

## CHAPTER- X

### CONCLUDING REMARKS

In my research work, described in this thesis, I have tried to investigate the solution properties of some biologically-active solutes and ionic salts in some aqueous and non-aqueous industrially important liquid systems respectively in terms of various interactions such as solute-solute/ion-ion, solute-solvent/ion-solvent and solvent-solvent of some compounds. Molecular interactions have been examined with the help of thermodynamic and transport properties of solutions. Systematic study made on these properties has great importance in gaining a better knowledge of these interactions. Such study will find importance in chemical engineering areas especially to understand the mixing behaviour of different components in the mixture.

The volumetric, viscometric, interferometric, conductometric and refractive index studies helped us to evaluate the extent of molecular interaction in a particular solution quantitatively whereas the FT-IR measurements gave an insight into the type of molecular interaction occurring in any given systems. Various types of interactions exist between the ions in solutions, and of these, ion-ion and ion-solvent interactions are of current interest in all branches of chemistry. These interactions help in better understanding the nature of solute and solvent, that is, whether the solute modifies or distorts the structure of the solvent.

Different quantities strongly influenced by solvent properties could be derived from concentration dependence of the electrolyte conductivity. Consequently, a number of conductometric and related studies of different electrolytes in non-aqueous solvents, have been made for their optimal use in high-energy batteries and for understanding organic reaction mechanisms. Ionic association of electrolytes in solution depends upon the mode of solvation of its ions, which in turn depends on the nature of the solvent or solvent mixtures. Such solvent properties as viscosity and the relative permittivity have

been taken into consideration as these properties help in determining the extent of ion association and the solvent-solvent interactions.

In Chapter IV, after a thorough investigation of apparent molar volume, viscosities, limiting partial isentropic compressibility, viscosity  $B$ -coefficient and molar refraction of some amino acids (biologically-active solutes) like glycine, L-alanine and L-valine in different concentration of aqueous ascorbic acid solution (vitamin-C) at 298.15 K, reveals the fact that the presence of strong solute-solvent interactions which increases with the increase of the mass fractions of ascorbic acid in aqueous mixture. The size and number of carbon atoms of the alkyl chain groups of the amino acids also play a pivotal role in determining the nature and strength of the interactions in these solvent media.

In Chapter V, the behaviour of carbohydrates (D-glucose, D-mannitol and D-sucrose) in aqueous binary solutions of nicotinic acid (NA) was observed at 298.15, 308.15, and 318.15 K temperature from volumetric, viscometric and refractometric measurements. Nicotinic acid is an important compound which plays a crucial role in various physiological effects, biosynthesis, metabolic reactions, and several drug preparations. This study indicates the presence of strong solute-solvent and weak solute-solute interactions and these interactions are further strengthened at higher temperatures and higher concentration of nicotinic acid in the ternary solutions. Here carbohydrates under investigation act as a structure breaker when added to aqueous NA solution.

In chapter VI, the extensive study of Tetrabutylphosphonium tetrafluoroborate  $[Bu_4PBF_4]$  in dimethyl sulfoxide (DMSO), N,N-dimethyl acetamide (DMA) and N,N-dimethyl formamide (DMF) at 298.15 K through conductometric measurements. From the experimental measurements we have seen that the limiting molar conductance of  $[Bu_4PBF_4]$  in DMF is greater than that in DMA and DMSO, and the association constant ( $K_A$ ) of the electrolyte is greater in DMSO than in DMA than in DMF. Hence, this shows that there is more ion-solvent interaction in DMSO than that in the other two solvents. The reliable value of volumetric, viscometric and interferometric studies also suggests that in solution there is more ion-solvent interaction than the ion-ion interaction.

Qualitative and quantitative analyses of molecular interaction prevailing in ionic liquid [Bu<sub>4</sub>PMS] in dimethyl sulfoxide (DMSO), N,N-dimethyl acetamide (DMA) and N,N-dimethyl formamide (DMF), probed by electrical conductance and FT-IR measurements have been reported in chapter VII. In this chapter the extent of interaction is expressed in terms of the association constant ( $K_A$ ) and shows the ion-dipole interaction to be a function of viscosity and the FT-IR measurements were supplemented to explain the ion-dipole interaction in the solution. It was seen that the conductance of [Bu<sub>4</sub>PMS] was highest in case of dimethylformamide (DMF) in comparison to the other solvents. Greater ion-solvent interaction of the salt was seen in dimethylsulfoxide (DMSO). It can also be seen that in the conductometric studies in DMSO, DMA and DMF, the electrolyte remains as ion-pairs. The ionic conductivity value suggests the fact that the anions (MS<sup>-</sup>) conduct more than the cation [Bu<sub>4</sub>P<sup>+</sup>]. The diffusion coefficient and ionic mobility also show that in studied ionic liquid, the anions diffuse more due to high ionic mobility compared to cation because the size of the anion is smaller than that of the cation. In all the solvents, the electrolyte forms ion-dipole interactions as evidenced by the FT-IR studies.

Chapter VIII dealt with solvation behaviour of tetrabutylammonium tetrafluoroborate [Bu<sub>4</sub>NBF<sub>4</sub>] in acetonitrile (CH<sub>3</sub>CN), methanol (CH<sub>3</sub>OH), dimethyl sulfoxide (DMSO) and 1,3-dioxolane(1,3-DO) at 298.15 K which was realised by conductometric study. The observed molar conductivities were explained by the formation of ion-pairs ( $M^+ + X^- \leftrightarrow MX$ ) and triple-ions ( $2M^+ + X^- \leftrightarrow M_2X^+$ ;  $M^+ + 2X^- \leftrightarrow MX_2^-$ ). From the study we get a clear idea that the electrolyte was more solvated by DMSO than other three solvents. During the conductometric studies triple-ion formation was seen in case of 1,3-dioxolane and the major portion of electrolyte was exists as ion-pairs in CH<sub>3</sub>CN, CH<sub>3</sub>OH and DMSO. The classical Fuoss-Kraus theory of triple-ion formation which occurs in low dielectric solvent was found to be valid in the study. The tendency of the ion-pair and triple-ion formation of electrolyte depends on the size and charge distribution of the ions.

Chapter IX quantifies the precise measurements on electrical conductance of tetrabutylammonium tetrafluoroborate [Bu<sub>4</sub>NBF<sub>4</sub>] and tetrabutylammonium

perchlorate  $[Bu_4NClO_4]$  in nitromethane, N-methylformamide, and formamide at 298.15 K. From the experimental data it is evident that the conductance for the electrolytes is highest in the case of nitromethane and lowest in the case of formamide. Among the two electrolytes,  $[Bu_4NBF_4]$  is associated most with the studied solvents, and the highest association is seen between  $[Bu_4NBF_4]$  and formamide. This illustrates that the electrolytes are solvated more by formamide, due to its highest viscosity value among the studied solvents. It is also seen that, with an increase in the size of the anion, the extent of salvation also increases. The present study also reveals that the greater share of the conductance holds the  $[Y]^-$  ion than the  $[Bu_4N]^+$  as clear from their ionic conductance values. In all of the investigated solvents, the electrolytes shows ion-dipole interactions observed from the FT- IR and conductance studies.

The volumetric behaviour of solutes has been proven to be very useful in elucidating the various interactions occurring in aqueous and nonaqueous solutions. Studies on the apparent and partial molar volumes of electrolytes and the dependence of viscosity on concentration of solutes and temperature of solutions have been employed as a function of studying ion-ion and ion-solvent interactions. It has been found that the addition of electrolyte could either break or make the structure of a liquid. Because a liquid's viscosity depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at different concentrations and temperatures.

More extensive studies of the different thermodynamic and transport properties of the electrolytes will be of sufficient help in understanding the nature of the ion-solvent interactions and the role of solvents in different chemical processes.

The proper understanding of the ion-ion and ion-solvent interactions may form the basis of explaining quantitatively the influence of the solvents and ions in solution and thus pave the way for real understanding of different phenomena associated with solution chemistry. However, it is necessary to remember that molecular interactions are very complex in nature. There are strong forces existing in the molecule and it is not really possible to separate them all. Nevertheless, if careful judgement is used, valid

conclusions can be drawn in many cases relating to degree of structure and order of the system.

To conclude it may be stated that extensive studies of the different physico-chemical, biological or pharmaceutical activity between different components of a given mixture will be of immense help in understanding the nature of the different interactions prevailing in mixed systems. The proper understanding of the ion-ion and ion-solvent interactions may form the basis of explaining quantitatively the influence of the solvents and ions in solution and thus pave the way for real understanding of different phenomena associated with solution chemistry.