

## ABSTRACT

Ionic liquids have some properties found in polar solvents or in apolar solvent. They were called "green" solvents because they have a very low vapor pressure that minimizes the release of chemical in the atmosphere when they are used as solvent.

Recent years ionic liquids have been using as a new generation of solvents to replace the traditional organic solvents. They are presented as novel solvents for the replacement of organic solvents and the formation of smart liquids. The investigation also proposed nano- and atom-scale structuring of ionic liquids, a feature that appears to totally underpin their unique behavioural characteristics and facilitate accurate predictions of trends.

The exploration of molecular interaction in fluids by physicochemical approaches has attracted attention, as thermodynamic parameters are convenient for interpreting intermolecular interaction patterns in non-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents. The different sequence of solubility, difference in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have open vistas for chemists and interest in the organic solvents transcends the traditional boundaries of physical, inorganic, organic, analytical and electrochemistry.

In '*Solution Chemistry*' broadly three types of approaches have been made 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, the second is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated with solvation can be elucidated, and the third is to use spectroscopic measurements where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature.

The mixing of different solute or solvent with another solvent/solvent mixtures gives rise to solutions that generally do not behave ideally. This deviation from ideality is expressed in terms of 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. In particular, they 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. The extent of ion-solvation is dependent upon the interactions taking place between solute-solute, solute-solvent, solvent-solvent species. The assesment of ion-pairing in these systems is important because of its effect on the ionic mobility and hence on the ionic conductivity of the ions in solution. These phenomenon thus paves the path for research in solution chemistry to elucidate the nature of interaction through experimental studies involving densitometry, viscometry, interferrometry, refractometry and other suitable methods and to interpret the experimental data collected. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute, solute-solvent and solvent-solvent

interactions are elucidated and thus the present research work is intimately related to the studies of solute-solute, and solvent-solvent interactions in some industrially important liquid systems.

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

## **A.1 CHOICE AND IMPORTANCE OF ELECTROLYTES/SOLUTES AND SOLVENTS USED**

### ***A.1.1 Ionic liquids, electrolytes and non-electrolytes***

The ionic liquids, electrolytes and non-electrolytes used in the research work are

#### **A.1.1.1 Ionic liquids**

The most noteworthy ionic liquids have been used as electrolytes during the research work are

- (a) 1-Butyl-2,3dimethylimidazoliumtetrafluoroborate
- (b) 1-Butyl-pyridinium bromide
- (c) Tetrabutylphosphonium methanesulfonate
- (d) 1-Methyl-3-octyl imidazolium chloride
- (e) N-Butyl-4-methylpyridinium chloride

### **A.1.1.2 Electrolytes**

tetrabutylammonium tetraphenylborate

### **A.1.1.3 Non-electrolytes**

- a. Amino acids, viz. glycine, L-alanine, L-valine
- b.  $\beta$ -cyclodextrin

### **A.1.2 Solvents**

The universal solvent water has been used throughout the work and the non-aqueous solvent e.g., Methyl cellosolve, Tetrahydrofuran, 1,4 Dioxane, Nitromethane, N,N-dimethylacetamide, Formamide, Methanol, Acetonitrile, and aqueous solution of 1-butylpyridinium bromide([BPy]Br) and Beta-Cyclodextrin.

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

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

To make use of different experimental techniques to get a better approaching into the phenomena of solvation and different interactions prevailing in solution systems. So, I have tried to employ some important physicochemical methods, namely, *Densitometry*, *Ultrasonic Interferometric*, *Surface chemistry (surface tension)*; transport properties *viz.*, *Viscometric*, *Conductometric*; optical property *Refractometric* and spectroscopic properties *FTIR*, *UV-Visible* and *NMR Spectroscopic* method to examine, probing, exploring of various interactions occurring in the solution systems.

### A.3 PHYSICO-CHEMICAL PARAMETERS AND THEIR SIGNIFICANCE

Apparent molar volume ( $\phi_V^0$ ) is estimated from experimental density values. The sign and magnitude of apparent molar volume ( $\phi_V^0$ ) provides information about the nature and magnitude of ion-solvent interaction while the experimental slope ( $S_V^*$ ) provides information about ion-ion interactions.

Viscosity  $B$ -coefficients are another tool gives the useful scheme of ion-solvent interaction, estimated from experimental viscosity values.

From experimental speed of sound values, deviation in isentropic compressibility ( $\beta_s$ ), limiting apparent molar isentropic compressibility ( $\phi_k^o$ ) and the experimental slope  $S_k^*$  can be estimated. These parameters also give an idea about the ion-solvent and ion-ion interaction in the solution.

The optical property as refractive index and spectroscopic property as FTIR spectroscopy is are used as supporting parameters to confirm the interaction occurring in the solution systems.

Limiting molar conductance ( $\Lambda_0$ ) obtained from specific conductance as well as molar conductance gives a central idea about the ion-solvent interaction the solution. More the magnitude of conductance of the solution less is the ion-solvent interaction. Another parameter obtained from the conductance study i.e. association constant ( $K_A$ ) gives an idea about the solvation of the ions by the solvent molecules.

## A.4 SUMMARY OF THE WORKS EMPHASIZE IN THE DISSERTATION

### **CHAPTER-I**

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

### **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 physicochemical properties viz., *density, viscosity, ultrasonic speed, refractive index and conductance*. 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's, structure, source, purification and uses of the ionic liquids, electrolytes/non-electrolytes or solutes, and solvents have been used throughout the entire research work. It is also restrains the details of the instruments, procedure, working principle and equations that are employed to understand the thermophysical/thermodynamic, transport, acoustic, optical and spectroscopic properties.

### **CHAPTER-IV**

The chapter deals with precise measurements of electrolytic conductivities, densities, viscosities, and FT-IR studies of 1-butyl-2,3 dimethylimidazolium tetrafluoroborate ([bmmim][BF<sub>4</sub>]) in Tetra hydro furan, Dimethyl acetamide and Methyl Cellosolve at different temperatures. The limiting molar conductivities, association constants, and the distance of closest approach of the ion have been evaluated using the Fuoss conductance equation (1978). The molar conductivities observed were explained by the formation of ion-pairs and triple ion formation. Ion-solvent interactions have been interpreted in terms of apparent molar volumes and viscosity *B*-coefficients which are obtained from the results supplemented with densities and viscosities, respectively. The limiting apparent molar volumes, experimental slopes 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. However, the deviation of the conductometric curves (*A* vs  $\sqrt{c}$ ) from linearity in tetrahydrofuran indicated triple-ion formation and therefore corresponding conductance data have been analyzed by the Fuoss-Kraus theory of triple-

ion. The limiting ionic conductances have been estimated from the appropriate division of the limiting molar conductivity value of tetrabutylammonium tetraphenylborate as the "reference electrolyte" method along with a numerical evaluation of ion-pair and triple-ion formation constants ( $K_P \approx K_A$  and  $K_T$ ). The FT-IR spectra for the solvents as well as the solute in solvent have also been studied. The results have been discussed in terms of ion-dipole interactions, hydrogen bonds formation, structural aspect, and configurational theory.

#### **CHAPTER-V**

This chapter discuss the experimental data evaluated from surface tension and conductance and with the evidence of those results the formation of inclusion complexes of  $\beta$ -Cyclodextrin with an Ionic Liquid, viz. N-butyl-4-methylpyridinium chloride ([C<sub>4</sub>mpy]Cl) in aqueous media have been reported. The limiting apparent molar volume, viscosity *B*-coefficient and limiting molar refraction have been studied to derive the appropriate parameters for the formation of inclusion complexes prevailing in the investigated solvent systems.

#### **CHAPTER-VI**

The chapter consists of the quantitative and qualitative analysis of molecular interactions prevailing in the ionic liquid tetrabutylphosphonium methanesulfonate [Bu<sub>4</sub>PCH<sub>3</sub>SO<sub>3</sub>] in aqueous (H<sub>2</sub>O) and non-aqueous solvents, i.e., acetonitrile (CH<sub>3</sub>CN), methanol (CH<sub>3</sub>OH), nitromethane (CH<sub>3</sub>NO<sub>2</sub>), and formamide (HCONH<sub>2</sub>) probed by precise measurements of electrical conductance ( $\lambda$ ) and FTIR spectroscopy respectively at 298.15K and atmospheric pressure. The conductance data have been analyzed by the Fuoss



conductance equation (1978) in terms of the limiting molar conductance ( $\Lambda_0$ ), the association constant ( $K_A$ ), and the association diameter ( $R$ ) for ion-pair formation. The limiting ionic conductance ( $\lambda_o^\pm$ ) of the ions ( $\text{Bu}_4\text{P}^+$  and  $\text{CH}_3\text{SO}_3^-$ ) have been estimated from the appropriate division of limiting molar conductance of tetrabutylammonium tetraphenylborate [ $\text{Bu}_4\text{NBPh}_4$ ] as "reference electrolyte" method along with a numerical evaluation of ion-pair formation constant. The molecular as well as ionic association have been discussed in terms of ion-dipole interactions, H-bonding formation, structural aspect, and configurational theory. The FTIR spectroscopic studies of the variational intensity of characteristic functional group of the solvents have been undertaken and the solvation phenomenon is evident by the shifting of the band intensity in presence of the ionic liquid.

## **CHAPTER-VII**

This chapter embraces the solute-Solvent interactions prevailing in  $\alpha$ -amino acids (glycine, L-alanine, L-valine) and aqueous solution of 1-butylpyridinium bromide([BPy]Br) by physico-chemical properties. The apparent molar volume ( $\phi_V$ ), viscosity B-coefficient, molal refraction ( $R_M$ ) and adiabatic compressibility ( $\phi_K$ ) of glycine, L-alanine, and L-valine have been studied in 0.001, 0.003, 0.005 mol  $\text{dm}^{-3}$  aqueous 1-butylpyridinium bromide([BPy]Br) solutions at 298.15 K from the values of densities ( $\rho$ ), viscosities( $\eta$ ), refractive index ( $n_D$ ) and speed of sound ( $u$ ) respectively. The limiting apparent molar volumes ( $\phi_V^0$ ), experimental slopes ( $S_V^*$ ) obtained from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The viscosity data were analyzed using the Jones-Dole equation, and the derived parameters A and B have also been interpreted in terms of solute-solvent and solute-solute interactions,

respectively in the mixed solutions. Molal refractions ( $R_M$ ) have been calculated using the Lorentz-Lorenz equation and discussed. The role of the solvent (aqueous ionic liquid solution) and the contribution of solute-solute and solute-solvent interactions to the solution complexes have also been analyzed through the derived properties.

### **CHAPTER-VIII**

Exploration of inclusion behaviour of a guest ionic liquid (IL) 1-methyl-3-octylimidazolium chloride into the host cavity of  $\beta$ -cyclodextrin in aqueous solution has been studied in this chapter. Surface tension and Conductivity measurements results showed that 1:1 hosts-guest inclusion complex is formed and favourable with the above system. The formation and nature of the inclusion complex has been also characterized using job method by ultraviolet spectroscopy and association constants has been evaluated for the formed inclusion complex by ultraviolet spectroscopy. The inclusion phenomenon has been confirmed by proton NMR study.

### **CHAPTER-IX**

Electrolytic conductivities, densities, viscosities, refractive index and FT-IR studies of 1-butyl-pyridinium bromide ([bupy]Br) have been reported in this chapter in 1,4 Dioxane, Tetrahydrofuran, and Acetonitrile at different temperatures. The molar conductivities observed were explained with the manifestation of the formation of ion-pairs and triple ion formation. The limiting ionic conductances have been estimated from the appropriate division of limiting molar conductance of tetrabutylammonium tetraphenylborate as "reference electrolyte" method along with a numerical evaluation of ion-pair and triple-ion formation constants ( $K_P \approx K_A$  and  $K_T$ ). Ion-solvent interactions have been interpreted in

terms of apparent molar volumes, viscosity  $B$ -coefficients and molar refraction which are obtained from the results supplemented with densities, viscosities and refractive index respectively. The FT-IR spectra of the solvents as well as solutions have also been studied. The results have been discussed in terms of ion-dipole interactions, structural aspect and configurational theory.

### ***CHAPTER-X***

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