

CHAPTER - X

CONCLUDING REMARKS

In this thesis, I have studied the molecular as well as ionic interaction on ionic liquids and amino acids in some liquid systems. The molecular interactions occurring in the solution systems have been studied with the help of thermophysical, thermodynamic, transport and optical properties along with FTIR spectroscopic studies.

The research reported in this dissertation explains the procedures and results as well as the studies of the molecular interactions that have been carried out on ionic liquids and amino acids. The overall goal of initiating an understanding of the structure property relationship of ionic liquids has been reached. This was done through work on several ionic liquids differing mainly in their cationic and anionic parts. By looking at thermophysical, thermodynamic and transport properties of these materials, a more complete knowledge of phosphonium, ammonium, imidazolium, pyridinium and pyrrolidinium -based ionic liquids and simple α -amino acids was achieved.

The volumetric, viscometric, interferometric, conductometric refractive index studies helped us to evaluate the extent of molecular interaction in a particular solution quantitatively whereas the FTIR measurements gave an insight into the type of molecular interaction occurring in any solution 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.

Mixed solvents enabled the variation of properties such as dielectric constant or viscosity, and therefore the ion-ion and ion-solvent interactions occurring in the solutions systems could be better understood. Moreover, different quantities strongly influenced by solvent properties could be derived from concentration dependence of the electrolytic conductivity. Consequently, a number of conductometric and related studies of different electrolytes in 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 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. Thus, extensive studies on electrical conductance in mixed organic solvents have been performed to examine the nature and magnitude of ion-ion and ion-solvent interactions.

Thus the discussion of the molecular interaction throughout the dissertation has been concluded **chapter** wish as follow:

The present *Chapter IV*, reveals an extensive study on the ion-solvation behaviour of the tetrabutylphosphonium tetrafluoroborate [Bu₄PBF₄] in ACN + THF, ACN+1,3-DO, and THF+1,3-DO mixtures through the conductometric measurements. It becomes clear that the electrolyte exists as ion-pairs for former two cases and as triple-ions for latter one. The tendency of the ion-pair and triple-ion formation depends on the size and the charge distribution of the ions. The effective size of the electrolyte increases in THF, 1,3-DO and their binary mixtures due to preferential solvation in such a way that the sizes of the solvated ions follow their crystallographic radii. The degree of ion-solvent interaction also indicates that the salt prefers cyclic ether THF and 1,3-DO than ACN in their solvation or coordination sphere.

In *Chapter V* the extensive qualitative and quantitative analysis on the ion-solvation phenomenon of the typical 1-ethyl-3-methylimidazolium based ionic liquids {[emim][Y]; where Y= NO₃⁻, CH₃SO₃⁻ and Tos⁻} in industrially important non-aqueous polar solvents acetonitrile (CH₃CN), methanol (CH₃OH), nitromethane (CH₃NO₂), methylamine solution (CH₃NH₂) with the help of conductometric and FTIR measurements. Precise examine on all the observed conductometric consequence, it has been obvious that studied ionic liquids (ILs) exists as ion-pair in acetonitrile, methanol, nitromethane, and as triple-ion in methylamine solution. The ionic size, the charge distribution of the anions (NO₃⁻, CH₃SO₃⁻ and Tos⁻) for the common cation ([emim]⁺), and structural aspects, i.e: functional group of the solvents, are the key factor in formation of ion-pair and triple-ion. The decreasing tendency of the transport properties as fluidity, diffusion coefficient (D_{\pm}) and ionic mobility (i_{\pm}) from acetonitrile to nitromethane for ions {[emim]⁺, NO₃⁻, CH₃SO₃⁻ and Tos⁻}, suggests the greater extent of ion-solvent interaction or ion-association in nitromethane than the other two studied solvents. For a particular solvent the order of ion-association of anions for the common cation [emim]⁺ are as follow:



In all the chosen solvents, the selected ionic liquids interact with hydrogen bonding and ion-dipole interactions as evident from the FTIR spectroscopic studies. After all, it is very clear to state that the ion-solvent interactions dominant over the ion-ion interactions. All the derived parameters determined by analyzing different valid equations enhancement with experimental data uphold the same climax as discussed and explained in this text, which challenging the distinctiveness of the effort and such information is particularly pertinent to the design of the appropriate (IL+molecular solvent) binary system for a diligent application.

In summary, ϕ_V^0 and viscosity B -coefficient values for citric acid indicate the presence of strong solute-solvent interactions, and these interactions are further strengthened at higher temperatures and higher concentrations of cetrimonium bromide in the ternary solutions has been reported in the **Chapter VI**. Also, citric acid was found to act as a structure breaker in the ternary mixtures studied, and cetrimonium bromide has a dehydration effect on the hydrated citric acid.

The present **Chapter VII**, deals the extensive study of physicochemical properties of the ionic liquid tetrabutylphosphonium tetrafluoroborate in 1,3-DO, THF, AN and their binaries shows that the ion association of the investigated ionic liquid and the solvent mixtures is greater in 1,3-DO, than in THF which is, in turn, greater than that in AN. The reliable value of volumetric, viscometric and interferometric studies also suggests the ion-solvent interaction dominates over the ion-ion interaction in solutions.

In **Chapter VIII**, 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 of in the number of carbon atoms of the studied amino acids in methanoic acid. The refractive index and the molar refraction values suggest that L-leucine molecules are more tightly packed in the solution leading to higher solute-solvent interaction than the other studied amino acids.

The **Chapter IX** disclose the extensive study of thermophysical and thermodynamic properties of simple amino acids in aqueous β -CD binary mixture were done. It is evident that the association of the investigated amino acids, the L-valine is greater than L-alanine which is, in turn, greater than that glycine. The reliable values of derivative obtained from the studies of thermophysical properties suggest that the solute-solvent interaction is dominant over the solute-solute interaction in solutions.

The structural effect of β -CD gives the favourable support in the molecular interaction with retention of configuration. Above all this study demands a novelty of some amino acids prevailing in the aqueous solutions of β -CD.

More extensive studies of the different thermophysical, 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 study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics and industrial products etc. is essential for confirming that their viscosity is appropriate for the contemplated used of the products.

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.

In the near future we endeavour to extend our research work with ionic liquids which I hope will certainly compliment our present findings. In recent years, with the advent of new synthetic technologies such as catalytic symmetric/asymmetric synthesis, phase transfer catalysis, and catalysis, the diversity of molecular interactions that can be studied has increased to the highest degree. I hope this thesis provides a substantial launching point for the reader to begin their own investigation into the chemical natures of remarkable, however natural amino acids and ionic liquids. As more and more interesting and unusual ionic liquids (ILs) and amino acid ionic liquids (AAILs) are discovered, the possibility for development of synthetic methods for these useful in academic, research area, industry and biologically important ionic liquids and amino acids grows up as well.