

CHAPTER-VIII

CONCLUDING REMARKS

The main objective of the work embodied in this thesis was to investigate various molecular interactions such as solute-solute, solute-solvent and solvent-solvent interactions prevailing in aqueous, non-aqueous and mixed solvent systems in various concentration regions.

In Chapter IV-A, a thorough investigation of apparent molar volume, viscosities, apparent molal isentropic compressibility, transfer of volume, transfer of compressibility, number of hydrated molecules and the viscosity *B*-coefficient of glycine, L-alanine, L-valine and L-leucine in different concentration of resorcinol solutions at 298.15 K, reveals the fact that the partial molar quantities of amino acids increase with the increase of concentration of resorcinol. The contribution of the zwitterions (NH_3^+ , COO^-) group to the value of the partial molar volumes is larger in comparison to the (CH_2) group in the studied amino acids and increases with the increasing concentration of resorcinol solution. The study reveals that although ion-ion or hydrophilic-hydrophilic group interactions are predominant for glycine and L-alanine, ion-hydrophobic or hydrophobic-hydrophobic group interactions are predominant for L-valine and L-leucine in aqueous resorcinol solutions. These interactions are a function of the molality of resorcinol in the ternary solutions. Also, it is evident that resorcinol has a dehydration effect on these amino acids in aqueous resorcinol solutions. 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 IV-B, we have studied the ion-solvent and ion-ion interactions of tetra n-butylammonium bromide (TBAB) in (0.00, 0.05, 0.10 and 0.15) mol·dm⁻³ aqueous ascorbic acid solutions at temperatures over the range (298.15 to 318.15) K. The study reveals the presence of strong ion-solvent and weak ion-ion

interactions. The ion-solvent interactions are further strengthened at higher temperature and increased amount of ascorbic acid in the mixtures, suggesting larger electrostriction and absence of 'caging/packing effect'. TBAB predominantly acts as a structure maker due to hydrophobic hydration in the presence of ascorbic acid and ascorbic acid has a dehydration effect on the hydrated TBAB.

In Chapter IV-C, the behaviour of nicotinamide in aqueous binary solutions of citric acid monohydrate was observed at different temperatures. Nicotinamide is an interesting molecule containing two nitrogen atoms- one in the heterocyclic ring and the other as the amide group. This study indicates the presence of strong solute-solvent interactions and these interactions are further strengthened at higher temperatures and higher molarity of citric acid monohydrate in the ternary solutions. Nicotinamide also acts as a water-structure promoter due to hydrophobic hydration in the presence of citric acid monohydrate. This structure-promoting propensity of nicotinamide may also be assigned to the presence of its - CONH₂ group. It is, however, interesting to note that citric acid monohydrate has dehydration effect on the hydrated nicotinamide.

In Chapter V-A, the excess/deviation properties of the binary mixtures of acrylonitrile with cinnamaldehyde, anisaldehyde, and benzaldehyde was studied at 298.15, 308.15, and 318.15K under atmospheric pressure. The study of mixtures of acrylonitrile in various solvents is of interest because of its wide use as an important industrial monomer for polyacrylonitrile, as well as for investigating the effect of the simultaneous presence of the C=C double bond and the polar nitrile C≡N group on the molecular interactions. The study reveals that acrylonitrile behaves differently towards the binary mixtures depending on the different substitution and nature of the mixing components. The strength of specific interaction for the binaries follows the order: acrylonitrile + benzaldehyde > acrylonitrile + cinnamaldehyde > acrylonitrile + anisaldehyde.

In Chapter V-B, the studies for the ternary systems consisting of eight ternary mixtures of tetrahydrofuran (THF), dimethylsulphoxide (DMSO) and monoalkanols: methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), 1-

butanol (1-BuOH), 2-butanol (2-BuOH), amyl alcohol (AmOH), *i*-amyl alcohol (*i*-AmOH) at 298.15 K under atmospheric pressure revealed that the derived excess/deviation properties are quite systematic and functions of the composition of the ternary mixtures. From the experimental measurements of we get a clear idea about the type and amount of molecular interactions between them and also throw light on antagonism and antagonistic index I_A , which are derived by the equations developed by Kalentunc-Gencer and Peleg and Howell, respectively. The explanation of this behavior is based on the known phenomenon of molecular dissociation, as a consequence of weakening the non-covalent bonding formed between the molecules producing a decrease in size of the molecular package. The strength of specific interaction for the ternaries follows the order: (THF) + (DMSO) + MeOH > EtOH > 2-PrOH > 1-PrOH > 2-BuOH > 1-BuOH > *i*-AmOH > AmOH. The similarity in the working formula of antagonistic interaction index and viscosity deviation would probably indicate that the two properties are similar but a close comparison between these two parameters has given the clear distinction.

In Chapter VI-A, an extensive study was done on the behavior of the tetraalkylammonium bromides, (R_4NBr) viz. tetra *n*-butylammonium bromide (Bu_4NBr), tetra *n*-pentylammonium bromide (Pen_4NBr), tetra *n*-hexylammonium bromide (Hex_4NBr) and tetra *n*-heptylammonium bromide (Hep_4NBr) in THF + C_6H_6 mixtures with 10, 20, 30 and 40 mass percent of C_6H_6 at 298.15 K through conductometric measurements. It becomes clear that major portion of the electrolyte exists as ion-pairs with a minor portion as triple-ions. The tendency of the ion-pair and triple-ion formation of R_4NX depends on the size of the ions. Further, it was found that Hep_4NBr had the tendency to form maximum amount of triple-ions and minimum number of ion-pairs in different binary solvent mixtures of THF + C_6H_6 as compared to the other electrolytes.

In Chapter VI-B, precise measurements on electrical conductances of tetraalkylammonium iodides, R_4NI ($R = n$ -butyl to *n*-heptyl) in different mass % (0-100) of dichloromethane (DCM) + *N,N*-dimethylformamide (DMF) at 298.15 K have been performed. In a particular solvent mixture the limiting molar conductances Λ_0 ,

of the electrolytes under investigation decreases as the size of the alkyl group increases, in contraposition to the conductance behaviour of the alkali metal cations, as tetraalkylammonium salts are characterized by their low surface charge density. There is a marked characteristic behaviour in the K_A values. The K_A for all salts increases as the concentration of DCM increases in the mixture, which supports significant association. The results further indicate that the Coulombic forces play a major role in the ion association processes. These electrolytes solutions, in general, show an increase in the association constant values with an increase in concentration of DCM in the solvent mixtures. Further, the effect of concentration of DCM on limiting equivalent conductance of tetraalkylammonium ions is less pronounced as compared to that of the alkali metal ion in the present mixed solvent media.

In Chapter VII, study of Fourier Transform Infra Red (FTIR) spectra of tetra n-pentylammonium bromide (Pe_4NBr), tetra n-pentylammonium iodide (Pe_4NI), tetra n-hexylammonium bromide (He_4NBr), tetra n-hexylammonium iodide (He_4NI), tetra n-heptylammonium bromide (Hp_4NBr) and tetra n-heptylammonium iodide (Hp_4NI) in pure acrylonitrile at various concentrations revealed that the structure-making effect increases with decrease in size of the cations as it increases the charge to surface density. When the ionic charge predominates by a considerable amount, electrostriction occurs in which solvent molecules are immobilized to a considerable extent around the ion to form a solvation sheath. The smaller cations and the larger anions with large charge-surface ratios are less effective as structure-breakers and act as good structure-makers. Electrostriction causes decrease in volume, so smaller ions are effectively more solvated. It thus supports the fact that ion-solvent association with the cationic nitrogen of the tetraalkylammonium halides is an important mechanism of relaxation in the non-aqueous medium of acrylonitrile. Henceforth, Pe_4N^+ and I^- may be considered as the most effective structure makers in acrylonitrile.

Most of the present day knowledge on non-aqueous solutions have come from studies on various thermodynamic properties, e.g., density, transport

properties, e.g., viscosity, conductance as well as acoustic properties, e.g., ultrasonic speed. It, however, is necessary to remember that molecular interactions are very complex in nature and quite difficult to explore and interpret. Numerous forces may operate between the molecules in a solvent mixture and it is really hard to separate and assign them all. Nevertheless, if careful experimental technique and methodology is used, valid conclusions may be drawn related to nature of structure and order of the systems in solution phase.

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, ion-solvent and solvent-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.

