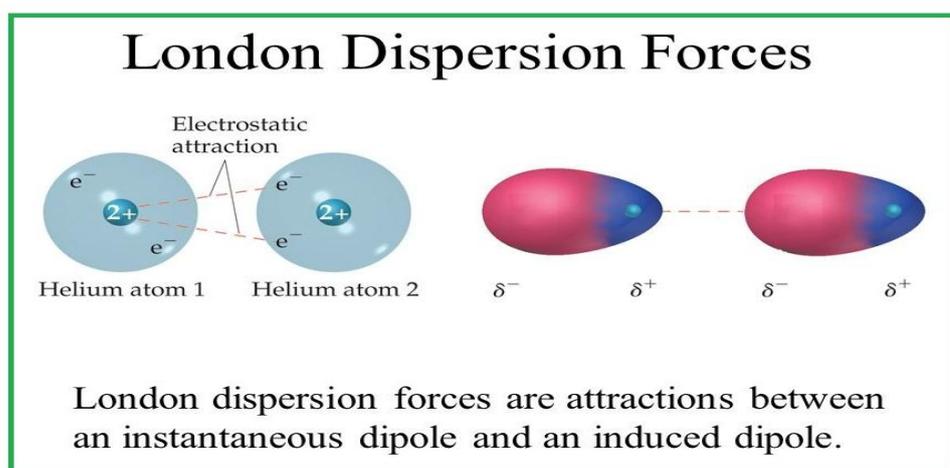


Figure 5. London Dispersion Forces

f. **Metallic Bonding:** Valence electrons in metals are rampant. Forces between the atoms in metallic solids belong to another category. They are not limited to certain atoms or bonds. Rather they run freely in the entire solid, providing good conductivity for heat and electric energy. These behaviours of electrons results in special properties such as mechanical strength and ductility to metals.

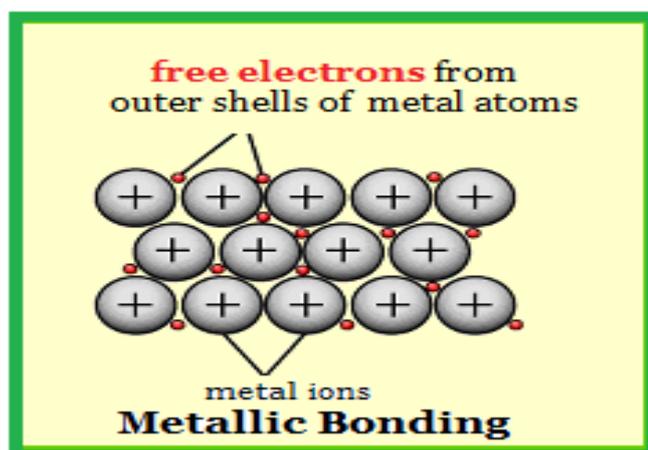


Figure 6. Metallic Bonding

The majority of reactions occurring in solutions are of 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 intensive studies in aqueous, non-aqueous and mixed solvents [4,5]. 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.

2.3. Interactions in the Solution Phase

There are three types of interactions in the solution process:

Solvent – Solvent Interactions: The energy required to break weak bonds between solvent molecules.

Solute – Solute Interactions: The energy required to break intermolecular bonds between the solute molecules.

Solute – Solvent Interactions: ΔH is negative since bonds are formed between them.

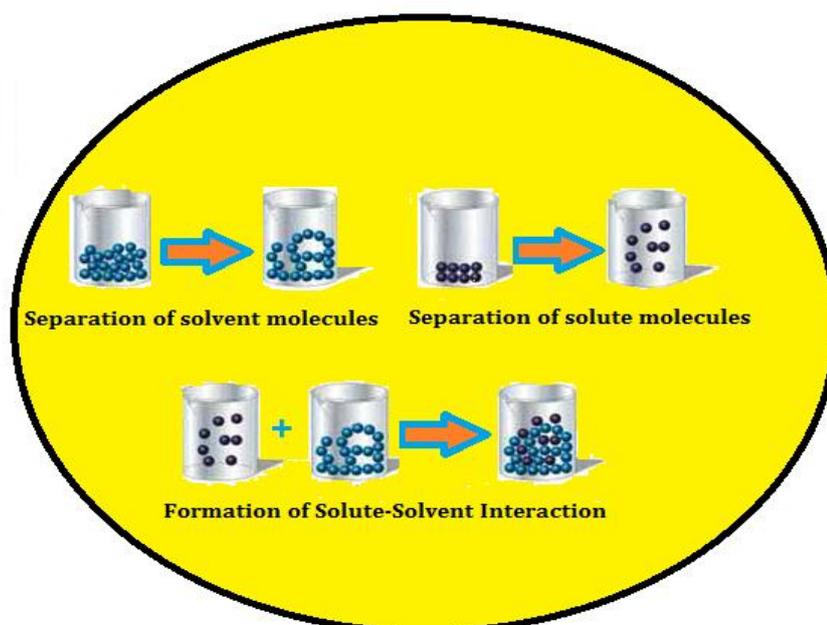


Figure 7. Interactions in the Solution Phase in Liquid Phase Involving Solute and Solvent Molecules

Furthermore, Solubility is affected by (a) Energy of attraction (due Ion-dipole force) affects the solubility, also called hydration energy, (b) Size of the ion- large ions mean smaller lattice energy. (c) Lattice energy: energy holding the ions together in the lattice and (d) Charge on ions; larger charge means higher lattice energy.

For liquid systems, the microscopic structure is often much less studied, whereas the macroscopic properties are usually quite well known. The liquid phase is characterized by local order and long-range disorder and to study the

A molecule ABC may suffer 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).

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 provide an important step in this direction. Naturally, in the development of theories, dealing with electrolyte solutions, much attention has been devoted to ion-solvent interactions which are the controlling forces in infinitely dilute solutions where ion-ion interactions are absent. It is 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 play a very important role to understand the physico-chemical properties of solutions.

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.

2.3.2. Ion-solvent Interaction

Ion-solvation is a phenomenon of primary interest in many contexts of chemistry because solvated ions are omnipresent on Earth. Ions solvated in organic solvents or mixtures of water and organic solvents are also very common [6]. 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. The exchange of solvent molecules around ions in solutions is fundamental to the understanding of the reactivity of ions in solution [8]. Solvated ions also play a key role in electrochemical applications, where for instance the conductivity of electrolytes depends on ion-solvent interactions [9].

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.

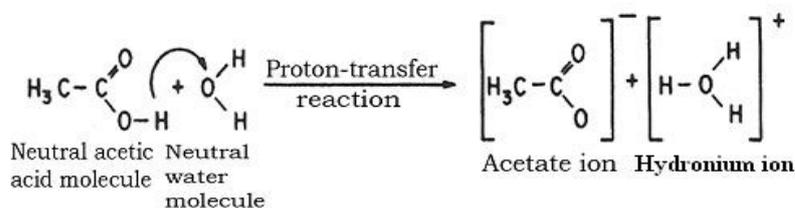


Figure 9. Chemical Method of Producing Ionic Solutions

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 [10-18].

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 [19,20] 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 donor-acceptor properties

[21, 22], hydrogen bonding [23] hard and soft acid-base principles [24] 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 also be studied by spectrometry [25, 26]. 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.

2.3.3. 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.

2.3.4. 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 [27] 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 Bellemans [28] 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. 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. Treszczanowicz *et al.* [30] 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 [31, 32]. It is observed in many systems that there is no simple correlation between the strength of interaction and the observed properties. Rastogi *et al.* [33] 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 [34], L. Huggins [35] 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.* [36-38] 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. A more successful approach is due to Flory who made the use of certain features of cell theory [39-41] 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. The more recent independent effort is the perturbation theory of Baker and Henderson [42]. Patterson and Dilamas [43] 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 [44-46] 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.* [40-42]. Subsequently the ERAS model has been successfully applied by many workers [47-49] 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 [50]. 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 [50, 51]. Gepert *et al.* [52] applied this model for studying some binary systems containing alcohols.

2.4. Density

The physico-chemical 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 [53], hydrophobic hydration [54], micellization [55] and co-sphere overlap during solute-solvent interactions [56] have been derived and interpreted from the partial molar volume data of many compounds.

2.4.1. Apparent and Partial Molar Volumes

Density data can be used for the calculation of molar volume of a pure substance. 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 [57].

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

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 [58]:

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

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 [59], the Redlich-Meyer equation [60], the Owen-Brinkley equation [61], and the Pitzer equation [31]. 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 [62] and nearly all ϕ_V data in non-aqueous [63-67] 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 expressed 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 , 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 obtained by the following equation:

$$\phi_E^0 = \delta \phi_V^0 / \delta T_p = a_1 + 2a_2 T \quad (5)$$

The limiting apparent molar expansibilities (ϕ_E^0) change in magnitude with the change of temperature. During the past few years it has been emphasized by a number of workers that S_V^* is not the sole criterion for determining the

structure-making or breaking tendency of any solute. Helper [68] developed a technique of examining the sign of $(\delta\phi_E^0/\delta T)_p$ 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:

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

If the sign of $(\delta\phi_E^0/\delta T)_p$ is positive or small negative the electrolyte is a structure maker and when the sign of $(\delta\phi_E^0/\delta T)_p$ is negative, it is a structure breaker. Redlich and Meyer [60] 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

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

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

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

The Redlich-Meyer's extrapolation equation [60] adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies [60-71] 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 [61] 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 [61] 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 [71] 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 :

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

where the symbols have their usual significance.

2.4.2. 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.* [73] 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 ϕ_{v,R_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:

$$\phi_{v_{R_4NX}}^0 = bM_{R_4N^+} + \phi_{v_{X^-}}^0 \quad (13)$$

The extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions $\phi_{v_{X^-}}^0$. Uosaki *et al.* [74] used this method for the separation of some literature values and of their own $\phi_{v_{R_4NX}}^0$ values into ionic contributions in organic electrolyte solutions. Krumgalz [75] applied the same method to a large number of partial molar volume data for non-aqueous electrolyte solutions in a wide temperature range.

2.4.3. 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 [76, 77]

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

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 [16]. 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.

2.5. 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 [78, 79]. 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.

2.5.1. 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.

2.5.2. Early Theoretical Considerations on Liquid Viscosity

The theoretical development of liquid viscosity in early stages has been reviewed Andrade [80] and Frenkel [81]. 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 [80] developed equations which checked well against data on mono atomic metals at the melting point. Frenkel [81] 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 [82] assumed the momentum transfer to take place by the irregular Brownian movement of the holes [83] 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:

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

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 [81] and Ewell and Eyring [84] Auluck, De and Kothari [85] 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 [86].

2.5.3. 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 [87, 88] and further expanded by Pople [89]. 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 [90].

2.5.4. 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 [91-92] Mayer and Montroll [93], Mayer [94], Born and Green [95] and the considerations on the basis of the general kinetic theory led Born and Green [95, 96] to develop a viscosity equation which provided explanation for several empirical equations [79, 80, 82] proposed for liquid viscosity. In this connection the theoretical contributions of Kirkwood and coworkers [83, 97-103] Zwanzig *et al.*, [104] Rice and coworkers [105-108] Longuet- Higgins and Valleau [109] and Davis and Coworkers [110, 111] are worth mentioning.

2.5.5. 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 [112] 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 [113], Boon and Thomaes [114-116] Boon, Legros and Thomaes [117], and Hollman and Hijmans [118] are worth mentioning.

2.5.6. 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 [119] showed that the viscosity of the liquid is given by:

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

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

$$\eta = \frac{N_A h (2\pi m k T)^{\frac{1}{2}}}{V h} \frac{b R T V^{\frac{1}{3}}}{N_A^{\frac{1}{3}} \Delta E_{vap}} \exp \frac{\Delta E_{vap}}{n R T} \quad (17)$$

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] have summarized all the working relations.

2.5.7. The Significant Structure Theory and Liquid Viscosity

Eyring and coworkers [122-125] improved the "holes in solid" model theory [121-126] 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 [127, 128].

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

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 [128]. Eyring and Ree [129] have discussed in detail the evaluation of η_s from the reaction rate theory of Eyring [119] assuming that a solid molecule can jump into all neighbouring empty sites. The expression for η_s takes the following form [130]

$$\eta = \frac{N_A h}{Z_K} \frac{V}{V_s} \frac{6}{2^{\frac{1}{2}}} \frac{1}{V - V_s} \frac{1}{1 - e^{-\frac{\theta}{T}}} \exp \frac{a E_s V_s}{(V - V_s) RT} \quad (19)$$

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 [130] by the relation:

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

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

2.5.8. 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 [131] 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 [132] suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations (c):

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

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 [133] of inter-ionic attractions in 1923. The A -coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory [134-136] and is given by the Falkenhagen Vernon [136] equation:

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

where the symbols have their usual significance. In very accurate work on aqueous solutions [137], 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 [138]. A -coefficient suggesting that should be calculated from conductivity measurements. Crudden *et al.* [139] 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) [140, 141] within experimental errors. At higher concentrations the extended Jones-Dole equation (25), involving an additional coefficient D , originally used by Kaminsky, 142 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 $(\eta/\eta_o - 1)/\sqrt{c}$ 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 [141,145,146]. 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 [132]. 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 [147, 148]:

- (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 solvation of ions is sterically hindered in high molal volume solvents or if either ion of a binary electrolyte cannot be specifically solvated.

2.5.9. 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:

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

The several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration range [149-154] and the equation suggested by Angell [155-156] 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.* [157-159] introducing the limiting condition, that is $N \rightarrow 0$, $\eta \rightarrow \eta_o$; which is the viscosity of the pure solvent.

Thus, we have:

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

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 [152] 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.

2.5.10. 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 [160-190]. 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 [191] 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 [192] and also of Kaminsky [142] 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 [193], however preferred RbCl or CsCl to KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron [143] is based on the assumption that the Et_4N^+ ion in water is probably closest to be neither structure breaker not a structure maker. Thus, they suggest that it is possible to apply with a high degree of accuracy of the Einstein's equation [194],

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

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 [195]. They also adopted $B_{Me_4N^+}^{25} = 0.25$ as the initial value for acetonitrile solutions.

(b) For acetonitrile solutions, Tuan and Fuoss [196] proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer *et al.* [197], $\lambda_{25}^o(Bu_4N^+) = 61.4$ and $\lambda_{25}^o(Ph_4B^-) = 58.3$ in acetonitrile.

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

(c) Gopal and Rastogi [147] 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 [146] assuming:

$$B_{[(i-pe)_3Bu_4N^+]} = B_{Ph_4B^-} = \frac{1}{2} B_{[(i-pe)_3BuNPh_4B]} \quad (37)$$

at all temperatures.

Wide use of this method has been made by other authors for dimethyl sulphoxide, sulpholane, hexamethyl phosphotriamide and ethylene carbonate [198] solutions. The methods, however, have been strongly criticized by Krungalz [199]. 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 [199, 200] 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 [201, 202] 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:

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

$a = B_{X^-} B$ 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:

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \quad (39)$$

$$\frac{B_{R_4N^+}}{B_{R'_4N^+}} = \frac{r^3_{R_4N^+}}{r^3_{R'_4N^+}} \quad (40)$$

The radii of the tetraalkylammonium ions have been calculated from the conductometric data [203]. Gill and Sharma [181] 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^+ (5.00Å) 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:

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

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

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:

$$B_{[(i-Am)_3Bu_4N^+]} = B_{Ph_4B^-} = \frac{1}{2} B_{[Bu_4NPh_4B]} \quad (43)$$

Recently, Lawrence and Sacco [184] used tetrabutylammonium tetrabutylborate ($Bu_4NB Bu_4$) 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:

$$\frac{B_{Bu_4N^+}}{B_{Bu_4B^-}} = \frac{V_{W(Bu_4N^+)}}{V_{W(Bu_4B^-)}} \quad (44)$$

$$B_{Bu_4N^+} = \frac{B_{Bu_4NBPh_4}}{\left[1 + \frac{V_{W(Bu_4B^-)}}{V_{W(Bu_4N^+)}} \right]} \quad (45)$$

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 $B_{R_4NBr} = B_{Br^-} + a[f_x R_4N^+]$ 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 $Bu_4NB Bu_4$ 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 [204] 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 [205] and 'volcano plots' of Morris [206]. The principle was extended to derive absolute single ion B coefficients for alkali metals and halides in water. They also observed that $B_{Cs^+} = B_{I^-}$ suggested by Krumgalz [201] to be more reliable than $B_{K^+} = B_{Cl^-}$ 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.

2.5.11. 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 [207], A, B, C Zones of Frank and Wen [208] and hydrated radius of Nightingale [193].

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_0) 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 [199] 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 [209] used the entropy of hydration to correlate ionic B values and Nightingale [193] 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.* [210] to assign single ion B -coefficients so that a plot of ΔS_e^o [211, 212] 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 $\Delta S_{I,II}^o$ 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.

2.5.12. Thermodynamics of Viscous Flow

Assuming viscous flow as a rate process, the viscosity (η) can be represented from Eyring's [213] approaches as:

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

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 [214] 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:

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

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

ΔE_V^{\neq} 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.* [215] have suggested an alternative formulation based on the transition state treatment of the relative viscosity of electrolytic solution. They suggested the following expression:

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

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

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

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:

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

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

2.5.13. 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 [194] 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 [216] 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:

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

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:

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

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.

2.5.14. Viscosity of Non-Electrolytic Solutions

The equations of Vand [217], Thomas [218] 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 [219-221]. These equations are:

Vand equation:
$$\ln \eta_r = \frac{\alpha}{1-Q} = \frac{2.5V_h c}{1-QV_h c}$$

(66)

Thomas equation:
$$\eta_r = 1 + 2.5V_h c + 10.05cV_h^2 c$$

(67)

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

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 :

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

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

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

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

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

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

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 [222-228].

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

The correlation of ternary is modified to the following form:

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

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

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

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.

2.5.15. 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 [229], the deviations in viscosities ($\Delta\eta$) from the ideal mixture values can be calculated as:

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

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.

2.5.16. Gibbs Excess Energy of Activation for Viscous Flow

Quantitatively, the Gibbs excess energy of activation for viscous flow, ΔG^* can be calculated as [230]:

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

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.

2.5.17. Viscous Synergy and Antagonism

Rheology is the branch of science that studies [231] material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products, [232-241] and to establish their stability and even bio-availability, since it has been firmly established that viscosity influences the drug absorption rate in the body [242, 243]. 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 [244, 245].

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 [246] 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 [247].

In order to secure more comparable viscous synergy results, the so-called synergic interaction index (I_S) as introduced by Howell [248] 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:

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

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.

2.6. 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.

2.6.1. 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 solutions²⁴⁹⁻²⁵³ 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]:

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

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 [255, 256]. 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 [257, 258] 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^0 values have

been reported in aqueous non-electrolyte [259] and non-aqueous non-electrolyte [260] solutions.

2.6.2. Deviation in Isentropic Compressibility

The deviation in isentropic compressibility (ΔK_s) can be calculated using the following equation [261-263]:

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

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 [264]. The resultant values of ΔK_s for the mixtures are due to the net effect of the combination of (i) to (iii) [265].

Moreover, the excess or deviation properties ($V_m^E, \Delta\eta, \Delta G^E$ and ΔK_s) have been fitted to Redlich-Kister [266] polynomial equation using the method of least squares involving the Marquardt algorithm [267] and the binary coefficients, α_i were determined as follows :

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

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.

2.7. 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.

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 [268] 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:

$$\Lambda = \Lambda_0 - S\sqrt{c} \quad (88)$$

where,

$$S = \alpha\Lambda_0 + \beta \quad (89)$$

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

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

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 [269]. In the subsequent years, Pitts (1953) [270] and Fuoss and Onsager (1957) [271] independently worked out the solution of the problem of electrolytic

conductance accounting for both long-range and short-range interactions. However, the Λ_0 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 [272,273]. The original Fuoss-Onsager equation was further modified by Fuoss and Hsia [274] 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:

$$\Lambda = \frac{\Lambda_0 - \alpha\Lambda_0\sqrt{c}}{(1 + \kappa\alpha)} \left(\frac{1 + \kappa\alpha}{\sqrt{2}} \right) - \frac{\beta\sqrt{c}}{(1 + \kappa\alpha)} + G(\kappa\alpha) \quad (91)$$

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

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \ln c + J_1c + J_2\sqrt[3]{c} \quad (92)$$

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 [275,276]. Further correction of the equation (92) was made by Fuoss and Accascini. They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \ln c + J_1c + J_2\sqrt[3]{c} - FAc \quad (93)$$

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

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 [277].

2.7.1. 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 $\Lambda_{o\text{exp}}$ is greater than $\Lambda_{o\text{theo}}$, 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 ($\Lambda_{o\text{exp}} < \Lambda_{o\text{theo}}$) or positive deviation from the Onsager limiting tangent ($\alpha\Lambda_o + \beta$) 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 $\Lambda_{o\text{exp}}$ and $\Lambda_{o\text{theo}}$ would be considerable with increasing association [278].

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_o has been determined using Fuoss-Kraus equation [279] or Shedlovsky's equation [280].

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

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

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

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

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

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

The equation was modified by Justice [281]. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

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

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

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

The conductance parameters are obtained from a least square treatment after

$$\text{setting, } R = q = \frac{e^2}{2\epsilon kT} \quad (\text{Bjerrum's critical distance}).$$

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 [282]:

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

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 [283].

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

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 [284].

2.7.2. Ion Size Parameter and Ionic Association

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

$$A_1 = A + S\sqrt{c} - Ec \ln c = A_0 + J_1c + J_2\sqrt[3]{c} = A_0 + J_1c \quad (106)$$

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' [285] 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 [286]. Fuoss [287] in 1975 proposed a new conductance equation. Latter 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 equation constants for eq. 107 are:

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

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

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:

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

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:

$$A = \gamma \left[A_o \left(\frac{1 + \Delta X}{X} \right) \right] + \Delta A_e \quad (114)$$

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 [287]. 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).

2.7.3. Lee-Wheaton Conductance Equation

As Fuoss 1978 conductance equation contained a boundary condition error, [288, 289] Fuoss introduced a slight modification to his model [290, 291]. 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 [292(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 [292(b)]. The conductance data were analyzed by means of the Lee-Wheaton conductance equation [293] in the form:

$$\Lambda = \alpha_i \left[\frac{A_o}{1 + \kappa R} \left\{ 1 + C_4 \beta \kappa + C_5 (\beta \kappa)^2 + \frac{\kappa R}{12} \right\} \right] \quad (121)$$

The mass action law association [294] 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 [295], 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 [295]:

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

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

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

where the symbols have their usual significance [296].

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 [297]. 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 [298] 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:

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

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 [299]. R was generally varied by a step 0.1 \AA and the iterative process was continued with equation (118).

2.7.4. 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:

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

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.,

$$\lambda_o^+ = t_+ \Lambda_0 \quad \text{and} \quad \lambda_o^- = t_- \Lambda_0 \quad (129b)$$

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 Krungalz [300] and some important points are mentioned as follows:

(i) Walden equation [301]

$$(\lambda_o^\pm)_{\text{water}}^{25} \cdot \eta_{o,\text{water}} = (\lambda_o^\pm)_{\text{acetone}}^{25} \cdot \eta_{o,\text{acetone}} \quad (130)$$

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

$$\text{based on } \lambda_{o,\text{Et}_4\text{N}_{\text{pic}}} = 0.563$$

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 good in nitrobenzene and in mixture with CCl_4 but not realized in methanol, acetonitrile and nitromethane.

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

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 Gill³⁰⁴ is:

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

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 [300(a)]. In a paper, [300(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.

$$(vi) \quad \lambda_o^{25} [i-Am_3 BuN^+] = \lambda_o^{25} Ph_4B^- \quad [305] \quad (135)$$

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 $i-Am_4B^-$, 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 A_o values

2.7.5. 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.

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

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

Assuming Stokes' relation to hold well, the ionic solvated volume can be obtained, because of the packing effects [307], 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 [308-311] have been suggested in order to apply it to most of the ions.

2.7.6. 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 of a spherical ion of radius R_i moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

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

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 [312]. 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 [313], Nightingale [193] and others [314-316] 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 [317] was invoked without much success [318, 319] 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 [320, 321]. Gill [322] has pointed out the inapplicability of the Zwanzig theory [323] 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 [322, 323].

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:

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

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

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 [280] 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 [310] 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:

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

where ϵ_r^o 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 [324] that λ_o^i passes through a maximum of $27^{1/4} A / 4B^{1/4}$ 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 [325]:

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

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

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 [324-329]. 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) 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.

(ii) 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 [326].

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 [324-334] mixtures and other aqueous binary mixtures [335-338]. To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts [339] 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 not possible to account for some specific properties of different kinds of ions and solvent molecules and

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

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

[340] 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 [341] 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 [342, 343] 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.

2.7.7. 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:

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

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

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

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

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

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^o can also be calculated using the following equation:

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

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

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.

2.7.8. 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 [344-348]. 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.

A. Galindo *et al.* [349,350] 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.* [351] of the University of Barcelona, Spain, have compared several “Preferential Solvation Models” specially for describing the polarity of dipolar hydrogen bond acceptor-cosolvent mixture.

2.7.9. Conductance-Some Recent Trends

Recently Blum, Turq and coworkers [352,353] 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.* [354]. 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 [355] 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).

2.8. 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 [356].

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 [357] 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:

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

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 [358].

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

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 [359]. Similar to that obtained for the salt + solvent solutions was used to represent ternary refractive indices:

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

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

There is no 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 σ 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. Grossfield, P. Ren, J. W. Ponder, *J. Am. Chem. Soc.* **2001**, *125*, 15671.
2. (a) J. D. Pandey, A. Yasmin, *Proc. Ind. Acad. Sci.* **1997**, *109*, 289.
(b) J. D. Pandey, Y. Akhtar, A. K. Sharma, *Ind. J. Chem* **1998**, *37A*, 1094 .
3. J. I. Kim, *J. Phys. Chem.* **1978**, *82*, 191.
4. B.E. Conway, R.G. Barradas, *Chemical Physics of Ionic Solutions*, Wiley, New York, **1966**.
5. J. J. Lagowski, *The Chemistry of Non-Aqueous Solvents*, Academic, New York, **1966**.
6. K. Ibuki, M. Nakahara, *J. Phys. Chem.* **1990**, *94*, 8370.
7. D.T. Richens, *The Chemistry of Aqua Ions*, Wiley, New York, **1997**.
8. A. Henni, J.H. Jonathan, T. Paitoon, C. Amit, *J. Chem. Eng. Data* **2003**, *48*, 1062.
9. J. Burgess, *Metal Ions in Solutions*; Ellis Horwood, New York, **1978**.
10. R.G. Bates, *J. Electroanal. Chem.* **1972**, *29*, 1.
11. G.S. Kell, C.M. Daries, J. Jarynski, *Water and Aqueous Solutions, Structure, Thermodynamics and Transport process*, Wiley, New York, **1972**.
12. E.S. Amis, J.F. Hinton, *Solvent effects on Chemical Phenomena*, Academic, New York, **1973**.
13. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York, **1958**.
14. J. J. Lagowski, *The Chemistry of Non-Aqueous Solvents*, Academic, New York, **1966**.
15. B.E. Conway, R.G. Barradas, *Chemical Physics of Ionic Solutions*, Wiley, New York, **1966**.
16. J.S. Muishead-Gould, K.J. Laidler, *Chemical Physics of Ionic Solutions*, Wiley, New York, **1966**.
17. J.F. Coetzee, C.D. Ritchie, *Solute-Solvent Interactions*, Marcel Dekker, New York, **1969**.

18. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York, **1973**.
19. F. Franks, *Physico-Chemical processes in Mixed Aqueous Solvents*, Heinemann, London, **1967**.
20. F. Franks, *Water—A Comprehensive Treatise*, Plenum Press, New York, **1973**.
21. V. Gutmann, *Electrochim. Acta.* **1967**, 21,661.
22. U. Mayer, V. Gutmann, *Adv. Inorg.Chem. Radiochem.* 1975, 17, 189.
23. J.E. Gordon, *The Organic Chemistry of Electrolyte Solutions*, Wiley-Interscience, New York, **1975**.
24. R.G. Pearson, *Hard and Soft Acids and Bases*, Strondsburgh, **1973**.
25. G.R. Behbehani, M. Dillon, J. Symth, W.E. Waghorne, *J. Solution Chem.* **2002**, 31, 811.
26. C. Guha, J.M. Chakraborty, S. Karanjai, B. Das, *J. Phys. Chem. B* **2003**, 107, 12814.
27. L. Jones, J.F. Devonshire, *A. F. Proc. Royal Soc.* **1937**.
28. I. Prigogine, A. Belleman, *J. Phys. Chem.* **1953**, 21, 561.
29. I. Prigogine, S. Garikian, *Physica* **1950**, 16, 239.
30. A.J. Treszczanowicz, G.C. Benson, *Fluid Phase Equilib.* **1985**, 23, 117.
31. Wen-Lu Weng, *J. Chem. Eng. Data* **2002**, 45, 606.
32. P.S. Nikam, S.J. Kharat, *J. Chem. Eng. Data* **2005**, 50, 455.
33. R.P. Rastogi, J. Nath, J. Mishra, *J. Phys. Chem.* **1966**, 71, 1277.
34. K.S. Pitzer, G. Mayora, *J. Phys. Chem.* **1973** 77, 2300.
35. D. Cook, L-Higgins, *H. C. Proc. Royal. Soc.* **1951**, A209, 28.
36. J.S. Rowlinson, *Liquid and Liquid Mixtures*, Scientific Publications, London **1959**.
37. J.S. Rowlinson, *Proc. Royal. Soc.* **1952**, A214,192.
38. J.L. Lebowitz, J. S. Rowlinson, *J. Chem. Phys.* **1964**, 41,133.
39. P.J. Flory, R.A. Orwoll, A. Vrij, *J. Am. Chem. Soc.* **1964**, 86, 3507.
40. P.J. Flory, A. Abe, *J. Am. Chem. Soc.* **1964**, 86, 3563.
41. P.J. Flory, *J. Am. Chem. Soc.* **1965**, 87, 1833.

42. J.A. Barker, D.J. Henderson, *J. Phys. Chem.* **1967**, 47, 4714.
43. D. Patterson, G. Delmas, *Discuss. Faraday Soc.* **1970**, 49, 98.
44. A. Heintz, *Ber. Bunsenges. J. Phys.* **1985**, 89, 172.
45. H. Funke, M. Wetzal, A. Heintz, *J. Pure. Appl. Chem.* **1989**, 61, 1429.
46. A. Heintz, D. Papaioannou, *Thermochimica Acta.* **1998**, 310, 69.
47. A. Heintz, P.K. Naicker, S.P. Verevkin, R. Pfestrof, B. Bunsenges, *Phys. Chem.* **1998**, 102, 953.
48. S. Villa, N. Riesco, I. Garcia de la Fuente, J.A. Gonzalaz, J.C. Cobos, *Fluid Phase Equilib.* **2004**, 216, 123.
49. S.L. Oswal, *J. Thermochim. Acta.* **2005**, 425, 59.
50. A. Pineiro, A. Amigo, R. Bravo, P. Brocos, *Fluid Phase Equilib.* **2000**, 173, 211.
51. A. Pineiro, *Fluid Phase Equilib.* **2004**, 216, 245.
52. M. Gepert, B. Stachowska, *J. Sol. Chem.* **2006**, 35, 425.
53. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolyte Solutions*, Reinhold Publishing Corporation, New York, **1943**.
54. C. Tanford, *Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Wiley-Interscience, New York, **1980**.
55. E. Vikingstad, *Aggregation Process in Solutions*, Elsevier, Amsterdam, **1983**.
56. J.E. Desnoyers, M. Arel, H. Perron, C. Jolicoenn, *J. Phys. Chem.* **1969**, 73, 3347.
57. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York, **1973**.
58. D.K. Hazra, B. Das, *J. Chem. Eng. Data* **1991**, 36, 403.
59. D.O. Masson, *Phil. Mag.* **1929**, 8, 218.
60. O. Redlich, D.M. Meyer, *Chem. Rev.* **1964**, 64, 221.
61. B.B. Owen, S.R. Brinkley, *J. Ann. N. Y. Acad. Sci.* **1949**, 51, 753.
62. F.J. Millero, *Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes*, Wiley- Interscience, New York, **1972**.
63. R. Gopal, M.A. Siddiqi, *J. Phys. Chem.* **1969**, 73, 3390.

64. J. Padova, I. Abrahmen, *J. Phys. Chem.*, **1967**, *71*, 2112.
65. R. Gopal, D.K. Agarwal, R. Kumar, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1973.
66. R. Gopal, P.P. Rastogi, *Z. Phys. Chem. (N.F.)*. **1970**, *69*, 1.
67. B. Das, D.K. Hazra, *J. Chem. Eng. Data*, **1991**, *36*, 403.
68. L. G. Hepler, *Can. J. Chem.* **1969**, *47*, 4617.
69. L.G. Hepler, J.M. Stokes, R.H. Stokes, *Trans. Faraday Soc.* **1965**, *61*, 20.
70. F.H. Spedding, M.J. Pikal, B.O. Ayres, *J. Phys. Chem.* **1966**, *70*, 2440.
71. L.A. Dunn, *Trans. Faraday Soc.* **1968**, *64*, 2951.
72. R. Pogue, G. Atkinson, *J. Chem. Eng. Data*, **1988**, *33*, 370.
73. B.E. Conway, R.E. Verral, J.E. Desnoyers, *Trans. Faraday Soc.* **1966**, *62*, 2738.
74. K. Uosaki, Y. Koudo, N. Tokura, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 871.
75. B.S. Krungal, *J. Chem. Soc. Faraday Trans. I.* **1980**, *76*, 1887.
76. A.W. Quin, D.F. Hoffmann, P. Munk, *J. Chem. Eng. Data* **1992**, *37*, 55.
77. Z. Atik, *J. Sol. Chem.* **2004**, *33*, 1447.
78. R.H. Stokes, R. Mills, *Viscosity of Electrolytes and Related Properties*, Pergamon, Great Britain, **1965**.
79. F. Vaslow, *Water and Aqueous Solutions*, Wiley- Interscience, New York, **1972**.
80. E.N.da C. Andrade, *Phil. Mag.* **1934**, *17*, 698.
81. J. Frankel, *Kinetic Theory of Liquids*, Dover Publications, New York, **1955**.
82. R. Furth, *Proc. Camb. Phil. Soc.* **1941**, *37*, 281.
83. R. Furth, *Proc. Camb. Phil. Soc.* **1941**, *37*, 252.
84. R.H. Ewell, H. Eyring, *J. Chem. Phys.* **1937**, *5*, 726.
85. F.C. Auluck, S.C. De, D.S. Kothari, *Proc. Natl. Inst. Sci.* **1944**, *10(4)*, 397.
86. R. Eisenschitz, *Proc. Roy. Soc.* **1952**, *215A*, 29.
87. J.E. Lennard-Jones, A.F. Devonshire, *Proc. Roy. Soc.* **1937**, *163A* , 53.
88. J.E. Lennard-Jones, A.F. Devonshire, *Proc. Roy. Soc.*, **1938**, *165A* , 1
89. J.A. Pople, *Proc. Roy. Soc.* **1952**, *215A* ,67.
90. R. Eisenchitz, *Proc. Phys. Soc.* **1949**, *62A*, 41.
91. J.G. Kirkwood, *J. Chem. Phys.* **1946**, *14* ,180.

92. J.G. Kirkwood, *Theory of Liquids*, Science Publishers, New York, **1968**.
93. J.E. Mayer, E. Montroll, *J. Chem. Phys.* **1941**, 9, 2.
94. J.E. Mayer, *J. Chem. Phys.* **1947**, 15, 187.
95. M. Born, H.S. Green, *Proc. Roy. Soc.* **1946**, 188A, 10.
96. M. Born, H.S. Green, *Proc. Roy. Soc.* **1947**, 190A, 455.
97. J.G. Kirkwood, F.P. Buff, M.S. Green, *J. Chem. Phys.* **1949**, 17, 988.
98. J.G. Kirkwood, *J. Chem. Phys.* **1935**, 3, 300.
99. J.G. Kirkwood, *J. Chem. Phys.* **1939**, 7, 919.
100. J.G. Kirkwood, Z.W. Salsburg, *Faraday Soc. Discuss.* **1953**, 15, 25.
101. J.G. Kirkwood, E.M. Boggs, *J. Chem. Phys.* **1942**, 10, 394.
102. J.G. Kirkwood, E.K. Maun, B.J. Alder, *J. Chem. Phys.* **1950**, 18, 1040.
103. J.G. Kirkwood, V.A. Lewinson, B.J. Alder, *J. Chem. Phys.* **1952**, 20, 929.
104. R.W. Zwanzig, J.G. Kirkwood, K.F. Stripp, I. Oppenheim, *J. Chem. Phys.* **1953**, 21, 2050.
105. 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**.
106. 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**.
107. S.A. Rice, A.R. Allnatt, *J. Chem. Phys.* **1961**, 34, 2144.
108. A.R. Allnatt, S.A. Rice, *J. Chem. Phys.* **1961**, 34, 2156.
109. H.C. Longuet-Higgins, J.P. Valleau, *Mol. Phys.* **1958**, 1, 284.
110. H.T. Davis, S.A. Rice, J.V. Sengers, *J. Chem. Phys.* **1961**, 35, 2210.
111. H.T. Davis, K.D. Luks, *J. Phys. Chem.* **1965**, 69, 869.
112. 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**.
113. J.D. Rogers, F.G. Brickwedde, *Physica* **1966**, 32, 100.
114. J.P. Boon, G. Thomaes, *Physica* **1963**, 29, 208.
115. J.P. Boon, G. Thomaes, *Physica* **1962**, 28, 1074.

116. J.P. Boon, G. Thomaes, *Physica* **1963**, 29,123.
117. J.P. Boon, J. C. Legros, G. Thomaes, *Physica* **1967**, 33, 547.
118. T.H. Holleman, J. Hijmans, *Physica* **1962**, 28, 604.
119. H. Eyring, *J. Chem. Phys.* **1936**, 4, 283.
120. H. Eyring, J.O. Hirschfelder, *J. Phys. Chem.* **1937**, 41, 249.
121. J.F. Kincaid, H. Eyring, A.E. Stearn, *Chem. Rev.* **1941**, 28, 301.
122. H. Eyring, T. Ree, N. Hirai, *Proc. Natl. Acad. Sci.* **1958**, 44, 683.
123. E.J. Fuller, T. Ree, H. Eyring, *Proc. Natl. Acad. Sci.* **1959**, 45, 1594.
124. C.M. Carlson, H. Eyring, *Proc. Natl. Acad. Sci.* **1960**, 46, 333.
125. T.R. Thomson, H. Eyring, T. Ree, *Proc. Natl. Acad. Sci.* **1960**, 46, 336.
126. J. Walter, H. Eyring, *J. Chem. Phys.* **1941**, 9, 393.
127. T. Ree, H. Eyring, *Ind. Eng. Chem.* **1958**, 50, 1036.
128. C.M. Carlson, H. Eyring, T. Ree, *Proc. Natl. Acad. Sci.* **1960**, 46, 649
129. H. Eyring, T. Ree, *Proc. Natl. Acad. Sci.* **1961**, 47, 526.
130. H. Eyring, M.S. John, *Significant Liquid Structures*, John Willey & Sons, New York, **1969**.
131. Gruneisen, Wiss, Abhaudl, *Physik-tech. Reich-austatt.* **1905**, 4, 239.
132. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, 51, 2950.
133. P. Debye, E. Hückel, *Z. Phys. Chem.* **1923**, 24, 185.
134. H. Falkenhagen, M. Dole, *Phys. Z.* **1929**, 30, 611.
135. H. Falkenhagen, E.L. Vernon, *Phys. Z.* **1932**, 33, 140.
136. H. Falkenhagen, E.L. Vernon, *Phil. Mag.* **1983**, 14, 537.
137. M. Kaminsky, *Discuss Faraday Soc.* **1957**, 24, 171.
138. D. Feakins, D.J. Freemantle, K.G. Lawrence, *J. Chem. Soc. Faraday Trans. I.* **1974**, 70, 795.
139. J. Crudden, G.M. Delancy, D. Feakins, P.J. O'Relly, W. E. Waghorne, K. G. Lawrence, *J. Chem. Soc. Faraday Trans. I.* **1986**, 82, 2195.
140. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York, **1973**.
141. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York, **1958**.

142. M. Kaminsky, *Z. Phys. Chem.* **1957**, *12*, 206.
143. J. Desnoyers, G. Perron, *J. Solution Chem.* **1972**, *1*, 199.
144. R.J.M. Bicknell, K.G. Lawrence, D. Feakins, *J. Chem. Soc. Faraday I.* **1980**, *76*, 637.
145. R.L. Kay, T. Vituccio, C. Zawoyski, D.F. Evans, *J. Phys. Chem.* **1966**, *70*, 2336.
146. N.P. Yao, D.N. Bennion, *J. Phys. Chem.* **1971**, *75*, 1727.
147. M. Kaminsky, *Discussions Faraday Soc.* **1957**, *24*, 171.
148. D. Feakins, K.G. Lawrence, *J. Chem. Soc.* **1966**, *A*, 212.
149. V. Vand, *J. Phys. Chem.* **1948**, *52*, 277.
150. D.G. Thomas, *J. Colloid Sci.* **1965**, *20*, 267.
151. S.P. Moulik, *J. Ind. Chem. Soc.* **1972**, *49*, 483.
152. D. England, G. Pilling, *J. Phys. Chem.* **1972**, *76*, 1902.
153. D.E. Goldsack, R.C. Franchetto, *Can. J. Chem.* **1977**, *55*, 1062.
154. D.E. Goldsack, R.C. Franchetto, *Can. J. Chem.* **1978**, *56*, 1442.
155. C.A. Angell, *J. Phys. Chem.* **1966**, *70*, 2793.
156. C.A. Angell, *J. Chem. Phys.* **1967**, *46*, 4673.
157. K.R. Chowdhury, D.K. Majumdar, *Electrochim. Acta.* **1983**, *28*, 23.
158. K.R. Chowdhury, D.K. Majumdar, *Electrochim. Acta.* **1983**, *28*, 597.
159. K.R. Chowdhury, D.K. Majumdar, *Electrochim. Acta.* **1984**, *29*, 1371.
160. P.P. Rastogi, *Bull. Chem. Soc. Japan*, **1970**, *43*, 2442.
161. R. Gopal, P.P. Rostogi, *Z. Phys. Chem. (N.F.)* **1970**, *69*, 1.
162. C.M. Criss, M.J. Mastroianni, *J. Phys. Chem.* **1971**, *75*, 2532.
163. K. Tamaski, Y. Ohara, Y. Isomura, *Bull. Chem. Soc. Japan* **1973**, *46*, 951.
164. P.P. Deluca, T.V. Rabagay, *J. Phys. Chem.* **1975**, *79*, 2493.
165. B.N. Prasad, N.P. Singh, M.M. Singh, *Ind. J. Chem.* **1976**, *14A*, 322.
166. B.N. Prasad, M.M. Agarwal, *Ind. J. Chem.* **1976**, *14A*, 343.
167. R.T.M. Bicknell, K.G. Lawrence, M.A. Scelay, D. Feakins, L. Werblan, *J. Chem. Soc. Faraday I.* **1976**, *72*, 307.
168. J.M. Mcdowall, N. Martinus, C.A. Vincent, *J. Chem. Soc. Faraday I.* **1976**, *72*, 654.
169. A. Sacco, G. Petrella, M. Castagnola, *J. Phys. Chem.* **1976**, *80*, 749.

170. R.L. Blokhra, Y.P. Segal, *Ind. J. Chem.* **1977**, *15A*, 36.
171. N.C. Das, P.B. Das, *Ind. J. Chem.* **1977**, *15A*, 826.
172. A. Sacco, G. Petrella, M. Della Monica, M. Castagnola, *J. Chem. Soc. Faraday I.* **1977**, *73*, 1936.
173. P.K. Mandal, B.K. Seal, A.S. Basu, *Z. Phys. Chem.* **1977**, *258*, 809.
174. J.I. Kim, *J. Phys. Chem.* **1978**, *82*, 191.
175. S.K. Vijaylakshamna, *Indian J. Chem.* **1979**, *17A*, 511.
176. A. Sacco, G. Petrella, M.D. Monica, *J. Chem. Soc. Faraday I.* **1979**, *75*, 2325.
177. P.T. Thomson, M. Durbana, J.L. Turner, R.H. Wood, *J. Sol. Chem.* **1980**, *9*, 955.
178. K. Kurotaki, S. Kawamura, *J. Chem. Soc. Faraday I.* **1981**, *77*, 217.
179. N. Martinus, C.A. Vincent, *J. Chem. Soc. Faraday I.* **1981**, *77*, 141.
180. A. Sacco, A. D. Giglio, A. D. Atti, *J. Chem. Soc. Faraday I.* **1981**, *77*, 2693.
181. D.S. Gill, A.N. Sharma, *J. Chem. Soc. Faraday I.* **1982**, *78*, 78475.
182. A. Sacco, G. Petrella, A.D. Atti, M. Castagnolo, *J. Chem. Soc. Faraday I.* **1980**, *78*, 955.
183. A. Sacco, A.D. Giglio, A.D. Atti, M. Castagnolo, *J. Chem. Soc. Faraday I.* **1983**, *79*, 431.
184. K.G. Lawrence, A. Sacco, *J. Chem. Soc. Faraday I.* **1981**, *77*, 615.
185. K. Miyajima, M. Sawada, M. Nakagaki, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 827.
186. J. Doenech, S. Rivera, *J. Chem. Soc. Faraday I.* **1984**, *80*, 1249.
187. D. Dasgupta, S. Das, D.K. Hazra, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1246.
188. S. Taniewska-Osinska, M. Jozwaik, *J. Chem. Soc. Faraday Trans I.* **1989**, *85*, 2147.
189. D. Nandi, D.K. Hazra, *J. Chem. Soc. Faraday Trans I.* **1989**, *85*, 4227.
190. I. Ibulci, M. Nakahara, *J. Phys. Chem.* **1990**, *94*, 8370.
191. W.M. Cox, J. H. Wolfenden, *Proc. Roy. Soc. London* **1934**, *145A*, 475.
192. R.W. Gurney, *Ionic Processes in Solution*, Mc Graw Hill, New York, **1953**.
193. E.R. Nightingale, *J. Phys. Chem.* **1959**, *63*, 1381.
194. A. Einstein, *Ann. Phys.* **1906**, *19*, 289.
195. G.S. Benson, A.R. Gordon, *J. Chem. Phys.* **1945**, *13*, 473.

196. [D.F.T. Tuan, R.M. Fuoss, *J. Phys. Chem.* **1963**, 67, 1343.
197. C.H. Springer, J.F. Coetzee, R.L. Key, *J. Phys. Chem.* **1969**, 78, 471.
198. G. Petrella, A. Sacco, *J. Chem. Soc. Faraday I.* **1978**, 74, 2070.
199. B.S. Krumgalz, *J. Chem. Soc. Faraday I.* **1980**, 76, 1275.
200. B.S. Krumgalz, *Russ. J. Phys. Chem.* **1972**, 46, 858.
201. B.S. Krumgalz, *Russ. J. Phys. Chem.* **1973**, 47, 956.
202. B.S. Krumgalz, *Russ. J. Phys. Chem.* **1974**, 48, 1163.
203. B.S. Krumgalz, *Russ. J. Phys. Chem.* **1971**, 45, 1448.
204. H.D.B. Jenkins, M.S.F. Pritchett, *J. Chem. Soc. Faraday I.* **1984**, 80, 721.
205. K. Fajan, *Naturwissenschaften* **1921**, 9, 729.
206. D.F.C. Morris, *Struct. Bonding* **1969**, 6, 157.
207. R.W. Gurney, *Ionic Processes in Solutions*, Doves, New York, **1962**.
208. H.S. Frank, W.Y. Wen, *Disc. Farad. Soc.* **1957**, 24, 133.
209. Z. Asmus, *Naturforsch.* **1949**, 4A, 589.
210. M.H. Abraham, J. Liszi, E. Papp, *J. Chem. Soc. Faraday I.* **1982**, 78, 197.
211. M.H. Abraham, J. Liszi, L. Meszaros, *J. Chem. Phys.* **1979**, 70, 249.
212. M.H. Abraham, J. Liszi, *J. Chem. Soc. Faraday I.* **1980**, 76, 1219.
213. S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw Hill, New York, **1941**.
214. E.R. Nightingale, R.F. Benck, *J. Phys. Chem.* **1959**, 63, 1777.
215. D. Feakins, D.J. Freemantle, K.G. Lawrence, *J. Chem. Soc. Faraday I.* **1974**, 70, 795.
216. R. Sinha, *J. Phys. Chem.* **1940**, 44, 25.
217. V. Vand, *J. Phys. Chem.* **1948**, 52, 277.
218. D.G. Thomas, *J. Colloid Sci.* **1965**, 20, 267.
219. S.P. Moulik, *J. Phys. Chem.* **1968**, 72, 4688.
220. S.P. Moulik, *Electrochim. Acta.* **1972**, 17, 1491.
221. S.P. Moulik, *J. Indian Chem. Soc.* **1972**, 49, 483.
222. R.J. Fort, W.R. Moore, *Trans. Faraday Soc.* **1966**, 62, 1112.
223. G.R. Naidu, P.R. Naidu, *Ind. J. Chem.* **1983**, 22A, 324.
224. O. Redlich, A.T. Kister, *Ind. Eng. Chem.* **1948**, 40, 345.

225. L. Pikkarainen, *J. Chem. Eng. Data* **1983**, 28, 344.
226. L. Pikkarainen, *J. Chem. Eng. Data* **1983**, 28, 381.
227. L.S. Manjeshwar, T. Aminabhavi, *J. Chem. Eng. Data* **1988**, 33, 184.
228. K.P. Rao, K.S. Reddy, *J. Chem. Eng. Data* **1988**, 33, 130.
229. S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw Hill, New York, **1941**.
230. D.S. Gill, T.S. Kaur, H. Kaur, I.M. Joshi, J. Singh, *J. Chem. Soc. Faraday Trans.* **1993**, 89, 1737.
231. J.V. Herraez, R. Belda, *J. Soln. Chem.* **2004**, 33, 117.
232. J. Ferguson, Z. Kemblonski, *Applied Fluid Rheology*, Elsevier, Cambridge, **1991**.
233. H.A. Barnes, J.F. Hutton, K. Walters, *An Introduction to Rheology*, Elsevier, Amsterdam, **1993**.
234. C.W. Macosk, *Rheology. Principles, Measurements and Applications* (VCH), New York, **1994**.
235. M. Garcia-Velarde, *Revista Esp. Fisica* **1995**, 9, 12.
236. R. Shukla, M. Cheryan, *J. Membrane Sci.* **2002**, 198, 104.
237. J.M. Resa, C. Gonzalez, J. Lanz, *J. Food Eng.* **2002**, 51, 113.
238. M.J. Assael, N.K. Dalaouti, I. Metaxa, *Fluid Phase Equilibria.* **2002**, 199, 237.
239. A. Darr, *Technología Farmacéutica.*, S.A. Acribia, Zaragoza, **1979**.
240. R. Voight, S.A. Acribia, *Tratado de Tecnología Farmacéutica.* Zaragoza, **1982**.
241. C.K. Z'eborg-Mikkelsen, S.E. Quiñones-Cisneros, S.H. Stenby, *Fluid Phase Equilibria.*, **2002**, 1191, 194.
242. C. Fauli-Trillo, *Tratado de Farmacia Galénica*, S.A. Lujan, Madrid, **1993**.
243. J. Swarbrik, J.C. Boyland, *Encyclopedia of Pharmaceutical Technology*, Marcel Dekker, New York, **1993**.
244. J. Pellicer, *Sinergia Viscosa*, Valencia, Spain, **1997**.
245. G. Copetti, R. Lapasin, E.R. Morris, *Proceedings of the Fourth European Rheology Conference*, Seville, Spain, **1994**.
246. G. Kalentunc-Gencer, M. Peleg, *J. Texture Studies.* **1986**, 17, 61.

247. D.D. Christianson, *Hydrocolloidal Interactions with Starches*, Wesport. Conn., **1982**.
248. N.K. Howell, *Proceedings of the Seventh International Conference*, Wales, **1993**.
249. J.G. Mathieson, B.E. Conway, *J. Sol. Chem.* **1974**, 3, 455.
250. S. Bhowmik, R.K. Mohanty, *Ind. J. Chem.* **1986**, 25A, 416.
251. M.V. Kaulgud, K.S. Mohan Rao, *Ind. J. Chem.* **1988**, 27A, 12.
252. K.J. Patil, A.B. Wazalwar, G.R. Mehta, *Ind. J. Chem.* **1988**, 27A, 799.
253. M. Iqbal, R.E. Verral, *Can. J. Chem.* **1989**, 67, 727.
254. M. Kikuchi, M. Sakurai, K. Nitta, *J. Chem. Eng. Data* **1996**, 41, 1439.
255. B.E. Conway, R.E. Verral, *J. Phys. Chem.* **1966**, 70, 3952.
256. K. Gekko, H. Noguchi, *J. Phys. Chem.* **1979**, 83, 2706.
257. W.L. Masterson, *J. Chem. Phys.* **1954**, 22, 1830.
258. L.G. Hepler, *Can. J. Chem.* **1969**, 47, 4613.
259. M.V. Kaulgud, K.J. Patil, *J. Phys. Chem.* **1976**, 80, 138.
260. K.J. Patil, G.R. Mehta, R.K. Chandewar, *Ind. J. Chem.* **1986**, 25A, 1147.
261. C. Lafuente, B. Ginar, A. Villares, I. Gascon, P. Cea, *Int. J. Thermophys.* **2004**, 25, 1735.
262. G. Douheret, A. Pal, M.I. Davis, *J. Chem. Thermodyn.* **1990**, 22, 99.
263. I. Gascon, S. Martin, P. Cea, M.C. Lopez, F.M. Royo, *J. Sol. Chem.* **2002**, 31, 905.
264. R. Mehra, M. Pancholi, *J. Ind. Chem. Soc.* **2005**, 82, 791.
265. S.L. Oswal, K.D. Prajapati, *J. Chem. Eng. Data* **1998**, 43, 367.
266. K. Hsu-Chen, T. Chein-Hsium, *J. Chem. Eng. Data* **2005**, 50, 608.
267. D.W. Marquardt, *J. Soc. Ind. Appl. Math.* **1963**, 11, 431.
268. L. Onsager, *Z. Phys. Chem.* **1927**, 28, 277.
269. R.M. Fuoss, *Rev. Pure Appl. Chem.* **1968**, 18, 125.
270. E. Pitts, *Proc. Roy. Soc.* **1953**, 217A, 43.
271. R.M. Fuoss, L. Onsager, *J. Phys. Chem.* **1957**, 61, 668.
272. R.M. Fuoss, *Chemical Physics of Ionic Solutions*, Wiley, New York, **1966**.
273. E. Pitts, R.E. Tabor, J. Daly, *Trans. Faraday Soc.* **1969**, 65, 849.

274. (a) R.M. Fuoss, K.L. Hsia, *Proc. Natl. Acad. Sci.* **1967**, 57, 1550.
(b) R.M. Fuoss, K.L. Hsia, *J. Am. Chem. Soc.* **1968**, 90, 3055.
275. R. Fernandez-Prini, *J.E. Prue. Z. Phys. Chem.* **1965**, 228, 373.
276. R. Fernandez-Prini, *J.E. Prue. Z. Phys. Chem.* **1965**, 228, 473.
277. D.F. Evans, R.L. Kay, *J. Phys. Chem.* **1966**, 70, 366.
278. D. F. Arrington, E. Griswold, *J. Phys. Chem.* **1970**, 74, 123.
279. R.M. Fuoss, C.A. Kraus, *J. Am. Chem. Soc.* **1933**, 55, 476.
280. T. Shedlovsky, J. Franklin, *Instt.* **1938**, 225, 739.
281. (a) J.C. Justice, *J. Chem. Phys.* **1968**, 65, 353.
(b) J.C. Justice, R. Bury, C. Treiner, *J. Chem. Phys.* **1968**, 65, 1708.
282. R.M. Fuoss, F. Accascina, *Electrolytic Conductance*, Wiley, New York, **1959**.
283. N.K. Bjerrum, Dan. Vidensk. Selek. *Mat.Fys.Medd.* **1926**, 7, 9.
284. M. Tissier, G. Douheret, *J. Soln. Chem.* **1978**, 7, 87.
285. R. Fernandez-Prini, *J. Prue, Trans. Faraday Soc.* **1962**, 66, 1257.
286. (a) R.M. Fuoss, L. Onsager, *J. Phys. Chem.* **1962**, 66, 1722.
(b) R.M. Fuoss, L. Onsager, *J. Phys. Chem.* **1963**, 67, 621.
287. R.M. Fuoss, *J. Phys. Chem.* **1975**, 49, 525.
288. P.C. Carman, D.P. Laurie, *J. Sol. Chem.* **1976**, 5, 457.
289. R.M. Fuoss, *J. Phys. Chem.* **1977**, 81, 1829.
290. R.M. Fuoss, *Proc. Nat. Acad. Sci.* **1978**, 75, 16.
291. R.M. Fuoss, *J. Phys. Chem.* **1957**, 82, 2427.
292. (a) W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday II.* **1978**, 74, 743.
(b) W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday II.* **1978**, 74, 1456.
293. W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday Trans. I.* **1979**, 75, 1128.
294. W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday Trans. II.* **1978**, 74, 1456.
295. A.D. Pethybridge, S.S. Tara, *J. Chem. Soc. Faraday I.* **1980**, 76, 368.
296. M. Bester-Rogac, R. Neueder, J. Barthel, *J. Solution Chem.* **1999**, 28, 1071.
297. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York, **1964**.
298. E. Balaguruswami, *Numerical Methods*, Tata McGraw-Hill Publishing Company, New Delhi, **2007**.

299. M.N. Roy, B. Sinha, V.K. Dakua, *Pak. J. Sci. Ind. Res.* **2006**, 49,153.
300. (a) B.S. Krumgalz, *J. Chem. Soc. Faraday I.* **1983**, 79,571.
(b) B.S. Krumgalz, *J. Chem. Soc. Faraday I.* **1985**, 81, 241.
301. P. Walden, H. Ulich, D. Bush, *Z. Phys. Chem.* **1926**, 123, 429.
302. R.M. Fuoss, E. Hirsch, *J. Am. Chem. Soc.* **1960**, 82, 1018.
303. S. Takezawa, Y. Kondo, N. Tokura, *J. Phys. Chem.* **1973**, 77,2133.
304. (a) D.S. Gill, *J. Chem. Soc. Faraday I.* **1981**, 74,751.
(b) D.S. Gill, N. Kumari, M.S. Chauhan, *J. Chem. Soc. Farada Trans I.* **1985**, 81,687.
305. M.A. Coplan, R.M. Fuoss, *J. Phys. Chem.* **1964**, 68, 1177.
306. J.F. Coetzee, G.P. Cunningham, *J. Am. Chem. Soc.* **1965**, 87, 2529.
307. R.H. Stokes, R.A. Robinson, *Trans. Faraday Soc.* **1957**, 53,301.
308. M. Born, *Z. Phys. Chem.* **1920**, 1, 221.
309. R.H. Boyd, *J. Chem. Phys.* **1961**, 35,1281.
310. R. Zwanzig, *J. Chem. Phys.* **1963**, 38,1603.
311. E.J. Passeron, *J. Phys. Chem.* **1964**, 68, 2728.
312. (a) P. Walden, *Z. Phys. Chem.* **1906**, 55,207.
(b) P. Walden, *Z. Phys. Chem.* **1912**, 78, 257.
313. R.A. Robinson, R.H. Stokes, *Electrolyte Solutions*, Butterworths, London, **1959**.
314. R. Gopal, M.M. Hussain, *J. Ind. Chem. Soc.* **1963**, 40, 981.
315. L.G. Longsworth, *J. Phys. Chem.* **1963**, 67, 689.
316. M. Della Monica, U. Lamauna, L. Seutatore, *J. Phys. Chem.* **1968**, 72, 2124.
317. S. Brocus, *J. Chem. Phys.* **1958**, 28, 1158.
318. D.G. Miller, *J. Phys. Chem.* **1960**, 64, 1598.
319. G.J. Hills, *Chemical Physics of Ionic Solutions*, Wiley, New York, **1966**.
320. R.H. Stokes, I.A. Weeks, *Aust. J. Chem.* **1964**, 17, 304.
321. R.H. Stokes, *The Structure of Electrolytic Solutions*, Wiley, New York, **1959**.
322. D.S. Gill, *J. Chem. Soc. Faraday Trans. I.* **1981**, 77, 751.
323. R. Zwanzig, *J. Chem. Phys.* **1970**, 52, 3625.
324. H.S. Franks, *Chemical Physics of Ionic Solutions*, Wiley, New York, **1966**.

325. G. Atkinson, S.K. Koz, *J. Phys. Chem.* **1965**, *69*, 128.
326. R.L. Kay, G.P. Cunningham, D.F. Evans, *Hydrogen bonded Solvent Systems*, Taylor and Francis, London, **1968**.
327. R.L. Kay, B.J. Hales, G.P. Cunningham, *J. Phys. Chem.* **1967**, *71*, 3925.
328. R.L. Kay, C. Zawoyski, D.F. Evans, *J. Phys. Chem.* **196**, *69*, 4208.
329. D. F. Evans, J. L. Broadwater, *J. Phys. Chem.* **1968**, *72*, 1037.
330. M. Spiro, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York, **1973**.
331. R. Fernandez-Prini, G. Atkinson, *J. Phys. Chem.* **1971**, *75*, 239.
332. L. Bahadur, M.V. Ramanamurti, *J. Chem. Soc. Faraday I.* **1980**, *76*, 1409.
333. L. Bahadur, M.V. Ramanamurti, *J. Electrochem. Soc.* **1981**, *128*, 339.
334. L. Bahadur, M.V. Ramanamurti, *Can. J. Chem.* **1984**, *62*, 1051.
335. J.L. Broadwater, R.L. Kay, *J. Phys. Chem.* **1970**, *74*, 3803.
336. S. Das, D.K. Hazra, *Indian J. Chem.* **1988**, *274*, 1073.
337. S. Das, D.K. Hazra, *J. Ind. Chem. Soc.* **1988**, *L XV*, 100.
338. (a) R.L. Kay, J.L. Broadwater, *Electrochim. Acta.* **1971**, *16*, 667.
(b) R.L. Kay, J.L. Broadwater, *J. Sol. Chem.* **1976**, *5*, 57.
339. A.D. Aprano, R.M. Fuoss, *J. Phys. Chem.* **1963**, *67*, 1704.
340. P. Hemmes, *J. Phys. Chem.* **1974**, *78*, 907.
341. J. Hubbard, L. Onsager, *J. Chem. Phys.* **1977**, *53*, 4850.
342. N. Islam, M.R. Islam, M. Ahmed, *Z. Phys. Chem.* **1981**, *262*, 129.
343. D.S. Gill, A.N. Sharma, H. Schneider, *J. Chem. Soc. Faraday I.* **1982**, *78*, 465.
344. C.J. Cramer, D.G. Truhlar, *J. Am. Chem. Soc.* **1991**, *113*, 8305.
345. D.J. Giesen, J.W. Stores, C.J. Cramer, D.G. Truhlar, *J. Am. Chem. Soc.* **1995**, *117*, 1057.
346. (a) C.J. Cramer, D.G. Truhlar, *J. Org. Chem.* **1996**, *61*, 8720.
(b) C.J. Cramer, D.G. Truhlar, *Erratum.* **1999**, *101*, 309.
347. G.D. Hawkins, C.J. Cramer, D.G. Truhlar, *J. Phys. Chem. B* **1997**, *101*, 7147.
348. G.D. Hawkins, C.J. Cramer, D.G. Truhlar, *J. Phys. Chem. B* **1998**, *102*, 3257.
349. A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burgess, *J. Chem. Phys.* **1997**, *106*, 4168.

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

CHAPTER -III

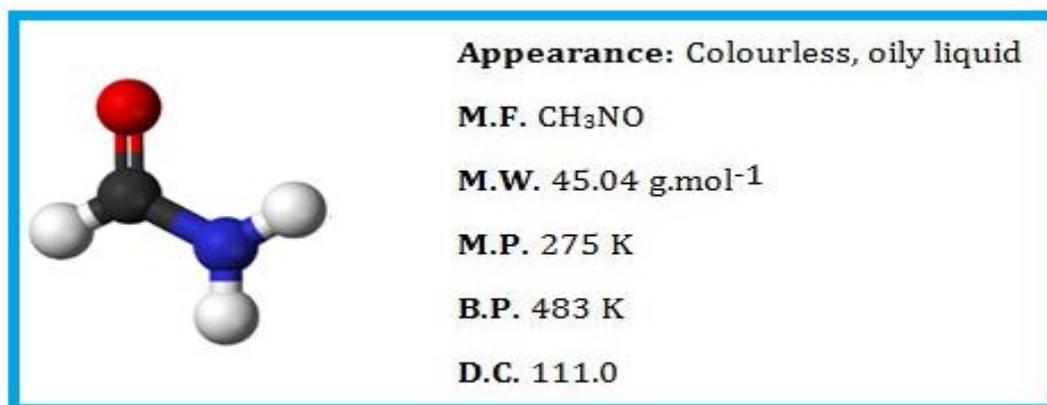
EXPERIMENTAL SECTION

3.1. NAME, STRUCTURE, PHYSICAL PROPERTIES, PURIFICATION AND APPLICATION OF THE USED SOLVENTS AND SOLUTES.

3.1.1. Solvents

Formamide:

It is also known as methanamide, is an amide with a chemical formula CH_3NO , derived from formic acid. It is a clear liquid being miscible with water and has an ammonia-like odour. It is hygroscopic in nature. It is used as a solvent for many ionic compounds.



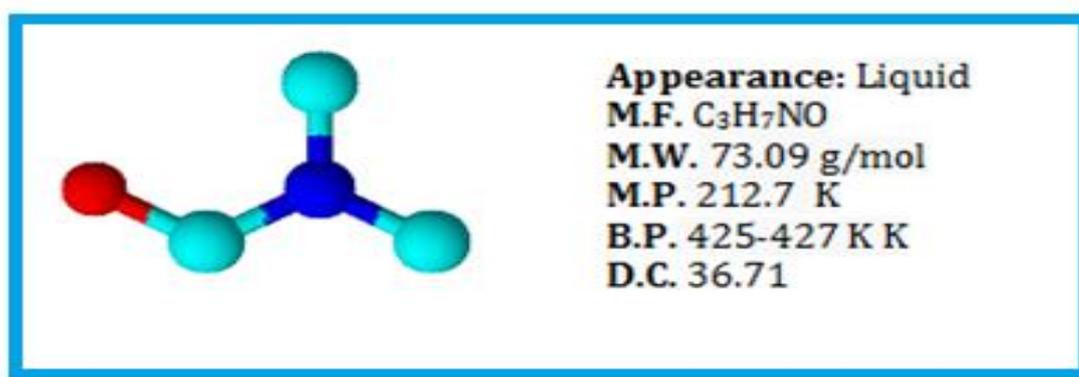
Source: S.D. Fine Chemicals Ltd. Mumbai, India.

Purification: It was dried by the passage through a column of 3A molecular sieves followed by the deionization with a mixed-bed-ion-exchange resin loaded with H^+ and HCONH^- ions [1].

Application: Formamide is the chemical feedstock for the manufacture of sulfa drugs, other pharmaceuticals, pesticides and herbicides. It is also used as an RNA stabiliser in gel electrophoresis by deionizing RNA. In capillary electrophoresis, it is used for stabilizing (single) strands of denatured DNA. It is also importantly used as a solvent for resins and plasticizers [2] and the electrostatic self-assembly of polymer nano-films [3].

N, N, Dimethylformamide:

N, N, Dimethylformamide is commonly abbreviated as DMF. DMF is a polar (hydrophilic) aprotic solvent with a high boiling point with the molecular formula C_3H_7NO . This colourless liquid is miscible with water and the majority of organic liquids. Pure dimethylformamide is odourless 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. It facilitates those reactions involving polar mechanisms, such as S_N2 reactions.



Source: Thomas Baker, India

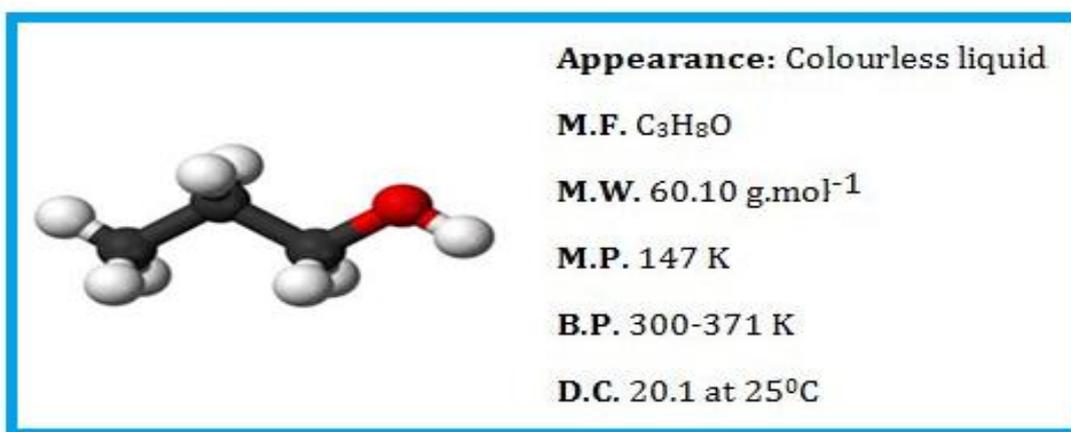
Purification: It was dried by passing through Linde 4Å molecular sieves and then distilled [1].

Application: DMF is used in the production of acrylic fibers and plastics. The primary use of dimethylformamide is as a solvent with low evaporation rate. 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 [4]. 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. 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. 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.

n-Propanol:

Propanol, technically known as 1-Propanol, is a primary alcohol with the formula $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$. It is formed naturally in small amounts during many fermentation processes. This colorless liquid is also known as propan-1-ol, 1-propyl alcohol, n-propyl alcohol, and n-propanol. It is isomeric with isopropanol (2-propanol, isopropyl alcohol).



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

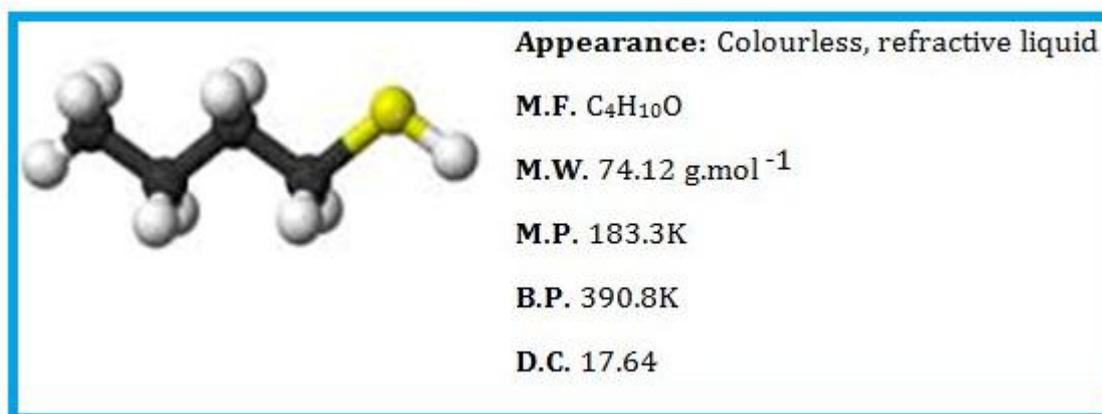
Purification: It was dried by adding drying agent CaSO_4 followed by filtration and then distillation [1].

Application: n-Propanol is used as a solvent for waxes, vegetable oils, resins, cellulose esters, and ethers. It is found in inks, brake fluids and polishing compounds and has been used as a degreasing agent, an antiseptic, and a chemical intermediate. More recently, it is being used as a hand disinfectant by health care workers.

n-Butanol:

n-Butanol or n-butyl alcohol is a primary alcohol with a 4-carbon structure with the chemical formula $\text{C}_4\text{H}_9\text{OH}$. Its isomers include isobutanol, 2-butanol, and tert-

butanol. Butanol is one of the group of "fusel alcohols" (from the German for "bad liquor"), which have more than two carbon atoms and have significant solubility in water. n-Butanol occurs naturally as a minor product of the fermentation of sugars and other carbohydrates [5] and is present in many foods and beverages.



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

Purification: It was dried by adding drying agent CaSO₄ followed by filtration and then distillation [1].

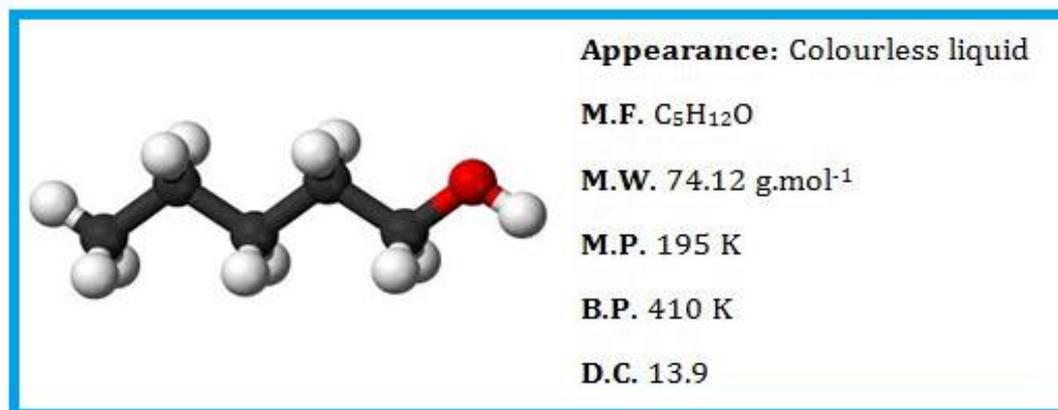
Application: n-Butanol is used as a solvent for waxes, vegetable oils, resins, cellulose esters, and ethers. It is used in inks, brake fluids and polishing compounds and has been utilized as a degreasing agent, an antiseptic and a chemical intermediate. More recently, it is being used as a hand disinfectant by health care workers.

n-Pentanol:

1-Pentanol (or n-pentanol), is an alcohol with five carbon atoms with the molecular formula C₅H₁₂O. 1-Pentanol is a colorless liquid with an unpleasant aroma. To reduce the use of fossil fuels, research is underway to discover cost-effective methods of utilizing fermentation to produce Bio-Pentanol.

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

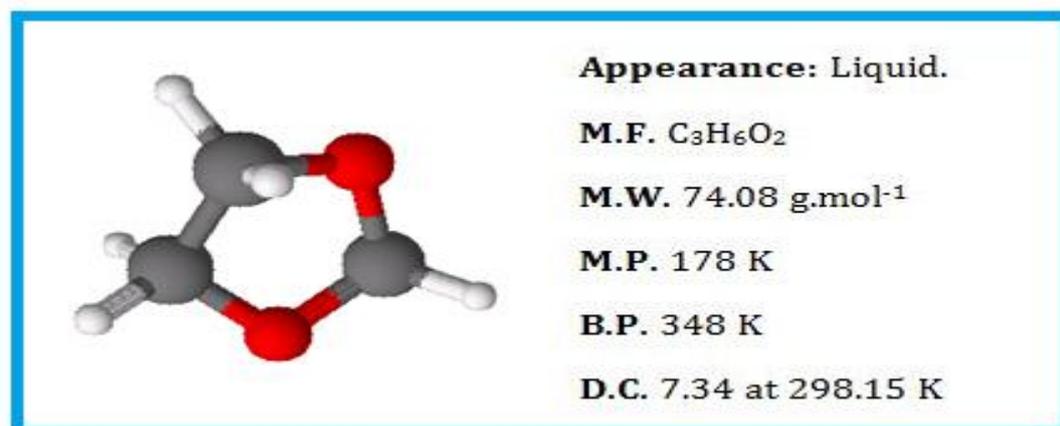
Purification: It was dried by adding drying agent CaSO₄ followed by filtration and then distillation [1].



Application: Pentanol can be used as a solvent for coating CDs and DVDs. Another use is a replacement for gasoline.

1,3-Dioxolane

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



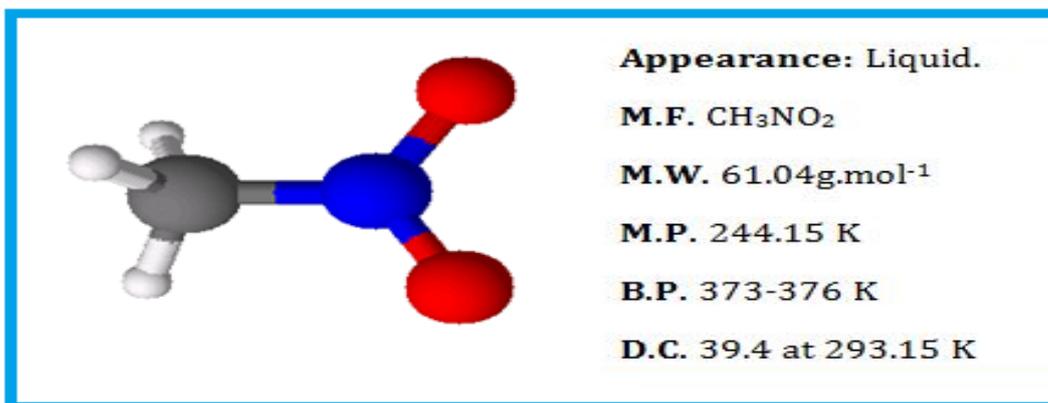
Source: S.D. Fine Chemicals, India.

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

Application: It is a very crucial as the lithium battery electrolyte solvent component. This is also important in pharmaceutical manufacturing. It is used as a replacement for many chlorinated solvents, 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.

Nitromethane

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



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

Purification: It is dried with CaSO₄ followed by distillation [1].

Application: The chief use of nitromethane is as a stabilizer for chlorinated solvents, which are used in dry cleaning, semiconductor processing, and degreasing. It is also used 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.

Dimethyl Sulphoxide

Dimethyl sulfoxide (DMSO) is an organosulfur compound with the formula (CH₃)₂SO. 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.



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

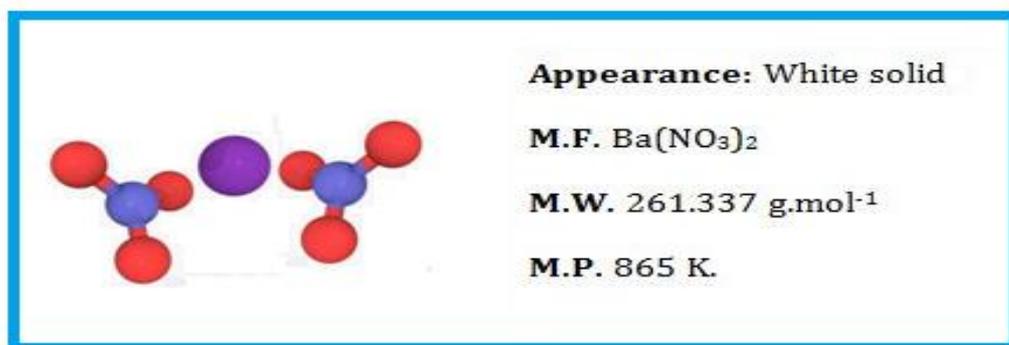
Purification: It was dried by passing through Linde 4Å molecular sieves[1].

Application: In medicine, DMSO is predominantly used as a topical analgesic, a vehicle for topical application of pharmaceuticals, as an anti-inflammatory, and an antioxidant [6]. 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. 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.

3.1.2. Solutes

Barium Nitrate:

Barium nitrate with chemical formula Ba(NO₃)₂ is a salt composed of barium and the nitrate ion. Barium nitrate exists as a white solid at room temperature. It is soluble in water, and like other soluble barium compounds, is toxic.



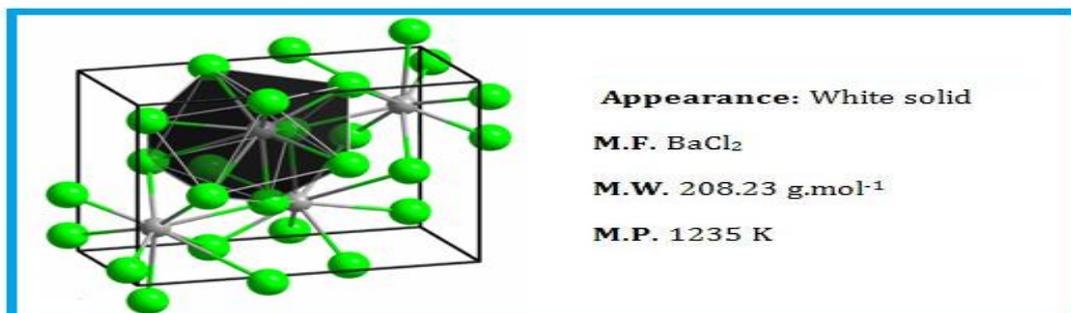
Source: Sigma Aldrich, Germany.

Purification: A method of preparing purified barium nitrate includes precipitating barium nitrate crystals from a solution including barium ions, and washing the barium nitrate crystals with an aqueous solution including at least 10 wt % nitric acid.

Application: Barium nitrate finds wide application in the laboratory. Barium nitrate is used to produce a 'green fire' and green signal flares, pyrotechnic devices and tracer bullets. It also has uses in the vacuum tube industry. Barium Nitrate is used to manufacture other barium compounds. However, its toxicity limits its applicability.

Barium Chloride:

Barium chloride is the inorganic compound with the formula BaCl_2 . It is one of the most common water-soluble salts of barium. Like other barium salts, it is toxic and imparts a yellow-green coloration to a flame. It is also hygroscopic.



Source: Sigma Aldrich, Germany.

Purification: Recrystallised from aqueous Ethanol solution followed by drying under vacuum at 348 K and it was stored over P_2O_5 in a desiccator.

Application: As an inexpensive, soluble salt of barium, barium chloride finds wide application in the laboratory. It is commonly used as a test for sulfate ion. In industry, barium chloride is mainly used in the purification of brine solution in caustic chlorine plants and also in the manufacture of heat treatment salts, case hardening of steel, in the manufacture of pigments, and in the manufacture of other barium salts. $BaCl_2$ is also used in fireworks to give a bright green color. However, its toxicity limits its applicability.

Lithium Perchlorate: Lithium perchlorate is the inorganic compound with the chemical formula $LiClO_4$. It is a white crystalline solid being highly soluble in water and in alcohol.



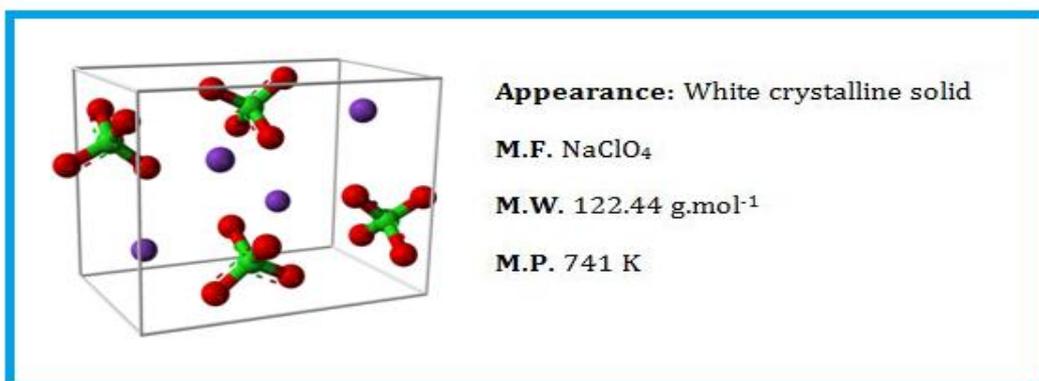
Source: Sigma Aldrich, Germany.

Purification: Used as purchased.

Application: Lithium perchlorate is used as an electrolyte in lithium-ion batteries. Lithium perchlorate is chosen over alternative electrolytes such as lithium hexafluorophosphate or lithium tetrafluoroborate when its superior electrical impedance, conductivity, hygroscopicity, and anodic stability properties are of importance to the specific application. One of the most promising potential applications of lithium perchlorate is in the manufacture of chemical sources of energy (i.e. fuel cells) for electric cars [7].

Sodium Perchlorate:

Sodium perchlorate is the most soluble common perchlorate salt with the chemical formula NaClO_4 . It is a hygroscopic, white crystalline solid that is highly soluble in water and in alcohol. It usually comes as the monohydrate, which has a rhombic crystal system.



Source: Sigma Aldrich, Germany.

Purification: Used as purchased.

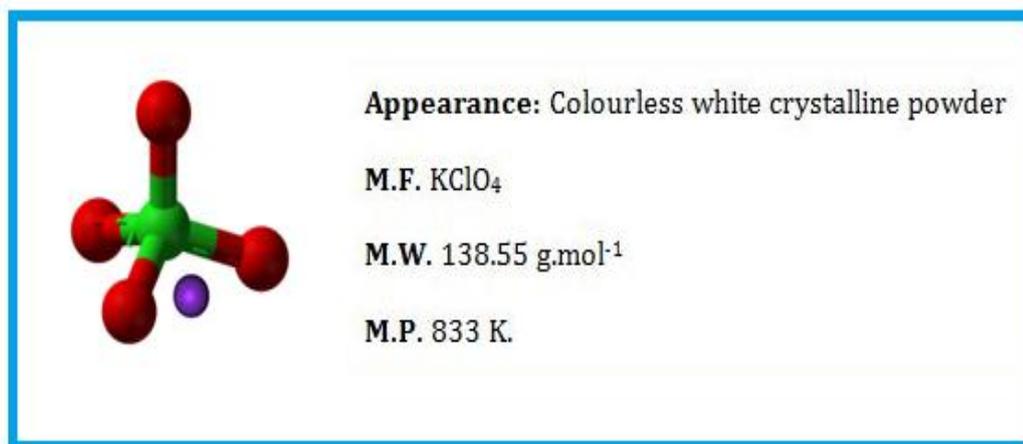
Application: Sodium perchlorate can be used to block iodine uptake before administration of iodinated contrast agents in patients with subclinical hyperthyroidism. NaClO_4 has a variety of uses in the laboratory, often as a nonreactive electrolyte. For example, it is used in standard DNA extraction and hybridization reactions in molecular biology.

Potassium Perchlorate:

Potassium perchlorate is the colorless, crystalline solid inorganic salt with the chemical formula KClO_4 . Like other perchlorates, this salt is a strong oxidizer although it usually reacts very slowly with organic substances. KClO_4 has the lowest solubility among the alkali metal perchlorates.

Source: Sigma Aldrich, Germany.

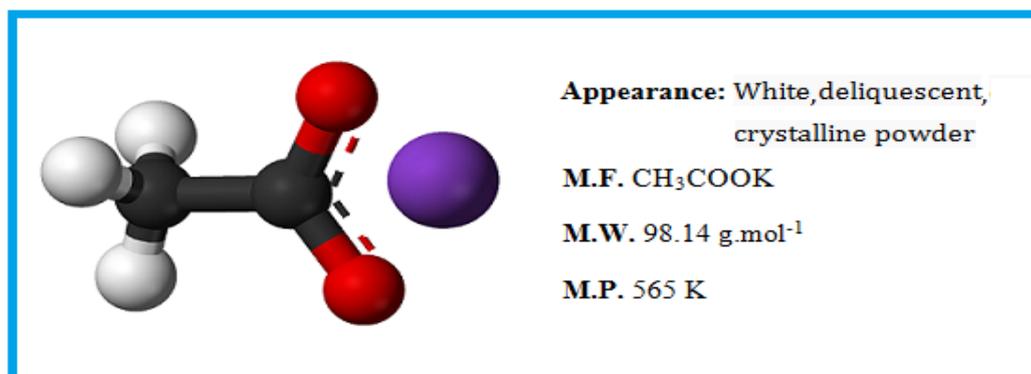
Purification: Used as purchased.



Application: KClO_4 is a common oxidizer used in fireworks, ammunition percussion caps, explosive primers, and is used variously in propellants, flash compositions and sparklers. It has been used as a solid rocket propellant. KClO_4 can be used as an antithyroid agent used to treat hyperthyroidism, usually in combination with one other medication.

Potassium Acetate:

Potassium Acetate (CH_3COOK) is the potassium salt of acetic acid. It is the salt that is formed along with water as acetic acid and potassium hydroxide are neutralized together. It appears as white, deliquescent, crystalline powder.



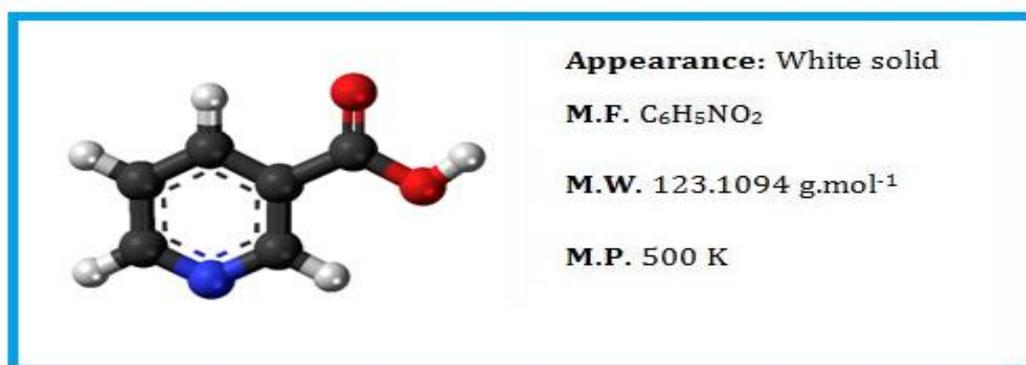
Source: Sigma Aldrich, Germany.

Purification: Used as purchased.

Application: Potassium acetate is used as a catalyst in the production of polyurethanes [8]. Potassium acetate is also the extinguishing agent used in class-K fire extinguishers because of its ability to cool and form a crust over burning oils. It is used as a food additive as a preservative and acidity regulator. In medicine, potassium acetate is used as part of replacement protocols in the treatment of diabetic ketoacidosis because of its ability to break down into bicarbonate and help neutralize the acidotic state. In molecular biology, potassium acetate is used to precipitate dodecyl sulfate (DS) and DS-bound proteins, allowing the removal of proteins from DNA. It is also used as a salt for the ethanol precipitation of DNA.

Nicotinic Acid:

Nicotinic acid is a B vitamin (vitamin B3) with the chemical formula $C_6H_5NO_2$. It appears as white translucent crystals. This is a water-soluble solid is a derivative of pyridine, with a carboxyl group (COOH) at the 3-position. It occurs naturally in plants and animals. It is also added to many foods as a vitamin supplement. It is also present in many multiple vitamins and nutritional supplements. It cannot be directly converted to nicotinamide, but both compounds are precursors of the coenzymes nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP) in vivo. [9]



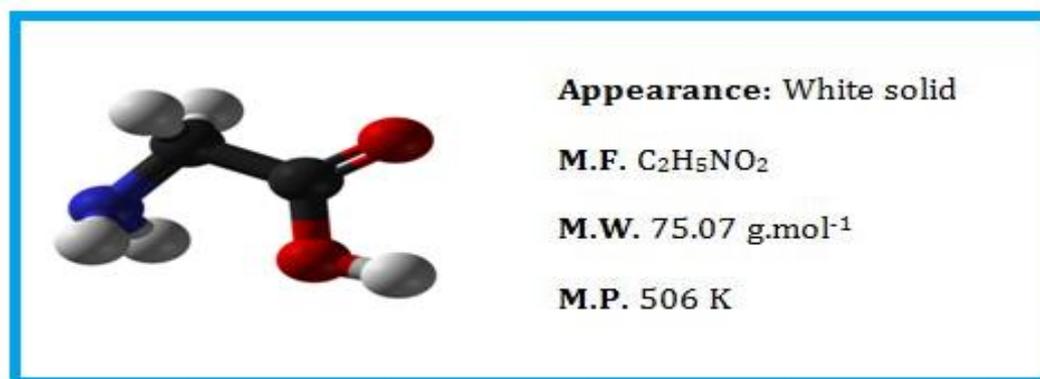
Source: Sigma Aldrich, Germany.

Purification: Used as purchased.

Application: As a treatment, higher amounts of nicotinic acid can improve cholesterol levels and lower cardiovascular risks. It is alternatively known as 'Niacin'. It can boost levels of good HDL cholesterol and lower triglycerides as well or better than some prescription drugs. Niacin also modestly lower the bad LDL cholesterol. It is very often prescribed in combination with statins for cholesterol control, such as Crestor, Lescol or Lipitor. Chronic niacin deficiency leads to a disease called pellagra.

Glycine:

Glycine is an important organic amino acid with the formula $\text{NH}_2\text{CH}_2\text{COOH}$. Having a hydrogen substituent in its side-chain, glycine is the smallest of the 20 amino acids commonly found in proteins and indeed is the smallest possible. Glycine is a colourless, sweet-tasting crystalline solid. It is non-chiral in nature. It can fit into hydrophilic or hydrophobic environments, due to its minimal side chain of only one hydrogen atom.



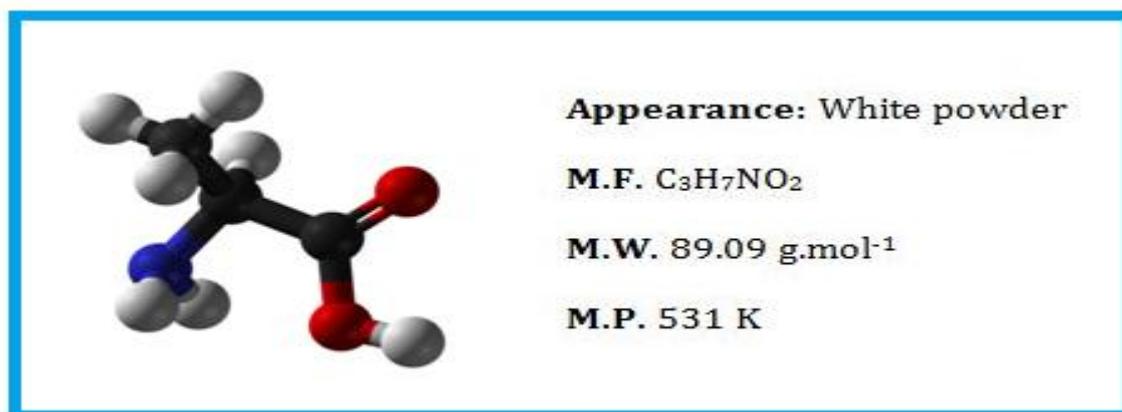
Source: S.D. Fine Chemicals Ltd. Mumbai, India.

Purification: Used as purchased.

Application: Glycine is used as an additive in pet food and animal feed. Certain food supplements and protein drinks contain glycine. Pharmaceutical grade glycine is used for intravenous injections. In industry technical grade glycine acts

as an agent in metal complexing and finishing. For humans, glycine is sold as a sweetener/taste enhancer. Certain drug formulations include glycine to improve gastric absorption of the drug. Glycine serves as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, and toiletries. Many miscellaneous products use glycine or its derivatives, such as the production of rubber sponge products, fertilizers, metal complexants.

L-alanine: Alanine is a non-polar α -amino acid with the chemical formula $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$. The L-isomer is one of the 20 amino acids encoded by the genetic code. L-Alanine is second only to leucine in rate of occurrence, accounting for 7.8% of the primary structure in a sample of 1,150 proteins.



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

Purification: Used as purchased.

Application: L-alanine plays a decisive role as a building block of important proteins. Mostly synthesized by the muscle cells from lactic acid it is considered the most important nutrient for the amino acid metabolism in the blood together with L-Glutamine. Once synthesized L-alanine is absorbed via the liver and converted to a pyruvate. This compound is critical for the production of glucose and hence blood sugar management. L-alanine supplements are therefore often used in cases of hypoglycaemia to prevent the organism from suffering low blood sugar or insuline shocks. They enable rapid energy delivery by stimulating the immediate release of glucose into the blood stream. Other important

functions of this amino acid are the support of the immune system and prevention of kidney stones. Alanine increases in duration and strengthens the immune system.

L-valine:

Valine is an essential α -amino acid with the chemical formula $\text{HO}_2\text{CCH}(\text{NH}_2)\text{CH}(\text{CH}_3)_2$. L-Valine is one of 20 proteinogenic amino acids. This essential amino acid is non-polar. Human dietary sources are any proteinaceous foods such as meats, dairy products, soy products, beans and legumes. Along with leucine and isoleucine, valine is a branched-chain amino acid. It is named after the plant valerian.



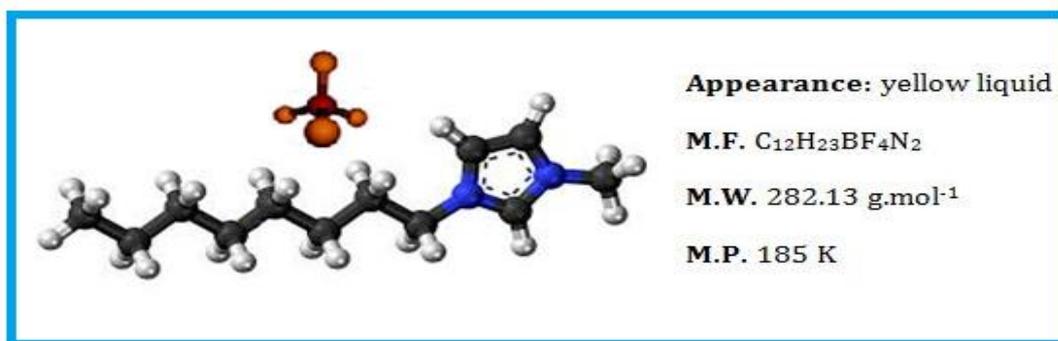
Source: S.D. Fine Chemicals Ltd. Mumbai, India.

Purification: Used as purchased.

Application: L-valine is a branched chain amino acid being very important for supplying energy to muscles. The branched chain amino acids enhance energy, increase endurance and aid in muscle tissue recovery and repair. Being a branched chain amino acid, L-valine is important for optimal growth in infants and children and nitrogen balance in adults. Branched chain preparations are used in sports nutrition and health foods.

1-Methyl-3-Octylimidazoliumtetrafluoroborate:

It is a 'Room temperature ionic liquid' (RTIL) based on the imidazolium cation with tetrafluoroborate as the anionic counterpart. It is highly polar, nonvolatile, nonflammable, stable in air or water and recyclable.



Source: Sigma Aldrich, Germany.

Purification: Used as purchased.

Application: 1-Methyl-3-octylimidazolium tetrafluoroborate is 'green' replacement for volatile organic solvents used in reactions involving inorganic and bio catalytic reactions. It is also utilized as electrically conductive liquids in electrochemistry. Moreover, It is vastly important in multiphase bioprocess operations, batteries, fuel cells.

Tetrabutylphosphonium Tetrafluoroborate:

It is a 'Room temperature ionic liquid' (RTIL) based on the phosphonium cation with tetrafluoroborate as the anionic counterpart. It is highly polar, nonvolatile, nonflammable, stable in air or water and recyclable. They are highly polar, nonvolatile, nonflammable, stable in air or water and recyclable.



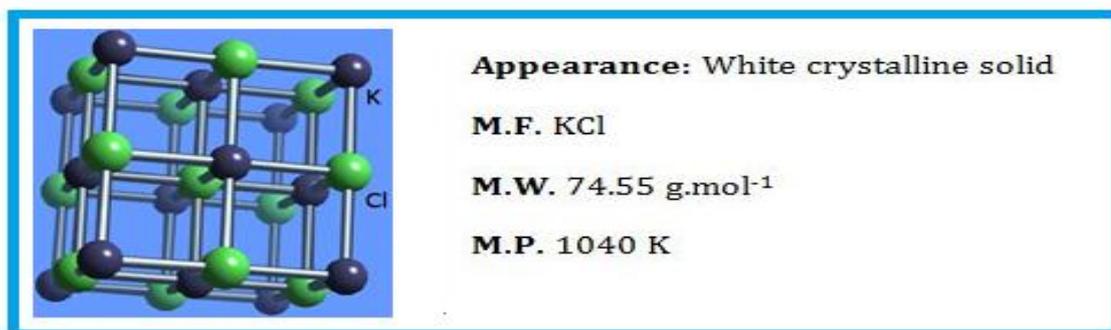
Source: Sigma Aldrich, Germany.

Purification: Used as purchased.

Application: Tetrabutylphosphonium Tetrafluoroborate (Bu_4PBF_4) is 'green' replacement for volatile organic solvents used in reactions involving inorganic and bio catalytic reactions. It is also utilized as non-aqueous electrolyte in electrochemistry. It can be used to adjust the selectivity and enhance resolution of HPLC, High Performance Liquid Chromatography, the preferred technique used in explosive analysis. It is also used as heat-transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells).

Potassium Chloride:

Under standard conditions in its pure state potassium chloride is odourless having white or colourless, vitreous crystal appearance. The solid dissolves readily in water and its solutions have a salt-like taste.



Source: Sigma Aldrich, Germany.

Purification: It was purified by re-crystallizing twice from conductivity water and then dried in vacuum desiccator over P_2O_5 for 24 hours before use.

Application: The majority of the potassium chloride produced is used for making fertilizer, since the growth of many plants is limited by their potassium intake. As an important chemical feedstock, it is used for the manufacture of potassium hydroxide and potassium metal. It is also used in medicine, lethal injections, scientific applications, food processing, and as a sodium-free substitute for table salt for persons concerned about its health effects. It is sometimes used in water as a completion fluid in petroleum and natural gas operations, as well as being an alternative to sodium chloride in household water softener units.

Potassium Bromide:

Under standard conditions, potassium bromide is a white crystalline powder. It is freely soluble in water. In a dilute aqueous solution, potassium bromide tastes sweet, at higher concentrations it tastes bitter, and tastes salty when the concentration is even higher. These effects are mainly due to the properties of the potassium ion.



Source: Sigma Aldrich, Germany.

Purification: It was purified by re-crystallizing twice from conductivity water and then dried in vacuum desiccator over P₂O₅ for 24 hrs before use.

Application: KBr helps characterize liquid compounds using infrared spectroscopy. Infrared spectroscopy, like all types of spectroscopy, is a technique used to identify compounds and investigate sample compositions. Every molecule has a unique absorbance profile determined by passing a beam of infrared light through the sample. Potassium bromide is a salt used to make photographic papers and plates and for process engraving. Found in general purpose and print developing solutions, potassium bromide is a highly soluble alkaline accelerator in solutions for X-ray films, continuous tone films requiring higher than normal contrast, intensifier solutions recommended for increasing the printing density of thin negatives, cold and warm tone developer solutions and universal developers for projection and contact papers.

Potassium Iodide:

Potassium iodide is an inorganic compound with the chemical formula KI. It is less hygroscopic (absorbs water less readily) than sodium iodide, making it easier to work with. Potassium iodide occurs naturally in kelp.



Source: Sigma Aldrich, Germany.

Purification: It was purified by re-crystallizing twice from conductivity water and then dried in vacuum desiccator over P₂O₅ for 24 hrs before use.

Application: KI is used with silver nitrate to make silver iodide an important chemical in film photography. KI is a component in some disinfectants and hair treatment chemicals. KI is also used as a fluorescence quenching agent in biomedical research, an application that takes advantage of collisional quenching of fluorescent substances by the iodide ion. However, for several fluorophores addition of KI in μM -mM concentrations results in increase of fluorescence intensity, and iodide acts as fluorescence enhancer. Potassium iodide is a component in the electrolyte of dye sensitized solar cells (DSSC) along with iodine. Potassium iodine finds its most important applications in organic synthesis mainly in the preparation of aryl iodides in the Sandmeyer reaction, starting from aryl amines.

3.2. EXPERIMENTAL METHODS

3.2.1. Preparation of Solvent Mixtures

Pure components were taken separately in glass stoppered bottles and thermostated at the desired temperature for sufficient time. After the attainment

of thermal equilibrium, 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 from experimental densities of the solvents at experimental temperature. It was then stoppered and the mixed contents were shaken well before use. Same procedure was adopted throughout the entire work while preparing different solvent mixtures. The physical properties of different pure and mixed solvents have been given 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).



Figure 1: 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 precision of $0.0005 \text{ g}\cdot\text{cm}^{-3}$.



Figure 2: Anton Paar Density-Meter (DMA 4500M)

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,

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

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 . 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 by means of a suspended Ubbelohde-type viscometer,

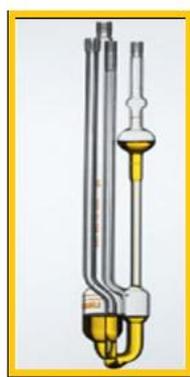


Figure 3: Suspended Ubbelohde-type Viscometer

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 precision 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.



Figure 4: Brookfield DV-III Ultra Programmable Rheometer & 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.



Figure 5: Thermostatic Water Bath (Science India, Kolkata)

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.

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.



Figure 6: The Multifrequency Ultrasonic Interferometer

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. 6 shows the Multifrequency Ultrasonic Interferometer i.e. (a) Cross-section of the measuring cell, (b) 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 (c) Electronic circuit diagram of the instrument is as follows.

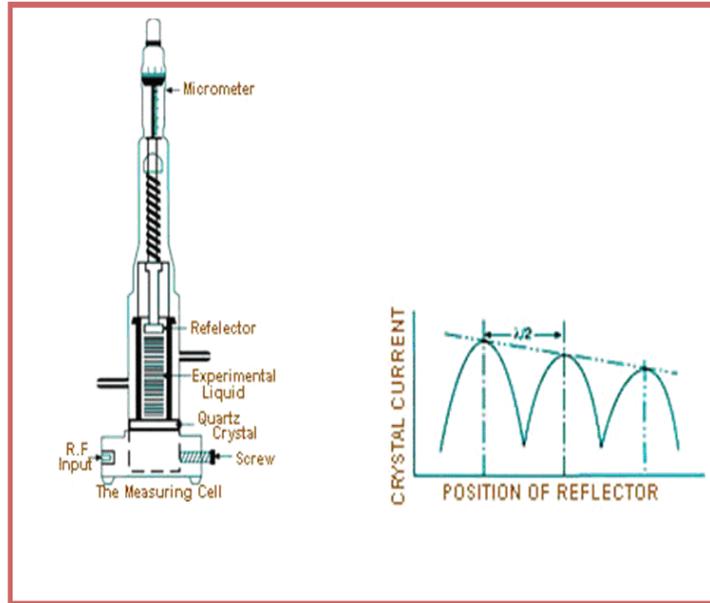


Figure 6(a): Cross section of the Measuring Cell and 6(b) Position of Reflector Versus Crystal Current

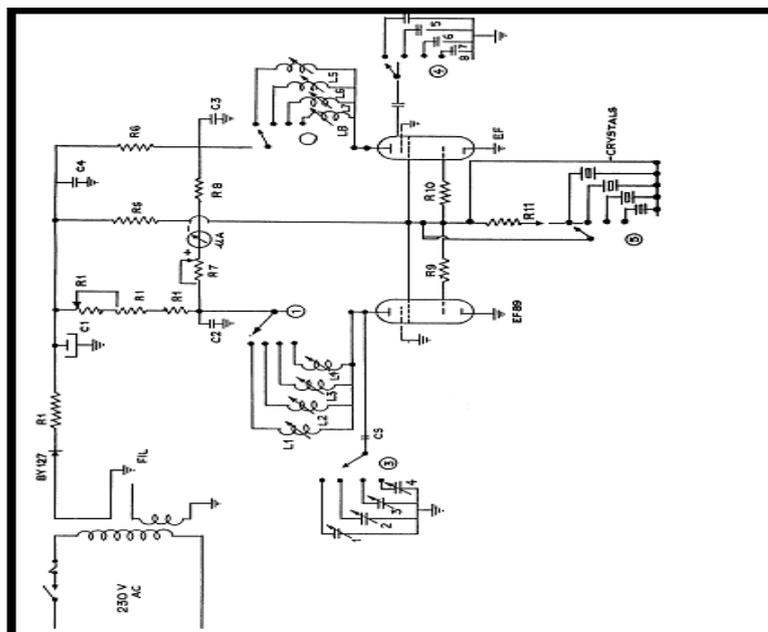


Figure 6(c): Electronic Circuit Diagram of the Instrument

3.2.8. Conductivity Measurement

Conductivity measurement was done using Systronics Conductivity TDS meter-308. It can provide both automatic and manual temperature compensation.



Figure 7: Systronics Conductivity TDS meter-308.

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 [10]. 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 thermoregulator [11].

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.

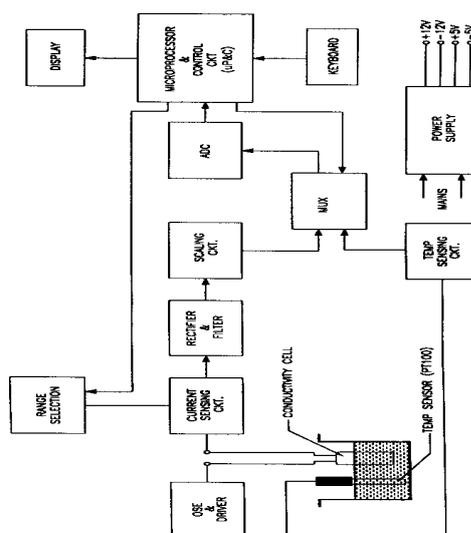


Figure 8: Block Diagram of Systronics Conductivity-TDS meter 308.

3.2.9. Refractive Index Measurement

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



Figure 9: 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.

References

1. D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd Ed., Pergamon Press, Oxford, England, **1988**.
2. A. Hohn, "Formamide". In Kroschwitz, Jacqueline I. Kirk-Othmer *Concise Encyclopedia of Chemical Technology*, 4th ed., John Wiley & Sons Inc., New York, **1999**.
3. V. K. Kamineni, Y. M. Lvov, T. A. Dobbins, *Langmuir* **2007**, 23 (14), 7423.
4. C. Redlich, W. S. Beckett, J. Sparer, K. W. Barwick, C. A. Riely, H. Miller, S. L. Sigal, S. L. Shalat, M. R. Cullen, (1988). *Annals of Internal Medicine* **1988**, 108 (5), 680.
5. J. M. Daran, A. J. A. van Maris, J. T. Pronk, J. R. Dickinson, *Appl. Environ. Microbiol.* **2008**, 74 (8), 2259.
6. J. A. M. Bleeker, J. Geiss, M. C. E. Huber, *The Century of Space Science*, Kluwer Academic Publishers, Netherlands, **2001**.
7. M. Jotanovic, Z. Andric, G. Tadric, V. Micic, *Peer-Reviewed and Open Access Journal* **2010**, 3, 15.
8. H. Cheung, R. S. Tanke, G. P. Torrence, "Acetic Acid" in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2005**.
9. M. M. Cox, A. L. Lehninger, D. R. Nelson, *Lehninger principles of biochemistry*, Worth Publishers, New York, **2000**.
10. J.E. Lind Jr., J.J. Zwolenik, R.M. Fuoss, *J. Chem. Soc. Faraday Trans I.* **1959**, 81, 1557.
11. B. Das, N. Saha, *J. Chem. Eng. Data* **2000**, 45, 2.

CHAPTER-IV

STUDY OF SOLVATION CONSEQUENCES OF α -AMINO ACIDS IN AQUEOUS IONIC LIQUID SOLUTION PROBED BY PHYSICO-CHEMICAL APPROACH

4.1. Introduction

Amino acids are molecules that contain an amine group, a carboxylic acid group and a side-chain varying between different amino acids. They play a key role in biochemistry, where the term usually refers to α -amino acids. One of the most important function is to serve as the building blocks of proteins, which are linear chains of amino acids. Amino acids are very much important in nutrition and are commonly used in nutrition supplements, fertilizers, food technology and industry.

Ionic liquids have unique intrinsic properties, such as negligible vapour pressure, large liquid range, ability of dissolving a variety of chemicals, high thermal stability, large electrochemical window and their potential as 'designer solvents' and 'green' replacements for volatile organic solvents [1-3] used in reactions involving inorganic and bio-catalysis etc. They are also utilized as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells) [4-6]. In the modern technology, the application of the salt is well understood by studying the ionic solvation or ion association. Ionic association of electrolytes in solution depends on the mode of solvation of its ions [7-10] which in turn depends on the nature of the solvent/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. The non-aqueous system has been of immense importance [11,12] to the technologist and theoretician as many chemical processes occur in these systems. The volumetric, viscometric and interferometric behavior of solutes has been found 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 studied to obtain information on solute-solute, solute-solvent, and solvent-solvent interactions [13-17].

In view of the above and in continuation of our studies, we have performed a systematic study on the density, viscosity, refractive index and ultrasonic speed of some amino acids in aqueous Bu_4PBF_4 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 aqueous Bu_4PBF_4 solution.

4.2. Experimental Section

4.2.1. Source and Purity of Samples

Tetrabutyl phosphonium tetrafluoroborate (Bu_4PBF_4) of puriss grade was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of Bu_4PBF_4 was ≥ 0.99 . The amino acids Glycine (S.D. Fine Chemicals, > 0.99), L-Alanine (S.D. Fine Chemicals, > 0.985), and L-Valine (Loba Chemie, India, > 0.99) were used for the present study and were used as such without further purification. Bu_4PBF_4 was recrystallized twice from aqueous ethanol solution and dried under vacuum at $T = 348$ K for 6 hours. Thereafter, it was stored over P_2O_5 in a desiccator before used [18]. Triply distilled water with a specific conductance $< 10^{-6}$ S cm^{-1} was used for the preparation of different aqueous Bu_4PBF_4 solutions. The physical properties of different mass fraction of aqueous Ionic liquid mixture are listed in Table 2.

4.2.2. Apparatus and Procedure

The measurement of Density (ρ) was done by means of vibrating-tube Anton Paar Density-Meter (DMA 4500M) with a precision of $0.00005 \text{ g}\cdot\text{cm}^{-3}$. It was calibrated by double-distilled water and dry air [19]. The temperature was automatically kept constant within $\pm 0.01 \text{ K}$.

The viscosity (η) was measured with the help 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 $\pm 0.1 \text{ s}$. 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 $\pm 0.01 \text{ mg}$. The precision of density measurements was $\pm 3 \cdot 10^{-4} \text{ g}\cdot\text{cm}^{-3}$.

Viscosity of the solution is obtained from the following equation [20].

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

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 $\pm 0.003 \text{ mPa}\cdot\text{s}$.

Refractive index was analysed with the help of a Digital Refractometer Mettler Toledo. The light source was LED, $\lambda=589.3 \text{ nm}$. 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 determined 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. [21] and Kiyoharo et al. [22,23] The obtained velocities were corrected for diffraction errors as given by Subrahmayan et al. [24]. The maximum uncertainty in the velocity is $\pm 0.5 \text{ m s}^{-1}$. The temperature was controlled within $\pm 0.01 \text{ K}$ using a Lauda thermostat for velocity measurements.

The solutions investigated here were prepared by mass and the conversion of molarity into molality was accomplished [15] 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 3 and the derived parameters are reported in Table 4 and Table 5.

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 [25].

$$\phi_V = M / \rho - 1000(\rho - \rho_0) / m\rho\rho_0 \quad (2)$$

where M is the molar mass of the solute, m is the molality of the solution ρ_0 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 [26].

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

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 5.

A perusal of Table 5 shows that ϕ_V^0 values for amino acids are positive and increase with an increase in concentration in aqueous Bu_4PBF_4 mixture. The positive ϕ_V^0 value indicates the presence of stronger solute-solvent interaction between amino acids and the aqueous Bu_4PBF_4 than solute-solute interaction. The solute solvent interactions are further strengthened with the increase in mass fraction of Bu_4PBF_4 in its aqueous mixture. The trend in the solute-solvent interaction is in the following order



This shows that with the increase in the number of carbon atoms in the studied amino acids, the solute-solvent interaction also increases. In the case of ($\text{Bu}_4\text{PBF}_4 + \text{water}$) mixture the solvation of anion $[\text{BF}_4]^-$ is not taking place in appreciable extent, having a positive central B atom well shielded from the interactions with F atoms. So the only interaction occurring here is between P atom of Bu_4P^+ and the oxygen atom of carboxylic part of amino acid. Owing to the greater +I effect of alkyl chain in L-Valine in comparison with other two studied amino acids negative charge density becomes maximum on the oxygen atom of the carboxylic part. So the solute-solvent interaction of L-Valine with Bu_4P^+ ion is highest among the three and thereby supporting the order of interactions mentioned above. Similar results were found for amino acid in methanoic acid (Formic acid) [27].

The S_V^* values of the amino acid solution given in Table 5 decreases with increases in the number of carbon atoms of the studied amino acids and with increases in the mass fraction of Bu_4PBF_4 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 Bu_4PBF_4 in the mixture

suggests that solute-solvent interactions dominate over solute-solute interactions.

A plausible mechanism of interaction between the ionic liquid and different amino acids as evident from the experimental observation explained and discussed above is given in **Scheme 1**.

4.3.2. Viscosity Calculation

The viscosity data has been analyzed using Jones-Dole equation [28].

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

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 Glycine to L-Valine) and with the increase in mass fraction of Bu_4PBF_4 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 [29,30]. 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 5 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 Bu_4PBF_4 in the solvent mixture, are 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 [31].

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

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 [32] as mentioned by Deetlefs et al [33].

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 Bu_4PBF_4 in solvent mixture refractive index value also increases. Hence a perusal of Table 3 & Table 4 we found that the refractive index and the molar refraction values respectively are higher for L-Valine compare to other two amino acid, 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 acids in aqueous mixture of Bu_4PBF_4 is

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 M is the molar mass and 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 5. Since the values of ϕ_K^0 and S_K^* are measures of solute-solvent and solute-solute interactions respectively, a perusal of Table 5 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) indicates 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 Bu_4PBF_4 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. T. Welton, *Chem. Rev.* **1999**, *99*, 2071.
2. M. J. Earle, K. R. Seddon, *Pure Appl. Chem.* **2000**, *72*, 1391.
3. J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667.
4. N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123.
5. F. Endres, S. El Abedin Zein, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101.
6. P. Wang, S. M. Zakeeruddin, J. E. Moser, M. Gratzel, *J. Phys. Chem. B.* **2003**, *107*, 13280.
7. D. Das, B. Das, D. K. Hazra, *J. Solution Chem.* **2002**, *31*, 425.
8. C. Guha, J. M. Chakraborty, S. Karanjai, B. Das, *J. Phys. Chem. B* **2003**, *107*, 12814.
9. D. Das, B. Das, D. K. Hazra, *J. Solution Chem.* **2003**, *32*, 77.
10. M. N. Roy, D. Nandi, D. K. Hazra, *J. Indian Chem. Soc.* **1993**, *70*, 123.
11. O. Popvysh, R. P. T. Tomkins, *Nonaqueous Solution Chemistry*, Wiley-Interscience, New York, **1981**, Ch-4.
12. A. J. Matheson, *Molecular Acoustics*, Wiley-Interscience: London, **1971**.
13. J. M. McDowall, C.A. Vincent, *J. Chem. Soc., Faraday Trans. 1.* **1974**, *70* 1862.
14. M.R. J. Deck, K.J. Bird, A.J. Parker, *Aust. J. Chem.* **1975**, *28*, 955.
15. M.N. Roy, B. Sinha, R. Dey, A. Sinha, *Int. J. Thermophy.* **2005**, *26*, 1549.
16. M. N. Roy, R. Dewan, P. K. Roy, D. Biswas, *J. Chem. Eng. Data.* **2010**, *55*, 3617.
17. M. N. Roy, A. Bhattacharjee, P. Chakraborti, *Thermochim. Acta.* **2010**, *507*, 135.
18. C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.* **2005**, *37*, 37.
19. A. Bhattacharjee, M. N. Roy, *Phys. Chem. Chem. Phys.* **2010**, *12*, 14534.
20. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data.* **2004**, *49*, 291.
21. E. B. Freyer, J. D. Hubbard, D. H. Andrews, *J. Am. Chem. Soc.* **1929**, *51*, 759.
22. O. Kiyohara, K. Arakawa, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3037.
23. O. Kiyohara, J. P. E. Grolier, G. C. Benson, *Can. J. Chem.* **1974**, *52*, 2287.
24. N. M. Murthy, S. V. Subrahmanyam, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2589.
25. E. Ayranci, *J. Chem. Eng. Data.* **1997**, *42*, 934.
26. D.O. Masson, *Phil. Mag.* **1929**, *8*, 218.

27. M. N. Roy, D. Ekka , R. Dewan, *Acta Chim. Slov.* **2011**, 58, 792.
28. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, 51, 2950.
29. F. J. Millero, Molal volumes of electrolytes. *Chem. Rev.* **1971**, 71, 147.
30. F. J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.* **1978**, 82, 784.
31. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, **1970**.
32. M. Born, E. Wolf, *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*, 7th ed., Cambridge University Press, London, **1999**.
33. M. Deetlefs, K. Seddon , M. Shara, *Phys. Chem. Chem. Phys.* **2006**,8, 642.

Table 1. Sample Table

Name of the Chemicals	Initial Mass-fraction	Source of the compounds	Purification Method used	Final Mass-Fraction
Bu ₄ PBF ₄	≥ 0.98	Sigma-Aldrich, Germany	Purified by Standard Methods [18]	≥ 0.99
Glycine	> 0.99	S.D.Fine Chemicals	Used as purchased	> 0.99
L-Alanine	> 0.985	S.D. Fine Chemicals	Used as purchased	> 0.985
L-Valine	> 0.99	Loba Chemie, India	Used as purchased	> 0.99

Table 2. The values of Density (ρ), Viscosity (η), Refractive index (n_D) and Speed of sound (u) in different mass fraction of Bu₄PBF₄ at Temperature (^a T) 298.15K and Experimental Pressure 0.1MPa.

Mass-fraction of Bu ₄ PBF ₄	^b $\rho \times 10^{-3}$ (kg m ⁻³)	^c η (mPa s)	^d n_D	^e u (ms ⁻¹)
$w_1 = 0.001$	0.99716	0.901	1.3326	1498.9
$w_1 = 0.003$	0.99867	0.909	1.3333	1502.6
$w_1 = 0.005$	1.00005	0.914	1.3341	1507.5

^a uncertainty in the temperature values: ± 0.01 K

^b uncertainty in the density values: ± 0.01 kg m⁻³

^c uncertainty in the viscosity values: ± 0.003 mPas

^d uncertainty in the refractive index values: ± 0.0002 units

^e uncertainty in the speed of sound: ± 0.2 m.s⁻¹

Table 3. Experimental values of Molality (m), Density (ρ), Viscosity (η), Refractive Index (n_D) and Ultrasonic Speed (u) of Glycine, L-Alanine and L-Valine in different mass fraction of the solvent mixture (Bu₄PBF₄ + Water) at Temperature (T) 298.15K and Experimental Pressure 0.1MPa.

^g m (mol kg ⁻¹)	^h $\rho \times 10^{-3}$ (kg m ⁻³)	ⁱ η (mPas)	^j n_D	^k u (m s ⁻¹)	^g m (mol kg ⁻¹)	^h $\rho \times 10^{-3}$ (kg m ⁻³)	ⁱ η (mPas)	^j n_D	^k u (m s ⁻¹)
w ₁ = 0.001					w ₁ = 0.003				
Glycine					Glycine				
0.1002	0.99741	0.907	1.3327	1503.9	0.1001	0.99886	0.915	1.3338	1508.1
0.1584	0.99782	0.913	1.3331	1518.0	0.1583	0.99918	0.919	1.3342	1523.8
0.2005	0.99825	0.917	1.3334	1538.1	0.2003	0.99953	0.923	1.3345	1546.1
0.2352	0.9987	0.921	1.3337	1564.8	0.2350	0.99991	0.927	1.3348	1575.6
0.2654	0.99917	0.925	1.3334	1595.6	0.2652	1.00029	0.931	1.3351	1611.4
0.2925	0.99965	0.929	1.3343	1633.8	0.2924	1.00069	0.935	1.3354	1654.0
L-Alanine					L-Alanine				
0.1002	0.99738	0.910	1.3329	1503.0	0.1001	0.99880	0.919	1.3339	1507.2
0.1585	0.99775	0.919	1.3333	1516.0	0.1584	0.99905	0.928	1.3343	1522.1
0.2005	0.99814	0.928	1.3336	1535.3	0.2004	0.99935	0.936	1.3346	1544.2
0.2353	0.99856	0.937	1.3339	1560.1	0.2351	0.99969	0.945	1.3349	1572.4

0.2655	0.99899	0.945	1.3342	1590.8	0.2654	1.00005	0.953	1.3352	1606.5
0.2927	0.99944	0.954	1.3345	1627.5	0.2926	1.00043	0.963	1.3355	1648.3
L-Valine					L-Valine				
0.1002	0.99730	0.911	1.3331	1501.8	0.1001	0.99873	0.924	1.334	1506.0
0.1585	0.99757	0.925	1.3336	1514.5	0.1584	0.99891	0.938	1.3346	1519.8
0.2007	0.99788	0.938	1.334	1532.5	0.2006	0.99916	0.952	1.335	1540.4
0.2355	0.99823	0.950	1.3344	1556.4	0.2353	0.99946	0.966	1.3354	1568.2
0.2659	0.99860	0.964	1.3348	1585.1	0.2657	0.99981	0.981	1.3358	1601.9
0.2932	0.99901	0.977	1.3352	1618.6	0.2930	1.00018	0.996	1.3362	1640.4
w ₁ = 0.005									
Glycine									
0.1000	1.0002	0.920	1.3349	1513.5					
0.1582	1.00046	0.925	1.3353	1530.8					
0.2002	1.00075	0.930	1.3357	1556.4					
0.2349	1.00107	0.935	1.336	1589.6					
0.2651	1.0014	0.940	1.3363	1628.4					
0.2922	1.00175	0.945	1.3366	1677.4					
L-Alanine									

0.1000	1.00013	0.924	1.335	1512.6
0.1583	1.00033	0.933	1.3354	1529.1
0.2003	1.00059	0.943	1.3358	1553.2
0.2350	1.0009	0.952	1.3361	1584.9
0.2652	1.00124	0.961	1.3364	1625.0
0.2924	1.0016	0.971	1.3367	1673.2
L-Valine				
0.1001	1.00007	0.930	1.3351	1511.3
0.1583	1.00020	0.946	1.3357	1526.1
0.2004	1.00042	0.961	1.3361	1549.4
0.2352	1.00070	0.978	1.3365	1578.6
0.2655	1.00103	0.994	1.3369	1617.3
0.2928	1.00142	1.008	1.3373	1663.7

^f uncertainty in the temperature values: ± 0.01 K

^g uncertainty in the molality: ± 0.0001 mol kg⁻¹

^h uncertainty in the density values: ± 0.01 kg m⁻³

ⁱ uncertainty in the viscosity values: ± 0.003 mPas

^j uncertainty in the refractive index values: ± 0.0002 units

^k uncertainty in the speed of sound: ± 0.2 m.s⁻¹

Table 4. Molality (m), 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 Glycine, L- Alanine and L-Valine in Bu₄PBF₄ at Temperature ($^m T$) 298.15K and Experimental Pressure 0.1MPa.

$^1 m$	$\phi_v \times 10^6$	$(\eta/\eta_0-1)/m^{1/2}$	R	$\beta \times 10^{10}$	$\phi_k \times 10^{10}$
(mol kg ⁻¹)	(m ³ mol ⁻¹)	(kg ^{1/2} mol ^{-1/2})	(m ³ mol ⁻¹)	(Pa ⁻¹)	(m ³ mol ⁻¹ Pa ⁻¹)
$w_1 = 0.001$					
Glycine					
0.1002	50.2126	0.070	15.4690	4.4329	-2.8523
0.1584	48.8086	0.081	15.4795	4.3491	-4.3653
0.2005	47.9562	0.089	15.4855	4.2343	-5.5212
0.2352	47.2041	0.096	15.4912	4.0892	-6.6007
0.2654	46.4877	0.101	15.4712	3.9310	-7.4058
0.2925	45.9063	0.107	15.5017	3.7476	-8.2250
L-Alanine					
0.1002	67.2811	0.096	18.3685	4.4383	-2.2313
0.1585	65.6765	0.127	18.3818	4.3609	-3.8180
0.2005	64.7740	0.149	18.3896	4.2503	-5.0476
0.2353	63.8167	0.168	18.3968	4.1114	-6.0669
0.2655	63.1264	0.185	18.4039	3.9555	-6.9816

0.2927	62.4438	0.201	18.4106	3.7774	-7.7994
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L-Valine

0.1002	103.4438	0.111	24.1691	4.4445	-1.3242
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0.1585	101.0369	0.165	24.1954	4.3703	-3.2828
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0.2007	99.4324	0.202	24.2142	4.2669	-4.4763
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0.2355	97.9737	0.233	24.2320	4.1354	-5.5334
--------	---------	-------	---------	--------	---------

0.2659	96.8536	0.262	24.2493	3.9856	-6.4015
--------	---------	-------	---------	--------	---------

0.2932	95.6570	0.287	24.2656	3.8207	-7.1415
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 $w_1 = 0.003$

Glycine

0.1001	56.1447	0.052	15.4929	4.4018	-3.0660
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0.1583	54.7428	0.062	15.5048	4.3102	-4.7506
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0.2003	53.6413	0.070	15.5120	4.1853	-6.0078
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0.2350	52.5945	0.077	15.5187	4.0285	-7.1617
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0.2652	51.9963	0.083	15.5254	3.8500	-8.1312
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0.2924	51.3736	0.089	15.5318	3.6528	-8.9803
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L-Alanine

0.1001	76.1913	0.083	18.3924	4.4073	-2.4244
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0.1584	73.9884	0.113	18.4078	4.3264	-4.2571
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0.2004	72.1860	0.135	18.4173	4.1963	-5.6488
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0.2351	70.6385	0.153	18.4260	4.0458	-6.7668
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0.2654	69.4681	0.170	18.4343	3.8745	-7.7041
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0.2926	68.4752	0.187	18.4423	3.6790	-8.5952
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L-Valine

0.1001	111.2980	0.129	24.1936	4.4147	-1.5346
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0.1584	107.6932	0.176	24.2287	4.3341	-3.5594
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0.2006	105.0397	0.213	24.2489	4.2179	-4.9643
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0.2353	102.9233	0.243	24.2678	4.0684	-6.2115
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0.2657	100.9986	0.276	24.2856	3.8977	-7.2317
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0.2930	99.5177	0.303	24.3028	3.7155	-8.0275
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 $w_1 = 0.005$

Glycine

0.1000	60.0670	0.052	15.5184	4.3646	-3.2854
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0.1582	58.6671	0.065	15.5311	4.2654	-5.1327
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0.2002	57.5671	0.077	15.5434	4.1250	-6.6274
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0.2349	56.5217	0.087	15.5511	3.9533	-7.8808
--------	---------	-------	---------	--------	---------

0.2651	55.7815	0.095	15.5585	3.7659	-8.8208
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0.2922	55.0672	0.104	15.5657	3.5478	-9.7911
--------	---------	-------	---------	--------	---------

L-Alanine

0.1000	81.0859	0.081	18.4229	4.3701	-2.6423
--------	---------	-------	---------	--------	---------

0.1583	77.8861	0.113	18.4391	4.2754	-4.6454
--------	---------	-------	---------	--------	---------

0.2003	75.5862	0.135	18.4543	4.1427	-6.1046
--------	---------	-------	---------	--------	---------

0.2350	73.6318	0.155	18.4635	3.9774	-7.3638
0.2652	72.0864	0.171	18.4721	3.7822	-8.5117
0.2924	70.8512	0.189	18.4804	3.5662	-9.5010

L-Valine

0.1001	115.1442	0.132	24.2334	4.3779	-1.4384
0.1583	111.1444	0.185	24.2696	4.2928	-3.3035
0.2004	107.8946	0.223	24.2904	4.1638	-4.6369
0.2352	105.3266	0.262	24.3098	4.0100	-5.7678
0.2655	103.1448	0.292	24.3280	3.8191	-6.7293
0.2928	101.0273	0.314	24.3447	3.6077	-7.6119

^l uncertainty in the molality: $\pm 0.0001 \text{ mol.kg}^{-1}$

^m uncertainty in the temperature values: $\pm 0.01 \text{ K}$.

Table 5. 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 Glycine, L-Alanine and L-Valine in aqueous Bu_4PBF_4 at Temperature ($^n T$) 298.15K and Experimental Pressure 0.1MPa.

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 ($\text{kg}^{1/2} \text{ mol}^{-1/2}$)	$\phi_K^0 \times 10^{10}$ ($\text{m}^3 \text{ mol}^{-1} \text{ Pa}^{-1}$)	$S_K^* \times 10^4$ ($\text{m}^3 \text{ mol}^{-3/2} \text{ Pa}^{-1} \text{ kg}^{1/2}$)
$w_1 = 0.001$						
Glycine	52.402	-22.23	0.0512	0.1893	0.0234	-24.050
L-Alanine	69.723	-24.922	0.0406	0.5457	0.7298	-29.005
L-Valine	107.44	-40.063	0.0200	0.9097	1.5833	-30.044
$W_1 = 0.003$						

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Glycine	58.675	-25.218	0.0259	0.2000	0.1007	-30.938
L-Alanine	80.321	-40.718	0.0128	0.5486	0.7981	-32.107
L-Valine	117.42	-61.492	0.0080	0.9259	1.8318	-33.942
<hr/> $W_1=0.005$ <hr/>						
Glycine	62.760	-26.295	0.0149	0.2694	0.1694	-34.037
L-Alanine	86.387	-53.702	0.0075	0.5511	0.9807	-35.694
L-Valine	122.61	-73.455	0.0057	0.9475	2.0421	-37.192

ⁿ uncertainty in the temperature values: ± 0.01 K

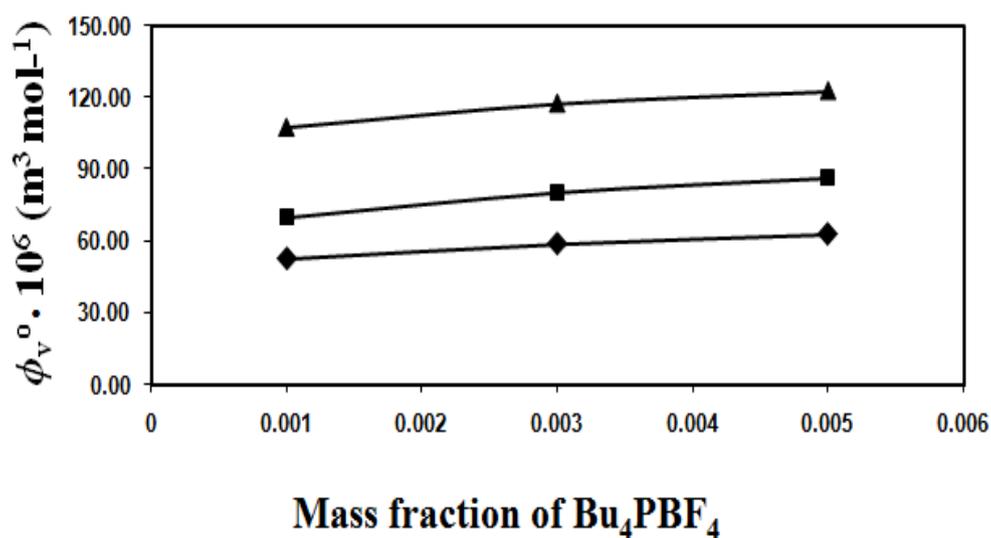


Figure 1. The plots of limiting apparent molar volumes (ϕ_v^0) for Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of Bu_4PBF_4 in aqueous mixture at 298.15K.

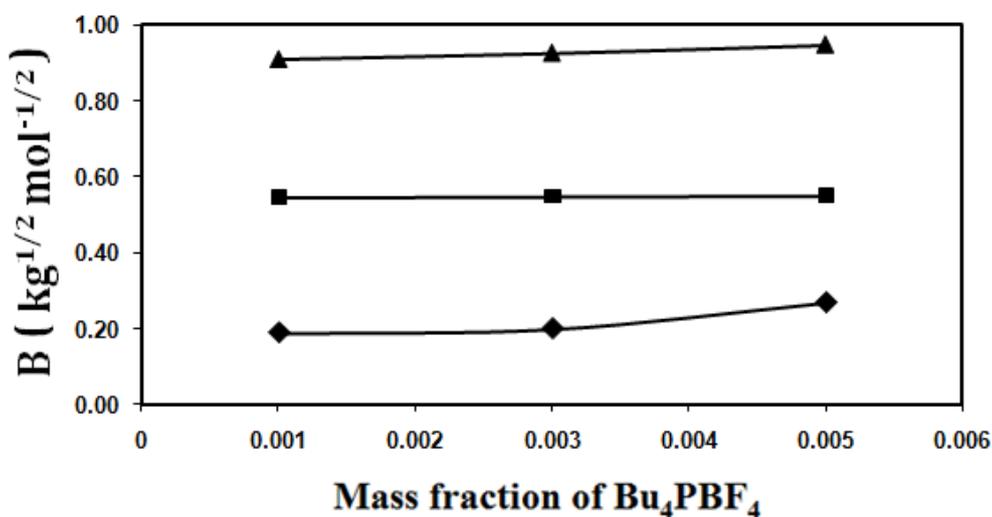


Figure 2. The plots of viscosity B -coefficient for Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of Bu_4PBF_4 in aqueous mixture at 298.15K.

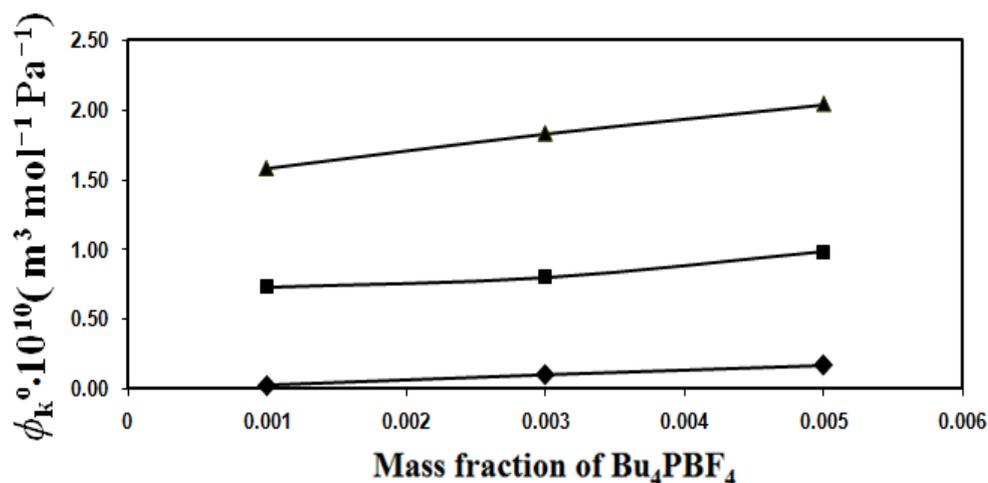
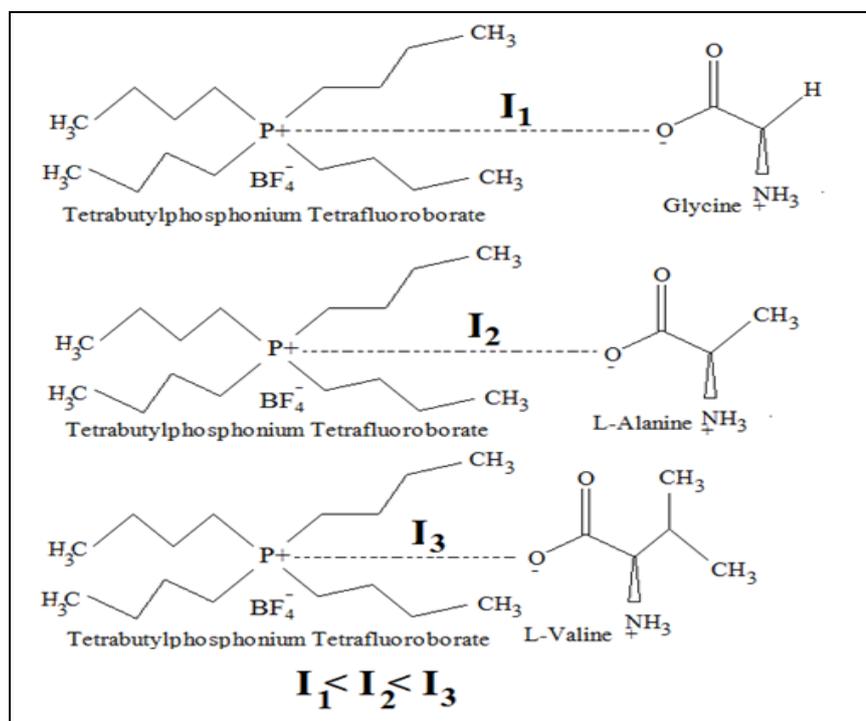


Figure 3. The plots of limiting partial adiabatic compressibility (ϕ_k^0) for Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of Bu₄PBF₄ in aqueous mixture at 298.15K.

Scheme:



Scheme 1. Plausible Mechanism of Interaction between the Ionic Liquid and Different Amino Acids

CHAPTER – V

PHYSICO-CHEMICAL STUDY OF SOLUTION BEHAVIOUR OF ALKALI METAL PERCHLORATES PREVAILING IN N, N- DIMETHYL FORMAMIDE WITH THE MANIFESTATION OF ION SOLVATION CONSEQUENCES

5.1. Introduction

Investigation on the transport properties of electrolytes has been utilized to understand the solvation and association behaviour of ions in different solvent media. Perchlorates are the high melting point inorganic salts easily soluble in protic solvents. Lithium Perchlorate is used in the manufacture of chemical sources of energy (i.e. fuel cells) for electric cars [1]. Sodium Perchlorate is extensively used to block iodine uptake for the patients with subclinical hyperthyroidism [2].

Measurement of Conductance has been employed to find out association and solvation behaviour of ions in solution. Volumetric, viscometric and interferometric studies help to investigate the molecular interactions in solution and to inspect the activities of the salt with different solvent concentrations. Studies of apparent and limiting apparent molar volumes along with the viscosity have been used to elucidate the ion-ion and ion-solvent interactions [3]. In conjunction with our investigation on electrical conductance of electrolytes [4-6] the present work deals with the transport and thermodynamic properties of Lithium Perchlorate, Sodium Perchlorate and Potassium Perchlorate in N,N-Dimethyl Formamide at 298.15 K.

5.2. Experimental Methods

5.2.1. Materials

LiClO_4 , NaClO_4 and KClO_4 of puriss grade were obtained from Aldrich, Germany and used as purchased. N,N-Dimethyl Formamide of spectroscopy grade was procured from Sd. fine Chemicals and purified using standard methods [7].

5.2.2 Apparatus and Procedure

A stock solution for each of the metal perchlorates was prepared by mass obtained by mass dilution at 298.15K. The conversion of molarity to molality was done using density values. The uncertainty of molarity of different solutions is found to be $\pm 0.0001 \text{ mol dm}^{-3}$. The density (ρ) was measured by a vibrating-tube Anton Paar density-meter (DMA 4500M) with a precision of 0.0005 g/cm^3 . The calibration was done by double-distilled water and dry air and uncertainty in density was $\pm 0.00005 \text{ g cm}^{-3}$.

Solvent viscosities were measured by means of a Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 having an accuracy of 1.0% and fitted to a Brookfield Digital Bath TC-500 at 298K using density and viscosity values from the literature [8-10]. The uncertainty in viscosity measurements is within $\pm 0.003 \text{ mPa s}$.

Conductance measurements were performed in a Systronic-308 conductivity bridge (accuracy $\pm 0.01 \%$) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 0.001) . A water bath maintained within $T = (298.15 \pm 0.01) \text{ K}$ was used and the cell was calibrated by the method proposed by Lind et al [11]. The conductance data were reported at a frequency of 1 kHz and were uncertain to $\pm 0.3 \%$.

Speeds of sound were recorded by multifrequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 1 MHz with a precision of 0.2 m.s^{-1} . Its calibration was carried out with three solvents namely water, methanol, and benzene at 298.15 K. The full details of the methods and techniques have been revealed earlier [12-14]. The uncertainty of ultrasonic speed measurements was $\pm 0.2 \text{ m.s}^{-1}$. The uncertainty for the working temperature was $\pm 0.02 \text{ K}$.

5.3. Results and Discussion

5.3.1. Conductance Calculation

The experimental values of physical properties of the pure solvent were in good agreement with those found in the literature, as in Table 1. The values of

equivalent conductances (Λ) at various concentrations are reported in Table 2 and the conductance data for LiClO_4 , NaClO_4 and KClO_4 in N,N-Dimethyl Formamide have been investigated with the help of Fuoss conductance equation [15,16]. Three adjustable parameters limiting molar conductance (Λ_0), the association constant (K_A) and the distance of closest approach of ions (R) are derived for a given set of conductivity values ($c_j, \Lambda_j, j=1, \dots, n$) from the following set of equations.

$$\Lambda = P\Lambda_0[(1+R_x) + E_L] \quad (2)$$

$$P = 1 - \alpha(1 - \gamma) \quad (3)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (4)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (5)$$

$$\beta = e^2 / (\varepsilon k_B T) \quad (6)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (7)$$

where the relaxation field effect is denoted by R_x , E_L represents the electrophoretic counter current, k^{-1} denotes the radius of the ion atmosphere, e is the electron charge, ε is the relative permittivity of the solvent mixture, k_B is the Boltzmann constant, c is the molarity of the solution, K_A is the overall pairing constant, K_R is the association constant of the solvent-separated pairs, K_S is the association constant of the contact-pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, β is twice the Bjerrum distance, f is the activity coefficient and T is the absolute temperature. The computations were done with the help of programs suggested by Fuoss. Shedlovsky extrapolation of the data were employed to obtain the initial Λ_0 values for the iteration procedure. Input for the program is the set ($c_j, \Lambda_j, j=1, \dots, n$), n, ε, η, T , initial values of Λ_0 , and an instruction to cover a pre-selected range of R values.

For the minimization of standard deviation all the calculations are performed by finding the values of Λ_0 and α .

$$\delta^2 = \sum [A_j(\text{cal}) - A_j(\text{obs})]^2 / (n-2) \quad (8)$$

For a sequence of R values and then plotting δ against R , the minimum of the δ versus R curve represents the best-fit R . Hence, approximate runs are

carried out over a fairly wide range of R values using 0.1 increments for the location of the minimum, but no significant minima were detected in the δ - R curves for LiClO_4 , NaClO_4 and KClO_4 , in N,N-Dimethyl Formamide ; R values are assumed to be $R = (a + d)$, where the sum of the crystallographic radii of the ions is represented by a and the average distance corresponding to the side of a cell occupied by a solvent molecule is denoted by d . This 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_0 , K_A , and R attained by this procedure are reported in Table 3.

Inspection of Table 3 shows that the limiting molar conductance Λ_0 is found to have an increasing order whilst moving from LiClO_4 , NaClO_4 followed by KClO_4 . The Table also reveals that the association in N,N-Dimethyl Formamide is highest for LiClO_4 and lowest for KClO_4 and intermediate in the case of NaClO_4 . Hence the ion-solvent interaction in N,N-Dimethyl Formamide is maximum in the case of LiClO_4 and minimum for KClO_4 . The ion-solvent interaction of NaClO_4 exists between LiClO_4 and KClO_4 . This leads to the fact that lowering of conductance of KClO_4 is found to be highest and lowest for LiClO_4 . The lowest viscosity of N,N-Dimethyl Formamide for KClO_4 also supports the above observation because with lowering of viscosity the Λ_0 value should increase [17].

The above trend in Λ_0 values can be supported through another characteristic function called the Walden product, $\Lambda_0 \eta$ given in Table 4. Even though the viscosity of N,N-Dimethyl Formamide for LiClO_4 is more than that of NaClO_4 and KClO_4 , the $\Lambda_0 \eta$ is found to attain an increasing order from LiClO_4 to KClO_4 which points out the predominance of Λ_0 over η .

ΔG° is given by the following relationship [18] and is given in Table 4.

$$\Delta G^\circ = - RT \ln K_A \quad (10)$$

The explanation of negative values of ΔG° can be made by considering the participation of specific covalent interaction in the ion-association process. The decrease in the value of ΔG° in N,N-Dimethyl Formamide for LiClO_4 than KClO_4

indicates the highest degree of association in LiClO₄. K_A values are indicative of significant ion-association in the media. The ion-association process is exothermic. As a result Gibbs Free Energy change is negative and the ion-association becomes favourable.

5.3.2. Density Calculation

The experimental value of densities of LiClO₄, NaClO₄ and KClO₄ in N,N-Dimethyl Formamide, as a function of concentration at 298.15K is listed in Table 5. limiting apparent molar volume is essential to investigate the interactions of LiClO₄, NaClO₄ and KClO₄ in different concentrations of pure solvent. The apparent molar volumes ϕ_V given in Table 5 were found out from the solution densities using the following equation

$$\phi_V = M / \rho - (\rho - \rho_o) / c\rho\rho_o \quad (11)$$

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 volumes ϕ_V^0 were calculated in accordance with a least-squares treatment to the plots of ϕ_V versus \sqrt{c} using the following Masson equation [19]

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{c} \quad (12)$$

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 the square root of the molar concentration \sqrt{c} were found to be linear with negative slopes which are shown in Figure 1.

The values of ϕ_V^0 and S_V^* along with the standard errors are reported in Table 5. The extent of ion-solvent interaction can be examined by taking the ϕ_V^0 values. A perusal of Table 5 indicates that the ϕ_V^0 values are positive and is highest in case of LiClO₄ in N,N-Dimethyl Formamide. This indicates that maximum ion-solvent interaction in N,N-Dimethyl Formamide is found in the case of LiClO₄ and the same is minimum for KClO₄. The said interaction of NaClO₄ becomes in between LiClO₄ and KClO₄ shown in the **Scheme 1** where **I₁**, **I₂** and **I₃**

are the extent of ion-solvent interaction of KClO_4 , NaClO_4 and LiClO_4 in N,N-Dimethyl Formamide respectively. The highest charge density and smallest size of Li^+ ion than that of Na^+ and K^+ favours the accessibility towards N,N-Dimethyl Formamide rendering to the highest ion solvent interaction which is enhanced by the following scheme and order. So the interaction of N,N-Dimethyl Formamide with Li^+ ion is maximum for LiClO_4 and minimum in the case of K^+ in KClO_4 .

On the other hand, S_V^* indicates the extent of ion-ion interaction. The S_V^* values are negative due to the disappearance of ion-ion attractive force at infinite dilution. The decrease in ion-ion interactions with the increase in dilution can be attributed to the increase in distance between ions at infinite dilution. The values of S_V^* indicate that the extent of ion-ion interaction in N,N-Dimethyl Formamide is highest for KClO_4 and lowest for LiClO_4 . From the comparison of the magnitude of ϕ_V^0 values with that of S_V^* , the former is found to be far greater than the latter in the solutions. This implies that ion-solvent interactions predominate over ion-ion interactions in all the solutions. Furthermore, the values of ϕ_V^0 lead to the fact that the lowest ion-solvent interaction of KClO_4 results in higher conductance than that of NaClO_4 whereas NaClO_4 exhibits higher conductance than LiClO_4 in N,N-Dimethyl Formamide.

5.3.3.. Viscosity Calculation

The viscosity data has been examined using Jones-Dole equation [20]

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B\sqrt{c} \quad (13)$$

where η and η_0 are the viscosities of the solution and solvent respectively. The values of A and B are acquired by a computerised least-square method and recorded in Table 6. This can be achieved from the straight line by plotting $(\eta/\eta_0 - 1)/\sqrt{c}$ against \sqrt{c} as depicted in Figure 2.

A perusal of Table 6 reveals that the A coefficients are smaller than the viscosity B -coefficients for all the solutions under investigation. This points towards weak ion-ion interactions in the solution. The viscosity B coefficient [21] describes the effects of ion-solvent interactions. Positive values of the viscosity B

coefficients for LiClO₄, NaClO₄ and KClO₄ in N,N-Dimethyl Formamide reflects the presence of strong ion-solvent interactions. The viscosity *B*-coefficient value is found to be lowest for KClO₄ supporting the fact that the conductance is highest KClO₄.

5.3.4. Ultrasonic Speed Calculation

The adiabatic compressibility (β_s) was calculated from the following equation:

$$\beta_s = 1 / u^2 \rho \quad (15)$$

Where *u* is the speed of sound in the solution and ρ is the density of solution. The apparent molar adiabatic compressibility (ϕ_K) of the solutions was found out from the relation,

$$\phi_K = M \beta_s / \rho + \int 1000(\beta_s \rho_o - \beta_o \rho) / c \rho \rho_o \quad (16)$$

Where β_s, β_o are the adiabatic compressibilities of the solution and solvent respectively and *c* is the molarity of the solution. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) and experimental slopes (S_K^*) were achieved by fitting ϕ_K against the square root of molarity (\sqrt{c}) of the electrolyte employing the method of least squares.

$$\phi_K = \phi_K^0 + S_K^* \cdot \sqrt{c} \quad (17)$$

The values of β_s and ϕ_K are recorded in Table 7. Since the values of ϕ_K^0 and S_K^* are the measure of ion-solvent and ion-ion interactions respectively, a perusal of Table 7 and Figure 3 reveals that the values are in agreement with results drawn from the values of ϕ_V^0 and S_V^* discussed earlier.

5.4. Conclusion

Extensive investigation of LiClO₄, NaClO₄ and KClO₄ in N,N-Dimethyl Formamide reveals that LiClO₄ is more associated in Formamide than the other two perchlorates and it remains as ion-pairs. The ion-association is found minimum in the case of KClO₄ in N,N-Dimethyl Formamide. The said interaction of NaClO₄ arises in the intermediacy of LiClO₄ and KClO₄. The volumetric, viscometric and interferometric studies reveal the predominance of ion-solvent interaction over the ion-ion interaction in all the studied solutions.

References

1. M. Jotanovic, Z. Andric, G. Tadric, V. Micic, *Peer-Reviewed and Open Access Journal* **2010**, 3, 15.
2. Becker C. *Radiologie* **2007**, 47(9), 768.
3. F.J. Millero, in: R.A. Horne (Ed.), *Structure Transport Process in Water Aqueous Solutions*, Wiley, New York, **1972**.
4. M.N. Roy, B. Sinha, V.K. Dakua, A. Sinha, *Pak. J. Sci. Ind. Res.* **2006**, 49, 153.
5. M.N. Roy, P. Pradhan, R.K. Das, P.G. Guha, *J. Chem. Eng. Data* **2008**, 53, 1417.
6. R. Chanda, M.N. Roy, *Fluid Phase Equilib.* **2008**, 269, 134.
7. D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed. Pergamon Press, Oxford, **1988**.
8. B. Sinha, V.K. Dakua, M.N. Roy, *J. Chem. Eng. Data.* 2007, 52, 1768.
9. J.A. Dean, *Lange's Handbook of Chemistry*, 11th ed. McGraw-Hill Book Company, New York, **1973**.
10. B.D. Chatterjee, *J. Chem. Eng. Data.* **2006**, 51, 1352.
11. J.E. Lind Jr., J.J. Zwolenik, R.M. Fuoss, *J. Am. Chem. Soc.* **1959**, 81, 1557.
12. M.N. Roy, A. Jha, R. Dey, *J. Chem. Eng. Data.* **2001**, 46, 1327.
13. M.N. Roy, D.K. Hazra, *Indian J. Chem. Technol.* **1994**, 1, 93.
14. R.M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.* **1978**, 75, 16.
15. R.M. Fuoss, *J. Phys. Chem.* **1978**, 82, 2427.
16. J. Barthel, M.B. Rogac, R. Neueder, *J. Solut. Chem.* **1999**, 28, 1071.
17. M.N. Roy, R. Dewan, D. Ekka, I. Banik, *Thermochimica Acta.* **2013**, 559, 46.
18. R.M. Fuoss and C.A. Kraus, *J. Am. Chem. Soc.* **1933**, 55, 2387.
19. F.J. Millero, A.L. Surdo, C. Shin, *Phys. Chem.* **1978**, 82, 784.
20. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, 51, 2950.

21. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, **1970** .
22. M. I. Aralaguppi, C.V. Jadar, T.M. Aminabhavi, J.D. Ortego, S.C. Mehrotra, *J. Chem. Eng. Data* **1997**, *42* , 301.
23. V. A. Aminabhavi, T.M. Aminabhavi, R.H. Balundgi, *Ind. Eng. Chem. Res.* **1990**, *29*, 2106.

Table 1. Density (ρ), viscosity (η), refractive index (n_D) and dielectric constant (ϵ) of pure N,N Dimethyl Formamide at 298.15K.

Solvent	$\rho \times 10^{-3} (\text{kg m}^{-3})$		$\eta (\text{mPa s})$		$u (\text{ms}^{-1})$		ϵ
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	
DMF	0.94484	0.9449	0.819	0.8209[23]	1449.7	1451.0[22]	36.7
		[22]					

Table 2. The concentration (c) and molar conductance (Λ) of LiClO_4 , NaClO_4 and KClO_4 in N,N-Dimethyl Formamide at 298.15 K.

$c \times 10^4$ (mol.dm ⁻³)	$\Lambda \times 10^4$ (S. m ² .mol ⁻¹)	$c \times 10^4$ (mol.dm ⁻³)	$\Lambda \times 10^4$ (S. m ² .mol ⁻¹)	$c \times 10^4$ (mol.dm ⁻³)	$\Lambda \times 10^4$ (S. m ² .mol ⁻¹)
LiClO ₄		NaClO ₄		KClO ₄	
1.1990	10.74	1.8796	12.99	4.8312	12.88
1.4232	10.61	2.6147	12.77	5.4850	12.76
1.7796	10.44	3.2580	12.58	6.3303	12.58
2.0136	10.33	3.8064	12.36	6.9960	12.41
2.2052	10.22	4.1943	12.23	7.3495	12.34
2.3994	10.13	4.9195	12.01	7.8456	12.18
2.6929	9.97	5.5178	11.86	8.3002	12.06
2.9447	9.84	6.3353	11.62	9.1144	11.96
3.1648	9.71	6.9960	11.46	9.7157	11.81
3.5081	9.56	7.4748	11.31	10.2913	11.69
3.6749	9.47	7.7785	11.19	11.1890	11.49
3.9521	9.34	8.0316	11.15	11.8818	11.39
4.2477	9.18	8.6260	10.91	12.3482	11.24
4.4437	9.09	9.4741	10.70	13.0393	11.14

Table 3. Limiting molar conductivity (Λ°), association constant (K_A), co-sphere diameter (R) and standard deviations (δ) of experimental Λ of LiClO_4 , NaClO_4 and KClO_4 at 298.15 K from eqn (3).

Salts	Solvent	$\Lambda^\circ \times 10^4$ ($\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$)	K_A ($\text{dm}^3\cdot\text{mol}^{-1}$)	R (\AA)	δ
LiClO_4	N,N-Dimethyl Formamide	11.945	929.379	8.6285	0.05131
NaClO_4		14.237	466.821	8.9585	0.07266
KClO_4		15.057	389.625	9.3185	0.04347

Table 4. Walden product ($\Lambda^\circ\eta_0$) and Gibb's energy change (ΔG°) of LiClO_4 , NaClO_4 and KClO_4 in N,N-Dimethyl Formamide at 298.15 K.

Solute	$\Lambda^\circ\eta_0$ ($\text{Sm}^2\text{mol}^{-1}$ mPass)	$\Delta G^\circ \times 10^{-4}$ (J mol^{-1})
LiClO_4	9.783	-1.6942
NaClO_4	11.659	-1.5235
KClO_4	12.332	-1.4786

Table 5. Experimental values of densities (ρ), apparent molar volume (ϕ_V), limiting apparent molar volume (ϕ_V^0) and experimental slope (S_V^*) of LiClO₄, NaClO₄ and KClO₄ in N,N-Dimethyl Formamide at 298.15 K.

c (mol.dm ⁻³)	$\rho \times 10^{-3}$ (kg m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\phi_V^0 \times 10^6$ (m ³ ·mol ⁻¹)	$S_V^* \times 10^6$ (m ² ·mol ^{-3/2} L ^{1/2})
LiClO ₄ in N,N-Dimethyl Formamide				
0.0159	0.94516	90.02		
0.0318	0.94557	86.85		
0.0478	0.94605	84.14	98.42	-65.60
0.0638	0.94658	81.91		
0.0799	0.94716	79.86		
0.0959	0.94778	78.03		
NaClO ₄ in N,N-Dimethyl Formamide				
0.0157	0.94544	86.72		
0.0317	0.94614	83.54	94.42	-61.48
0.0476	0.9469	80.93		
0.0637	0.94771	78.88		
0.0796	0.94855	77.08		
0.0958	0.94944	75.43		
KClO ₄ in N,N-Dimethyl Formamide				
0.0160	0.94576	82.15		
0.0319	0.94677	78.71	89.93	-62.00
0.0479	0.94783	76.47		
0.0639	0.94895	74.27		
0.0799	0.95011	72.35		
0.0961	0.95131	70.74		

Table 6. Experimental values of concentration (c), viscosity (η), $(\eta/\eta_0 - 1)/c^{1/2}$, viscosity A,B- coefficients of LiClO₄, NaClO₄ and KClO₄ in N,N-Dimethyl Formamide at 298.15 K.

c (mol dm ⁻³)	η (mPa s)	$(\eta/\eta_0 - 1)/c^{1/2}$ (Kg ^{1/2} mol ^{-1/2})	A (L mol ⁻¹)	B (L ^{1/2} mol ^{-1/2})
LiClO ₄ in N,N-Dimethyl Formamide				
0.0159	0.836	0.165		
0.0318	0.852	0.226		
0.0478	0.868	0.274	0.010	1.211
0.0638	0.884	0.314		
0.0799	0.901	0.354		
0.0959	0.917	0.386		
NaClO ₄ in N,N-Dimethyl Formamide				
0.0157	0.829	0.097		
0.0317	0.838	0.130		
0.0476	0.847	0.157	0.015	0.650
0.0637	0.856	0.179		
0.0796	0.865	0.199		
0.0958	0.874	0.217		
KClO ₄ in N,N-Dimethyl Formamide				
0.0160	0.826	0.068		
0.0319	0.831	0.082		
0.0479	0.836	0.095	0.025	0.320
0.0639	0.841	0.106		
0.0799	0.846	0.117		
0.0961	0.851	0.126		

Table 7. Experimental values of speed of sound (u), adiabatic compressibility (β_s) and apparent molar adiabatic compressibility (ϕ_K), limiting apparent molar adiabatic compressibility (ϕ_K^0), and experimental slopes (S_K^*) of LiClO₄, NaClO₄ and KClO₄ in N,N-Dimethyl Formamide at 298.15 K.

c (mol dm ⁻³)	u (m s ⁻¹)	$\beta_s \times 10^{10}$ (Pa ⁻¹)	$\phi_K \times 10^{10}$ (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})
LiClO ₄ in N,N-Dimethyl Formamide					
0.0159	1453.5	5.0080	-1.413		
0.0318	1468.3	4.9054	-3.915		
0.0478	1491.6	4.7510	-5.910		
0.0638	1520.9	4.5671	-7.402	4.555	-47.50
0.0799	1559.6	4.3406	-8.870		
0.0959	1606.7	4.0872	-10.150		
NaClO ₄ in N,N-Dimethyl Formamide					
0.0157	1454.8	4.9976	-2.157		
0.0317	1471.3	4.8825	-4.717		
0.0476	1495.4	4.7226	-6.586		
0.0637	1526.8	4.5265	-8.109	3.619	-46.55
0.0796	1567.1	4.2929	-9.550		
0.0958	1615.3	4.0367	-10.736		
KClO ₄ in N,N-Dimethyl Formamide					
0.0160	1455.7	4.9897	-2.652		
0.0319	1472.9	4.8687	-5.169		
0.0479	1497.6	4.7041	-6.973		
0.0639	1530.8	4.4970	-8.594	3.061	-45.77
0.0799	1570.6	4.2667	-9.881		
0.0961	1619.5	4.0079	-11.039		

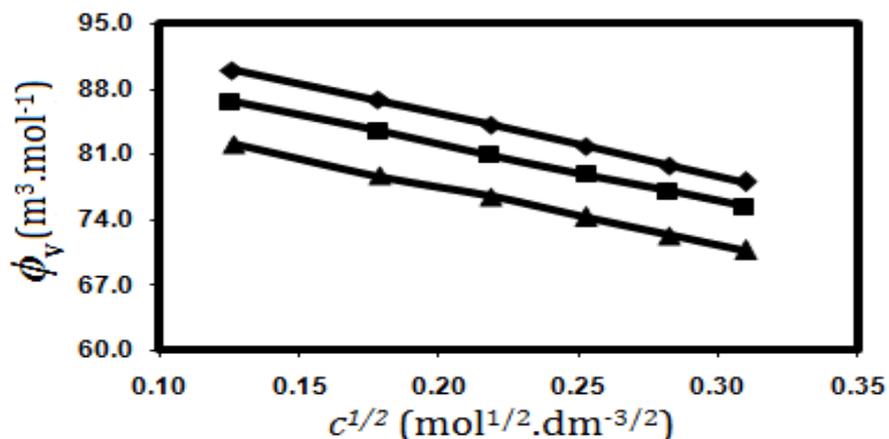


Figure 1: Apparent molar volume (ϕ_V) and the square root of concentrations (\sqrt{c}) for LiClO₄ (—◆—), NaClO₄ (—■—) and KClO₄ (—▲—) in N,N-Dimethyl Formamide at 298.15 K.

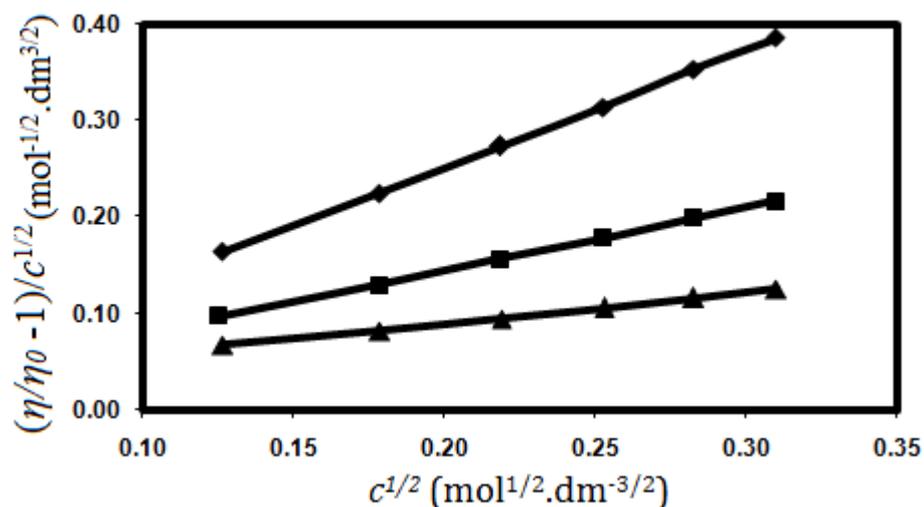


Figure 2: Plots of $(\eta/\eta_0 - 1)/\sqrt{c}$ versus \sqrt{c} for LiClO₄ (—◆—), NaClO₄ (—■—) and KClO₄ (—▲—) in N,N-Dimethyl Formamide at 298.15 K.

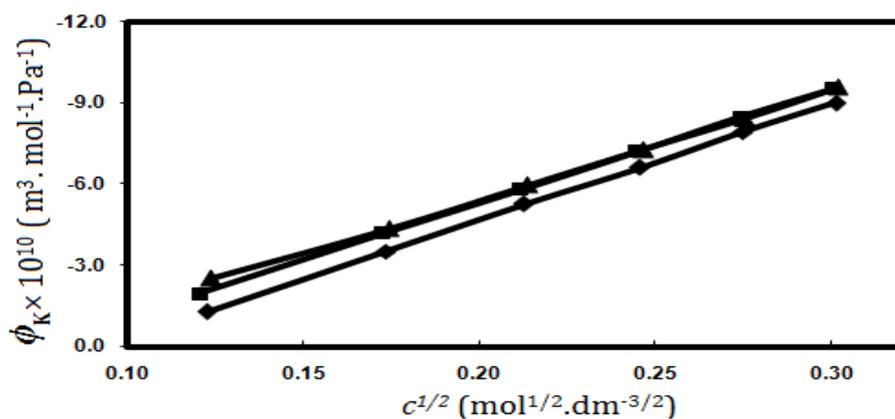
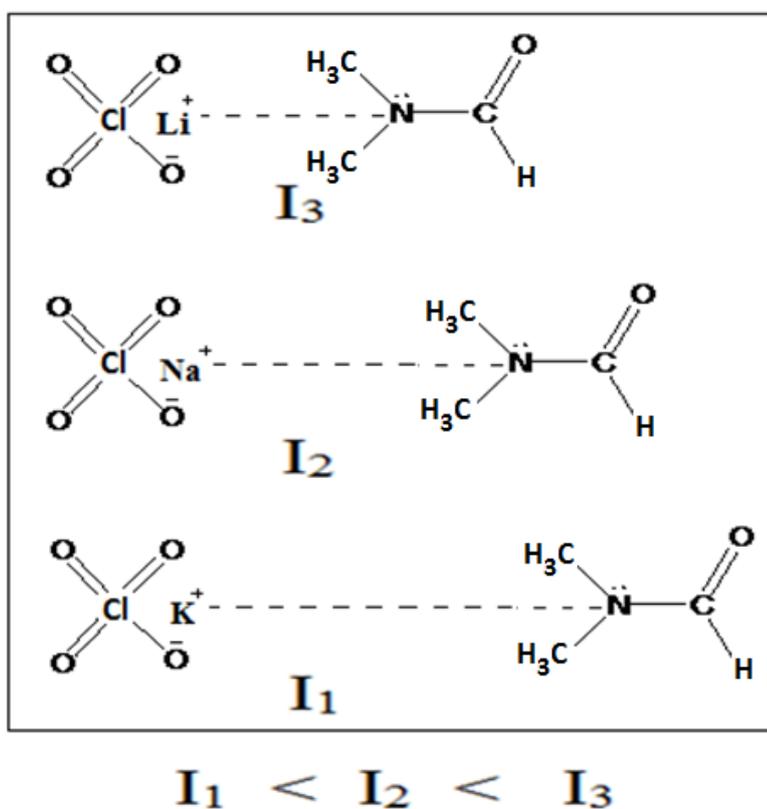


Figure 3: Apparent molar adiabatic compressibilities (ϕ_K) and the square root of concentrations (\sqrt{c}) for LiClO₄ (—◆—), NaClO₄ (—■—) and KClO₄ (—▲—) in N,N-Dimethyl Formamide at 298.15 K.



Scheme 1. Interaction of LiClO₄, NaClO₄ and KClO₄ with N,N-Dimethyl Formamide .

CHAPTER – VI

PHYSICO-CHEMICAL STUDY OF SOME BIO-ACTIVE SOLUTES IN AQUEOUS POTASSIUM ACETATE SOLUTION

6.1. Introduction

Amino acids are the biologically important molecules containing an amine group (-NH₂) and a carboxylic acid group (-COOH) attached to the same carbon atom with variable side-chain. Since the carboxylic acid group has a proton available for binding with the electrons of another atom, and the amino group has electrons available for binding with a proton from another atom, the amino acid behaves as an acid and a base simultaneously. Carbon, hydrogen, oxygen, and nitrogen are the key elements of an amino acid. In biochemistry the term usually refers to *alpha-amino acids* being important in metabolism. Amino acids combine into peptide chains to form the building blocks of linear array of proteins. Because of the key role in biochemistry, amino acids are commonly used in nutrition supplements, fertilizers, food technology and also in the manufacture of biodegradable plastic and drugs in industry.

Potassium Acetate (CH₃COOK) is the potassium salt of acetic acid. In recent years, Potassium Acetates are widely used as an additive to dialysis fluids, in the manufacture of fire extinguishers and in the petroleum industry. Besides it is used as a food additive as a preservative and acidity regulator.

The volumetric, viscometric and interferometric behavior of solutes has been proved 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 [1-5].

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 Potassium Acetate 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 aqueous Potassium Acetate solution.

6.2. Experimental Methods

6.2.1. Source and Purity of Samples

Potassium Acetate of puriss grade was procured from Sigma-Aldrich, Germany and was used as purchased. The mass fraction purity of Potassium Acetate was ≥ 0.99 . The amino acids 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. The recrystallization of Potassium Acetate was performed twice from aqueous ethanol solution and dried under vacuum at $T = 348$ K for 6 hours. Then it was stored over P_2O_5 in a desiccator before used [6]. Triply distilled water with a specific conductance $<10^{-6}$ S cm^{-1} was used for the preparation of different aqueous Potassium Acetate solutions. The physical properties of different mass fraction of aqueous Potassium Acetate mixture are listed in Table 1.

6.2.2. Apparatus and Procedure

The Density (ρ) measurement was done by means of vibrating-tube Anton Paar Density-Meter (DMA 4500M) with a precision of 0.00005 g. cm^{-3} . Its calibration was made by double-distilled water and dry air [7]. The temperature was automatically kept constant within ± 0.01 K.

Refractive index measurement was performed 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.

A suspended Ubbelohde type viscometer was employed to measure the viscosity (η) after being 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 ± 0.0003 g·cm⁻³.

Viscosity of the solution is evaluated using the following equation [8].

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

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 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. [9] and Kiyoharo et al. [10,11] The obtained velocities were corrected for diffraction errors as given by Subrahmayan et al. [12]. 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 [1] from the 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.

6.3. Results and Discussions

6.3.1 Density Calculation

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

$$\phi_v = M / \rho - 1000(\rho - \rho_0) / m\rho\rho_0 \quad (2)$$

where M is the molar mass of the solute, m is the molality of the solution ρ_0 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 [14].

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

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 reveals that ϕ_v^0 values for amino acids are positive and increase with an increase concentrations in aqueous Potassium Acetate mixture, indicate the presence of strong solute-solvent interactions and these interactions are further strengthened as increases the mass fraction of Potassium Acetate in the mixture. The trend in the solute-solvent interaction is



This indicates that with increases in the number of carbon atoms in the studied amino acids, the solute-solvent interaction also increases.

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 Potassium Acetate 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 Potassium Acetate in the mixture suggests the predominance of solute-solvent interactions over solute-solute interactions.

6.3.2 Refractive Index Calculation

The molar refraction, R can be evaluated from the Lorentz-Lorenz relation [18].

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

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 [19]. As stated by Deetlefs et al. [20]

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 Potassium Acetate in solvent mixture refractive index value also increases. Hence a perusal of Table 2 & Table 3 we found that the refractive index and the molar refraction values respectively are higher for L-Valine compare to other two amino acid, 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 Potassium Acetate is

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Glycine < L-Alanine < L-Valine.

6.3.3 Viscosity Calculation

The viscosity data has been analyzed using Jones-Dole equation [15].

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

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 Glycine to L-Valine) and with the increase in mass fraction of Potassium Acetate 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 [16, 17]. 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 Potassium Acetate in the solvent mixture, are agreement with the results obtained from ϕ_v^0 values discussed earlier.

6.3.4 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.

$$\phi_K = M\beta / \rho + 1000 \beta \rho_0 - \beta_0 \rho / m \rho \rho_0 \quad (7)$$

where β_0, 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.

6.4. Conclusion

The values of the limiting apparent molar volume (ϕ_V^0), viscosity B -coefficients and limiting partial isentropic compressibility (ϕ_K^0) are indicative of 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 Potassium Acetate 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, B. Sinha, R. Dey, A. Sinha, *Int. J. Thermophy.* **2005**, 26, 1549.
2. M.R. J. Deck, K.J. Bird, A.J. Parker, *Aust. J. Chem.* **1975**, 28, 955.
3. M. N. Roy, R. Dewan, P. K. Roy, D. Biswas, *J. Chem. Eng. Data.* **2010**, 55, 3617.
4. J. M. McDowall, C.A. Vincent, *J. Chem. Soc., Faraday Trans. 1.* **1974**, 70, 1862.
5. M. N. Roy, A. Bhattacharjee, P. Chakraborti, *Thermochim. Acta.* **2010**, 507, 135.
6. C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.* **2005**, 37, 37.
7. A. Bhattacharjee, M. N. Roy, *Phys. Chem. Chem. Phys.* **2010**, 12, 14534.
8. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data.* **2004**, 49, 291.
9. E. B. Freyer, J. D. Hubbard, D. H. Andrews, *J. Am. Chem. Soc.* **1929**, 51, 759.
10. O. Kiyohara, K. Arakawa, *Bull. Chem. Soc. Jpn.* **1970**, 43, 3037.
11. O. Kiyohara, J. P. E. Grolier, G. C. Benson, *Can. J. Chem.* **1974**, 52, 2287.
12. N. M. Murthy, S. V. Subrahmanyam, *Bull. Chem. Soc. Jpn.* **1977**, 50, 2589.
13. E. Ayranci, *J. Chem. Eng. Data.* **1997**, 42, 934.
14. D.O. Masson, *Phil. Mag.* **1929**, 8, 218.
15. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, 51, 2950.
16. F. J. Millero, Molal volumes of electrolytes. *Chem. Rev.* **1971**, 71, 147.
17. F. J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.* **1978**, 82, 784.
18. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, **1970**.
19. M. Born, E. Wolf, *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*, 7th ed., Cambridge University Press, London, **1999**.
20. M. Deetlefs, K. Seddon, M. Shara, *Phys. Chem. Chem. Phys.* **2006**, 8, 642.

Table 1. The values of Density (ρ), Viscosity (η), Refractive index (n_D), and Speed of sound (u) in different mass fraction of Potassium acetate at 298.15K

Mass-fraction	$\rho \times 10^{-3}$	η	n_D	U
Potassium Acetate	(kg m^{-3})	(mPa s)		(ms^{-1})
$w_1 = 0.01$	0.99736	0.907	1.3328	1510.3
$w_1 = 0.03$	0.99845	0.913	1.3335	1514.5
$w_1 = 0.05$	0.99953	0.919	1.3343	1518.9

Table 2. Experimental values of Densities (ρ), Viscosities (η), Refractive Index (n_D) and Ultrasonic Speed (u) of Glycine, L-Alanine and L-Valine in different mass fraction of Potassium acetate at 298.15K

molality (mol kg ⁻¹)	$\rho \times 10^{-3}$ (kg m ⁻³)	η (mPa s)	n_D	u (m s ⁻¹)	molality (mol kg ⁻¹)	$\rho \times 10^{-3}$ (kg m ⁻³)	η (mPas)	n_D	u (m s ⁻¹)
$w_1 = 0.01$					$w_1 = 0.03$				
Glycine					Glycine				
0.1002	0.99761	0.910	1.3329	1515.3	0.1001	0.99866	0.917	1.3340	1519.9
0.1584	0.99802	0.913	1.3333	1529.4	0.1583	0.99901	0.920	1.3344	1535.9
0.2005	0.99847	0.916	1.3336	1549.5	0.2004	0.99940	0.923	1.3347	1559.0
0.2351	0.99893	0.918	1.3339	1576.2	0.2350	0.99981	0.926	1.3350	1588.0
0.2654	0.99941	0.921	1.3342	1607.0	0.2652	1.00023	0.929	1.3353	1623.2
0.2925	0.99992	0.924	1.3345	1645.2	0.2924	1.00070	0.932	1.3356	1666.2
L-Alanine					L-Alanine				
0.1002	0.99757	0.912	1.3331	1514.4	0.1001	0.99860	0.921	1.3341	1518.8
0.1585	0.99794	0.920	1.3335	1527.4	0.1584	0.99891	0.928	1.3345	1533.5

0.2005	0.99836	0.927	1.3338	1546.7	0.2004	0.99928	0.936	1.3348	1554.5
0.2352	0.99880	0.933	1.3341	1571.5	0.2351	0.99970	0.944	1.3351	1582.0
0.2655	0.99929	0.940	1.3344	1602.2	0.2654	1.00016	0.951	1.3354	1615.1
0.2927	0.99979	0.946	1.3347	1638.9	0.2926	1.00065	0.959	1.3357	1656.3
L-Valine					L-Valine				
0.1002	0.99749	0.916	1.3333	1513.2	0.1001	0.99853	0.928	1.3342	1517.9
0.1585	0.99778	0.929	1.3338	1525.6	0.1584	0.99877	0.942	1.3348	1531.4
0.2007	0.99812	0.942	1.3342	1543.9	0.2006	0.99909	0.956	1.3353	1551.2
0.2355	0.99851	0.954	1.3346	1567.8	0.2353	0.99947	0.970	1.3357	1577.0
0.2658	0.99895	0.966	1.3350	1596.5	0.2657	0.99992	0.985	1.3361	1610.7
0.2931	0.99943	0.979	1.3354	1630.0	0.2929	1.00041	0.998	1.3365	1648.3
$w_1 = 0.05$									
Glycine									
0.1001	0.99972	0.923	1.3351	1524.8					
0.1583	1.00006	0.927	1.3355	1542.5					
0.2003	1.00043	0.931	1.3358	1568.5					
0.2349	1.00083	0.934	1.3361	1600.9					

0.2651	1.00125	0.937	1.3364	1641.6
0.2922	1.00168	0.941	1.3367	1689.8
L-Alanine				
0.1001	0.99965	0.928	1.3352	1523.9
0.1583	0.99993	0.936	1.3356	1540.3
0.2003	1.00030	0.944	1.3359	1564.7
0.2350	1.00071	0.952	1.3363	1595.9
0.2652	1.00117	0.960	1.3366	1634.5
0.2924	1.00169	0.969	1.3369	1682.8
L-Valine				
0.1001	0.99958	0.930	1.3353	1523.1
0.1584	0.99982	0.946	1.3359	1539.1
0.2005	1.00020	0.961	1.3364	1562.7
0.2352	1.00065	0.978	1.3369	1593.8
0.2655	1.00117	0.994	1.3373	1633.7
0.2927	1.00178	1.008	1.3377	1679.9

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 Glycine, L- Alanine, and L-Valine in Potassium acetate 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)
$w_1 = 0.01$					
Glycine					
0.1002	50.2025	0.031	15.4743	4.36	-2.7874
0.1584	48.7988	0.040	15.4848	4.28	-4.2670
0.2005	47.4453	0.047	15.4905	4.17	-5.3980
0.2351	46.6477	0.052	15.4960	4.03	-6.4548
0.2654	45.9055	0.057	15.5012	3.87	-7.2437
0.2925	45.0713	0.062	15.5059	3.69	-8.0470
L-Alanine					
0.1002	68.2702	0.056	18.3751	4.37	-2.1797
0.1585	66.0644	0.085	18.3883	4.29	-3.7313
0.2005	64.2596	0.106	18.3955	4.18	-4.9341
0.2352	63.0747	0.121	18.4024	4.05	-5.9319
0.2655	61.6814	0.136	18.4084	3.89	-6.8279
0.2927	60.6619	0.147	18.4141	3.72	-7.6298
L-Valine					
0.1002	104.4257	0.097	24.1776	4.38	-1.2914
0.1585	100.6156	0.150	24.2035	4.30	-3.1388

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0.2007	98.4098	0.188	24.2216	4.20	-4.3741
0.2355	96.4957	0.217	24.2384	4.07	-5.4087
0.2658	94.6857	0.243	24.2540	3.92	-6.2591
0.2931	93.0427	0.269	24.2686	3.76	-6.9845

 $w_1 = 0.03$

Glycine

0.1001	54.1539	0.034	15.5044	4.33	-2.9361
0.1583	52.7518	0.044	15.5158	4.24	-4.6833
0.2004	51.3997	0.051	15.5224	4.11	-6.0003
0.2350	50.4209	0.057	15.5286	3.96	-7.0424
0.2652	49.7185	0.062	15.5347	3.79	-7.9396
0.2924	48.6749	0.066	15.5400	3.59	-8.7940

L-Alanine

0.1001	74.2050	0.069	18.4061	4.34	-2.1941
0.1584	70.7997	0.093	18.4204	4.25	-4.0451
0.2004	68.4461	0.114	18.4285	4.14	-5.3036
0.2351	66.4657	0.131	18.4358	3.99	-6.3993
0.2654	64.7618	0.145	18.4422	3.83	-7.3048
0.2926	63.3058	0.158	18.4482	3.64	-8.2001

L-Valine

0.1001	109.3194	0.125	24.2116	4.34	-1.4951
0.1584	104.5120	0.173	24.2452	4.26	-3.4064
0.2006	101.3070	0.209	24.2703	4.15	-4.6990
0.2353	98.7576	0.243	24.2873	4.02	-5.7794

0.2657	96.2993	0.272	24.3026	3.85	-6.8535
0.2929	94.2372	0.295	24.3169	3.68	-7.6354

 $w_1 = 0.05$

Glycine

0.1001	56.0964	0.036	15.5342	4.30	-3.1542
0.1583	53.8953	0.047	15.5458	4.20	-5.0828
0.2003	52.5947	0.055	15.5526	4.06	-6.5710
0.2349	51.4578	0.062	15.5590	3.89	-7.6991
0.2651	50.5223	0.067	15.5650	3.70	-8.7461
0.2922	49.7993	0.074	15.5709	3.49	-9.6307

L-Alanine

0.1001	77.1262	0.070	18.4417	4.30	-2.5244
0.1583	73.1244	0.097	18.4565	4.21	-4.4964
0.2003	69.8728	0.117	18.4646	4.08	-5.9812
0.2350	67.6673	0.134	18.4769	3.92	-7.1656
0.2652	65.6923	0.150	18.4834	3.73	-8.2026
0.2924	63.7082	0.165	18.4887	3.52	-9.2088

L-Valine

0.1001	112.2027	0.132	24.2584	4.31	-1.8982
0.1584	105.5996	0.182	24.2919	4.22	-4.0673
0.2005	100.4472	0.226	24.3154	4.09	-5.5625
0.2352	96.8319	0.259	24.3372	3.93	-6.8262
0.2655	93.7655	0.289	24.3508	3.74	-8.0052
0.2927	90.7221	0.319	24.3621	3.53	-8.9279

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 Potassium Acetate at 298.15 K

Salt	$\phi_V^0 \times 10^6$ (m ³ mol ⁻¹)	$S_V^* \times 10^6$ (m ³ mol ^{-3/2} kg ^{1/2})	A (kg mol ⁻¹)	B (kg ^{1/2} mol ^{-1/2})	$\phi_K^0 \times 10^{10}$ (m ³ mol ⁻¹ Pa ⁻¹)	$S_K^* \times 10^4$ (m ³ mol ^{-3/2} Pa ⁻¹ kg ^{1/2})
$w_1 = 0.01$						
L-Glycine	52.90	-26.65	0.014	0.158	0.028	-27.45
L-Alanine	72.28	-39.67	0.010	0.471	0.719	-28.38
L-Valine	110.0	-58.12	0.008	0.887	1.594	-29.53
$w_1 = 0.03$						
L-Glycine	57.09	-28.31	0.012	0.173	0.118	-30.46
L-Alanine	79.82	-56.68	0.007	0.478	0.900	-31.04
L-Valine	116.9	-77.82	0.006	0.916	1.683	-31.90
$w_1 = 0.05$						
L-Glycine	59.21	-32.71	0.009	0.195	0.234	-33.82
L-Alanine	84.05	-69.64	0.004	0.488	0.965	-34.66
L-Valine	123.1	-111.4	0.002	0.959	1.745	-36.54

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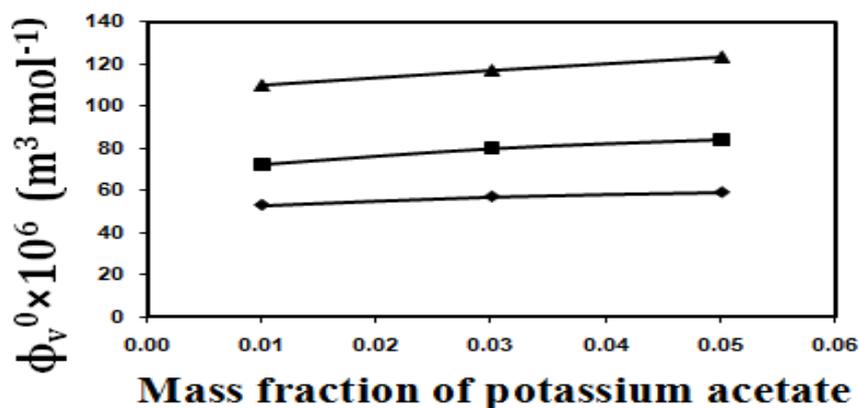


Figure 1. The plots of limiting apparent molar volumes (ϕ_v^0) for Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of Potassium Acetate in aqueous mixture at 298.15K.

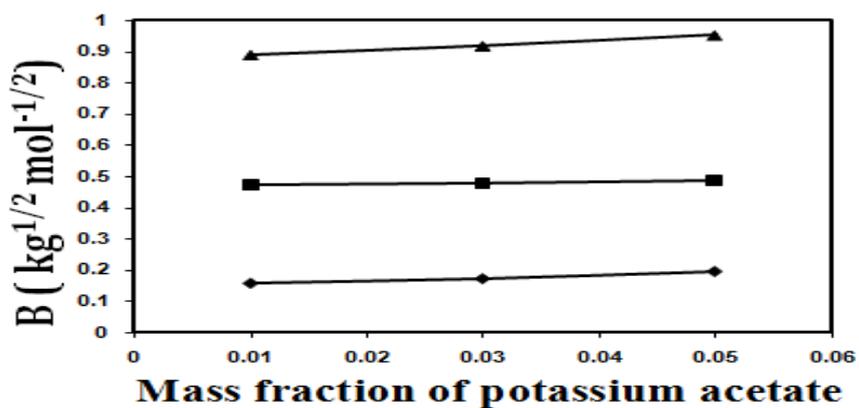


Figure 2. The plots of viscosity B -coefficient for Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of Potassium Acetate in aqueous mixture at 298.15K.

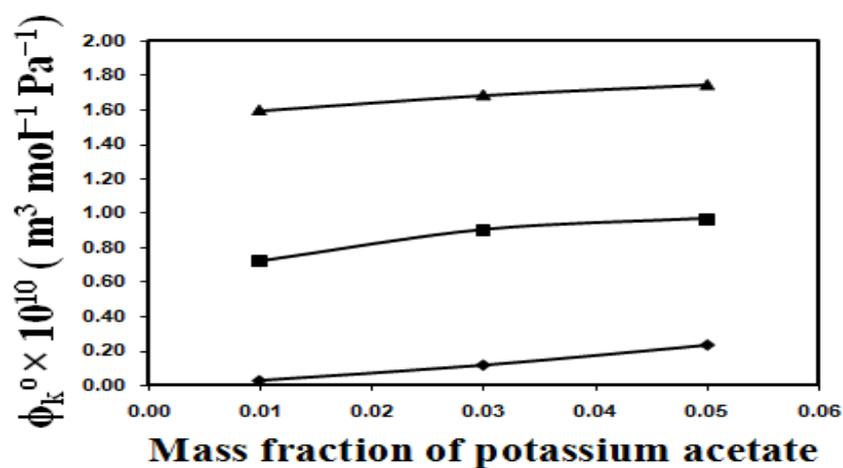


Figure 3. The plots of limiting partial adiabatic compressibility (ϕ_k^0) for Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of Potassium Acetate in aqueous mixture at 298.15K.

CHAPTER - VII

PROBING SOLUTE-SOLVENT INTERACTIONS OF SOME BIO-ACTIVE SOLUTES IN AQUEOUS BARIUM NITRATE SOLUTION ON THE BASIS OF PHYSICO-CHEMICAL CONTRIVANCES

7.1. Introduction

Amino acids are the bioactive compounds playing central roles both as building blocks of proteins and as intermediates in metabolism. They are very much useful in food technology and industry.

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) of a solute reflect the cumulative effects [1-5] of the interactions like ion-ion, ion-solvent, and solvent-solvent interactions in solutions. In this paper we have attempted to study these properties for three amino acids namely Glycine, L-Alanine, and L-Valine in aqueous Barium Nitrate solutions at 298.15 K to understand the solute-solute and solute-solvent interactions.

7.2. Experimental Methods

7.2.1. Source and Purity of Samples

The mass fraction of purity of Barium Nitrate of puriss grade (Sigma-Aldrich, Germany) was ≥ 0.99 . It was recrystallised from aqueous Ethanol solution after being dried under vacuum at $T = 348$ K and it was stored over P_2O_5 kept in a desiccators [6]. The three amino acids namely Glycine, L-Alanine and L-Valine (S.D. Fine Chemicals, >99%) were taken without any further purification. Barium Nitrate solution was prepared with freshly distilled conductivity water. Table 1. depicts the physical properties of different mass fraction of aqueous Barium Nitrate solution.

7.2.2. Apparatus and Procedure

Density (ρ) was measured with Vibrating-tube Anton Paar Density-Meter (DMA 4500M) with a uncertainty of $0.00005 \text{ g}\cdot\text{cm}^{-3}$ after being calibrated by double-distilled water and dry air [7]. The temperature was kept fixed within $\pm 0.01 \text{ K}$.

Ubbelohde type viscometer was used to measure the viscosity (η) whilst calibrated at 298.15 K with distilled water and pure Methanol. A thoroughly cleaned and dried viscometer containing the experimental liquid was placed vertically in a glass-walled thermostat (Bose Panda Instruments Pvt. Ltd.). The flow times were accurate to $\pm 0.1\text{s}$. Airtight-stopper bottles were used for the preparation of the mixtures. A triplicate measurement was taken into account with sufficient precautions to minimize the evaporation loss. A Mettler AG-285 electronic balance with a uncertainty of $\pm 0.01 \text{ mg}$ was used to measure the mass. The uncertainty of density measurements was $\pm 3\cdot 10^{-4} \text{ g}\cdot\text{cm}^{-3}$.

Viscosity of the solution is evaluated using the appropriate equation as reported earlier [8]. The uncertainty in viscosity measurements was within $\pm 0.003 \text{ mPa}\cdot\text{s}$.

Refractive index was calculated by means of Digital Refractometer Mettler Toledo. The light source was LED, $\lambda=589.3\text{nm}$. The calibration of refractometer was done twice using distilled water and being checked after every few measurements. The uncertainty of refractive index measurement was ± 0.0002 units.

An ultrasonic interferometer (Model M-83 from Mittal enterprises) was utilized to measure the ultrasonic velocities, u (ms^{-1}). The interferometer (2 MHz) is based on the principle used by Freyer et al. [9] and Kiyoharo et al. [10,11]. The obtained velocities were corrected for diffraction errors as given by Subrahmayan et al.[12]. The maximum uncertainty in the velocity was $\pm 0.5 \text{ m s}^{-1}$. The temperature control were carried out within $\pm 0.01 \text{ K}$ using a Lauda thermostat for velocity measurements.

The solutions under investigation were prepared by mass and the conversion of molarity into molality was accomplished [4] from the studied

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 listed in Table 3 and Table 4.

7.3. Results & Discussion

7.3.1. Density Calculation

The determination of Apparent molar volumes (ϕ_V) were done from the solution densities using the following equation [13].

$$\phi_V = M / \rho - 1000(\rho - \rho_0) / m\rho\rho_0 \quad (1)$$

where M is the molar mass of the solute, m is the molality of the solution ρ_0 and ρ are the densities of the solution and the mixture respectively. The limiting apparent molar volume ϕ_V^0 was obtained using a least-square treatment to the plot of ϕ_V versus \sqrt{m} with the help of Masson equation [14].

$$\phi_V = \phi_V^0 + S_V^* m^{1/2} \quad (2)$$

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. Values of ϕ_V^0 and S_V^* are reported in Table 4.

A perusal of Table 4 reveals that ϕ_V^0 values for amino acids are positive and increase with an increase in concentrations of aqueous Barium Nitrate mixture, indicating the presence of strong solute-solvent interactions and these interactions are further strengthened with the increase of the mass fraction of $\text{Ba}(\text{NO}_3)_2$ in the solvent mixture. The trend in the solute-solvent interaction is



This indicates that the solute-solvent interaction increases with the increase in the number of carbon atoms in the three amino acids.

The S_V^* values of the amino acid solution (Table 4) follow a decreasing order with the increase in the number of carbon atoms of the above mentioned amino

acids and also the mass fraction of Barium Nitrate in its aqueous mixture. Thus solute-solute interaction is minimized in the higher analogs.

The predominance of solute-solvent interactions over solute-solute interactions was cemented from the higher values of ϕ_V^0 than S_V^* obtained from Figure 1. The same result was obtained for each of the studied amino acids as well as mass fraction of Barium Nitrate in the mixture.

7.3.2. Viscosity Calculation

The viscosity data has been analyzed using Jones-Dole equation [15]

$$(\eta / \eta_0 - 1) / m^{1/2} = A + Bm^{1/2} \quad (3)$$

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 (starting from Glycine to L-Valine) and with the increase in mass fraction of Barium Nitrate in solvent mixture. The results reveal the presence of very weak solute-solute interactions. These results are in excellent agreement with those obtained from S_V^* values discussed earlier.

The effects of solute-solvent interactions on the solution viscosity can be inferred from the B -coefficient [16,17]. The viscosity B -coefficient is an important 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 for all the amino acids and increase with the increase of the size of the side chains. This is due to the greater structure breaking tendency of L-valine as compared to L-alanine [18]. The B -coefficients reflect the net structural effects of the charged groups and the hydrophobic CH_2 - groups on the amino acids. Thus solute-solvent interaction predominates and increases with the increase of mass fraction of $\text{Ba}(\text{NO}_3)_2$ in the

solvent mixture. This observation is in a fine agreement with the results obtained from ϕ_v^0 values discussed earlier.

7.3.3. Refractive Index Calculation

The molar refraction, R has been evaluated from Lorentz-Lorenz relation [19]

$$R = \left\{ (n_D^2 - 1) / (n_D^2 + 2) \right\} (M / \rho) \quad (4)$$

where R , n_D , ρ and M are the molar refraction, the refractive index, density and the molar mass of the solution respectively. According to Born et al.[20] the greater the refractive index of a substance, the more the light is refracted and it was further supported by Deetlefs et al.[21].

More tightly packed substance i.e. more denser solution has higher refractive index. So refractive index value rises with the increase of mass fraction of Barium Nitrate in solvent mixture. Hence from Table 2 & Table 3 it is clear that for L-Valine the refractive index and the molar refraction values are higher than the other two amino acids. Thus solute-solvent interaction predominates over solute-solute interaction. This fact also supports the results obtained from density and viscosity parameters discussed above. The studied amino acids in aqueous Barium Nitrate solution obey the same trend of solute solvent interaction i.e.

Glycine < L-Alanine < L-Valine.

7.3.4. Ultrasonic Speed Calculation

The adiabatic compressibility (β) was evaluated with the help of the following equation:

$$\beta = 1 / u^2 \rho \quad (5)$$

where u is the sound speed in the solution and ρ is the solution density. The apparent molal adiabatic compressibility (ϕ_K) of the solutions was analyzed from the relation.

$$\phi_K = M\beta / \rho + 1000(\beta \rho_o - \beta_o \rho) / m \rho \rho_o \quad (6)$$

where β and β_o are the adiabatic compressibility of the solution and solvent respectively and m is the molality of the solution. Limiting partial molal adiabatic compressibilities (ϕ_K^0) and experimental slopes (S_K^*) were achieved by fitting ϕ_K against the square root of molality of the electrolyte (\sqrt{m}) using the least-squares method.

$$\phi_K = \phi_K^0 + S_K^* m^{1/2} \quad (7)$$

The values of β and ϕ_K are enlisted in Table 3 and the values of ϕ_K^0 and S_K^* are presented in Table 4. The values of ϕ_K^0 and S_K^* also represent the extent of solute-solvent and solute-solute interactions respectively. An inspection of Table 4 and Figure 3 confirms that the ϕ_K^0 values are in an excellent agreement with those drawn from the values of ϕ_V^0 discussed earlier.

Owing to the greater +I effect of alkyl chain in L-Valine in comparison with other two studied amino acids negative charge density becomes maximum on the oxygen atom of the carboxylic part. So the solute-solvent interaction of L-Valine with Ba^{2+} ion is highest among the three and thereby supporting the order of interactions mentioned above.

7.4. Conclusions

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 amino acids and also with the increase of mass fraction of Barium Nitrate in the aqueous mixture. The refractive index and the molar refraction values indicate that molecules of L-Valine are more tightly packed in the solution resulting higher solute-solvent interaction than the other two amino acids.

References

1. M.N. Roy, B. Sinha, R. Dey, A. Sinha, *Int. J. Thermophys.* **2005**, 26, 1549.
2. M.R. J. Deck, K.J. Bird, A.J. Parker, *Aust. J. Chem.* **1975**, 28, 955.
3. M. N. Roy, R. Dewan, P. K. Roy, D. Biswas, *J. Chem. Eng. Data.* **2010**, 55, 3617.
4. J. M. McDowall, C.A. Vincent, *J. Chem. Soc., Faraday Trans. 1.* **1974**, 70 1862.
5. M. N. Roy, A. Bhattacharjee, P. Chakraborti, *Thermochim. Acta.* **2010**, 507, 135.
6. C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.* **2005**, 37, 37.
7. A. Bhattacharjee, M. N. Roy, *Phys. Chem. Chem. Phys.* **2010**, 12, 14534.
8. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data.* **2004**, 49, 291.
9. E. B. Freyer, J. D. Hubbard, D. H. Andrews, *J. Am. Chem. Soc.* **1929**, 51, 759.
10. O. Kiyohara, K. Arakawa, *Bull. Chem. Soc. Jpn.* **1970**, 43, 3037.
11. O. Kiyohara, J. P. E. Grolier, G. C. Benson, *Can. J. Chem.* **1974**, 52, 2287.
12. N. M. Murthy, S. V. Subrahmanyam, *Bull. Chem. Soc. Jpn.* **1977**, 50, 2589.
13. E. Ayrançi, *J. Chem. Eng. Data.* **1997**, 42, 934.
14. D.O. Masson, *Phil. Mag.* **1929**, 8, 218.
15. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, 51, 2950.
16. F. J. Millero, Molal volumes of electrolytes. *Chem. Rev.* **1971**, 71, 147.
17. F. J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.* **1978**, 82, 784.
18. B. Sinha, V. K. Dakua, M. N. Roy, *J. Chem. Eng. Data.* **2007**, 52, 1768.
19. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, **1970**.
20. M. Born, E. Wolf, *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*, 7th ed., Cambridge University Press, London, **1999**.
21. M. Deetlefs, K. Seddon, M. Shara, *Phys. Chem. Chem. Phys.* **2006**, 8, 642.

Table 1. The values of Density (ρ), Viscosity (η), Refractive index (n_D), and Speed of sound (u) in different mass fraction of Barium Nitrate at 298.15K and Experimental Pressure 0.1MPa.

Mass-fraction of Barium Nitrate	^a $\rho \times 10^{-3}$ (kg m ⁻³)	^b η (mPa s)	^c n_D	^d u (ms ⁻¹)
$w_1 = 0.01$	0.99737	0.904	1.3327	1512.7
$w_1 = 0.03$	0.99848	0.910	1.3334	1516.4
$w_1 = 0.05$	0.99956	0.916	1.3342	1519.3

^a uncertainty in the density values: ± 0.01 kg m⁻³

^b uncertainty in the viscosity values: ± 0.003 mPas

^c uncertainty in the refractive index values: ± 0.0002 units

^d uncertainty in the speed of sound: ± 0.2 m.s⁻¹

Table 2. Experimental values of Molality (m), Density (ρ), Viscosity (η), Refractive Index (n_D) and Ultrasonic Speed (u) of Glycine, L-Alanine and L-Valine in different mass fraction of Barium Nitrate in the solvent mixture [Ba(NO₃)₂+ Water] at 298.15K and Experimental Pressure 0.1MPa.

^e m	^f $\rho \times 10^{-3}$ g	η	^h n_D	ⁱ u	^e m	^f $\rho \times 10^{-3}$ g	η	^h n_D	ⁱ u
(mol kg ⁻¹)	(kg m ⁻³)	(mPas)		(m s ⁻¹)	(mol kg ⁻¹)	(kg m ⁻³)	(mPas)		(m s ⁻¹)
$w_1 = 0.01$					$w_1 = 0.03$				
Glycine					Glycine				
0.1001	0.99763	0.907	1.3328	1517.3	0.1001	0.99867	0.914	1.3339	1521.8
0.1584	0.99806	0.910	1.3332	1531.8	0.1583	0.99902	0.917	1.3343	1537.8
0.2004	0.99851	0.913	1.3335	1551.9	0.2003	0.99941	0.920	1.3346	1560.9
0.2351	0.99898	0.915	1.3338	1578.6	0.2350	0.99984	0.923	1.3349	1589.9
0.2653	0.99947	0.918	1.3341	1609.4	0.2652	1.00028	0.926	1.3352	1625.1
0.2925	0.99998	0.920	1.3344	1647.6	0.2923	1.00075	0.929	1.3355	1668.1

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L-Alanine					L-Alanine				
0.1002	0.99759	0.909	1.3330	1516.5	0.1001	0.99861	0.918	1.3340	1520.7
0.1584	0.99797	0.917	1.3334	1529.8	0.1584	0.99892	0.926	1.3344	1535.4
0.2005	0.99838	0.923	1.3337	1549.1	0.2004	0.99929	0.933	1.3347	1556.4
0.2352	0.99884	0.930	1.3340	1573.9	0.2351	0.99972	0.940	1.3350	1583.9
0.2655	0.99932	0.937	1.3344	1604.6	0.2654	1.00018	0.948	1.3354	1616.9
0.2927	0.99984	0.944	1.3346	1641.3	0.2925	1.00068	0.955	1.3356	1658.2
L-Valine					L-Valine				
0.1002	0.99750	0.913	1.3332	1515.5	0.1001	0.99854	0.925	1.3341	1519.8
0.1585	0.99779	0.926	1.3337	1528.0	0.1584	0.99878	0.939	1.3347	1533.3
0.2006	0.99814	0.939	1.3341	1546.3	0.2005	0.99911	0.953	1.3351	1553.1
0.2354	0.99852	0.951	1.3343	1570.2	0.2353	0.99952	0.967	1.3356	1578.9
0.2658	0.99899	0.963	1.3348	1598.9	0.2656	0.99995	0.982	1.3361	1612.6

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0.2931	0.99947	0.976	1.3354	1633.6	0.2929	1.00044	0.996	1.3365	1650.2
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$w_1 = 0.05$

Glycine									
0.1000	0.99974	0.920	1.335	1525.2					
0.1582	1.00007	0.924	1.3354	1542.9					
0.2002	1.00045	0.928	1.3357	1568.9					
0.2349	1.00086	0.931	1.3361	1601.3					
0.2651	1.00130	0.935	1.3364	1642.0					
0.2922	1.00176	0.938	1.3367	1690.2					
L-Alanine									
0.1001	0.99967	0.925	1.3351	1524.3					
0.1583	0.99994	0.933	1.3355	1540.7					
0.2003	1.00031	0.941	1.3358	1565.1					

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0.2350	1.00074	0.949	1.3362	1596.3
0.2652	1.00122	0.957	1.3365	1634.9
0.2924	1.00173	0.965	1.3368	1683.2
L-Valine				
0.1001	0.99960	0.932	1.3352	1523.5
0.1583	0.99983	0.948	1.3358	1539.5
0.2004	1.00020	0.963	1.3363	1563.1
0.2352	1.00064	0.978	1.3368	1594.2
0.2655	1.00116	0.995	1.3372	1634.1
0.2927	1.00175	1.010	1.3376	1680.3

^e uncertainty in the molality: $\pm 0.0001 \text{ mol kg}^{-1}$

^f uncertainty in the density values: $\pm 0.01 \text{ kg m}^{-3}$

^g uncertainty in the viscosity values: $\pm 0.003 \text{ mPas}$

^h uncertainty in the refractive index values: $\pm 0.0002 \text{ units}$

ⁱ uncertainty in the speed of sound: $\pm 0.2 \text{ m.s}^{-1}$

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Table 3. Molality (m), 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 Glycine, L- Alanine and L-Valine in Barium Nitrate at 298.15K and Experimental Pressure 0.1MPa.

m (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 (m ³ mol ⁻¹)	β x 10 ¹⁰ (Pa ⁻¹)	$\phi_k \times 10^{10}$ (m ³ mol ⁻¹ Pa ⁻¹)
$w_1 = 0.01$					
Glycine					
0.1001	49.1994	0.036	15.4698	4.3539	-2.6443
0.1584	47.5952	0.044	15.4800	4.2701	-4.2921
0.2004	46.6928	0.050	15.4857	4.1583	-5.4037
0.2351	45.9180	0.054	15.4910	4.0169	-6.4489
0.2653	45.1888	0.058	15.4961	3.8628	-7.2303
0.2925	44.4811	0.061	15.5008	3.6838	-8.0281
L-Alanine					
0.1002	67.2669	0.062	18.3697	4.3587	-2.0879
0.1584	65.2616	0.089	18.3827	4.2816	-3.7521
0.2005	64.0083	0.107	18.3902	4.1739	-4.9379
0.2352	62.5272	0.123	18.3967	4.0415	-5.9285
0.2655	61.3943	0.138	18.4078	3.8865	-6.8198
0.2927	60.1895	0.152	18.4082	3.7127	-7.6189
L-Valine					
0.1002	104.4246	0.100	24.1708	4.3649	-1.3100
0.1585	100.6146	0.153	24.1967	4.2925	-3.1623
0.2006	98.1582	0.192	24.2145	4.1901	-4.3847

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0.2354	96.4947	0.220	24.2184	4.0619	-5.4093
0.2658	94.2550	0.247	24.2399	3.9155	-6.2603
0.2931	92.6879	0.272	24.2676	3.7492	-7.0469
<hr/> w ₁ = 0.03 <hr/>					
Glycine					
0.1001	56.1554	0.034	15.5000	4.3237	-2.8432
0.1583	53.5514	0.044	15.5115	4.2327	-4.6445
0.2003	51.8989	0.052	15.5180	4.1068	-5.9740
0.2350	50.4194	0.058	15.5240	3.9566	-7.0214
0.2652	49.4308	0.063	15.5297	3.7854	-7.9215
0.2923	48.4377	0.067	15.5350	3.5911	-8.7771
L-Alanine					
0.1001	76.2058	0.069	18.4009	4.3302	-2.1035
0.1584	71.5988	0.096	18.4152	4.2464	-4.0186
0.2004	68.9448	0.115	18.4234	4.1311	-5.2920
0.2351	66.6458	0.131	18.4304	3.9871	-6.3949
0.2654	64.9029	0.146	18.4419	3.8243	-7.2973
0.2925	63.3039	0.159	18.4426	3.6343	-8.2015
L-Valine					
0.1001	111.3192	0.127	24.2048	4.3357	-1.4067
0.1584	105.3101	0.175	24.2384	4.2586	-3.3819
0.2005	101.5544	0.212	24.2567	4.1494	-4.6914
0.2353	98.3905	0.245	24.2795	4.0132	-5.7814
0.2656	96.2964	0.274	24.3019	3.8456	-6.8553
0.2929	94.2344	0.298	24.3162	3.6705	-7.6397
<hr/> w ₁ = 0.05 <hr/>					
Glycine					
0.1000	57.0951	0.036	15.5297	4.2999	-2.9682
0.1582	54.6941	0.047	15.5414	4.2004	-5.0326
0.2002	52.8433	0.055	15.5481	4.0608	-6.5580

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0.2349	51.4563	0.062	15.5585	3.8965	-7.7019
0.2651	50.2350	0.069	15.5643	3.7041	-8.7591
0.2922	49.2093	0.074	15.5697	3.4942	-9.6492
L-Alanine					
0.1001	78.1244	0.072	18.4363	4.3053	-2.3383
0.1583	73.9225	0.097	18.4513	4.2129	-4.4462
0.2003	70.3710	0.118	18.4594	4.0811	-5.9724
0.2350	67.6652	0.135	18.4714	3.9214	-7.1757
0.2652	65.4045	0.151	18.4775	3.7366	-8.2244
0.2924	63.5886	0.165	18.4830	3.5235	-9.2374
L-Valine					
0.1001	113.1998	0.132	24.2513	4.3101	-1.7034
0.1583	106.3968	0.184	24.2851	4.2201	-4.0238
0.2004	101.1945	0.221	24.3089	4.0920	-5.5660
0.2352	97.5566	0.254	24.3309	3.9322	-6.8507
0.2655	94.3344	0.288	24.3445	3.7405	-8.0430
0.2927	91.4255	0.313	24.3563	3.5356	-8.9733

^j uncertainty in the molality: $\pm 0.0001 \text{ mol.kg}^{-1}$

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 Glycine, L-Alanine, and L-Valine in aqueous Barium Nitrate at 298.15K and Experimental Pressure 0.1MPa.

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 ($\text{kg}^{1/2} \text{ mol}^{-1/2}$)	$\phi_K^0 \times 10^{10}$ ($\text{m}^3 \text{ mol}^{-1} \text{ Pa}^{-1}$)	$S_K^* \times 10^4$ ($\text{m}^3 \text{ mol}^{-3/2} \text{ Pa}^{-1} \text{ kg}^{1/2}$)
$w_1 = 0.01$						
Glycine	51.53	-24.01	0.023	0.131	0.151	-27.92
L-Alanine	71.05	-36.48	0.015	0.463	0.795	-28.68
L-Valine	110.30	-60.17	0.012	0.887	1.591	-29.61
$w_1 = 0.03$						
Glycine	60.01	-40.08	0.011	0.181	0.229	-30.82
L-Alanine	82.47	-66.5	0.008	0.477	1.012	-31.46
L-Valine	119.60	-88.43	0.007	0.920	1.796	-32.35
$w_1 = 0.005$						
Glycine	61.19	-41.27	0.009	0.197	0.478	-34.82
L-Alanine	85.84	-76.71	0.007	0.478	1.215	-35.72
L-Valine	124.30	-113.10	0.006	0.931	2.012	-37.72

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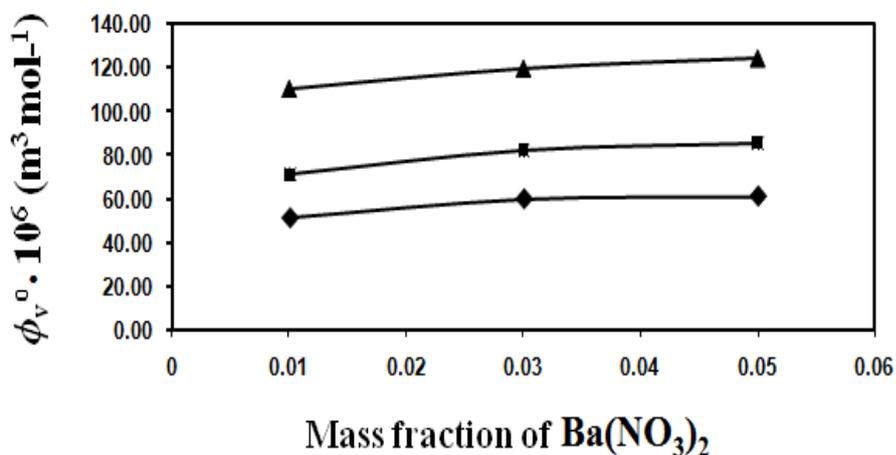


Figure 1. Plots of limiting apparent molar volumes (ϕ_v^0) for Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of $\text{Ba}(\text{NO}_3)_2$ in aqueous mixture at 298.15K.

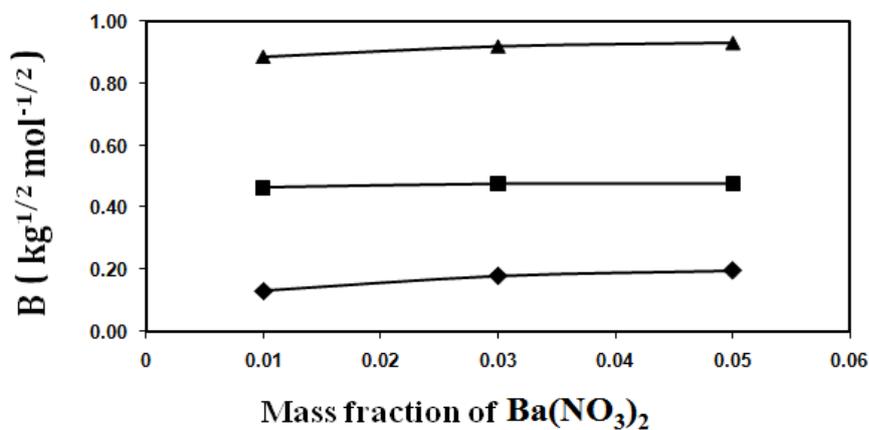


Figure 2. Plots of viscosity B -coefficient for Glycine (—◆—), L-Alanine (—■—), L-Valine (—▲—) in different mass fractions (w_1) of $\text{Ba}(\text{NO}_3)_2$ in aqueous mixture at 298.15K.

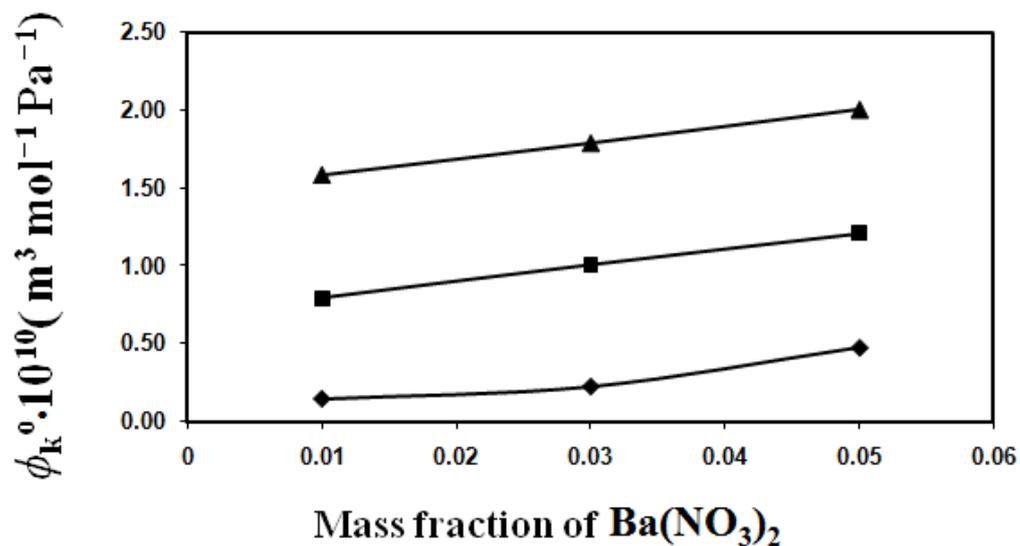


Figure 3. Plots of limiting partial adiabatic compressibility (ϕ_k^0) for Glycine (— \diamond —), L-Alanine (— \blacksquare —), L-Valine (— \blacktriangle —) in different mass fractions (w_1) of $\text{Ba}(\text{NO}_3)_2$ in aqueous mixture at 298.15K.

CHAPTER -VIII

STUDY ON INTERACTIONS OF POTASSIUM HALIDES PREVAILING IN AQUEOUS NICOTINIC ACID SOLUTION BY PHYSICO-CHEMICAL APPROACH

8.1. Introduction

Investigations on densities (ρ) and viscosities (η) of electrolyte solutions are of immense importance in exemplifying the properties and structural features of various solutions. The inclusion of an electrolyte to an aqueous organic solution amends the pattern of ion solvation and results in phenomenal changes in the behaviour of the dissolved electrolyte. Thus studies on the limiting apparent molar volume and viscosity B-coefficients of electrolyte enable us important information regarding ion-solvent, ion-ion, and solvent-solvent interactions [1-3]. It has been found by a number of workers [4-6] that the addition of an electrolyte could either make or break the structure of a liquid. As the viscosity of a liquid depends on the intermolecular forces, the structural aspects of the liquid can be gathered from the viscosity of solutions at various electrolyte concentrations and temperature.

In this exploration we have attempted to report the limiting apparent molar volume (ϕ_V^0), experimental slopes (S_V^*) and viscosity B-coefficients for potassium chloride, potassium bromide and potassium iodide in aqueous mixture of Nicotinic acid at 298.15, 308.15 and 318.15 K. Since potassium ion being a common cation for all of the electrolytes under investigation, the present work enables us to have a qualitative comparison of the role of anion in aqueous Nicotinic acid in terms of various derived parameters obtained from viscosity (η) and density (ρ) measurements.

8.2. Experimental Methods

8.1. Materials

Nicotinic acid (SD. Fine Chemicals) was purified by standard methods [7]. The purity of the solvent was checked by measuring the viscosity (η) and density (ρ) at 298.15 K which was in good agreement with the literature values. Doubly distilled, degassed and deionised water with a specific conductance of $1 \times 10^{-6} \Omega^{-1}$

cm⁻¹ was used. Potassium chloride, potassium bromide and potassium iodide (Sigma-Aldrich, Germany) were purified by re-crystallizing twice from conductivity water and then dried in a vacuum desiccator over P₂O₅ for 24 h before use. The experimental values of viscosity (η) and density (ρ) of aqueous mixtures of 0.01 M, 0.03 M and 0.05 M Nicotinic acid at different temperatures are listed in Table 1.

8.2. Apparatus and Procedure

Densities (ρ) were computed with an Anton Paar density-meter (DMA 4500M) with a precision of 0.0005 g/cm³. The calibration was done by double-distilled water and dry air and uncertainty in density was ± 0.00005 g cm⁻³. The measurements were done in a thermostat bath controlled to ± 0.01 K. Viscosity (η) was measured by means of Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 having an accuracy of 1.0% and fitted to a Brookfield Digital Bath TC-500 at 298K using density and viscosity values from the literature [8-10]. The uncertainty in viscosity measurements is within ± 0.003 mPa s. The mixtures were prepared by mixing known volume of pure liquids 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.

The electrolyte solutions studied here were prepared by mass and the conversion of molality into molarity was accomplished [3] using experimental density values. The experimental values of concentrations (c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in Table 2.

8. 3. Result and Discussion

8.3.1. Density Calculation

The apparent molar volumes (ϕ_v) were determined from the solution densities using the following Eq. [3]:

$$\phi_v = M / \rho - (\rho - \rho_o) / c \rho \rho_o \quad (1)$$

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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 limiting apparent molar volume ϕ_V^0 was calculated using a least-squares treatment to the plots of ϕ_V versus \sqrt{c} using the following Masson equation [11]:

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{c} \quad (2)$$

where (ϕ_V^0) is the apparent molar volume at infinite dilution and (S_V^*) is the experimental slope. The plots of (ϕ_V^0) against square root of molar concentration (\sqrt{c}) were found to be linear as depicted graphically in Figs. 1–9 with negative slopes. Values of ϕ_V^0 and S_V^* are reported in Table 3.

In these systems the ion–solvent and ion–ion interactions can be interpreted in terms of structural changes between various components of the solvent and solution systems. ϕ_V^0 can be used to interpret ion–solvent interactions. A perusal of Table 3 discloses that the ϕ_V^0 values are positive and increase with a rise in both the temperature and amount of Nicotinic acid in the mixtures. This indicates the presence of strong ion–solvent interactions and these interactions are further strengthened at higher temperatures and higher molar mass of Nicotinic acid in the mixtures, suggesting larger electrostriction at higher temperatures and in enhanced amount of Nicotinic acid.

A perusal of Table 3 also reveals that the S_V^* values are negative for all the solutions at all the experimental temperatures and S_V^* values decrease as the experimental temperature and amount of Nicotinic acid in the mixtures increases. Since S_V^* is a measure of ion–ion interactions, the results indicate the presence of weak ion–ion interactions in the solutions at all the experimental temperatures and these interactions further decrease with a rise in temperature and increase in molar mass Nicotinic acid in the mixtures. In other words, it may be said that the solvation of electrolyte/ions increases with the increase of Nicotinic acid content in water. This is probably due to more violent thermal agitation at higher temperatures, resulting in diminishing the force of ion–ion

interactions (ionic-dissociation) [12]. This implies that ion–solvent interactions predominate over ion–ion interactions in all the solutions and at all experimental temperatures.

The variation of ϕ_V^0 with temperature of potassium chloride, potassium bromide and potassium iodide in aqueous mixture of Nicotinic acid follows the polynomial,

$$\phi_V^0 = a_0 + a_1T + a_2T^2 \quad (3)$$

over the temperature range under study where T is the temperature in K. Values of coefficients of the above equation for potassium chloride, potassium bromide and potassium iodide in aqueous mixture of Nicotinic acid are reported in Table 4. The apparent molar expansibilities (ϕ_E^0) can be obtained by the following equation:

$$\phi_E^0 = \left(\frac{\partial \phi_V^0}{\partial T} \right)_P = a_1 + 2a_2T \quad (4)$$

The values of ϕ_E^0 for different solutions of the studied electrolytes at 298.15, 308.15 and 318.15 K are reported in Table 5. From the table it is evident that the values of ϕ_E^0 for potassium chloride increases with the increase in the amount of Nicotinic acid in the mixture. However, for potassium bromide and potassium iodide the ϕ_E^0 values were found to be rather complicated to explain. During the past few years it has been emphasized by a number of workers that S_V^* is not the sole criterion for determining the structure making or breaking tendency of any solute. Hepler [13] developed a technique of examining the sign of $\left(\frac{\partial \phi_E^0}{\partial T} \right)_P$ 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

$$\left(\frac{\partial \phi_E^0}{\partial T} \right)_P = 2a_2 \quad (5)$$

If the sign of $\left(\frac{\partial \phi_E^0}{\partial T} \right)_P$ is positive or small negative [14,15] the electrolyte is a structure maker and when the sign of $\left(\frac{\partial \phi_E^0}{\partial T} \right)_P$ is negative, it is a structure breaker. As is evident from Table 5, the electrolyte under investigation generally acts as a structure breaker.

8.3.2. Viscosity Calculation

The viscosity data of solutions for the electrolytes in 0.01 M, 0.03 M, 0.05 M Nicotinic acid have been analyzed using Jones–Dole [16] equation:

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B\sqrt{c} \quad (6)$$

where η_0 and η are the viscosities of the solvent and solution respectively. A and B are the constants estimated by least square method and are reported in Table 6. From the table it is evident that the values of the A-coefficient are very small for all the solutions under investigation at all experimental temperatures. These results indicate the presence of weak ion–ion interactions, and these interactions further decrease with both rise of experimental temperatures and amount of Nicotinic acid suggesting an increase in ion–solvation. Interestingly, values are found to be smallest for Potassium iodide and hence it may be concluded that solubility in aqueous Nicotinic acid solutions is maximum for Potassium iodide and minimum for Potassium chloride.

The effects of ion–solvent interactions on the solution viscosity can be inferred from the B-coefficient [17,18]. 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 6 it is evident that the values of the B-coefficient of potassium chloride, potassium bromide and potassium iodide in the studied solvent systems are more positive than A-coefficients, thereby suggesting the presence of strong ion–solvent interactions, and these type of interactions are strengthened with a rise in both temperature and amount of Nicotinic acid in solutions. These conclusions are in excellent agreement with those drawn from ϕ_V^0 values discussed earlier. It has been reported in a number of studies [19,20] that dB/dT is a better criterion for determining the structure-making/breaking nature of any solute rather than simply the value of the B-coefficient. It is found from Table 6 that the values of the B-coefficient increase with a rise in temperature (positive dB/dT) suggesting the structure-breaking tendency of potassium chloride, potassium bromide and potassium iodide in the solvent systems.

8. 4. Conclusions

Extensive study of potassium chloride, potassium bromide and potassium iodide in aqueous mixture of Nicotinic acid reveals that potassium iodide is more associated in Nicotinic acid than the other two halides. The ion-association is found minimum in the case of potassium chloride in Nicotinic acid. The said interaction of potassium bromide arises in the intermediacy of potassium iodide and potassium chloride. The present study reveals the predominance of ion-solvent interaction over the ion-ion interaction in all the solution under investigation.

References

1. J.M. Mc Dowali, C.A. Vincent, *J. Chem. Soc., Faraday Trans.* **1974**, 1, 1862.
2. M.R.J. Dack, K.J. Bird, A.J. Parker, *Aust. J. Chem.* **1975**, 28, 955.
3. M.N. Roy, B. Sinha, R. Dey, A. Sinha, *Int. J. Thermophys.* **2005**, 26, 1549.
4. R.H. Stokes, R. Mills, *Int. Encyclopedia of Physical Chemistry and Chemical Physics*, Pergamon Press, Oxford, New York, **1965**.
5. P.S. Nikam, H. Mehdi, *J. Chem. Eng. Data* **1988**, 33, 165.
6. M. N. Roy, D. Nandi, D. K. Hazra, *J. Indian Chem. Soc.* **1993**, 70, 123.
7. D.D. Perrin, W.L.F. Amarego, *Purification of Laboratory Chemicals*, third ed., Great Britain, **1988**.
8. B. Sinha, V.K. Dakua, M.N. Roy, *J. Chem. Eng. Data.* 2007, 52, 1768.
9. J.A. Dean, *Lange's Handbook of Chemistry*, 11th ed. McGraw-Hill Book Company, New York, **1973**.
10. B.D. Chatterjee, *J. Chem. Eng. Data.* **2006**, 51, 1352.
11. D.O. Masson, *Phil. Mag.* **1929**, 8, 218.
12. F.J. Millero, *Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes*, Wiley- Interscience, New York, **1972**.
13. L. G. Hepler, *Can. J. Chem.* **1969**, 47, 4617.
14. B.K. Sarkar, B. Sinha, M.N. Roy, *Russ. J. Phys. Chem* **2008**, 8, 960.
15. M.L. Parmar, D.S. Banyal, *Indian J. Chem.* **2005**, 44A, 1582.
16. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, 51, 2950.
17. F. J. Millero, *Chem. Rev.* **1971**, 71, 147.
18. F. J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.* **1978**, 82, 784.
19. R. Gopal, M.A. Siddiqi, *J. Phys. Chem.* **1969**, 73, 3390.
20. N. Saha, B. Das, *J. Chem. Eng. Data* **1997**, 42, 227.

Table 1. Density (ρ , kg m⁻³) and viscosity (η , mPa s) of aqueous mixtures of 0.01 M Nicotinic acid , 0.03 M Nicotinic acid, 0.05 M Nicotinic acid at different temperatures

Temperature (K)	$\rho \times 10^{-3}$ (kg m ⁻³)	η (mPa s)
0.01 M Nicotinic acid		
298.15 K	0.99738	0.903
308.15 K	0.99593	0.766
318.15 K	0.99451	0.634
0.03 M Nicotinic acid		
298.15 K	0.99887	0.910
308.15 K	0.99751	0.773
318.15 K	0.99589	0.640
0.05 M Nicotinic acid		
298.15 K	1.00031	0.917
308.15 K	0.99929	0.781
318.15 K	0.99759	0.647

Table 2. The concentration (c), density (ρ), viscosity (η), apparent molar volume (ϕ_v), and $(\eta/\eta_0-1)/c^{1/2}$ of potassium chloride, potassium bromide and potassium iodide in different aqueous mixtures 0.01 M Nicotinic acid, 0.03 M Nicotinic acid, 0.05 M Nicotinic acid at different temperatures

c (mol.dm ⁻³)	$\rho \times 10^{-3}$ (kg m ⁻³)	η (mPa s)	$\phi_v \times 10^6$ (m ³ . mol ⁻¹)	$(\eta/\eta_0-1)/c^{1/2}$ (kg ^{1/2} mol ^{-1/2})
Potassium chloride in aqueous mixture 0.01 M Nicotinic acid				
298.15K				
0.0149	0.99804	0.912	40.3180	0.082
0.0299	0.99862	0.917	38.0586	0.090
0.0448	0.99924	0.921	36.3141	0.094
0.0585	0.99985	0.925	35.1427	0.101
0.0748	1.00059	0.928	33.7883	0.101
0.0907	1.00132	0.932	32.3955	0.107
Potassium chloride in aqueous mixture 0.01 M Nicotinic acid				
308.15K				
0.0149	0.99639	0.774	43.7101	0.086
0.0299	0.99697	0.779	39.7467	0.098
0.0448	0.99761	0.784	36.9861	0.111
0.0585	0.99825	0.788	34.7917	0.119
0.0748	0.99906	0.793	32.5657	0.129
0.0907	0.99987	0.798	30.9376	0.139
Potassium chloride in aqueous mixture 0.01 M Nicotinic acid				
318.15K				
0.0149	0.99494	0.642	45.7642	0.103
0.0299	0.99551	0.648	41.1061	0.128
0.0448	0.99614	0.654	38.1133	0.149

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0.0585	0.99678	0.659	35.6482	0.163
0.0748	0.99759	0.665	33.2273	0.179
0.0907	0.99843	0.671	31.1419	0.194
Potassium bromide in aqueous mixture 0.01 M Nicotinic acid				
298.15K				
0.0151	0.99836	0.916	54.0174	0.117
0.0301	0.99944	0.925	50.4099	0.140
0.0451	1.00058	0.934	47.8324	0.162
0.0604	1.00177	0.942	46.0455	0.176
0.0756	1.00301	0.950	44.2004	0.189
0.0908	1.00431	0.959	42.2956	0.206
Potassium bromide in aqueous mixture 0.01 M Nicotinic acid				
308.15K				
0.0151	0.99681	0.778	60.6773	0.127
0.0301	0.99785	0.787	55.0704	0.158
0.0451	0.99901	0.796	50.4782	0.184
0.0604	1.00026	0.805	47.0061	0.207
0.0756	1.00158	0.814	43.8898	0.228
0.0908	1.00297	0.822	41.0283	0.243
Potassium bromide in aqueous mixture 0.01 M Nicotinic acid				
318.15K				
0.0151	0.99526	0.646	69.3858	0.154
0.0301	0.99625	0.656	61.1027	0.200
0.0451	0.99740	0.666	54.7087	0.238
0.0604	0.99867	0.676	49.8119	0.270
0.0756	1.00004	0.686	45.4462	0.298
0.0908	1.00154	0.696	41.0864	0.325
Potassium iodide in aqueous mixture 0.01 M Nicotinic acid				

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298.15K				
0.0153	0.99871	0.921	78.9482	0.161
0.0304	1.00013	0.935	75.2949	0.203
0.0454	1.00160	0.949	72.6908	0.239
0.0607	1.00314	0.962	70.6388	0.265
0.0758	1.00471	0.975	68.7232	0.290
0.0911	1.00634	0.989	66.9664	0.316
Potassium iodide in aqueous mixture 0.01 M Nicotinic acid				
308.15K				
0.0153	0.99702	0.783	94.7522	0.179
0.0304	0.99839	0.798	84.8877	0.240
0.0454	0.99991	0.813	77.9864	0.288
0.0607	1.00159	0.828	72.2614	0.329
0.0758	1.00333	0.842	67.7529	0.360
0.0911	1.00516	0.857	63.9416	0.394
Potassium iodide in aqueous mixture 0.01 M Nicotinic acid				
318.15K				
0.0153	0.99544	0.651	105.3634	0.217
0.0304	0.99674	0.667	92.5443	0.299
0.0454	0.99824	0.682	83.5377	0.355
0.0607	0.99995	0.698	75.8908	0.410
0.0758	1.00177	0.713	69.5726	0.453
0.0911	1.00373	0.729	63.9979	0.496
Potassium chloride in aqueous mixture 0.03 M Nicotinic acid				
298.15K				
0.0147	0.99905	0.917	62.3515	0.063
0.0297	0.99934	0.921	58.7470	0.070
0.0450	0.99971	0.925	55.8794	0.078

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0.0601	1.00015	0.929	53.2211	0.085
0.0751	1.00066	0.933	50.6557	0.092
0.0903	1.00122	0.936	48.4381	0.095

Potassium chloride in aqueous mixture 0.03 M Nicotinic acid

308.15K

0.0147	0.99759	0.780	69.2622	0.075
0.0297	0.99783	0.785	63.8883	0.090
0.0450	0.99818	0.790	59.7337	0.104
0.0601	0.99861	0.795	56.2807	0.116
0.0751	0.99915	0.799	52.7037	0.123
0.0903	0.99971	0.804	50.1415	0.133

Potassium chloride in aqueous mixture 0.03 M Nicotinic acid

318.15K

0.0147	0.99604	0.647	64.5605	0.090
0.0297	0.99644	0.653	56.1560	0.118
0.0450	0.99697	0.658	50.6053	0.133
0.0601	0.99769	0.664	44.5803	0.153
0.0751	0.99851	0.669	39.5792	0.165
0.0903	0.99949	0.674	34.5370	0.177

Potassium bromide in aqueous mixture 0.03 M Nicotinic acid

298.15K

0.0150	0.99907	0.922	105.7862	0.108
0.0305	0.9997	0.932	91.7836	0.138
0.0456	1.00062	0.941	80.5295	0.160
0.0608	1.00181	0.951	70.4625	0.183
0.0759	1.00322	0.960	61.4251	0.199
0.0911	1.00476	0.969	54.0155	0.215

Potassium bromide in aqueous mixture 0.03 M Nicotinic acid

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308.15K				
0.0150	0.99762	0.785	111.9347	0.127
0.0305	0.99832	0.796	92.5318	0.170
0.0456	0.99938	0.807	77.9372	0.206
0.0608	1.00079	0.817	64.8667	0.231
0.0759	1.00249	0.828	53.0914	0.258
0.0911	1.00436	0.838	43.4308	0.279
Potassium bromide in aqueous mixture 0.03 M Nicotinic acid				
318.15K				
0.0150	0.99597	0.652	114.1191	0.153
0.0305	0.99677	0.663	90.3202	0.206
0.0456	0.99804	0.674	71.7970	0.249
0.0608	0.99972	0.685	55.7622	0.285
0.0759	1.00174	0.696	41.5345	0.318
0.0911	1.00402	0.707	29.2714	0.347
Potassium iodide in aqueous mixture 0.03 M Nicotinic acid				
298.15K				
0.0141	0.99913	0.928	147.6707	0.167
0.0293	1.00018	0.944	121.2205	0.218
0.0447	1.00167	0.960	103.1199	0.260
0.0592	1.00344	0.975	88.4154	0.294
0.0746	1.00563	0.991	74.8622	0.326
0.0898	1.00799	1.007	63.8190	0.356
Potassium iodide in aqueous mixture 0.03 M Nicotinic acid				
308.15K				
0.0141	0.99769	0.790	153.5597	0.185
0.0293	0.99866	0.808	126.8256	0.265
0.0447	1.00019	0.826	105.8778	0.324

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0.0592	1.00209	0.842	88.2604	0.367
0.0746	1.00443	0.859	72.6878	0.407
0.0898	1.00694	0.876	60.3110	0.445
Potassium iodide in aqueous mixture 0.03 M Nicotinic acid				
318.15K				
0.0141	0.99597	0.657	160.9543	0.224
0.0293	0.99708	0.675	125.5876	0.319
0.0447	0.99884	0.693	99.8507	0.392
0.0592	1.00102	0.710	78.9093	0.450
0.0746	1.00369	0.727	60.7893	0.498
0.0898	1.00669	0.745	44.9386	0.547
Potassium chloride in aqueous mixture 0.05 M Nicotinic acid				
298.15 K				
0.0149	1.00043	0.925	66.9900	0.071
0.0304	1.0007	0.931	62.2015	0.088
0.0453	1.00105	0.936	58.6779	0.097
0.0611	1.00149	0.942	55.6804	0.110
0.0759	1.00196	0.947	53.2333	0.119
0.0912	1.00252	0.952	50.7172	0.126
Potassium chloride in aqueous mixture 0.05 M Nicotinic acid				
308.15 K				
0.0149	0.99942	0.789	66.3775	0.084
0.0304	0.99988	0.795	55.6550	0.103
0.0453	1.00052	0.801	47.8735	0.120
0.0611	1.00133	0.807	41.6031	0.135
0.0759	1.00226	0.813	35.8308	0.149
0.0912	1.00339	0.819	29.9803	0.161
Potassium chloride in aqueous mixture 0.05 M Nicotinic acid				

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318.15 K				
0.0149	0.99773	0.655	65.8007	0.101
0.0304	0.99822	0.662	54.3931	0.133
0.0453	0.99888	0.669	46.5765	0.160
0.0611	0.99977	0.676	39.3136	0.181
0.0759	1.00076	0.682	33.1784	0.196
0.0912	1.00189	0.689	27.7545	0.215
Potassium bromide in aqueous mixture 0.05 M Nicotinic acid				
298.15 K				
0.0155	1.00047	0.929	108.6296	0.105
0.0309	1.00124	0.939	88.8021	0.136
0.0463	1.00241	0.949	73.4806	0.162
0.0609	1.00381	0.959	61.3129	0.186
0.0761	1.00554	0.969	50.0188	0.206
0.0914	1.00755	0.978	39.5140	0.220
Potassium bromide in aqueous mixture 0.05 M Nicotinic acid				
308.15 K				
0.0155	0.99945	0.793	108.7299	0.123
0.0309	1.00034	0.804	84.9664	0.168
0.0463	1.00165	0.815	67.8799	0.202
0.0609	1.00335	0.825	52.1114	0.228
0.0761	1.00531	0.835	39.6269	0.251
0.0914	1.00748	0.846	29.1124	0.275
Potassium bromide in aqueous mixture 0.05 M Nicotinic acid				
318.15 K				
0.0155	0.99776	0.659	108.2482	0.149
0.0309	0.99892	0.670	75.9360	0.202
0.0463	1.00059	0.681	54.0168	0.244

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0.0609	1.00266	0.692	35.4533	0.282
0.0761	1.00521	0.703	18.5302	0.314
0.0914	1.00811	0.714	3.5943	0.343

Potassium iodide in aqueous mixture 0.05 M Nicotinic acid

298.15 K

0.0147	1.00049	0.935	153.6864	0.162
0.0306	1.00146	0.953	128.2455	0.224
0.0456	1.00289	0.970	109.1260	0.271
0.0602	1.00474	0.987	92.0015	0.311
0.0763	1.00702	1.005	77.5434	0.347
0.0901	1.00944	1.021	64.0973	0.378

Potassium iodide in aqueous mixture 0.05 M Nicotinic acid

308.15 K

0.0147	0.99949	0.799	152.4654	0.190
0.0306	1.00060	0.818	123.0881	0.271
0.0456	1.00224	0.836	101.0375	0.330
0.0602	1.00423	0.853	83.5314	0.376
0.0763	1.00683	0.871	66.6569	0.417
0.0901	1.00953	0.887	51.7771	0.452

Potassium iodide in aqueous mixture 0.05 M Nicotinic acid

318.15 K

0.0147	0.99781	0.665	151.3321	0.229
0.0306	0.99931	0.684	109.7336	0.327
0.0456	1.00152	0.703	79.4896	0.405
0.0602	1.00433	0.720	53.5404	0.460
0.0763	1.00768	0.739	33.1873	0.515
0.0901	1.01141	0.756	12.1090	0.561

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Table 3.

Limiting apparent molar volumes (ϕ_v^0) and experimental slopes (S_v^*) of potassium chloride, potassium bromide and potassium iodide in different aqueous mixtures 0.01 M Nicotinic acid, 0.03 M Nicotinic acid, 0.05 M Nicotinic acid at different temperatures

Molarity of Nicotinic acid	$\phi_v^0 \times 10^6$ ($\text{m}^3 \cdot \text{mol}^{-1}$)			$S_v^* \times 10^6$ ($\text{m}^2 \cdot \text{mol}^{-3/2} \text{L}^{1/2}$)		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
Potassium chloride						
0.01	45.63	52.25	55.39	-43.66	-71.64	-81.15
0.03	72.04	82.36	85.01	-77.71	-107.20	-165.9
0.05	77.92	90.71	91.44	-89.97	-200.10	-211.1
Potassium bromide						
0.01	61.75	74.12	88.51	-64.40	-110.10	-157.40
0.03	142.10	159.4	172.90	-291.41	-384.20	-475.70
0.05	157.01	164.5	180.2	-388.10	-451.10	-585.9
Potassium iodide						
0.01	87.05	115.4	133.4	-66.74	-173.20	-231.90
0.03	201.41	215.50	236.10	-462.80	-520.30	-641.90
0.05	215.10	220.70	244.91	-500.31	-560.20	-773.69

Table 4.

Values of the coefficients of Eq. (4) for potassium chloride, potassium bromide and potassium iodide in different aqueous mixtures 0.01 M Nicotinic acid, 0.03 M Nicotinic acid, 0.05 M Nicotinic acid at different temperatures

Molarity of Nicotinic acid	a_0 ($\text{m}^3 \cdot \text{mol}^{-1}$)	a_1 ($\text{m}^3 \cdot \text{mol}^{-1} \text{K}^{-1}$)	a_2 ($\text{m}^3 \cdot \text{mol}^{-1} \text{K}^{-2}$)
Potassium chloride			
0.01	-1750.368	11.2116	-0.0174
0.03	-3759.054	24.2836	-0.0383
0.05	-5843.471	37.8389	-0.0603
Potassium bromide			
0.01	620.875	-4.8866	0.0101
0.03	-2119.323	13.2497	-0.0190
0.05	3705.161	-24.1396	0.0410
Potassium iodide			
0.01	-5512.732	34.2110	-0.0517
0.03	2771.845	-18.3260	0.0325
0.05	8597.097	-55.8562	0.0930

Table 5.

Limiting partial molar expansibilities for potassium chloride, potassium bromide and potassium iodide in different aqueous mixtures 0.01 M Nicotinic acid, 0.03 M Nicotinic acid, 0.05 M Nicotinic acid at different temperatures

Molarity of Nicotinic acid	ϕ_E^0 (m ³ · mol ⁻¹)			$(\partial\phi_E^0 / \partial T)_P$ (m ³ · mol ⁻¹ K ⁻²)
	298.15 K	308.15 K	318.15 K	
Potassium chloride				
0.01	0.0836	0.4879	0.1399	-0.0348
0.03	1.4453	0.6793	-0.0867	-0.0766
0.05	1.8820	0.6760	-0.5299	-0.1206
Potassium bromide				
0.01	1.1360	1.3380	1.5401	0.0202
0.03	1.9199	1.5399	1.1601	-0.0380
0.05	0.3385	1.1595	1.9805	0.0820
Potassium iodide				
0.01	3.3823	2.3483	1.3143	-0.1034
0.03	1.0537	1.7037	2.3537	0.0650
0.05	-0.4003	1.4597	3.3197	0.1860

Table 6. Values of A and B coefficients for potassium chloride, potassium bromide and potassium iodide in different aqueous mixtures 0.01 M Nicotinic acid, 0.03 M Nicotinic acid, 0.05 M Nicotinic acid at different temperatures

Molarity of Nicotinic acid	B-coefficient ($\text{dm}^{3/2}\cdot\text{mol}^{-1/2}$)			A-coefficient ($\text{dm}^3\cdot\text{mol}^{-1}$)		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
Potassium chloride						
0.01	0.136	0.296	0.504	0.065	0.048	0.041
0.03	0.186	0.327	0.483	0.039	0.034	0.032
0.05	0.307	0.432	0.630	0.033	0.029	0.024
Potassium bromide						
0.01	0.489	0.656	0.957	0.056	0.045	0.035
0.03	0.602	0.852	1.087	0.033	0.022	0.017
0.05	0.658	0.848	1.095	0.022	0.018	0.010
Potassium iodide						
0.01	0.860	1.202	1.560	0.054	0.030	0.024
0.03	1.045	1.427	1.782	0.040	0.018	0.013
0.05	1.208	1.462	1.852	0.014	0.014	0.005

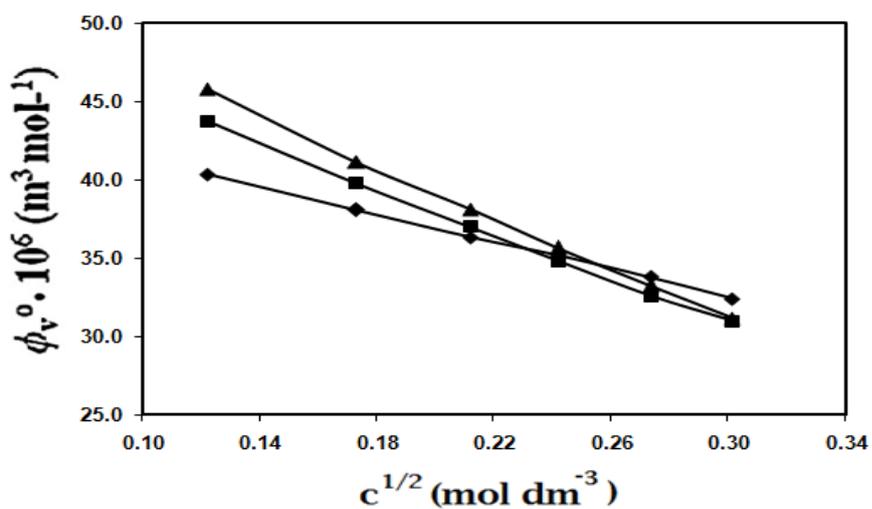


Figure 1: The apparent molar volume (ϕ_v) and the square root of concentrations (\sqrt{c}) for potassium chloride in different aqueous mixtures 0.01 M Nicotinic acid at 298.15 K (—◆—), 308.15 K (—■—) and 318.15 K (—▲—).

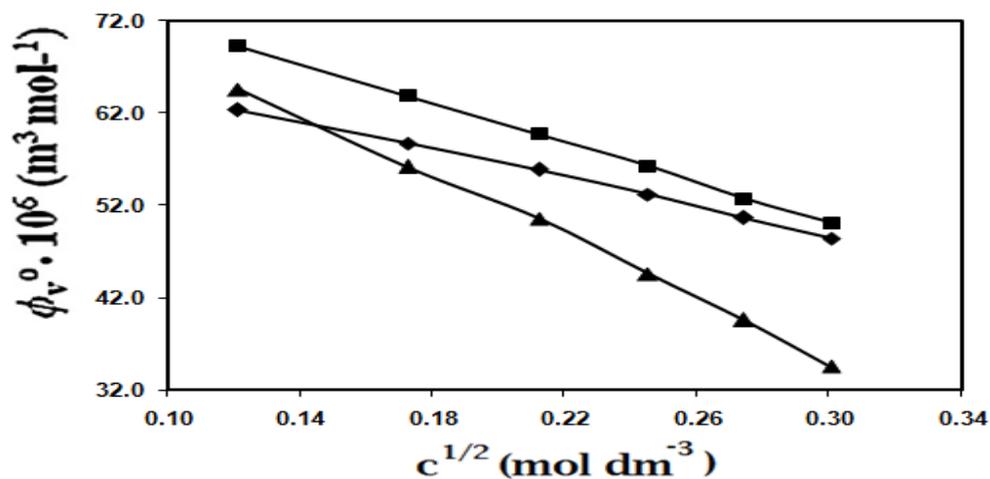


Figure 2: The apparent molar volume (ϕ_v) and the square root of concentrations (\sqrt{c}) for potassium chloride in different aqueous mixtures 0.03 M Nicotinic acid at 298.15 K (—◆—), 308.15 K (—■—) and 318.15 K (—▲—).

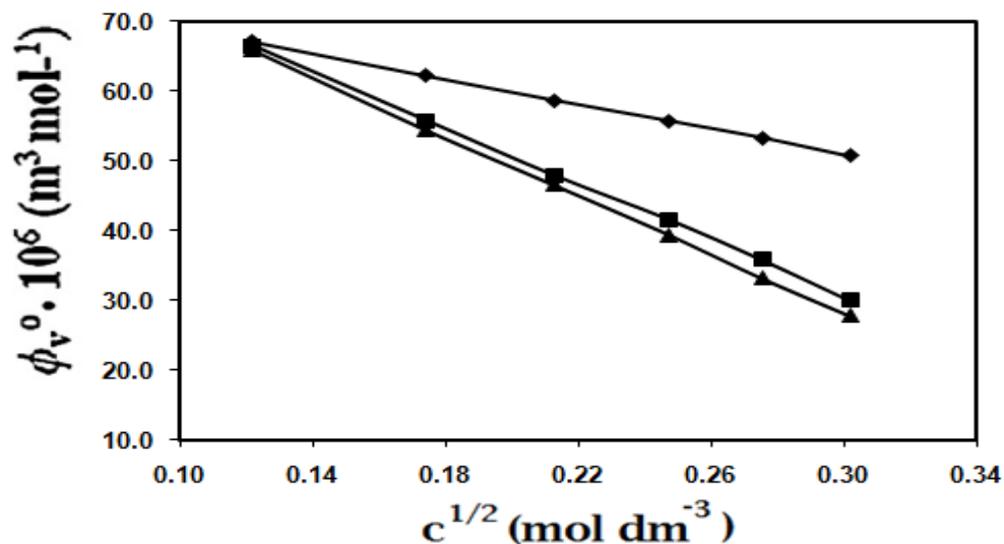


Figure 3: The apparent molar volume (ϕ_v) and the square root of concentrations (\sqrt{c}) for potassium chloride in different aqueous mixtures 0.05 M Nicotinic acid at 298.15 K (—◆—), 308.15 K (—■—) and 318.15 K (—▲—).

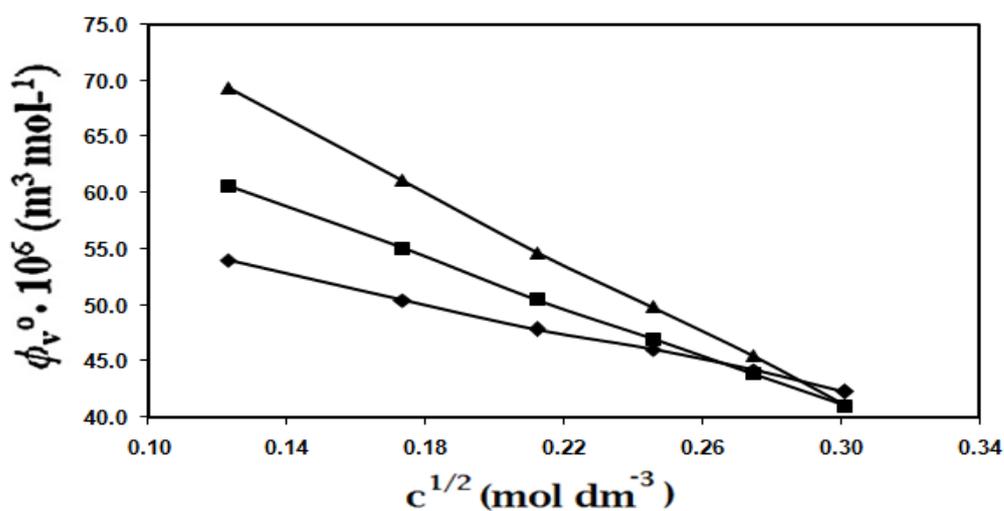


Figure 4: The apparent molar volume (ϕ_v) and the square root of concentrations (\sqrt{c}) for potassium bromide in different aqueous mixtures 0.01 M Nicotinic acid at 298.15 K (—◆—), 308.15 K (—■—) and 318.15 K (—▲—).

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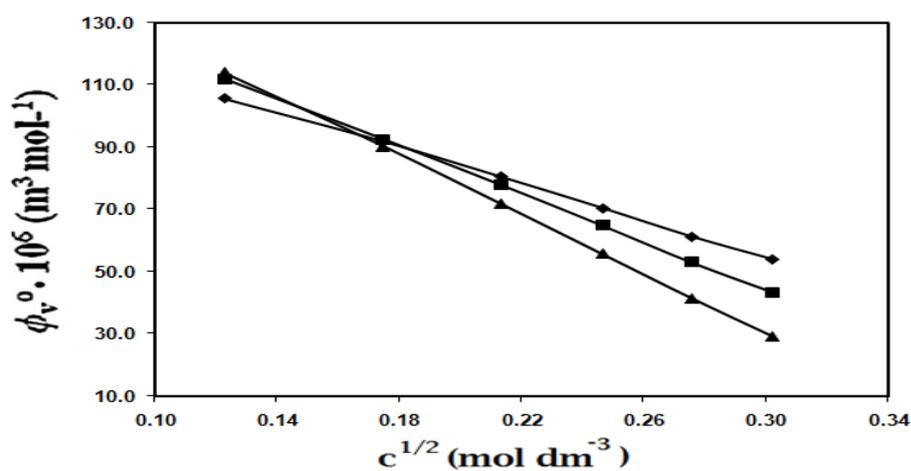


Figure 5: The apparent molar volume (ϕ_v) and the square root of concentrations (\sqrt{c}) for potassium bromide in different aqueous mixtures 0.03 M Nicotinic acid at 298.15 K (—◆—), 308.15 K (—■—) and 318.15 K (—▲—).

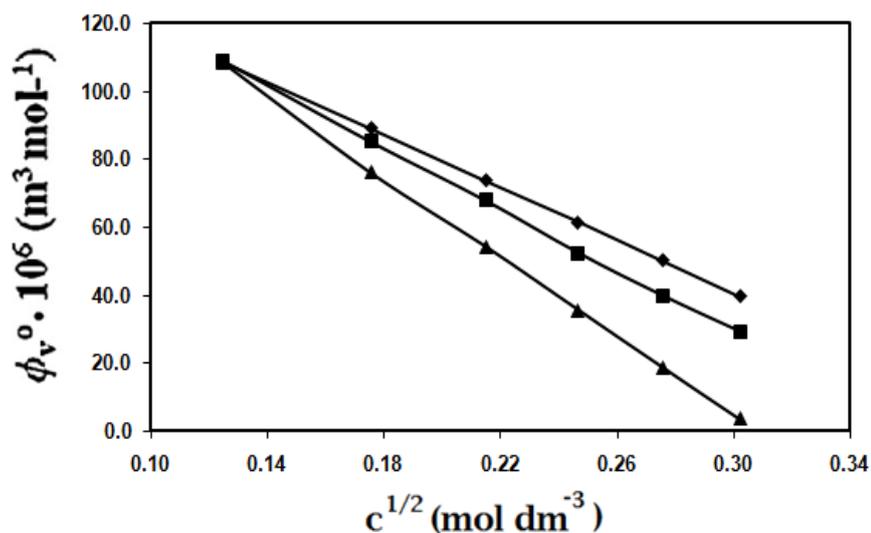


Figure 6: The apparent molar volume (ϕ_v) and the square root of concentrations (\sqrt{c}) for potassium bromide in different aqueous mixtures 0.05 M Nicotinic acid at 298.15 K (—◆—), 308.15 K (—■—) and 318.15 K (—▲—).

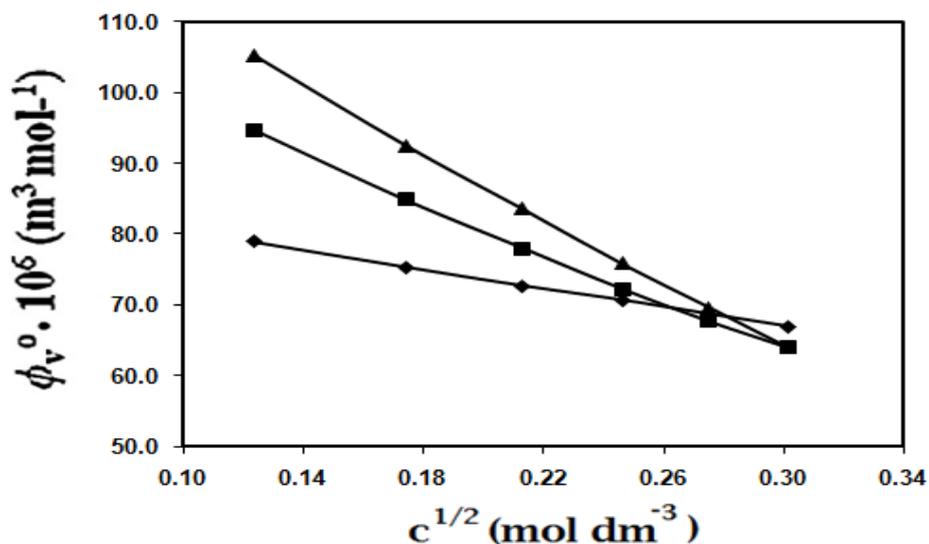


Figure 7: The apparent molar volume (ϕ_v) and the square root of concentrations (\sqrt{c}) for potassium iodide in different aqueous mixtures 0.01 M Nicotinic acid at 298.15 K (—◆—), 308.15 K (—■—) and 318.15 K (—▲—).

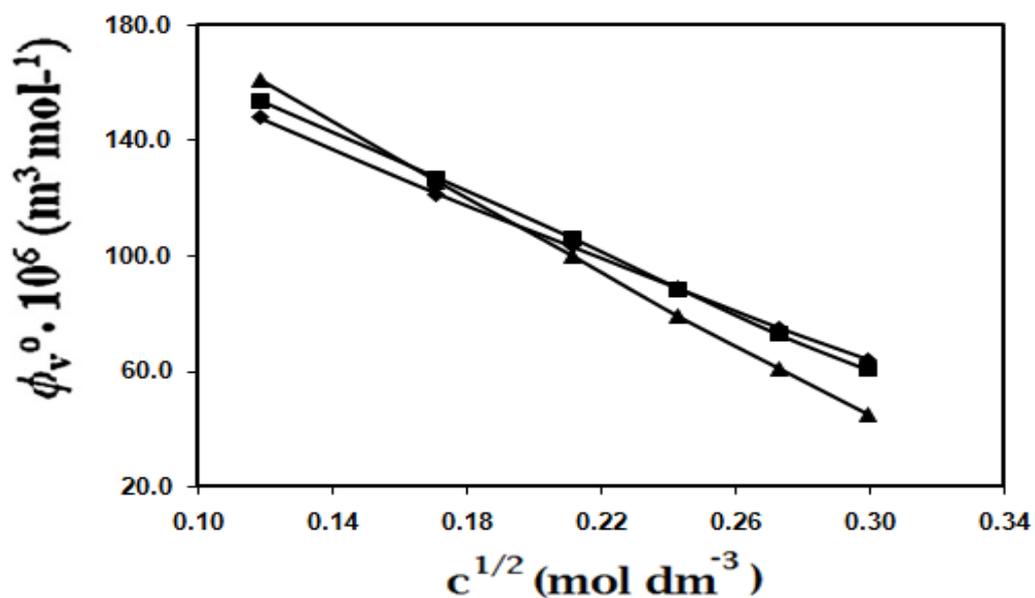


Figure 8: The apparent molar volume (ϕ_v) and the square root of concentrations (\sqrt{c}) for potassium iodide in different aqueous mixtures 0.03 M Nicotinic acid at 298.15 K (—◆—), 308.15 K (—■—) and 318.15 K (—▲—).

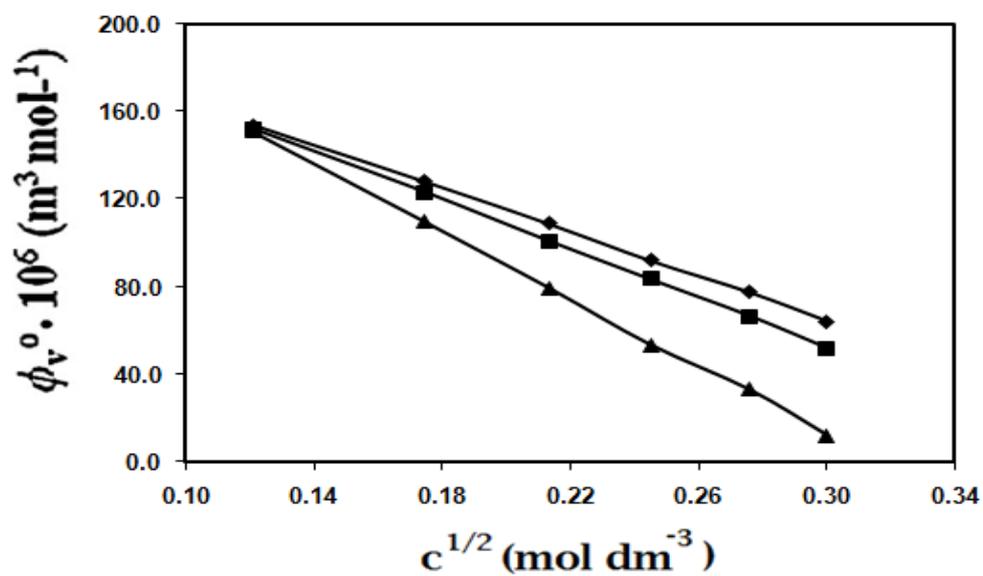


Figure 9: The apparent molar volume (ϕ_v) and the square root of concentrations (\sqrt{c}) for potassium iodide in different aqueous mixtures 0.05 M Nicotinic acid at 298.15 K (—◆—), 308.15 K (—■—) and 318.15 K (—▲—).

CHAPTER -IX

STUDY ON INTERACTIONS OF SOME METAL PERCHLORATES PREVAILING IN FORMAMIDE BY PHYSICO-CHEMICAL APPROACH

9.1. Introduction

Physicochemical study on the transport properties of electrolytes has been utilized to investigate the solvation and association behavior of ions in different solvent media. Electrolytic concentration and viscosity of the solvent plays a vital part in deciding the electrical conductivity in solvents.

Perchlorates are the high melting point inorganic salts easily soluble in water and protic solvents. One of the most promising potential applications of lithium perchlorate is in the manufacture of chemical sources of energy (i.e. fuel cells) for electric cars [1]. Sodium perchlorate can be used to block iodine uptake for the patients with subclinical hyperthyroidism [2].

Study of Conductance has been employed to measure association and behavior of ions in solution. Techniques such as volumetric, viscometric and interferometric studies help to investigate the molecular interactions in solution and to inspect the activities of the salt with different solvent concentrations. Study of apparent and limiting apparent molar volumes of the electrolyte along with the dependence of viscosity on the concentration of salt have been demonstrated as a function of ion-ion and ion-solvent interactions [3]. In conjunction with our investigation on electrical conductance of electrolytes [4-6] the present work deals with the transport and thermodynamic properties of Lithium Perchlorate, Sodium Perchlorate and Potassium Perchlorate in Formamide at 298.15 K.

9.2. Experimental Methods

9.2.1. Source and Purity of the Sample

LiClO_4 , NaClO_4 and KClO_4 of puriss grade were obtained from Aldrich, Germany and used as purchased. Formamide of spectroscopy grade was procured from Sd. fine Chemicals. Standard methods [7] were applied for the purification of the solvent.

9.2.2 Apparatus and Procedure

A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution at 298.15K. The conversion of molarity to molality was done using density values. The uncertainty of molarity of different solutions is found to be $\pm 0.0001 \text{ mol dm}^{-3}$. The density (ρ) was measured by a vibrating-tube Anton Paar density-meter (DMA 4500M) with a precision of 0.0005 g/cm^3 . The calibration was done by double-distilled water and dry air and uncertainty in density was $\pm 0.00005 \text{ g cm}^{-3}$.

Solvent viscosities were measured by means of a suspended Ubbelohde-type viscometer being calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature [8-10]. A perfectly dried and thoroughly cleaned viscometer filled with experimental solution was placed vertically in the glass-walled thermostat (Bose Panda Instruments Pvt. Ltd.) maintained to $\pm 0.01 \text{ K}$. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to $\pm 0.1 \text{ s}$. At least three repetitions of each data reproducible to $\pm 0.1 \text{ s}$ were taken to average the flow times. Viscosity of the solution, η can be determined using the following equation:

$$\eta = (Kt - L/t)\rho \quad (1)$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid respectively. The uncertainty in viscosity measurements is within $\pm 0.003 \text{ mPas}$.

Conductance measurements were performed in a Systronic-308 conductivity bridge (accuracy $\pm 0.01 \%$) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 0.001). A water bath maintained within $T = (298.15 \pm 0.01) \text{ K}$ was used and the cell was calibrated by the method proposed by Lind et al [11]. The conductance data were reported at a frequency of 1 kHz and were uncertain to $\pm 0.3 \%$.

Speeds of sound were recorded by multifrequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 1 MHz with a precision of 0.2 m.s⁻¹. Its calibration was carried out with three solvents namely water, methanol, and benzene at 298.15 K. The full details of the methods and techniques have been revealed earlier [12-14]. The uncertainty of ultrasonic speed measurements was ± 0.2 m.s⁻¹. The uncertainty for the working temperature was ± 0.02 K.

9.3. Result and Discussion

The experimental values of physical properties of the pure solvent were in good agreement with those found in the literature, as in Table 1. The values of equivalent conductances (Λ) at various concentrations are exhibited in Table 2 and the conductance data for LiClO₄, NaClO₄ and KClO₄ in Formamide have been examined with the help of the Fuoss conductance equation [15,16]. The limiting molar conductance (Λ_0), the association constant (K_A) and the distance of closest approach of ions (R) are derived for a given set of conductivity values ($c_j, \Lambda_j, j=1, \dots, n$) from the following set of equations.

$$\Lambda = P\Lambda_0[(1+R_X) + E_L] \quad (2)$$

$$P = 1 - \alpha(1 - \gamma) \quad (3)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (4)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (5)$$

$$\beta = e^2 / (\epsilon k_B T) \quad (6)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (7)$$

where the relaxation field effect is denoted by R_X , E_L corresponds to the electrophoretic counter current, k^{-1} denotes the radius of the ion atmosphere, e is the electron charge, ϵ is the relative permittivity of the solvent mixture, k_B is the Boltzmann constant, c is the molarity of the solution, K_A is the overall pairing constant, K_R is the association constant of the solvent-separated pairs, K_S is the association constant of the contact-pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, β is twice the Bjerrum distance, f is the activity coefficient and T is the absolute temperature. The computations were performed by dint of using a

program suggested by Fuoss. Shedlovsky extrapolation [17] of the data were used to obtain the initial Λ_0 values for the iteration procedure. Input for the program is the set $(c_j, \Lambda_j, j=1, \dots, n), n, \varepsilon, \eta, T$, initial values of Λ_0 , and an instruction to cover a pre-selected range of R values.

For the minimization of standard deviation all the calculations are performed by finding the values of Λ_0 and α .

$$\delta^2 = \sum [A_j(cal) - A_j(obs)]^2 / (n-2) \quad (8)$$

For a sequence of R values and then plotting δ against R , the minimum of the δ versus R curve represents the best-fit R . Hence, approximate runs are carried out over a fairly wide range of R values using 0.1 increments for the location of the minimum, but no significant minima were found in the δ - R curves for LiClO_4 , NaClO_4 and KClO_4 , in Formamide; R values are assumed to be $R = (a + d)$, where the sum of the crystallographic radii of the ions is represented by a and the average distance corresponding to the side of a cell occupied by a solvent molecule is designated by d . This 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_0 , K_A , and R attained by this procedure are reported in Table 3.

Inspection of Table 3 reveals that the limiting molar conductance Λ_0 is found to have an increasing order whilst moving from LiClO_4 , NaClO_4 followed by KClO_4 . It also implies that the association in Formamide is highest for LiClO_4 and lowest for KClO_4 and intermediate in the case of NaClO_4 . Hence the ion-solvent interaction in Formamide is maximum in the case of LiClO_4 and minimum for KClO_4 . The ion-solvent interaction of NaClO_4 exists between LiClO_4 and KClO_4 . This indicates that lowering of conductance of KClO_4 is found to be highest and least for LiClO_4 . The lowest viscosity of Formamide for KClO_4 also supports the above observation because with lowering of viscosity the Λ_0 value should increase [18].

The above trend in Λ_0 values can be verified through a characteristic function called the Walden product, $\Lambda_0 \eta$ given in Table 4. Even though the

viscosity of Formamide for LiClO_4 is more than that of NaClO_4 and KClO_4 , the $\Lambda_0 \eta$ is found to attain an increasing order from LiClO_4 to KClO_4 which points out the predominance of Λ_0 over η .

ΔG° is given by the following relationship [19] and is given in Table 4.

$$\Delta G^\circ = -RT \ln K_A \quad (10)$$

The explanation of negative values of ΔG° can be given considering the participation of specific covalent interaction in the ion-association process. The decrease in the value of ΔG° in formamide for LiClO_4 than KClO_4 indicates the highest degree of association in LiClO_4 . High K_A values indicate strong ion-association in the media. The ion-association process is exothermic. As a result Gibbs Free Energy change is negative and the ion-association becomes favourable.

The experimental value of densities of LiClO_4 , NaClO_4 and KClO_4 in Formamide, as a function of concentration at 298.15K is listed in Table 5. Limiting apparent molar volume is essential to study the interactions of LiClO_4 , NaClO_4 and KClO_4 in the pure solvent. The apparent molar volumes ϕ_V given in Table 5 were obtained from the solution densities using the following equation

$$\phi_V = M / \rho - (\rho - \rho_o) / c \rho \rho_o \quad (11)$$

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 pure solvent, respectively. The limiting apparent molar volumes ϕ_V^0 were evaluated in accordance with a least-squares treatment to the plots of ϕ_V versus \sqrt{c} using the following Masson equation [20]

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{c} \quad (12)$$

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 the square root of the molar concentration \sqrt{c} were found to be linear with negative slopes which are shown in Figure 1.

The values of ϕ_V^0 and S_V^* along with the standard errors are reported in Table 5. The extent of ion-solvent interaction can be examined by taking the ϕ_V^0 values. A perusal of Table 5 indicates that the ϕ_V^0 values are positive and is highest in case of LiClO₄ in Formamide. This indicates that maximum ion-solvent interaction in Formamide is found in the case of LiClO₄ and the same is minimum for KClO₄. The said interaction of NaClO₄ becomes in between LiClO₄ and KClO₄. These effects are further represented in the scheme 1 where I₁, I₂ and I₃ are the extent of ion-solvent interaction of KClO₄, NaClO₄ and LiClO₄ in Formamide respectively shown in **Scheme 1**. Li⁺ ion with highest charge density and smallest in size compared to Na⁺ and K⁺ favours the accessibility towards formamide rendering the highest ion solvent interaction exhibited by the following scheme. So the interaction of Formamide with Li⁺ ion is maximum for LiClO₄ and minimum in the case of K⁺ in KClO₄.

On the other hand, the S_V^* indicates the extent of ion-ion interaction. The S_V^* values are negative due to the disappearance of ion-ion attractive force at infinite dilution. The ion-ion interactions decrease with dilution which can be attributed to increase in distance between ions at infinite dilution. The values of S_V^* shows that the extent of ion-ion interaction in Formamide is maximum for KClO₄ and minimum for LiClO₄. From the comparison of the magnitude of ϕ_V^0 values with that of S_V^* , it is evident that ion-solvent interactions predominate over ion-ion interactions in all the solutions. Furthermore, the values of ϕ_V^0 lead to the fact that the lowest ion-solvent interaction of KClO₄ results in higher conductance than NaClO₄ whereas NaClO₄ exhibits higher conductance than LiClO₄ in Formamide. The viscosity data has been examined using Jones-Dole equation [21]

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B\sqrt{c} \quad (13)$$

where η and η_0 are the viscosities of the solution and solvent respectively. The values of A and B are acquired by a computerised least-square method

and recorded in Table 6. This can be achieved from the straight line by plotting $(\eta/\eta_0 - 1)/\sqrt{c}$ against \sqrt{c} as depicted in Figure 2.

A perusal of Table 6 reveals the negative values of A coefficient are generally negative for all of the solutions under investigation and point towards weak ion-ion interactions. The viscosity B coefficient [22] describes the effects of ion-solvent interactions. Positive values of the viscosity B coefficients for LiClO_4 , NaClO_4 and KClO_4 in Formamide reflects the presence of strong ion-solvent interactions. The viscosity B -coefficient value is found to be lowest for KClO_4 supporting the fact that the conductance is highest KClO_4 .

The adiabatic compressibility (β_s) was calculated from the following equation:

$$\beta_s = 1/u^2 \rho \quad (15)$$

where u is the speed of sound in the solution and ρ is the density of solution. The apparent molar adiabatic compressibility (ϕ_K) of the solutions was found out from the relation,

$$\phi_K = M \beta_s / \rho + (\beta_s \rho_o - \beta_o \rho) / c \rho \rho_o \quad (16)$$

where β_s, β_o are the adiabatic compressibilities of the solution and solvent respectively and c is the molarity of the solution. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) and experimental slopes (S_K^*) were achieved by fitting ϕ_K against the square root of molarity (\sqrt{c}) of the electrolyte employing the method of least squares.

$$\phi_K = \phi_K^0 + S_K^* \cdot \sqrt{c} \quad (17)$$

The values of β_s and ϕ_K are recorded in Table 7. Since the values of ϕ_K^0 and S_K^* are the measure of ion-solvent and ion-ion interactions respectively, a perusal of Table 7 and Figure 3 reveals that the values are in agreement with results drawn from the values of ϕ_V^0 and S_V^* discussed earlier.

9.4. Conclusion

Extensive investigation of LiClO_4 , NaClO_4 and KClO_4 in Formamide reveals that LiClO_4 is more associated in Formamide than the other two perchlorates and it remains as ion-pairs. The ion-association is found minimum in the case of KClO_4 in Formamide. The said interaction of NaClO_4 becomes in between LiClO_4 and KClO_4 . The volumetric, viscometric and interferometric studies reveal the predominance of ion-solvent interaction over the ion-ion interaction in all the studied solutions.

References

1. M. Jotanovic, Z. Andric, G. Tadic, V. Micic, *Peer-Reviewed and Open Access Journal*, **2010**, 3, 15.
2. C. Becker, *Radiologe*, **2007**,47(9), 768.
3. F.J. Millero, *Structure Transport Process in Water Aqueous Solutions*, R.A. Horne (Ed.), Wiley, New York **1972**.
4. M.N. Roy, B. Sinha, V.K. Dakua, A. Sinha, *Pak. J. Sci. Ind. Res.* **2006**, 49,153.
5. M.N. Roy, P. Pradhan, R.K. Das, P.G. Guha, *J. Chem. Eng. Data* **2008**, 53,1417.
6. R. Chanda, M.N. Roy, *Fluid Phase Equilib.* **2008**,269, 134.
7. H.K. Samanta, D. Engel, *J. Biochem. Biophys. Meth.***1987**, 14, 261.
8. B. Sinha, V.K. Dakua, M.N. Roy, *J. Chem. Eng. Data.***2007**, 52, 1768.
9. J.A. Dean, *Lange's Handbook of Chemistry*, 11th ed. McGraw-Hill Book Company, New York **1973**.
10. A. Chatterjee, B. Das, *J. Chem. Eng. Data.* **2006**, 51,1352.
11. J.E. Lind Jr., J.J. Zwolenik, R.M. Fuoss, *J. Am. Chem. Soc.* **1959**, 81, 1557.
12. M.N. Roy, A. Jha, R. Dey, *J. Chem. Eng. Data.***2001**, 46 , 1327.
13. M.N. Roy, D.K. Hazra, *Indian J. Chem. Technol.* **1994**, 1 ,93.
14. R.M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.* **1978**, 75 ,16.
15. R.M. Fuoss, *J. Phys. Chem.* **1978**, 82, 2427.
16. J. Barthel, M.B. Rogac , R. Neueder, *J. Solut. Chem.* **1999**, 28 , 1071.
17. R.M. Fuoss, T. Shedlovsky, *J. Am. Chem Soc.* **1949**, 71(4),1496.
18. M.N. Roy, R. Dewan, D. Ekka, I. Banik, *Thermochimica Acta.* **2013** , 559, 46.
19. R.M. Fuoss and C.A. Kraus, *J. Am. Chem. Soc.* **1933** , 55 , 2387.
20. F.J. Millero, A.L. Surdo, C. Shin, *Phys. Chem.* **1978** , 82 ,784.
21. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**,51, 2950.
22. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, **1970** .

23. A.M. Cases, ACG Marigliano, C.M. Bonatti, H.N. Solimo, *J.Chem. Eng. Data*. **2001**, *46*, 712.
24. D. Papamatthaiakis, F. Aroni, V. Havredaki, *J. Chem. Thermodyn.* **2008**, *40*, 107.

**Bibliographical Sketch*



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Table 1 Density (ρ), viscosity (η) and dielectric constant (ϵ) of pure Formamide at 298.15K.

Solute	$\rho \times 10^{-3} (\text{kg m}^{-3})$		$\eta (\text{mPa. s.})$		$u (\text{ms}^{-1})$		ϵ
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	
Formamide	1.12908	1.1291[23]	3.299	3.302[23]	1596.1	1597.8[24]	111.0

Table 2 The concentration (c) and molar conductance (Λ) of LiClO_4 , NaClO_4 and KClO_4 in Formamide at 298.15 K.

$c \times 10^4$ (mol.dm ⁻³)	$\Lambda \times 10^4$ (S. m ² . mol ⁻¹)	$c \times 10^4$ (mol.dm ⁻³)	$\Lambda \times 10^4$ (S. m ² . mol ⁻¹)	$c \times 10^4$ (mol.dm ⁻³)	$\Lambda \times 10^4$ (S. m ² . mol ⁻¹)
LiClO_4		NaClO_4		KClO_4	
1.3363	10.31	1.9825	12.38	5.0535	13.05
1.5725	10.16	2.7456	12.24	5.9000	12.85
1.9349	9.98	3.4040	12.01	6.8069	12.76
2.1815	9.88	3.9760	11.73	7.4966	12.56
2.4555	9.75	4.6010	11.53	7.9017	12.45
2.6830	9.64	5.0940	11.35	8.4042	12.38
2.9173	9.51	5.6882	11.23	8.8506	12.36
3.2005	9.37	6.5331	10.98	9.6783	12.14
3.4077	9.27	7.1770	10.86	10.3362	12.08
3.7288	9.10	7.7451	10.62	10.9362	12.01
3.9323	8.99	8.0770	10.64	11.8267	11.79
4.2230	8.85	8.4390	10.53	12.5670	11.73
4.5199	8.72	8.9820	10.31	13.3079	11.51
4.7263	8.63	9.6970	10.16	13.7789	11.44

Table 3 Limiting molar conductivity (Λ^0), association constant (K_A), co-sphere diameter (R) and standard deviations (δ) of experimental Λ of LiClO_4 , NaClO_4 and KClO_4 at 298.15 K.

Salts	Solvent	Λ^0 ($\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$)	K_A ($\text{dm}^3\cdot\text{mol}^{-1}$)	R (\AA)	δ
LiClO_4		11.529	921.322	7.6262	5.294
NaClO_4	Formamide	13.533	446.743	7.9561	6.168
KClO_4		14.567	248.296	8.3161	4.895

Table 4 Walden product ($\Lambda_0\eta_0$) and Gibb's energy change (ΔG°) of LiClO_4 , NaClO_4 and KClO_4 in Formamide at 298.15 K.

Solute	$\Lambda_0\eta_0$ ($\text{Sm}^2\text{mol}^{-1}$ mPas. s.)	$\Delta G^\circ \times 10^{-4}$ (J mol^{-1})
LiClO_4	38.034	-1.6939
NaClO_4	44.645	-1.5125
KClO_4	48.056	-1.3669

Table 5 Experimental values of densities (ρ), apparent molar volume(ϕ_v), limiting apparent molar volume (ϕ_v^0) and experimental slope (S_v^*) of LiClO₄, NaClO₄ and KClO₄ in Formamide at 298.15 K.

c (mol.dm ⁻³)	$\rho \times 10^{-3}$ (kg m ⁻³)	$\phi_v \times 10^6$ (m ³ . mol ⁻¹)	$\phi_v^0 \times 10^6$ (m ³ . mol ⁻¹)	$S_v^* \times 10^6$ (m ³ mol ^{-3/2} kg ^{1/2})
LiClO ₄ in Formamide				
0.0133	1.12940	75.33272		
0.0265	1.12981	72.67569		
0.0398	1.13029	70.41229	82.3	-59.68
0.0532	1.13082	68.54253		
0.0665	1.13140	66.83022		
0.0799	1.13201	65.39346		
NaClO ₄ in Formamide				
0.0132	1.12968	72.7480		
0.0263	1.13037	69.8869		
0.0397	1.13114	67.6158	79.42	-58.74
0.0529	1.13194	65.8661		
0.0663	1.1328	64.2178		
0.0798	1.13368	62.9683		
KClO ₄ in Formamide				
0.0134	1.13000	68.7985		
0.0266	1.13099	66.2733		
0.0399	1.13205	64.1524	75.39	-56.46
0.0533	1.13317	62.2918		
0.0665	1.13430	60.8549		
0.0801	1.13551	59.4029		

Table 6 Experimental values of concentration (c), viscosity (η), $(\eta/\eta_0-1)/c^{1/2}$, viscosity A,B- coefficients of LiClO₄, NaClO₄ and KClO₄ in Formamide at 298.15 K

c (mol dm ⁻³)	η (mPa s)	$(\eta/\eta_0-1)/c^{1/2}$ (kg ^{1/2} mol ^{-1/2})	A (kg. mol ⁻¹)	B (kg ^{1/2} mol ^{-1/2})
LiClO ₄ in Formamide				
0.0133	3.315	0.042	0.003	0.331
0.0265	3.330	0.058		
0.0398	3.345	0.070		
0.0532	3.360	0.080		
0.0665	3.375	0.089		
0.0799	3.390	0.098		
NaClO ₄ in Formamide				
0.0132	3.309	0.026	0.005	0.182
0.0263	3.318	0.036		
0.0397	3.327	0.043		
0.0529	3.335	0.047		
0.0663	3.344	0.053		
0.0798	3.352	0.057		
KClO ₄ in Formamide				
0.0134	3.306	0.018	0.010	0.067
0.0266	3.311	0.022		
0.0399	3.315	0.024		
0.0533	3.319	0.026		
0.0665	3.323	0.028		
0.0801	3.327	0.030		

Table 7 Experimental values of speed of sound (u), adiabatic compressibility (β_s) and apparent molar adiabatic compressibility (ϕ_K), limiting apparent molar adiabatic compressibility (ϕ_K^0), and experimental slopes (S_K^*) of LiClO_4 , NaClO_4 and KClO_4 in Formamide at 298.15 K.

c (mol dm^{-3})	u (m s^{-1})	$\beta_s \times 10^{10}$ (Pa^{-1})	$\phi_K \times 10^{10}$ ($\text{m}^3 \text{ mol}^{-1}$ Pa^{-1})	$\phi_K^0 \times 10^{10}$ ($\text{m}^3 \text{ mol}^{-1}$ Pa^{-1})	$S_K^* \times 10^{10}$ ($\text{m}^3 \text{ mol}^{-3/2}$ $\text{Pa}^{-1} \text{ kg}^{1/2}$)
LiClO ₄ in Formamide					
0.0133	1596.1	3.4766	-0.174		
0.0265	1600.2	3.4578	-1.751		
0.0398	1612.4	3.4045	-2.926		
0.0532	1631.9	3.3222	-3.869	3.372	-31.26
0.0665	1657.5	3.2188	-4.642		
0.0799	1688.5	3.1001	-5.449		
NaClO ₄ in Formamide					
0.0132	1601.3	3.4764	-0.561		
0.0263	1613.3	3.4522	-1.963		
0.0397	1632.4	3.3989	-3.048		
0.0529	1657.2	3.3176	-3.932	2.665	-28.46
0.0663	1687.1	3.2168	-4.648		
0.0798	1724.1	3.1014	-5.328		
KClO ₄ in Formamide					
0.0134	1601.4	3.4508	-2.567		
0.0266	1609.2	3.4145	-9.320		
0.0399	1620.4	3.3643	-14.833		
0.0533	1634.9	3.3016	-19.531	1.148	-15.74
0.0665	1651.9	3.2308	-23.329		
0.0801	1672.1	3.1498	-26.924		

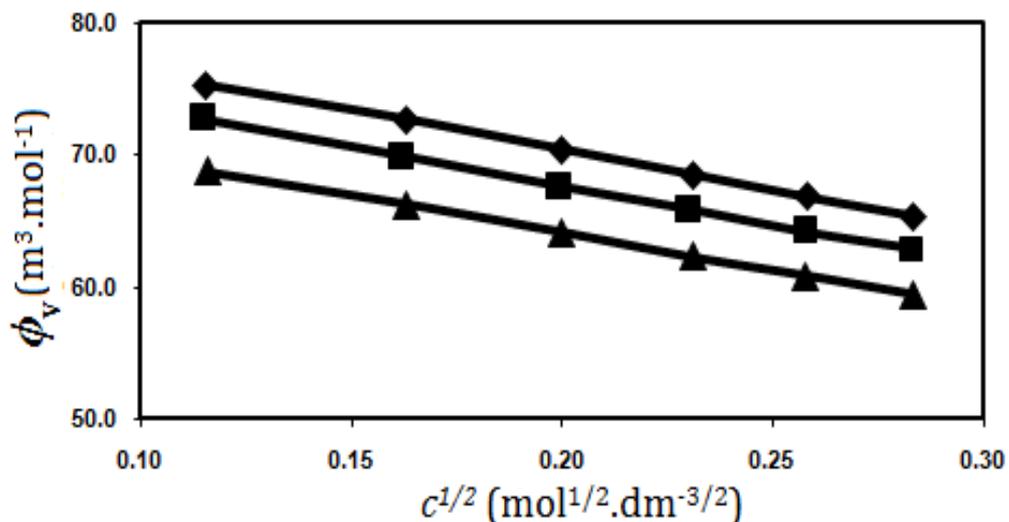


Figure 1: Apparent molar volume (ϕ_v), and the square root of concentrations (\sqrt{c}) for LiClO₄ (—◆—), NaClO₄ (—■—) and KClO₄ (—▲—) in formamide at 298.15 K.

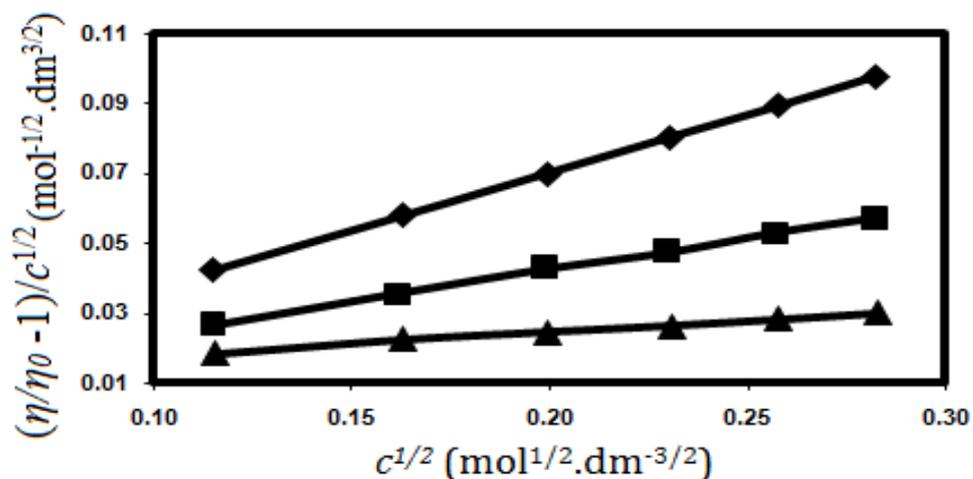


Figure 2: Plots of $(\eta/\eta_0 - 1)/\sqrt{c}$ versus \sqrt{c} for LiClO₄ (—◆—), NaClO₄ (—■—) and KClO₄ (—▲—) in formamide at 298.15 K.

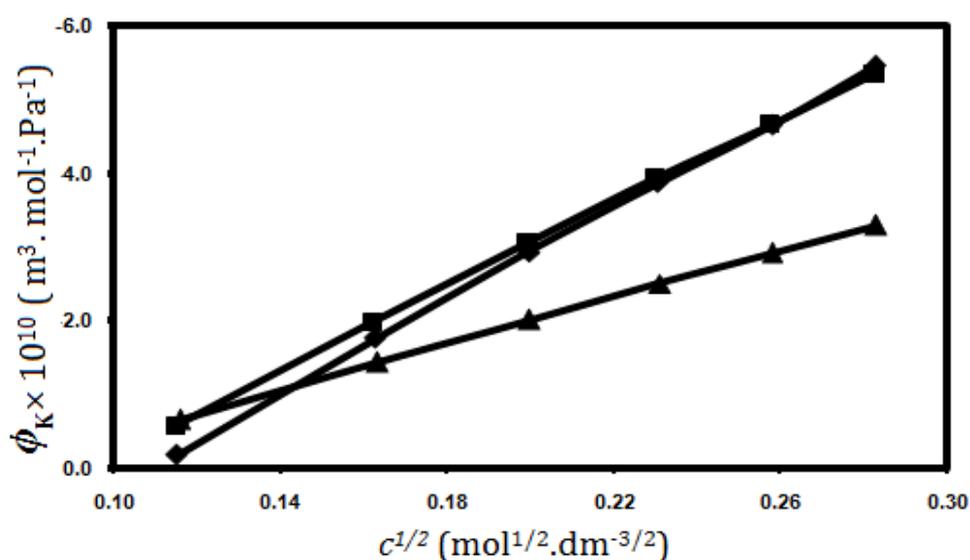
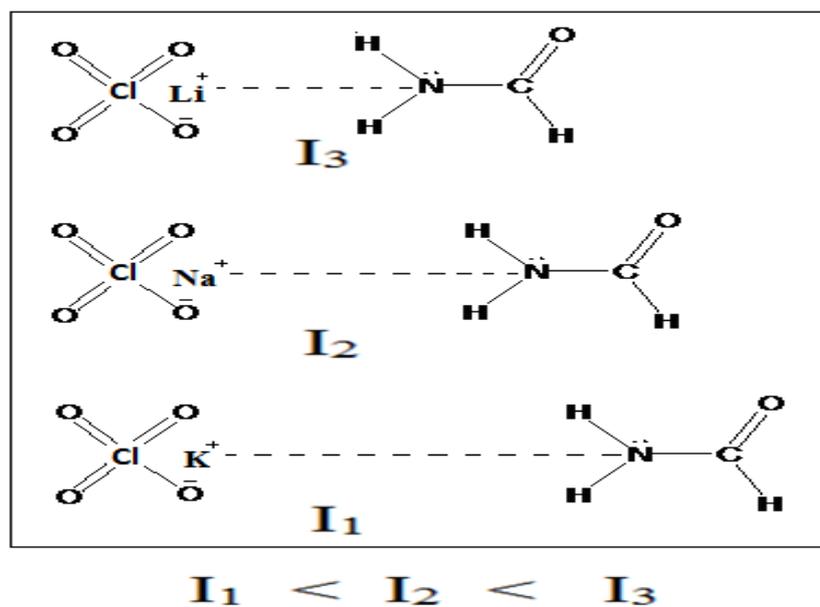


Figure 3: Apparent molar adiabatic compressibilities (ϕ_K) and the square root of concentrations (\sqrt{c}) for LiClO₄ (—◆—), NaClO₄ (—■—) and KClO₄ (—▲—) in formamide at 298.15 K.



Scheme 1. Interaction of LiClO₄, NaClO₄ and KClO₄ with Formamide .

CHAPTER -X

CONCLUDING REMARKS

In this thesis, I have studied the interactions of some biomolecules and simple molecules by physicochemical processes in liquid media. A detailed investigation has been done on different interactions, such as solute-solute, solute-solvent and solvent-solvent interactions in various solvent systems. Molecular interactions have been explored by dint of thermodynamic and transport properties of solutions. Systematic study made on the properties has an immense importance in gaining a better knowledge of these interactions. 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.

In **Chapter-IV**, after a systematic study of the density, viscosity, refractive index and ultrasonic speed of α -amino acids in aqueous Bu_4PBF_4 solution at 298.15 K, we have obtained a comprehensible idea about 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 Bu_4PBF_4 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.

Chapter V deals with the study on solution behaviour of alkali metal perchlorates (LiClO_4 , NaClO_4 and KClO_4) prevailing in N, N- dimethyl formamide with the manifestation of ion solvation consequence. Extensive investigation of LiClO_4 , NaClO_4 and KClO_4 in N,N-Dimethyl Formamide reveals that LiClO_4 is more associated in Formamide than the other two perchlorates and it remains as ion-pairs. The ion-association is found minimum in the case of KClO_4 in N,N-Dimethyl Formamide. The said interaction of NaClO_4 arises in

the intermediacy of LiClO_4 and KClO_4 . The volumetric, viscometric and interferometric studies reveal the predominance of ion-solvent interaction over the ion-ion interaction in all the studied solutions.

In **Chapter VI** discussion on the physico-chemical study of some bioactive solutes in aqueous potassium acetate solution have been made. The values of the limiting apparent molar volume (ϕ_V^0), viscosity B -coefficients and limiting partial isentropic compressibility (ϕ_K^0) are indicative of 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 Potassium Acetate 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.

The study in **Chapter-VII** demonstrates probing solute-solvent interactions of some bioactive solutes in aqueous barium nitrate solution on the basis of physicochemical contrivances. 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 amino acids and also with the increase of mass fraction of Barium Nitrate in the aqueous mixture. The refractive index and the molar refraction values indicate that molecules of L-Valine are more tightly packed in the solution resulting higher solute-solvent interaction than the other two amino acids.

The study in **Chapter-VIII** demonstrates that potassium iodide is more associated in Nicotinic acid than the other two halides. The ion-association is found minimum in the case of potassium chloride in Nicotinic acid. The said interaction of potassium bromide arises in the intermediacy of potassium iodide and potassium chloride. The present study reveals the

predominance of ion-solvent interaction over the ion-ion interaction in all the solution under investigation.

The study in **Chapter-IX** is associated with the study on interactions of some metal perchlorates prevailing in formamide by physicochemical approach. Extensive investigation of LiClO_4 , NaClO_4 and KClO_4 in Formamide reveals that LiClO_4 is more associated in Formamide than the other two perchlorates and it remains as ion-pairs. The ion-association is found minimum in the case of KClO_4 in Formamide. The said interaction of NaClO_4 becomes in between LiClO_4 and KClO_4 . The volumetric, viscometric and interferometric studies reveal the predominance of ion-solvent interaction over the ion-ion interaction in all the studied solutions.

Extensive investigations of the different transport and thermodynamic properties of the electrolytes will facilitate in understanding the scenery of the ion-solvent interactions and the role of solvents in various physicochemical processes.

Different phenomena associated with solution chemistry may be well understood by virtue of proper understanding of the ion-ion and ion-solvent interactions in the solution. However, it is compulsory to remember that molecular interactions are very complex in nature. There are strong forces existing in the molecule and it is not really feasible to separate them all. Nevertheless, if careful judgement is used, convincing conclusions can be strained in many cases involving the order of the system and degree of structure.

In my dissertation, an extreme importance has been given to Amino acids, the monomeric unit of the Polypeptide (protein) belonging to the class of Biomolecules, because of their key role in biochemistry, nutrition supplements, fertilizers, food technology, biodegradable plastic and drugs industry. I have also dealt with the 'Room Temperature Ionic liquids' being the current interest in all branches of chemistry because of their potential uses as 'designer solvents' and 'green' replacements for volatile organic

solvents in the reactions involving inorganic and bio-catalysis. They are also utilized as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells).

From my experimental observations, it is obvious that vital informations regarding various types of interactions i.e. ion-solvent interactions have been obtained successfully in different liquid media .These results are very important and useful in various industries such as modern battery, medicine as well as different types pharmaceutical, cosmetics products.

BIBLIOGRAPHY

Chapter I:

1. J.V. Herraez, R. Belda, *J. Solution Chem.* **2004**, *33*, 117.
2. C.K. Zeberg-Mikkelsen, S.E. Quinones-Cisneros, S.H. Stenby, *Fluid Phase Equil.* **2002**, *194*, 1191.
3. R. Shukla, M. Cheryan, *Journal of Membrane Science.* **2002**, *198*, 104.
4. M.J. Assael, N.K. Dalaouti, I. Metaxa, *Fluid Phase Equil.* **2002**, *199*, 237.
5. J.M. Resa, C. Gonzalez, J. Lanz, *Journal of Food Engineering* **2002**, *51*, 113.
6. M. Garcia-Velarde, *Revista Espanola de Fisica* **1995**, *9*, 12.
7. S.T. Young, *Phil. Mag.* **1882**, *33*, 153.
8. C. Fauli-Trillo, *Tratado de Farmacia Galencia*, Ed. S.A. Lujan, Madrid, **1993**.
9. J. Swarbrik, J.C. Boyland, *Encyclopedia of Pharmaceutical Technology*, Marcel Dekker, New York, **1993**.
10. E.R. Morris, *Food Gels - Applied Science*, Elsevier, London, **1984**.
11. J. Pellicer, *Sinergia Viscosa*, Valencia, Spain, October **1997**.
12. G. Copetti, R. Lapasin, E.R. Morris, *Proceedings of the 4th European Rheology Conference*, Seville, Spain, **1994**, 215.
13. O. Popovych, *Crit. Rev. Anal. Che.* **1973**, *1*, 73.
14. R.G. Bates, *Solute-Solvent Interactions*, Eds. J.J. Coetzee, C.D. Ritchie, Marcel Dekker, New York, **1969**.
15. D.K. Meck, *The Chemistry of Non-Aqueous Solvents*, Ed. J.J. Lagowski, Academic, New York, Vol-1, **1966**, Ch. 1.
16. F. Franks, *Physico-Chemical Processes in Mixed Aqueous Solvents*, Heinemann Educational Books Ltd., **1967**.
17. A.J. Parker, *Electrochim. Acta* **1976**, *21*, 671.
18. C.M. Criss, M. Salomon, *J. Chem. Edu.* **1976**, *53*, 763.
19. Y. Marcus, *Ion Solvation*, Wiley, Chinchester, **1986**.
20. R.R. Dogonadze, E. Kalman, A.A. Kornyshev, J. Ulstrup, *The Chemical Physics of Solvation*, Elsevier, Amsterdam, **1988**.
21. O. Popovych, R.P.T. Tomkins, *Non-Aqueous Solution Chemistry*, John Wiley and Sons, New York, **1981**.
22. E.J. King, *Acid-Base Equilibria*, Pergamon, Oxford, **1965**.
23. G.S. Kell, C.M. Daries, J. Jarynski, *Water and Aqueous Solutions, Structure, Thermodynamics and Transport Process*, Ed. R.A. Horne, Wiley, **1972**, Ch. 9 & 10.
24. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, **1973**.
25. A. Chandra, B. Bagchi, *J. Phys. Chem. B.* **2000**, *104*, 9067.

26. G. Atkinson, R. Garney, M.J. Taft, *Hydrogen Bonded Solvent Systems*, Eds. A.K. Covington, P. Jones, Taylor and Francis, London, **1968**.
27. W.E. Waghorne, *Chem. Soc. Rev.* **1993**, 22, 285.
28. Y. Marcus, *Ion Properties*, Dekker, New York, **1997**.
29. A. Masquez, A Vargas, P.B. Balbuena, *J. Electron. Soc.* **1998**, 45, 3328.
30. A.F.D. Namor, M.A.L. Tanco, M. Solomon, *J. Phys. Chem.* **1994**, 98, 11796.
31. K. Gunaseelau, S. Dev, K. Ismail, *Indian. J. Chem.* **2000**, 39A, 761.
32. M. Iqbal, R.E. Verral, *Can. J. Chem.* **1989**, 67, 727.
33. E.P. Georgios, I.Z. Ioannis, *J. Chem. Eng. Data* **1992**, 37, 167.
34. J.N. Nayak, M.I. Aralaguppi, T.J. Aminabhavi, *J. Chem. Eng. Data* **2003**, 48, 1489.
35. K. Hsu-Chen, T. Chein-Hsiun, *J. Chem. Eng. Data* **2005**, 50, 608.
36. A. Ali, A.K. Nain, *J. Pure. Appl. Ultrasonics.* **2000**, 22, 10.
37. J.H. Dymond, *Chem. Soc. Rev.* **1985**, 14, 317.
38. E.L. Herric, J.G. Brewer, *J. Chem. Eng. Data* **1969**, 14, 55.
39. P.K. Gessner, M.P. Shakarjian, *J. Pharm. Exptal. Therap.* **1985**, 32, 235.
40. H. Ohtaki and T. Radnai, *Chem.Rev.* **1993**, 93, 1157.
41. W.M. Cox and J.H. Wolfenden, *Proc. Roy, Soc., London* **1934**, 145A, 475.

Chapter II:

1. A. Grossfield, P. Ren, J. W. Ponder, *J. Am. Chem. Soc.* **2001**, 125, 15671.
2. (a) J. D. Pandey, A. Yasmin, *Proc. Ind. Acad. Sci.* **1997**, 109, 289.
(b) J. D. Pandey, Y. Akhtar , A. K. Sharma, *Ind. J. Chem* **1998**, 37A, 1094 .
3. J. I. Kim, *J. Phys. Chem.* **1978**, 82, 191.
4. B.E. Conway, R.G. Barradas, *Chemical Physics of Ionic Solutions*, Wiley, New York, **1966**.
5. J. J. Lagowski, *The Chemistry of Non-Aqueous Solvents*, Academic, New York, **1966**.
6. K. Ibuki, M. Nakahara, *J. Phys. Chem.* **1990**, 94, 8370.
7. D.T. Richens, *The Chemistry of Aqua Ions*, Wiley, New York , **1997**.
8. A. Henni, J.H. Jonathan, T. Paitoon, C. Amit, *J. Chem. Eng. Data* **2003**, 48, 1062.
9. J. Burgess, *Metal Ions in Solutions*; Ellis Horwood, New York, **1978**.
10. R.G. Bates, *J. Electroanal. Chem.* **1972**, 29, 1.
11. G.S. Kell, C.M. Daries, J. Jarynski, *Water and Aqueous Solutions, Structure, Thermodynamics and Transport process*, Wiley, New York , **1972**.
12. E.S. Amis, J.F. Hinton, *Solvent effects on Chemical Phenomena*, Academic, New York, **1973**.
13. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York, **1958**.
14. J. J. Lagowski, *The Chemistry of Non-Aqueous Solvents*, Academic, New York , **1966**.

15. B.E. Conway, R.G. Barradas, *Chemical Physics of Ionic Solutions*, Wiley, New York, **1966**.
16. J.S. Muishead-Gould, K.J. Laidler, *Chemical Physics of Ionic Solutions*, Wiley, New York, **1966**.
17. J.F. Coetzee, C.D. Ritchie, *Solute-Solvent Interactions*, Marcel Dekker, New York, **1969**.
18. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York, **1973**.
19. F. Franks, *Physico-Chemical processes in Mixed Aqueous Solvents*, Heinemann, London, **1967**.
20. F. Franks, *Water—A Comprehensive Treatise*, Plenum Press, New York, **1973**.
21. V. Gutmann, *Electrochim. Acta.* **1967**, 21,661.
22. U. Mayer, V. Gutmann, *Adv. Inorg.Chem. Radiochem.* 1975, 17, 189.
23. J.E. Gordon, *The Organic Chemistry of Electrolyte Solutions*, Wiley- Interscience, New York, **1975**.
24. R.G. Pearson, *Hard and Soft Acids and Bases*, Strondsburgh, **1973**.
25. G.R. Behbehani, M. Dillon, J. Symth, W.E. Waghorne, *J. Solution Chem.* **2002**, 31, 811.
26. C. Guha, J.M. Chakraborty, S. Karanjai, B. Das, *J. Phys. Chem. B* **2003**, 107, 12814.
27. L. Jones, J.F. Devonshire, *A. F. Proc. Royal Soc.* **1937**.
28. I. Prigogine, A. Belleman, *J. Phys. Chem.* **1953**, 21, 561.
29. I. Prigogine, S. Garikian, *Physica* **1950**, 16, 239.
30. A.J. Treszczanowicz, G.C. Benson, *Fluid Phase Equilib.* **1985**, 23 ,117.
31. Wen-Lu Weng, *J. Chem. Eng. Data* **2002**, 45, 606.
32. P.S. Nikam, S.J. Kharat, *J. Chem. Eng. Data* **2005**, 50, 455.
33. R.P. Rastogi, J. Nath, J. Mishra, *J. Phys. Chem.* **1966**, 71 ,1277.
34. K.S. Pitzer, G. Mayora, *J. Phys. Chem.* **1973** 77, 2300.
35. D. Cook, L-Higgins, *H. C. Proc. Royal. Soc.* **1951**, A209, 28.
36. J.S. Rowlinson, *Liquid and Liquid Mixtures*, Scientific Publications, London **1959**.
37. J.S. Rowlinson, *Proc. Royal. Soc.* **1952**, A214, 192.
38. J.L. Lebowitz, J. S. Rowlinson, *J. Chem. Phys.* **1964**, 41,133.
39. P.J. Flory, R.A. Orwoll, A. Vrij, *J. Am. Chem. Soc.* **1964**, 86 , 3507.
40. P.J. Flory, A. Abe, *J. Am. Chem. Soc.* **1964**, 86, 3563.
41. P.J. Flory, *J. Am. Chem. Soc.* **1965**, 87, 1833.
42. J.A. Barker, D.J. Henderson, *J. Phys. Chem.* **1967**, 47, 4714.
43. D. Patterson, G. Delmas, *Discuss. Faraday Soc.* **1970**, 49, 98.
44. A. Heintz, *Ber. Bunsenges. J. Phys.* **1985**, 89, 172.
45. H. Funke, M. Wetzell, A. Heintz, *J. Pure. Appl. Chem.* **1989**, 61,1429.
46. A. Heintz, D. Papaioannou, *Thermochimica Acta.* **1998**, 310, 69.
47. A. Heintz, P.K. Naicker, S.P. Verevkin, R. Pfestrof, B. Bunsenges, *Phys. Chem.* **1998**, 102 ,953.

48. S. Villa, N. Riesco, I. Garcia de la Fuente, J.A. Gonzalz, J.C. Cobos, *Fluid Phase Equilib.* **2004**, *216*, 123.
49. S.L. Oswal, *J. Thermochim. Acta.* **2005**, *425*, 59.
50. A. Pineiro, A. Amigo, R. Bravo, P. Brocos, *Fluid Phase Equilib.* **2000**, *173*, 211.
51. A. Pineiro, *Fluid Phase Equilib.* **2004**, *216*, 245.
52. M. Gepert, B. Stachowska, *J. Sol. Chem.* **2006**, *35*, 425.
53. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolyte Solutions*, Reinhold Publishing Corporation, New York, **1943**.
54. C. Tanford, *Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Wiley-Interscience, New York, **1980**.
55. E. Vikingstad, *Aggregation Process in Solutions*, Elsevier, Amsterdam, **1983**.
56. J.E. Desnoyers, M. Arel, H. Perron, C. Jolicoenn, *J. Phys. Chem.* **1969**, *73*, 3347.
57. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York, **1973**.
58. D.K. Hazra, B. Das, *J. Chem. Eng. Data* **1991**, *36*, 403.
59. D.O. Masson, *Phil. Mag.* **1929**, *8*, 218.
60. O. Redlich, D.M. Meyer, *Chem. Rev.* **1964**, *64*, 221.
61. B.B. Owen, S.R. Brinkley, *J. Ann. N. Y. Acad. Sci.* **1949**, *51*, 753.
62. F.J. Millero, *Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes*, Wiley- Interscience, New York, **1972**.
63. R. Gopal, M.A. Siddiqi, *J. Phys. Chem.* **1969**, *73*, 3390.
64. J. Padova, I. Abrahmen, *J. Phys. Chem.*, **1967**, *71*, 2112.
65. R. Gopal, D.K. Agarwal, R. Kumar, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1973.
66. R. Gopal, P.P. Rastogi, *Z. Phys. Chem. (N.F.)*. **1970**, *69*, 1.
67. B. Das, D.K. Hazra, *J. Chem. Eng. Data*, **1991**, *36*, 403.
68. L. G. Hepler, *Can. J. Chem.* **1969**, *47*, 4617.
69. L.G. Hepler, J.M. Stokes, R.H. Stokes, *Trans. Faraday Soc.* **1965**, *61*, 20.
70. F.H. Spedding, M.J. Pikal, B.O. Ayres, *J. Phys. Chem.* **1966**, *70*, 2440.
71. L.A. Dunn, *Trans. Faraday Soc.* **1968**, *64*, 2951.
72. R. Pogue, G. Atkinson, *J. Chem. Eng. Data*, **1988**, *33*, 370.
73. B.E. Conway, R.E. Verral, J.E. Desnoyers, *Trans. Faraday Soc.* **1966**, *62*, 2738.
74. K. Uosaki, Y. Koudo, N. Tokura, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 871.
75. B.S. Krumgalz, *J. Chem. Soc. Faraday Trans. I.* **1980**, *76*, 1887.
76. A.W. Quin, D.F. Hoffmann, P. Munk, *J. Chem. Eng. Data* **1992**, *37*, 55.
77. Z. Atik, *J. Sol. Chem.* **2004**, *33*, 1447.
78. R.H. Stokes, R. Mills, *Viscosity of Electrolytes and Related Properties*, Pergamon, Great Britain, **1965**.
79. F. Vaslow, *Water and Aqueous Solutions*, Wiley- Interscience, New York, **1972**.
80. E.N.da C. Andrade, *Phil. Mag.* **1934**, *17*, 698.

81. J. Frankel, *Kinetic Theory of Liquids*, Dover Publications, New York, **1955**.
82. R. Furth, *Proc. Camb. Phil. Soc.* **1941**, 37, 281.
83. R. Furth, *Proc. Camb. Phil. Soc.* **1941**, 37, 252.
84. R.H. Ewell, H. Eyring, *J. Chem. Phys.* **1937**, 5, 726.
85. F.C. Auluck, S.C. De, D.S. Kothari, *Proc. Natl. Inst. Sci.* **1944**, 10(4), 397.
86. R. Eisenschitz, *Proc. Roy. Soc.* **1952**, 215A, 29.
87. J.E. Lennard-Jones, A.F. Devonshire, *Proc. Roy. Soc.* **1937**, 163A, 53.
88. J.E. Lennard-Jones, A.F. Devonshire, *Proc. Roy. Soc.*, **1938**, 165A, 1
89. J.A. Pople, *Proc. Roy. Soc.* **1952**, 215A, 67.
90. R. Eisenchitz, *Proc. Phys. Soc.* **1949**, 62A, 41.
91. J.G. Kirkwood, *J. Chem. Phys.* **1946**, 14, 180.
92. J.G. Kirkwood, *Theory of Liquids*, Science Publishers, New York, **1968**.
93. J.E. Mayer, E. Montroll, *J. Chem. Phys.* **1941**, 9, 2.
94. J.E. Mayer, *J. Chem. Phys.* **1947**, 15, 187.
95. M. Born, H.S. Green, *Proc. Roy. Soc.* **1946**, 188A, 10.
96. M. Born, H.S. Green, *Proc. Roy. Soc.* **1947**, 190A, 455.
97. J.G. Kirkwood, F.P. Buff, M.S. Green, *J. Chem. Phys.* **1949**, 17, 988.
98. J.G. Kirkwood, *J. Chem. Phys.* **1935**, 3, 300.
99. J.G. Kirkwood, *J. Chem. Phys.* **1939**, 7, 919.
100. J.G. Kirkwood, Z.W. Salsburg, *Faraday Soc. Discuss.* **1953**, 15, 25.
101. J.G. Kirkwood, E.M. Boggs, *J. Chem. Phys.* **1942**, 10, 394.
102. J.G. Kirkwood, E.K. Maun, B.J. Alder, *J. Chem. Phys.* **1950**, 18, 1040.
103. J.G. Kirkwood, V.A. Lewinson, B.J. Alder, *J. Chem. Phys.* **1952**, 20, 929.
104. R.W. Zwanzig, J.G. Kirkwood, K.F. Stripp, I. Oppenheim, *J. Chem. Phys.* **1953**, 21, 2050.
105. 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**.
106. 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**.
107. S.A. Rice, A.R. Allnatt, *J. Chem. Phys.* **1961**, 34, 2144.
108. A.R. Allnatt, S.A. Rice, *J. Chem. Phys.* **1961**, 34, 2156.
109. H.C. Longuet-Higgins, J.P. Valleau, *Mol. Phys.* **1958**, 1, 284.
110. H.T. Davis, S.A. Rice, J.V. Sengers, *J. Chem. Phys.* **1961**, 35, 2210.
111. H.T. Davis, K.D. Luks, *J. Phys. Chem.* **1965**, 69, 869.
112. 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**.
113. J.D. Rogers, F.G. Brickwedde, *Physica* **1966**, 32, 100.
114. J.P. Boon, G. Thomaes, *Physica* **1963**, 29, 208.
115. J.P. Boon, G. Thomaes, *Physica* **1962**, 28, 1074.

116. J.P. Boon, G. Thomaes, *Physica* **1963**, 29,123.
117. J.P. Boon, J. C. Legros, G. Thomaes, *Physica* **1967**, 33, 547.
118. T.H. Holleman, J. Hijmans, *Physica* **1962**, 28, 604.
119. H. Eyring, *J. Chem. Phys.* **1936**, 4, 283.
120. H. Eyring, J.O. Hirschfelder, *J. Phys. Chem.* **1937**, 41, 249.
121. J.F. Kincaid, H. Eyring, A.E. Stearn, *Chem. Rev.* **1941**, 28, 301.
122. H. Eyring, T. Ree, N. Hirai, *Proc. Natl. Acad. Sci.* **1958**, 44, 683.
123. E.J. Fuller, T. Ree, H. Eyring, *Proc. Natl. Acad. Sci.* **1959**, 45, 1594.
124. C.M. Carlson, H. Eyring, *Proc. Natl. Acad. Sci.* **1960**, 46, 333.
125. T.R. Thomson, H. Eyring, T. Ree, *Proc. Natl. Acad. Sci.* **1960**, 46, 336.
126. J. Walter, H. Eyring, *J. Chem. Phys.* **1941**, 9, 393.
127. T. Ree, H. Eyring, *Ind. Eng. Chem.* **1958**, 50, 1036.
128. C.M. Carlson, H. Eyring, T. Ree, *Proc. Natl. Acad. Sci.* **1960**, 46, 649
129. H. Eyring, T. Ree, *Proc. Natl. Acad. Sci.* **1961**, 47, 526.
130. H. Eyring, M.S. John, *Significant Liquid Structures*, John Willey & Sons, New York, **1969**.
131. Gruneisen, Wiss, Abhaudl, *Physik-tech. Reich-austatt.* **1905**, 4, 239.
132. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, 51, 2950.
133. P. Debye, E. Hückel, *Z. Phys. Chem.* **1923**, 24, 185.
134. H. Falkenhagen, M. Dole, *Phys. Z.* **1929**, 30, 611.
135. H. Falkenhagen, E.L. Vernon, *Phys. Z.* **1932**, 33, 140.
136. H. Falkenhagen, E.L. Vernon, *Phil. Mag.* **1983**, 14, 537.
137. M. Kaminsky, *Discuss Faraday Soc.* **1957**, 24, 171.
138. D. Feakins, D.J. Freemantle, K.G. Lawrence, *J. Chem. Soc. Faraday Trans. I.* **1974**, 70, 795.
139. J. Crudden, G.M. Delancy, D. Feakins, P.J. O'Relly, W. E. Waghorne, K. G. Lawrence, *J. Chem. Soc. Faraday Trans. I.* **1986**, 82, 2195.
140. A.K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York, **1973**.
141. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York, **1958**.
142. M. Kaminsky, *Z. Phys. Chem.* **1957**, 12, 206.
143. J. Desnoyers, G. Perron, *J. Solution Chem.* **1972**, 1, 199.
144. R.J.M. Bicknell, K.G. Lawrence, D. Feakins, *J. Chem. Soc. Faraday I.* **1980**, 76, 637.
145. R.L. Kay, T. Vituccio, C. Zawoyski, D.F. Evans, *J. Phys. Chem.* **1966**, 70, 2336.
146. N.P. Yao, D.N. Bennion, *J. Phys. Chem.* **1971**, 75, 1727.
147. M. Kaminsky, *Discussions Faraday Soc.* **1957**, 24, 171.
148. D. Feakins, K.G. Lawrence, *J. Chem. Soc.* **1966**, A, 212.
149. V. Vand, *J. Phys. Chem.* **1948**, 52, 277.
150. D.G. Thomas, *J. Colloid Sci.* **1965**, 20, 267.
151. S.P. Moulik, *J. Ind. Chem. Soc.* **1972**, 49, 483.

152. D. England, G. Pilling, *J. Phys. Chem.* **1972**, 76, 1902.
153. D.E. Goldsack, R.C. Franchetto, *Can. J. Chem.* **1977**, 55, 1062.
154. D.E. Goldsack, R.C. Franchetto, *Can. J. Chem.* **1978**, 56, 1442.
155. C.A. Angell, *J. Phys. Chem.* **1966**, 70, 2793.
156. C.A. Angell, *J. Chem. Phys.* **1967**, 46, 4673.
157. K.R. Chowdhury, D.K. Majumdar, *Electrochim. Acta.* **1983**, 28, 23.
158. K.R. Chowdhury, D.K. Majumdar, *Electrochim. Acta.* **1983**, 28, 597.
159. K.R. Chowdhury, D.K. Majumdar, *Electrochim. Acta.* **1984**, 29, 1371.
160. P.P. Rastogi, *Bull. Chem. Soc. Japan*, **1970**, 43, 2442.
161. R. Gopal, P.P. Rostogi, *Z. Phys. Chem. (N.F.)* **1970**, 69, 1.
162. C.M. Criss, M.J. Mostroiani, *J. Phys. Chem.* **1971**, 75, 2532.
163. K. Tamaski, Y. Ohara, Y. Isomura, *Bull. Chem. Soc. Japan* **1973**, 46, 951.
164. P.P. Deluca, T.V. Rabagay, *J. Phys. Chem.* **1975**, 79, 2493.
165. B.N. Prasad, N.P. Singh, M.M. Singh, *Ind. J. Chem.* **1976**, 14A, 322.
166. B.N. Prasad, M.M. Agarwal, *Ind. J. Chem.* **1976**, 14A, 343.
167. R.T.M. Bicknell, K.G. Lawrence, M.A. Scelay, D. Feakins, L. Werblan, *J. Chem. Soc. Faraday I.* **1976**, 72, 307.
168. J.M. McDowall, N. Martinus, C.A. Vincent, *J. Chem. Soc. Faraday I.* **1976**, 72, 654.
169. A. Sacco, G. Petrella, M. Castagnola, *J. Phys. Chem.* **1976**, 80, 749.
170. R.L. Blokhra, Y.P. Segal, *Ind. J. Chem.* **1977**, 15A, 36.
171. N.C. Das, P.B. Das, *Ind. J. Chem.* **1977**, 15A, 826.
172. A. Sacco, G. Petrella, M. Della Monica, M. Castagnola, *J. Chem. Soc. Faraday I.* **1977**, 73, 1936.
173. P.K. Mandal, B.K. Seal, A.S. Basu, *Z. Phys. Chem.* **1977**, 258, 809.
174. J.I. Kim, *J. Phys. Chem.* **1978**, 82, 191.
175. S.K. Vijaylakshamna, *Indian J. Chem.* **1979**, 17A, 511.
176. A. Sacco, G. Petrella, M.D. Monica, *J. Chem. Soc. Faraday I.* **1979**, 75, 2325.
177. P.T. Thomson, M. Durbana, J.L. Turner, R.H. Wood, *J. Sol. Chem.* **1980**, 9, 955.
178. K. Kurotaki, S. Kawamura, *J. Chem. Soc. Faraday I.* **1981**, 77, 217.
179. N. Martinus, C.A. Vincent, *J. Chem. Soc. Faraday I.* **1981**, 77, 141.
180. A. Sacco, A. D. Giglio, A. D. Atti, *J. Chem. Soc. Faraday I.* **1981**, 77, 2693.
181. D.S. Gill, A.N. Sharma, *J. Chem. Soc. Faraday I.* **1982**, 78, 78475.
182. A. Sacco, G. Petrella, A.D. Atti, M. Castagnolo, *J. Chem. Soc. Faraday I.* **1980**, 78, 955.
183. A. Sacco, A.D. Giglio, A.D. Atti, M. Castagnolo, *J. Chem. Soc. Faraday I.* **1983**, 79, 431.
184. K.G. Lawrence, A. Sacco, *J. Chem. Soc. Faraday I.* **1981**, 77, 615.
185. K. Miyajima, M. Sawada, M. Nakagaki, *Bull. Chem. Soc. Jpn.* **1983**, 56, 827.
186. J. Doenech, S. Rivera, *J. Chem. Soc. Faraday I.* **1984**, 80, 1249.
187. D. Dasgupta, S. Das, D.K. Hazra, *Bull. Chem. Soc. Jpn.* **1989**, 62, 1246.
188. S. Taniewska-Osinska, M. Jozwaik, *J. Chem. Soc. Faraday Trans I.* **1989**, 85, 2147.

189. D. Nandi, D.K. Hazra, *J. Chem. Soc. Faraday Trans I.* **1989**, 85, 4227.
190. I. Ibulci, M. Nakahara, *J. Phys. Chem.* **1990**, 94, 8370.
191. W.M. Cox, J. H. Wolfenden, *Proc. Roy. Soc. London* **1934**, 145A, 475.
192. R.W. Gurney, *Ionic Processes in Solution*, Mc Graw Hill, New York, **1953**.
193. E.R. Nightingale, *J. Phys. Chem.* **1959**, 63, 1381.
194. A. Einstein, *Ann. Phys.* **1906**, 19, 289.
195. G.S. Benson, A.R. Gordon, *J. Chem. Phys.* **1945**, 13, 473.
196. [D.F.T. Tuan, R.M. Fuoss, *J. Phys. Chem.* **1963**, 67, 1343.
197. C.H. Springer, J.F. Coetzee, R.L. Key, *J. Phys. Chem.* **1969**, 78, 471.
198. G. Petrella, A. Sacco, *J. Chem. Soc. Faraday I.* **1978**, 74, 2070.
199. B.S. Krumgalz, *J. Chem. Soc. Faraday I.* **1980**, 76, 1275.
200. B.S. Krumgalz, *Russ. J. Phys. Chem.* **1972**, 46, 858.
201. B.S. Krumgalz, *Russ. J. Phys. Chem.* **1973**, 47, 956.
202. B.S. Krumgalz, *Russ. J. Phys. Chem.* **1974**, 48, 1163.
203. B.S. Krumgalz, *Russ. J. Phys. Chem.* **1971**, 45, 1448.
204. H.D.B. Jenkins, M.S.F. Pritchett, *J. Chem. Soc. Faraday I.* **1984**, 80, 721.
205. K. Fajan, *Naturwissenschaften* **1921**, 9, 729.
206. D.F.C. Morris, *Struct. Bonding* **1969**, 6, 157.
207. R.W. Gurney, *Ionic Processes in Solutions*, Doves, New York, **1962**.
208. H.S. Frank, W.Y. Wen, *Disc. Farad. Soc.* **1957**, 24, 133.
209. Z. Asmus, *Naturforsch.* **1949**, 4A, 589.
210. M.H. Abraham, J. Liszi, E. Papp, *J. Chem. Soc. Faraday I.* **1982**, 78, 197.
211. M.H. Abraham, J. Liszi, L. Meszaros, *J. Chem. Phys.* **1979**, 70, 249.
212. M.H. Abraham, J. Liszi, *J. Chem. Soc. Faraday I.* **1980**, 76, 1219.
213. S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw Hill, New York, **1941**.
214. E.R. Nightingale, R.F. Benck, *J. Phys. Chem.* **1959**, 63, 1777.
215. D. Feakins, D.J. Freemantle, K.G. Lawrence, *J. Chem. Soc. Faraday I.* **1974**, 70, 795.
216. R. Sinha, *J. Phys. Chem.* **1940**, 44, 25.
217. V. Vand, *J. Phys. Chem.* **1948**, 52, 277.
218. D.G. Thomas, *J. Colloid Sci.* **1965**, 20, 267.
219. S.P. Moulik, *J. Phys. Chem.* **1968**, 72, 4688.
220. S.P. Moulik, *Electrochim. Acta.* **1972**, 17, 1491.
221. S.P. Moulik, *J. Indian Chem. Soc.* **1972**, 49, 483.
222. R.J. Fort, W.R. Moore, *Trans. Faraday Soc.* **1966**, 62, 1112.
223. G.R. Naidu, P.R. Naidu, *Ind. J. Chem.* **1983**, 22A, 324.
224. O. Redlich, A.T. Kister, *Ind. Eng. Chem.* **1948**, 40, 345.
225. L. Pikkarainen, *J. Chem. Eng. Data* **1983**, 28, 344.
226. L. Pikkarainen, *J. Chem. Eng. Data* **1983**, 28, 381.

227. L.S. Manjeshwar, T. Aminabhavi, *J. Chem. Eng. Data* **1988**, *33*, 184.
228. K.P. Rao, K.S. Reddy, *J. Chem. Eng. Data* **1988**, *33*, 130.
229. S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw Hill, New York, **1941**.
230. D.S. Gill, T.S. Kaur, H. Kaur, I.M. Joshi, J. Singh, *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 1737.
231. J.V. Herraiez, R. Belda, *J. Soln. Chem.* **2004**, *33*, 117.
232. J. Ferguson, Z. Kemblonski, *Applied Fluid Rheology*, Elsevier, Cambridge, **1991**.
233. H.A. Barnes, J.F. Hutton, K. Walters, *An Introduction to Rheology*, Elsevier, Amsterdam, **1993**.
234. C.W. Macosk, *Rheology. Principles, Measurements and Applications* (VCH), New York, **1994**.
235. M. Garcia-Velarde, *Revista Esp. Fisica* **1995**, *9*, 12.
236. R. Shukla, M. Cheryan, *J. Membrane Sci.* **2002**, *198*, 104.
237. J.M. Resa, C. Gonzalez, J. Lanz, *J. Food Eng.* **2002**, *51*, 113.
238. M.J. Assael, N.K. Dalaouti, I. Metaxa, *Fluid Phase Equilibria.* **2002**, *199*, 237.
239. A. Darr, *Technologia Farmaceutica.*, S.A. Acribia, Zaragoza, **1979**.
240. R. Voight, S.A. Acribia, *Tratado de Tecnología Farmaceutica.* Zaragoza, **1982**.
241. C.K. Z'eborg-Mikkelsen, S.E. Quiñones-Cisneros, S.H. Stenby, *Fluid Phase Equilibria.*, **2002**, *1191*, 194.
242. C. Fauli-Trillo, *Tratado de Farmacia Galénica*, S.A. Lujan, Madrid, **1993**.
243. J. Swarbrik, J.C. Boyland, *Encyclopedia of Pharmaceutical Technology*, Marcel Dekker, NewYork, **1993**.
244. J. Pellicer, *Sinergia Viscosa*, Valencia, Spain, **1997**.
245. G. Copetti, R. Lapasin, E.R. Morris, *Proceedings of the Fourth European Rheology Conference*, Seville, Spain, **1994**.
246. G. Kalentunc-Gencer, M. Peleg, *J. Texture Studies.* **1986**, *17*, 61.
247. D.D. Christianson, *Hydrocolloidal Interactions with Starches*, Wesport. Conn., **1982**.
248. N.K. Howell, *Proceedings of the Seventh International Conference*, Wales, **1993**.
249. J.G. Mathieson, B.E. Conway, *J. Sol. Chem.* **1974**, *3*, 455.
250. S. Bhowmik, R.K. Mohanty, *Ind. J. Chem.* **1986**, *25A*, 416.
251. M.V. Kaulgud, K.S. Mohan Rao, *Ind. J. Chem.* **1988**, *27A*, 12.
252. K.J. Patil, A.B. Wazalwar, G.R. Mehta, *Ind. J. Chem.* **1988**, *27A*, 799.
253. M. Iqbal, R.E. Verral, *Can. J. Chem.* **1989**, *67*, 727.
254. M. Kikuchi, M. Sakurai, K. Nitta, *J. Chem. Eng. Data* **1996**, *41*, 1439.
255. B.E. Conway, R.E. Verral, *J. Phys. Chem.* **1966**, *70*, 3952.
256. K. Gekko, H. Noguchi, *J. Phys. Chem.* **1979**, *83*, 2706.
257. W.L. Masterson, *J. Chem. Phys.* **1954**, *22*, 1830.
258. L.G. Hepler, *Can. J. Chem.* **1969**, *47*, 4613.
259. M.V. Kaulgud, K.J. Patil, *J. Phys. Chem.* **1976**, *80*, 138.

260. K.J. Patil, G.R. Mehta, R.K. Chandewar, *Ind. J. Chem.* **1986**, 25A, 1147.
261. C. Lafuente, B. Ginar, A. Villares, I. Gascon, P. Cea, *Int. J. Thermophys.* **2004**, 25, 1735.
262. G. Douheret, A. Pal, M.I. Davis, *J. Chem. Thermodyn.* **1990**, 22, 99.
263. I. Gascon, S. Martin, P. Cea, M.C. Lopez, F.M. Royo, *J. Sol. Chem.* **2002**, 31, 905.
264. R. Mehra, M. Pancholi, *J. Ind. Chem. Soc.* **2005**, 82, 791.
265. S.L. Oswal, K.D. Prajapati, *J. Chem. Eng. Data* **1998**, 43, 367.
266. K. Hsu-Chen, T. Chein-Hsium, *J. Chem. Eng. Data* **2005**, 50, 608.
267. D.W. Marquardt, *J. Soc. Ind. Appl. Math.* **1963**, 11, 431.
268. L. Onsager, *Z. Phys. Chem.* **1927**, 28, 277.
269. R.M. Fuoss, *Rev. Pure Appl. Chem.* **1968**, 18, 125.
270. E. Pitts, *Proc. Roy. Soc.* **1953**, 217A, 43.
271. R.M. Fuoss, L. Onsager, *J. Phys. Chem.* **1957**, 61, 668.
272. R.M. Fuoss, *Chemical Physics of Ionic Solutions*, Wiley, New York, **1966**.
273. E. Pitts, R.E. Tabor, J. Daly, *Trans. Faraday Soc.* **1969**, 65, 849.
274. (a) R.M. Fuoss, K.L. Hsia, *Proc. Natl. Acad. Sci.* **1967**, 57, 1550.
(b) R.M. Fuoss, K.L. Hsia, *J. Am. Chem. Soc.* **1968**, 90, 3055.
275. R. Fernandez-Prini, *J.E. Prue. Z. Phys. Chem.* **1965**, 228, 373.
276. R. Fernandez-Prini, *J.E. Prue. Z. Phys. Chem.* **1965**, 228, 473.
277. D.F. Evans, R.L. Kay, *J. Phys. Chem.* **1966**, 70, 366.
278. D. F. Arrington, E. Griswold, *J. Phys. Chem.* **1970**, 74, 123.
279. R.M. Fuoss, C.A. Kraus, *J. Am. Chem. Soc.* **1933**, 55, 476.
280. T. Shedlovsky, J. Franklin, *Instt.* **1938**, 225, 739.
281. (a) J.C. Justice, *J. Chem. Phys.* **1968**, 65, 353.
(b) J.C. Justice, R. Bury, C. Treiner, *J. Chem. Phys.* **1968**, 65, 1708.
282. R.M. Fuoss, F. Accascina, *Electrolytic Conductance*, Wiley, New York, **1959**.
283. N.K. Bjerrum, Dan. Vidensk. Selek. *Mat.Fys.Medd.* **1926**, 7, 9.
284. M. Tissier, G. Douheret, *J. Soln. Chem.* **1978**, 7, 87.
285. R. Fernandez-Prini, *J. Prue, Trans. Faraday Soc.* **1962**, 66, 1257.
286. (a) R.M. Fuoss, L. Onsager, *J. Phys. Chem.* **1962**, 66, 1722.
(b) R.M. Fuoss, L. Onsager, *J. Phys. Chem.* **1963**, 67, 621.
287. R.M. Fuoss, *J. Phys. Chem.* **1975**, 49, 525.
288. P.C. Carman, D.P. Laurie, *J. Sol. Chem.* **1976**, 5, 457.
289. R.M. Fuoss, *J. Phys. Chem.* **1977**, 81, 1829.
290. R.M. Fuoss, *Proc. Nat. Acad. Sci.* **1978**, 75, 16.
291. R.M. Fuoss, *J. Phys. Chem.* **1957**, 82, 2427.
292. (a) W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday II.* **1978**, 74, 743.
(b) W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday II.* **1978**, 74, 1456.
293. W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday Trans. I.* **1979**, 75, 1128.
294. W.H. Lee, R.J. Wheaton, *J. Chem. Soc. Faraday Trans. II.* **1978**, 74, 1456.

295. A.D. Pethybridge, S.S. Tara, *J. Chem. Soc. Faraday I.* **1980**, 76, 368.
296. M. Bester-Rogac, R. Neueder, J. Barthel, *J. Solution Chem.* **1999**, 28, 1071.
297. H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York, **1964**.
298. E. Balaguruswami, *Numerical Methods*, Tata McGraw-Hill Publishing Company, New Delhi, **2007**.
299. M.N. Roy, B. Sinha, V.K. Dakua, *Pak. J. Sci. Ind. Res.* **2006**, 49,153.
300. (a) B.S. Krumgalz, *J. Chem. Soc. Faraday I.* **1983**, 79,571.
(b) B.S. Krumgalz, *J. Chem. Soc. Faraday I.* **1985**, 81, 241.
301. P. Walden, H. Ulich, D. Bush, *Z. Phys. Chem.* **1926**, 123, 429.
302. R.M. Fuoss, E. Hirsch, *J. Am. Chem. Soc.* **1960**, 82, 1018.
303. S. Takezawa, Y. Kondo, N. Tokura, *J. Phys. Chem.* **1973**, 77, 2133.
304. (a) D.S. Gill, *J. Chem. Soc. Faraday I.* **1981**, 74, 751.
(b) D.S. Gill, N. Kumari, M.S. Chauhan, *J. Chem. Soc. Farada Trans I.* **1985**, 81, 687.
305. M.A. Coplan, R.M. Fuoss, *J. Phys. Chem.* **1964**, 68, 1177.
306. J.F. Coetzee, G.P. Cunningham, *J. Am. Chem. Soc.* **1965**, 87, 2529.
307. R.H. Stokes, R.A. Robinson, *Trans. Faraday Soc.* **1957**, 53,301.
308. M. Born, *Z. Phys. Chem.* **1920**, 1, 221.
309. R.H. Boyd, *J. Chem. Phys.* **1961**, 35, 1281.
310. R. Zwanzig, *J. Chem. Phys.* **1963**, 38, 1603.
311. E.J. Passeron, *J. Phys. Chem.* **1964**, 68, 2728.
312. (a) P. Walden, *Z. Phys. Chem.* **1906**, 55, 207.
(b) P. Walden, *Z. Phys. Chem.* **1912**, 78, 257.
313. R.A. Robinson, R.H. Stokes, *Electrolyte Solutions*, Butterworths, London, **1959**.
314. R. Gopal, M.M. Hussain, *J. Ind. Chem. Soc.* **1963**, 40, 981.
315. L.G. Longworth, *J. Phys. Chem.* **1963**, 67, 689.
316. M. Della Monica, U. Lamauna, L. Seutatore, *J. Phys. Chem.* **1968**, 72, 2124.
317. S. Brocus, *J. Chem. Phys.* **1958**, 28, 1158.
318. D.G. Miller, *J. Phys. Chem.* **1960**, 64, 1598.
319. G.J. Hills, *Chemical Physics of Ionic Solutions*, Wiley, New York, **1966**.
320. R.H. Stokes, I.A. Weeks, *Aust. J. Chem.* **1964**, 17, 304.
321. R.H. Stokes, *The Structure of Electrolytic Solutions*, Wiley, New York, **1959**.
322. D.S. Gill, *J. Chem. Soc. Faraday Trans. I.* **1981**, 77, 751.
323. R. Zwanzig, *J. Chem. Phys.* **1970**, 52, 3625.
324. H.S. Franks, *Chemical Physics of Ionic Solutions*, Wiley, New York, **1966**.
325. G. Atkinson, S.K. Koz, *J. Phys. Chem.* **1965**, 69, 128.
326. R.L. Kay, G.P. Cunningham, D.F. Evans, *Hydrogen bonded Solvent Systems*, Taylor and Francis, London, **1968**.
327. R.L. Kay, B.J. Hales, G.P. Cunningham, *J. Phys. Chem.* **1967**, 71, 3925.

328. R.L. Kay, C. Zawoyski, D.F. Evans, *J. Phys. Chem.* **196**, 69, 4208.
329. D. F. Evans, J. L. Broadwater, *J. Phys. Chem.* **1968**, 72, 1037.
330. M. Spiro, *Physical Chemistry of Organic Solvent Systems*, Plenum Press, New York, **1973**.
331. R. Fernandez-Prini, G. Atkinson, *J. Phys. Chem.* **1971**, 75, 239.
332. L. Bahadur, M.V. Ramanamurti, *J. Chem. Soc. Faraday I.* **1980**, 76, 1409.
333. L. Bahadur, M.V. Ramanamurti, *J. Electrochem. Soc.* **1981**, 128, 339.
334. L. Bahadur, M.V. Ramanamurti, *Can. J. Chem.* **1984**, 62, 1051.
335. J.L. Broadwater, R.L. Kay, *J. Phys. Chem.* **1970**, 74, 3803.
336. S. Das, D.K. Hazra, *Indian J. Chem.* **1988**, 274, 1073.
337. S. Das, D.K. Hazra, *J. Ind. Chem. Soc.* **1988**, L XV, 100.
338. (a) R.L. Kay, J.L. Broadwater, *Electrochim. Acta.* **1971**, 16, 667.
(b) R.L. Kay, J.L. Broadwater, *J. Sol. Chem.* **1976**, 5, 57.
339. A.D. Aprano, R.M. Fuoss, *J. Phys. Chem.* **1963**, 67, 1704.
340. P. Hemmes, *J. Phys. Chem.* **1974**, 78, 907.
341. J. Hubbard, L. Onsager, *J. Chem. Phys.* **1977**, 53, 4850.
342. N. Islam, M.R. Islam, M. Ahmed, *Z. Phys. Chem.* **1981**, 262, 129.
343. D.S. Gill, A.N. Sharma, H. Schneider, *J. Chem. Soc. Faraday I.* **1982**, 78, 465.
344. C.J. Cramer, D.G. Truhlar, *J. Am. Chem. Soc.* **1991**, 113, 8305.
345. D.J. Giesen, J.W. Stores, C.J. Cramer, D.G. Truhlar, *J. Am. Chem. Soc.* **1995**, 117, 1057.
346. (a) C.J. Cramer, D.G. Truhlar, *J. Org. Chem.* **1996**, 61, 8720.
(b) C.J. Cramer, D.G. Truhlar, *Erratum.* **1999**, 101, 309.
347. G.D. Hawkins, C.J. Cramer, D.G. Truhlar, *J. Phys. Chem. B* **1997**, 101, 7147.
348. G.D. Hawkins, C.J. Cramer, D.G. Truhlar, *J. Phys. Chem. B* **1998**, 102, 3257.
349. A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burgess, *J. Chem. Phys.* **1997**, 106, 4168.
350. A. Galindo, L.A. Davies, A. Gil-Villegas, G. Jackson, *Mol. Phys.* **1998**, 93, 241.
351. M. Roses, C. Rafols, J. Ortega, E. Bosch, *J. Chem. Soc. Perkin Trans.* **1997**, 2, 1607.
352. O. Bernard, W. Kunz, P. Turq, L. Blum, *J. Phys. Chem.* **1992**, 96, 3833.
353. S. Durand-Vidal, P. Turq, O. Bernard, *J. Phys. Chem.* **1996**, 100, 17345.
354. H.L. Bianchi, I. Dujovne, R. Fernandez-Prini, *J. Sol. Chem.* **2000**, 29, 237.
355. A. Chandra, B. Bagchi, *J. Phys. Chem. B.* **2000**, 104, 9067
356. W. Heller, *J. Phys. Chem.* **1965**, 69, 1123.
357. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, **1970**.
358. O. Redlich, A. Kister, *Ind. Eng. Chem.* **1948**, 40, 345.
359. J.F. Comesaña, J.J. Otero, E. Camesella, A. Correa, *J. Chem. Eng. Data* **2001**, 46, 1153.

Chapter III:

1. D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd Ed., Pergamon Press, Oxford, England, **1988**.
2. A. Hohn, "Formamide". In Kroschwitz, Jacqueline I. Kirk-Othmer *Concise Encyclopedia of Chemical Technology*, 4th ed., John Wiley & Sons Inc., New York, **1999**.
3. V. K. Kamineni, Y. M. Lvov, T. A. Dobbins, *Langmuir* **2007**, 23 (14), 7423.
4. 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* **1988**, 108 (5), 680.
5. J. M. Daran, A. J. A. van Maris, J. T. Pronk, J. R. Dickinson, *Appl. Environ. Microbiol.* **2008**, 74 (8), 2259.
6. J. A. M. Bleeker, J. Geiss, M. C. E. Huber, *The Century of Space Science*, Kluwer Academic Publishers, Netherlands, **2001**.
7. M. Jotanovic, Z. Andric, G. Tadic, V. Micic, *Peer-Reviewed and Open Access Journal* **2010**, 3, 15.
8. H. Cheung, R. S. Tanke, G. P. Torrence, "Acetic Acid" in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2005**.
9. M. M. Cox, A. L. Lehninger, D. R. Nelson, *Lehninger principles of biochemistry*, Worth Publishers, New York, **2000**.
10. J.E. Lind Jr., J.J. Zwolenik, R.M. Fuoss, *J. Chem. Soc. Faraday Trans I.* **1959**, 81, 1557.
11. B. Das, N. Saha, *J. Chem. Eng. Data* **2000**, 45, 2.

Chapter IV :

1. T. Welton, *Chem. Rev.* **1999**, 99, 2071.
2. M. J. Earle, K. R. Seddon, *Pure Appl. Chem.* **2000**, 72, 1391.
3. J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, 102, 3667.
4. N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, 37, 123.
5. F. Endres, S. El Abedin Zein, *Phys. Chem. Chem. Phys.* **2006**, 8, 2101.
6. P. Wang, S. M. Zakeeruddin, J. E. Moser, M. Gratzel, *J. Phys. Chem. B.* **2003**, 107, 13280.
7. D. Das, B. Das, D. K. Hazra, *J. Solution Chem.* **2002**, 31, 425.
8. C. Guha, J. M. Chakraborty, S. Karanjai, B. Das, *J. Phys. Chem. B* **2003**, 107, 12814.
9. D. Das, B. Das, D. K. Hazra, *J. Solution Chem.* **2003**, 32, 77.
10. M. N. Roy, D. Nandi, D. K. Hazra, *J. Indian Chem. Soc.* **1993**, 70, 123.
11. O. Popvych, R. P. T. Tomkins, *Nonaqueous Solution Chemistry*, Wiley-Interscience, New York, **1981**, Ch-4.
12. A. J. Matheson, *Molecular Acoustics*, Wiley-Interscience: London, **1971**.

13. J. M. McDowall, C.A. Vincent, *J. Chem. Soc., Faraday Trans. 1.* **1974**, 70 1862.
14. M.R. J. Deck, K.J. Bird, A.J. Parker, *Aust. J. Chem.* **1975**, 28, 955.
15. M.N. Roy, B. Sinha, R. Dey, A. Sinha, *Int. J. Thermophy.* **2005**, 26, 1549.
16. M. N. Roy, R. Dewan, P. K. Roy, D. Biswas, *J. Chem. Eng. Data.* **2010**, 55, 3617.
17. M. N. Roy, A. Bhattacharjee, P. Chakraborti, *Thermochim. Acta.* **2010**, 507, 135.
18. C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.* **2005**, 37, 37.
19. A. Bhattacharjee, M. N. Roy, *Phys. Chem. Chem. Phys.* **2010**, 12, 14534.
20. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data.* **2004**, 49, 291.
21. E. B. Freyer, J. D. Hubbard, D. H. Andrews, *J. Am. Chem. Soc.* **1929**, 51, 759.
22. O. Kiyohara, K. Arakawa, *Bull. Chem. Soc. Jpn.* **1970**, 43, 3037.
23. O. Kiyohara, J. P. E. Grolier, G. C. Benson, *Can. J. Chem.* **1974**, 52, 2287.
24. N. M. Murthy, S. V. Subrahmanyam, *Bull. Chem. Soc. Jpn.* **1977**, 50, 2589.
25. E. Ayranci, *J. Chem. Eng. Data.* **1997**, 42, 934.
26. D.O. Masson, *Phil. Mag.* **1929**, 8, 218.
27. M. N. Roy, D. Ekka, R. Dewan, *Acta Chim. Slov.* **2011**, 58, 792.
28. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, 51, 2950.
29. F. J. Millero, *Chem. Rev.* **1971**, 71, 147.
30. F. J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.* **1978**, 82, 784.
31. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, **1970**.
32. M. Born, E. Wolf, *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*, 7th ed., Cambridge University Press, London, **1999**.
33. M. Deetlefs, K. Seddon, M. Shara, *Phys. Chem. Chem. Phys.* **2006**, 8, 642.

Chapter V:

1. M. Jotanovic, Z. Andric, G. Tadic, V. Micic, *Peer-Reviewed and Open Access Journal* **2010**, 3, 15.
2. Becker C. *Radiologe* **2007**, 47(9), 768.
3. F.J. Millero, in: R.A. Horne (Ed.), *Structure Transport Process in Water Aqueous Solutions*, Wiley, New York, **1972**.
4. M.N. Roy, B. Sinha, V.K. Dakua, A. Sinha, *Pak. J. Sci. Ind. Res.* **2006**, 49, 153.
5. M.N. Roy, P. Pradhan, R.K. Das, P.G. Guha, *J. Chem. Eng. Data* **2008**, 53, 1417.
6. R. Chanda, M.N. Roy, *Fluid Phase Equilib.* **2008**, 269, 134.
7. D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed. Pergamon Press, Oxford, **1988**.

8. B. Sinha, V.K. Dakua, M.N. Roy, *J. Chem. Eng. Data*. 2007, 52,1768.
9. J.A. Dean, *Lange's Handbook of Chemistry*, 11th ed. McGraw-Hill Book Company, New York, **1973**.
10. B.D. Chatterjee, *J. Chem. Eng. Data*.**2006**, 51,1352.
11. J.E. Lind Jr., J.J. Zwolenik, R.M. Fuoss, *J. Am. Chem. Soc.* **1959**, 81, 1557.
12. M.N. Roy, A. Jha, R. Dey, *J. Chem. Eng. Data*.**2001**, 46, 1327.
13. M.N. Roy, D.K. Hazra, *Indian J. Chem. Technol.* **1994**, 1, 93.
14. R.M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.* **1978**, 75, 16.
15. R.M. Fuoss, *J. Phys. Chem.* **1978**, 82, 2427.
16. J. Barthel, M.B. Rogac , R. Neueder, *J. Solut. Chem.* **1999**, 28, 1071.
17. M.N. Roy, R. Dewan, D. Ekka, I. Banik, *Thermochimica Acta.* **2013**, 559, 46.
18. R.M. Fuoss and C.A. Kraus, *J. Am. Chem. Soc.* **1933**, 55, 2387.
19. F.J. Millero, A.L. Surdo, C. Shin, *Phys. Chem.* **1978**, 82, 784.
20. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, 51, 2950.
21. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, **1970** .
22. M. I. Aralaguppi, C.V. Jadar, T.M. Aminabhavi, J.D. Ortego, S.C. Mehrotra, *J. Chem. Eng. Data* **1997**, 42 , 301.
23. V. A. Aminabhavi, T.M. Aminabhavi, R.H. Balundgi, *Ind. Eng. Chem. Res.* **1990**, 29, 2106.

Chapter VI:

1. M.N. Roy, B. Sinha, R. Dey, A. Sinha, *Int. J. Thermophy.* **2005**, 26, 1549.
2. M.R. J. Deck, K.J. Bird, A.J. Parker, *Aust. J. Chem.* **1975**, 28, 955.
3. M. N. Roy, R.Dewan, P. K. Roy, D. Biswas, *J. Chem. Eng. Data.* **2010**, 55, 3617.
4. J. M. McDowall, C.A. Vincent, *J. Chem. Soc., Faraday Trans. 1.* **1974**, 70, 1862.
5. M. N. Roy, A. Bhattacharjee, P. Chakraborti, *Thermochim. Acta.* **2010**, 507, 135.
6. C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.* **2005**, 37, 37.
7. A. Bhattacharjee, M. N. Roy, *Phys. Chem. Chem. Phys.* **2010**, 12, 14534.
8. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data.* **2004**, 49, 291.
9. E. B. Freyer, J. D. Hubbard, D. H. Andrews, *J. Am. Chem. Soc.* **1929**, 51, 759.
10. O. Kiyohara, K. Arakawa, *Bull. Chem. Soc. Jpn.* **1970**, 43, 3037.

11. O. Kiyohara, J. P. E. Grolier, G. C. Benson, *Can. J. Chem.* **1974**, *52*, 2287.
12. N. M. Murthy, S. V. Subrahmanyam, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2589.
13. E. Ayranci, *J. Chem. Eng. Data.* **1997**, *42*, 934.
14. D.O. Masson, *Phil. Mag.* **1929**, *8*, 218.
15. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, *51*, 2950.
16. F. J. Millero, Molal volumes of electrolytes. *Chem. Rev.* **1971**, *71*, 147.
17. F. J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.* **1978**, *82*, 784.
18. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, **1970**.
19. M. Born, E. Wolf, *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*, 7th ed., Cambridge University Press, London, **1999**.
20. M. Deetlefs, K. Seddon, M. Shara, *Phys. Chem. Chem. Phys.* **2006**, *8*, 642.

Chapter VII:

1. M.N. Roy, B. Sinha, R. Dey, A. Sinha, *Int. J. Thermophy.* **2005**, *26*, 1549.
2. M.R. J. Deck, K.J. Bird, A.J. Parker, *Aust. J. Chem.* **1975**, *28*, 955.
3. M. N. Roy, R. Dewan, P. K. Roy, D. Biswas, *J. Chem. Eng. Data.* **2010**, *55*, 3617.
4. J. M. McDowall, C.A. Vincent, *J. Chem. Soc., Faraday Trans. 1.* **1974**, *70*, 1862.
5. M. N. Roy, A. Bhattacharjee, P. Chakraborti, *Thermochim. Acta.* **2010**, *507*, 135.
6. C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.* **2005**, *37*, 37.
7. A. Bhattacharjee, M. N. Roy, *Phys. Chem. Chem. Phys.* **2010**, *12*, 14534.
8. M. N. Roy, A. Jha, A. Choudhury, *J. Chem. Eng. Data.* **2004**, *49*, 291.
9. E. B. Freyer, J. D. Hubbard, D. H. Andrews, *J. Am. Chem. Soc.* **1929**, *51*, 759.
10. O. Kiyohara, K. Arakawa, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3037.
11. O. Kiyohara, J. P. E. Grolier, G. C. Benson, *Can. J. Chem.* **1974**, *52*, 2287.
12. N. M. Murthy, S. V. Subrahmanyam, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2589.
13. E. Ayranci, *J. Chem. Eng. Data.* **1997**, *42*, 934.
14. D.O. Masson, *Phil. Mag.* **1929**, *8*, 218.
15. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, *51*, 2950.
16. F. J. Millero, Molal volumes of electrolytes. *Chem. Rev.* **1971**, *71*, 147.
17. F. J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.* **1978**, *82*, 784.
18. B. Sinha, V. K. Dakua, M. N. Roy, *J. Chem. Eng. Data.* **2007**, *52*, 1768.
19. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, **1970**.
20. M. Born, E. Wolf, *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*, 7th ed., Cambridge University Press, London, **1999**.
21. M. Deetlefs, K. Seddon, M. Shara, *Phys. Chem. Chem. Phys.* **2006**, *8*, 642.

Chapter VIII:

1. J.M. Mc Dowali, C.A. Vincent, *J. Chem. Soc., Faraday Trans.* **1974**, *1*, 1862.
2. M.R.J. Dack, K.J. Bird, A.J. Parker, *Aust. J. Chem.* **1975**, *28*, 955.
3. M.N. Roy, B. Sinha, R. Dey, A. Sinha, *Int. J. Thermophys.* **2005**, *26*, 1549.
4. R.H. Stokes, R. Mills, *Int. Encyclopedia of Physical Chemistry and Chemical Physics*, Pergamon Press, Oxford, New York, **1965**.
5. P.S. Nikam, H. Mehdi, *J. Chem. Eng. Data* **1988**, *33*, 165.
6. M. N. Roy, D. Nandi, D. K. Hazra, *J. Indian Chem. Soc.* **1993**, *70*, 123.
7. D.D. Perrin, W.L.F. Amarego, *Purification of Laboratory Chemicals*, third ed., Great Britain, **1988**.
8. B. Sinha, V.K. Dakua, M.N. Roy, *J. Chem. Eng. Data.* **2007**, *52*, 1768.
9. J.A. Dean, *Lange's Handbook of Chemistry*, 11th ed. McGraw-Hill Book Company, New York, **1973**.
10. B.D. Chatterjee, *J. Chem. Eng. Data.* **2006**, *51*, 1352.
11. D.O. Masson, *Phil. Mag.* **1929**, *8*, 218.
12. F.J. Millero, *Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes*, Wiley- Interscience, New York, **1972**.
13. L. G. Hepler, *Can. J. Chem.* **1969**, *47*, 4617.
14. B.K. Sarkar, B. Sinha, M.N. Roy, *Russ. J. Phys. Chem* **2008**, *8*, 960.
15. M.L. Parmar, D.S. Banyal, *Indian J. Chem.* **2005**, *44A*, 1582.
16. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, *51*, 2950.
17. F. J. Millero, *Chem. Rev.* **1971**, *71*, 147.
18. F. J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.* **1978**, *82*, 784.
19. R. Gopal, M.A. Siddiqi, *J. Phys. Chem.* **1969**, *73*, 3390.
20. N. Saha, B. Das, *J. Chem. Eng. Data* **1997**, *42*, 227.

Chapter IX:

1. M. Jotanovic, Z. Andric, G. Tadic, V. Micic, *Peer-Reviewed and Open Access Journal*, **2010**, *3*, 15.
2. C. Becker, *Radiologe*, **2007**, *47*(9), 768.
3. F.J. Millero, *Structure Transport Process in Water Aqueous Solutions*, R.A. Horne (Ed.), Wiley, New York **1972**.
4. M.N. Roy, B. Sinha, V.K. Dakua, A. Sinha, *Pak. J. Sci. Ind. Res.* **2006**, *49*, 153.
5. M.N. Roy, P. Pradhan, R.K. Das, P.G. Guha, *J. Chem. Eng. Data* **2008**, *53*, 1417.

6. R. Chanda, M.N. Roy, *Fluid Phase Equilib.* **2008**, 269, 134.
7. H.K. Samanta, D. Engel, *J. Biochem. Biophys. Meth.* **1987**, 14, 261.
8. B. Sinha, V.K. Dakua, M.N. Roy, *J. Chem. Eng. Data.* **2007**, 52, 1768.
9. J.A. Dean, *Lange's Handbook of Chemistry*, 11th ed. McGraw-Hill Book Company, New York **1973**.
10. A. Chatterjee, B. Das, *J. Chem. Eng. Data.* **2006**, 51, 1352.
11. J.E. Lind Jr., J.J. Zwolenik, R.M. Fuoss, *J. Am. Chem. Soc.* **1959**, 81, 1557.
12. M.N. Roy, A. Jha, R. Dey, *J. Chem. Eng. Data.* **2001**, 46, 1327.
13. M.N. Roy, D.K. Hazra, *Indian J. Chem. Technol.* **1994**, 1, 93.
14. R.M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.* **1978**, 75, 16.
15. R.M. Fuoss, *J. Phys. Chem.* **1978**, 82, 2427.
16. J. Barthel, M.B. Rogac, R. Neueder, *J. Solut. Chem.* **1999**, 28, 1071.
17. R.M. Fuoss, T. Shedlovsky, *J. Am. Chem. Soc.* **1949**, 71(4), 1496.
18. M.N. Roy, R. Dewan, D. Ekka, I. Banik, *Thermochimica Acta.* **2013**, 559, 46.
19. R.M. Fuoss and C.A. Kraus, *J. Am. Chem. Soc.* **1933**, 55, 2387.
20. F.J. Millero, A.L. Surdo, C. Shin, *Phys. Chem.* **1978**, 82, 784.
21. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, 51, 2950.
22. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, **1970**.
23. A.M. Cases, ACG Marigliano, C.M. Bonatti, H.N. Solimo, *J. Chem. Eng. Data.* **2001**, 46, 712.
24. D. Papamatthaiakis, F. Aroni, V. Havredaki, *J. Chem. Thermodyn.* **2008**, 40, 107.

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