

CHAPTER XIII

Concluding Remarks

The aim of the works embodied in this thesis was to investigate the viscous synergy and antagonism and various type of interactions prevailing in mono, binary and ternary solvent systems.

After a thorough study in chapter IV, of the behavior of monoalkanols on aqueous DMF solution, we get a clear idea about the type and amount of molecular interactions between them and also given us an idea about synergy. The lower monoalkanols are found to associate more with others molecules whereas self-association between the alcohol molecules was found to increase with increasing chain length.

After a thorough study in chapter V, of the behavior of some ether on DMF + C₆H₆ mixtures we get a clear idea about the type and amount of molecular interactions between them and also given us an idea about antagonism. 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. It also seen that though there is a 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.

An extensive study was done in chapter VI, on the behavior of the tetraalkylammonium halides in THF + CCl₄ mixtures through conductometric measurements. It becomes clear that a 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 R₄NX depends on the size and the charge distribution of the ions. Further, it was found that Oct₄NCl had the highest amount of triple-ions and the lowest number of ion-pairs formed in different binary solvent mixtures of THF + CCl₄ as compared to the other electrolytes.

The study in chapter VII revealed that proteins are complex molecules and their behaviour in solutions is governed by a combination of many specific interactions. To

study the interactions in systems containing smaller biomolecules, such as amino acids, 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.

The study in chapter VIII revealed that for ammonium, sodium and potassium ions, the Stokes' radii are much higher than their crystallographic radii suggesting that these ions are significantly solvated in both aqueous THF and aqueous 1,3 DO solvent mixtures. The Stokes' radius of the thiocyanate ion is, however, found to be either very close to or smaller than their corresponding crystallographic radii. This observation indicates that this ion is scarcely solvated in both solvent mixtures. This also supports our earlier contention, derived from the Walden products of those ions. It also shown that the aqueous THF mixtures have higher ΔG° than aqueous 1,3 DO mixtures. This indicates greater degree of ion-pair formation and lower extent of association in presence of THF molecules, attributing to its higher D than 1,3 DO. The results further indicate that the coulombic forces play a major role in the ion association processes.

In chapter IX an attempt has been made to reveal the nature of various types of interactions prevailing in solutions of some sulphate salts in formamide + water mixtures. The sulphates under investigation were found has a positive value of $(\delta^2 V_\phi^\circ / \delta T^2)_p$, indicating all are structure maker in the given mixture. Also the compressibility data indicated electrostriction of the solvent molecules around the cations.

Study of electrical conductances of some tetraalkylammonium halides have been measured in chapter X indicate that Hep_4NBr had the highest amount of triple-ions and the lowest number of ion-pairs formed in different binary solvent mixtures of THF + C_6H_6 as compared to the other electrolytes. It is observed for all the salts in all solvent composition that the amount of triple-ions in the solution mixture increases with the increase in concentration of the salt as well as increase in the amount of benzene the

solvent mixture. The large association between the ions may be due to the coulombic interactions as well as to covalent bonding forces between the ions ($R_4N^+ \dots X^-$).

The study of V_ϕ° and viscosity B -coefficient values for different thiocyanate, in chapter XI indicate the presence of strong ion–solvent interactions and these interactions are further strengthened with rise in temperature and with decrease in the amount of 1,3-dioxolane in the mixtures. It also seen that all studied thiocyanate salts in different composition of 1,3-Dioxolane + water mixture acts as a structure breaker.

Study in chapter XII reveals that the order of specific interaction for the binary mixtures of formamide follows the order: formamide + 1,2-dimethoxyethane > formamide + acetonitrile > formamide + 2-methoxyethanol > formamide + dimethylsulfoxide > formamide + acetophenone. This may be attributed to intermolecular hydrogen bonding and interstitial accommodation between the mixing components. The graded pattern can also be partly due to the difference in the dielectric constants of the mixing components.

In recent years to interpreting the intermolecular interactions and the mechanism of such interactions among mixed components at microscopic and macroscopic levels thermodynamic, transport and acoustic studies on mono, binary and ternary solvent systems are highly useful. Numerous forces may operate between the molecules in solvent mixtures 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 immense help in understanding the nature of 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.

