

ABSTRACT

Ionic solids may be defined as a customary salt in solid state having symmetric cation and anion. Ionic solids are mainly made up by the chemical combination of **metallic** and **non-metallic** elements. "Salt"- a broad chemical expression refers to ionic compounds (ionic solids) created when a reaction between acid and base occurs. The unique properties of ionic solids signify strong forces between the particles and it takes a lot of energy to move them all relative to each other. In case of ionic solid the three dimensional lattice is held together strongly by electrostatic forces of attraction between positive and negative ions. At present, salt extends to be of leading monetary corollary, with thousands of uses in accumulation to senescing and conserving food.

Ionic Liquids (ILs) are liquid salts that consist of combinations of organic/organic or organic/inorganic cation/anions are found a variety of industrial applications, as in chemical industry, pharmaceuticals, cellulose processing, gas handling, gas treatment, solar thermal energy, nuclear fuel processing, food and biproducts, waste recycling, batteries etc. *Amino acids* serve as the building blocks of proteins, peptides, polypeptides, essential for human body, they are used in nutrition supplements, fertilizers, food technology, industry, include the production of biodegradable plastics, drugs, and chiral catalysts.

'*Solution Chemistry*' is an imperative branch of the physical chemistry, which deal the change in properties that arise when one substance dissolves in another substance. The investigation have been done for the solubility of substances and studied how it is affected in both the physical and chemical nature for the solute and solvent. There are three types of approach have been made to estimate the extent of salvation in physical chemistry. The first one is involves the studies of transport properties as viscosity, conductance, diffusion coefficient, ionic mobility etc., of the electrolytes in aqueous and non-aqueous solvents and the derivation of various factors associated with ionic salvation; the second one is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated

with solvation can be explain; and the third one is to use spectroscopic study where the spectral line shifts or the chemical shifts of the functional group of electrolytes or non-electrolytes in solvents has been resolved qualitatively and quantitatively with their nature/mode of interactions.

'*Host-guest chemistry*' majorly describes complexes that are composed of two or more molecules which are held together in unique structural relationships by non covalent interactions. Yet as its innovation, the notion of supramolecular chemistry has concerned plenty of interest from chemists, biologists, and material scientists, where they exploit the noncovalent interactions, together with hydrogen-bonding communication, π - π stacking interface, electrostatic interface, van der Waals force and hydrophobic/hydrophilic attraction. In an emblematic host-guest inclusion complex, a host molecule affords a cavity to encapsulate a guest molecule through noncovalent communications. Due to having a variety of noncovalent interfaces in host-guest complexation, host-guest interaction based on macrocyclic molecules is an extremely imperative incident that has been widely explored. Two or more chemical moieties can be incorporated together during such host-guest inclusion, in a facile and reversible manner which provides immense potential for the edifice of new-fangled supramolecular structures.

In the modern era, there have been increasing interests in the interacting behaviour of electrolytes in aqueous/non-aqueous and mixed solvent systems with the outlook to examining ion-ion or solute-solute and ion-solvent or solute-solvent interactions in various conditions. However, unlike succession of solubility, variation in solvating power and possibilities of physical, chemical or electrochemical reactions, are foreign in aqueous chemistry, have open vistas for physical chemists and interests in these organic solvents transcend the traditional boundaries of physical, inorganic, organic, analytical and electrochemistry etc.

Studies of thermodynamic properties of ionic solids and ionic liquids, based on the considered parameters from physicochemical as well as spectroscopic study, provides valuable information about molecular interactions occurring in solution systems. The

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influence of the ion-solvent interactions is amply huge to reason dramatic changes in chemical reactions involving ions. The changes in ionic solvation by the solvent molecules have vast application in miscellaneous areas, for example organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extraction etc.

Knowledge of various types of interactions in aqueous, non-aqueous solutions and mixed solvents used in industries is very important in many practical problems concerning energy transport, heat transport, mass transport and fluid flow. Besides finding applications in engineering branch, the study is important from practical and theoretical point of view in understanding liquid theory. The non-aqueous systems have been of immense importance to the technologist and theoretician as many chemical processes occur in these systems. This is helpful for scientists in optimal choice of solvents as well as solutes used in industries. Even though solvents studied during the course of my research work have drawn much focus in recent years as solvents for thermophysical investigations, still a lot remains to be explored.

Using mixed solvents in these studies enable the variation of thermophysical properties such as dielectric constant, viscosity, and therefore the ion-ion and ion-solvent interactions could be better studied. Furthermore, the quantities strongly influenced by solvent properties could be derived from concentration dependence of the electrolyte conductivity. Accordingly, a number of conductometric and related studies of different electrolytes in aqueous/nonaqueous solvents, especially mixed organic solvents, have been made for their optimal use in high-energy batteries and for understanding organic reaction mechanisms. Ionic association of electrolytes in solution systems depends upon the mode of solvation, charge distribution, dipole moment, columbic force and electrostriction of its respective ions; which in turn depends on the nature of the solvents/solvent mixtures. The solvent properties such as viscosity and the relative permittivity have been taken into account as these properties helpful in determining the degree of ion-association and the solvent-solvent interactions. Hence, extensive studies on electrical conductance in mixed organic solvents have been

performed to examine the manner and magnitude of ion-ion and ion-solvent interactions.

SUMMARY OF THE WORKS EMPHASIZE IN THE THESIS

CHAPTER-I

This chapter contains the *objective, utility and applications of the research work*, the important solutes and solvents used and methods of investigation. This also occupies the summary of the works done allied with the thesis.

CHAPTER-II

The chapter encloses *the general introduction* of the thesis and forms the strong background of the work embodied in the thesis. A brief review of noteworthy works in the field of molecular as well as ionic interaction has been given. The discussion includes ion-solvent/solute-solvent, ion-ion/solute-solute and solvent-solvent interactions in binary, ternary mixed solvent systems and of electrolytes in pure and non-aqueous solvent systems at various temperatures in terms of various derived parameters, estimated from the experimentally observed thermodynamic properties viz., *density, viscosity, ultrasonic speed, refractive index, conductance and another important properties such as Surface Tension, FTIR Spectroscopy and NMR Spectroscopy*. Several semi-empirical models to estimate dynamic viscosity of binary liquid mixtures have been discussed. Ionic association and its dependence on ion-size parameters as well as relation between solution viscosity and limiting conductance of an ion has been discussed using Stokes' law and Walden rule. Crucial assessment of different methods on the relative merits and demerits on the basis of various assumption employed from time to time of acquiring the single ion values (viscosity *B*-coefficient and limiting equivalent conductance) and their implications have been discussed. The molecular interactions are interpreted based on various derived parameters.

CHAPTER-III

The chapter comprises *the experimental section* which principally involves the basic information, structure, source, purification and uses of the ionic solids, ionic liquids and solvents have been used throughout the entire research work. It also restrains the details of the instruments, procedure, working principle and equations that are employed to understand the thermodynamic, transport, acoustic, optical and spectroscopic properties.

CHAPTER-IV

The chapter deals precise measurements on electrolytic conductivities, densities and viscosities of lithium salts (LiI, LiClO₄ and LiAsF₆) in (0.25, 0.50 and 0.75) mass fraction of acetonitrile (AN) in diethyl carbonate (DEC) at 298.15K. The limiting molar conductivities (Λ^0), association constants (K_A) and the distance of closest approach of the ions (R) have been evaluated using the Fuoss conductance equation (1978). The Walden product are obtained and discussed. However, the deviation of the conductometric curves (Λ versus \sqrt{c}) from linearity for the electrolytes in 0.25 mass fraction of acetonitrile (AN) in diethyl carbonate (DEC) indicated triple-ion formation, and therefore the corresponding conductance data have been analysed by the Fuoss-Kraus theory of triple ions. The observed molar conductivities were explained by the ion-pair ($M^+ + X^- \leftrightarrow MX$) and triple-ion ($2M^+ + X^- \leftrightarrow M_2X^+$, $M^+ + 2X^- \leftrightarrow MX_2^-$) formation. The limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) derived from the Masson equation and viscosity A and B-coefficients using the Jones-Dole equation have been interpreted in terms of ion-ion and ion-solvent interactions respectively.

CHAPTER-V

In this chapter, we present conductivities (Λ), densities (ρ) and viscosities (η) of Hept₄NI in o-Toluidine, o-Xylene and 2-Nitrotoluene at 298.15 K. Limiting molar conductivity (Λ^0), association constant (K_A), distance of closest approach of the ions (R),

for Hept₄NI in 2-Nitrotoluene have been evaluated using the Fuoss conductance equation (1978). The Walden product and Gibb's energy change are obtained and discussed. Deviation of the conductometric curves (Λ versus \sqrt{c}) from linearity for Hept₄NI in o-Toluidine and o-Xylene indicates triple-ion formation, therefore the corresponding conductance data have been analysed by the Fuoss-Kraus theory of triple-ions. Observed molar conductivities have been explained by the ion-pair ($M^+ + X^- \leftrightarrow MX$) and triple-ion ($2M^+ + X^- \leftrightarrow M_2X^+$, $M^+ + 2X^- \leftrightarrow MX_2^-$) formation. Limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) derived from the Masson equation and viscosity A and B -coefficients using the Jones-Dole equation have been interpreted in terms of ion-ion and ion-solvent interactions respectively.

CHAPTER-VI

The chapter embraces Interface properties of an IL, 1-butyl-1-methylpyrrolidinium chloride ([bmp]Cl) in different concentrations of aqueous carbohydrate solutions at diverse temperatures. In spite of having "green solvent" property toxicity of ILs has been revealed. So the interface of ILs with biomolecules is a progressive research topic. Gibbs free energy (ΔG_A^0), enthalpy (ΔH_A^0), entropy (ΔS_A^0) of ion-pair formation, limiting partial molal transfer volumes, $\Delta_v \phi_V^0$ and dB/dT have been determined. Through ¹H NMR study, changes in terms of size and structure of carbohydrates and IL by means of the interaction between IL and biomolecules, the potential toxicity of ILs originate.

CHAPTER-VII

In this chapter precise measurements on electrical conductance of solutions of 1-butyl-1-methylpyrrolidinium bromide in formamide, N, N-dimethyl formamide and N, N-dimethyl acetamide have been studied at 298.15 K. The conductance data have been analyzed by the Fuoss conductance equation (1978) in terms of limiting molar conductance, association constant, and association diameter for ion-pair formation. The

apparent molar volume, viscosity B -coefficient, molar refraction and adiabatic compressibility have also been studied, supplemented from the values of density, viscosity, refractive index and ultrasonic speed respectively, to interpret the ion-ion and ion-solvent interactions. Limiting apparent molar volumes, experimental slopes have been obtained from the Masson equation. The viscosity data have been analyzed using Jones-Dole equation to derive A and B coefficients. Molar refractions have been determined with the help of Lorentz-Lorenz equation and limiting apparent molar adiabatic compressibilities in all three solvents at infinite dilution have been evaluated and discussed. IR study of the functional group of solvents in presence and absence of IL has also been taken into account for interpretation.

CHAPTER-VIII

This chapter involves host-guest inclusion complex construction of an ionic solid (*viz.*, tetrabutyl ammonium iodide) with α and β -cyclodextrins by various physicochemical and spectroscopic methods. Which act as preservative, transporter and regulatory releaser of the guest molecules. Surface tension and conductivity studies proposed 1:1 stoichiometry of the inclusion complexes and ^1H NMR and FT-IR studies substantiate the inclusion phenomenon. Density, viscosity and refractive index studies characterize the interactions of cyclodextrin with ionic salt which also indicates greater extent of encapsulation in case of β -cyclodextrin than that in α -cyclodextrin. Hydrophobic effect, structural effect, electrostatic force and H-bonding interfaces were mainly exploited to explicate the development of inclusion complex.

CHAPTER-IX

In this chapter self assembly of inclusion complexes and interfaces phenomenon of a surface active ionic liquid (SAIL) *n*-dodecyl-*n*, *n*-dimethyl-3-ammonio-1-propanesulfonate (DDAPS) as a guest insight into the favorably fitted host cavity of hollow cylinder oligosaccharides such as α - and β -cyclodextrins in aqueous media, have been characterized and explored on recent research gaining far achievement outcome.

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The interfacial inclusion complex formation have been established with the manifested by surface tension and conductance measurements. These two experimentally determined parameters have been revealed that the formation of 1:1(CD/IL) stoichiometric inclusion complex is suggested itself by IL with α - and β -CDs. The variation of the thermodynamic parameters with guest size and state are used to draw inferences about contributions to the overall binding from the driving forces, viz., hydrophobic and hydrophilic interfaces, van der Waals force, H-bonding, electrostatic force, structural effect and configurational theory.

CHAPTER-X

This chapter presents Electrolytic conductivity, density, viscosity and FTIR study of an ionic liquid, 1-butyl-4-methylpyridinium hexafluorophosphate ([bmpy]PF₆) have been measured in diverse industrially significant solvents viz. acetonitrile, tetrahydrofuran and 1,3 dioxolane at various temperatures. In acetonitrile, the ion-pair formation of the IL was analyzed by Fuoss conductance equation. In Tetrahydrofuran and 1,3 Dioxolane systems, triple-ion formation analyzed by the Fuoss-Kraus theory. Ion-solvent interactions have been inferred in terms of limiting apparent molal volumes and viscosity *B*-coefficients. The results obtained from the experimental study, have been conferred in terms of ion-dipole interactions, structural aspect, configurational theory and solvatochromic effect.

CHAPTER-XI

This chapter contains the concluding remarks of the works related or detailed described in the thesis.