CHAPTER XII

Concluding Remarks

The aim of the works embodied in this thesis was to investigate the viscous synergy and antagonism of some liquid mixtures along with the physico-chemical properties of some solute-solvent and solvent-solvent systems.

The study in chapter IV revealed that ion-solvent interactions are predominant over ion-ion interactions for sodium molybdate in different aqueous binary mixtures of 1,3-dioxolane at all experimental temperatures. Also, the electrolyte under study was found to act as structure breaker in the solvent mixtures studied.

The study in chapter V revealed that while 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 in aqueous TMAI solutions. These interactions are a function of the molarity of TMAI in the ternary solutions. Also it is evident that TMAI has a dehydration effect on these amino acids in aqueous TMAI 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 VI revealed that amine systems are characterized by the presence of strong hydrogen bond interaction between the mixing liquids and the strength of interaction follows the order: primary amine > secondary amine; also steric and other effects play a pivotal role in this regard. On the contrary, alkoxyethanols systems are characterized by the presence of weak hydrogen bond interaction or dispersive forces in the studied binary systems. The reason is probably the formation of intramolecular associates in these molecules by the interaction of the etheric oxygen and hydrogen of --OH group in the same alkoxyethanol molecule.

The study in chapter VII revealed that the strength of interaction in the mixtures is in the order: 1-butanol>2-methyl-1-propanol>2-butanol>2-methyl-2-propanol and the strength of interaction increases with the

increase in temperature. The above order may be attributed to the increase in branching in the alcohol molecules.

The study in chapter VIII revealed that all the electrolytes under investigation are highly associated in these solvent mixtures. Smaller cations are relatively more solvated that the larger ones. The same trend was observed for the anions too. Also the variation of Walden product indicated preferential salvation at higher mole fraction of 1,4-dioxane justifying specific ion-solvent interactions in these media.

We have studied the ion-ion and ion-solvent interactions of sodium molybdate in aqueous binary mixtures of 1,4-dioxane and 1, 3-dioxolane in chapters IV and IX respectively at different temperatures. The study reveals the presence of strong ion-solvent and weak ion-ion interactions. Also, the ion-solvent interactions are further strengthened at higher temperature and increased amount of the cyclic diether, suggesting larger electrostriction and absence of 'caging/packing' effect. Sodium molybdate behaves as a structure breaker in lower mass% of 1,4-dioxane but behaves as a structure maker at 30 mass% of the same.

The excess properties of the binary mixtures of 1,3-dioxolane and 1,4-dioxane with butyl acetate, butyric acid, butylamine and 2-butanone studied at 298.15 K reveals that the cyclic diethers behave differently towards the other mixing component. This may be due to their structural difference (One methylene group short in 1,3-dioxolane) and dipolar and quadrupolar order subject to the difference in the position of the –O- groups in their respective structures.

The study of the molecular interactions between butylamine and N, N-dimethyformamide (DMF) with some alkyl acetates in chapter XI indicated that the specific interaction between the unlike molecules is predominated by hydrogen bonding and the degree of specific intermolecular interactions decreases as the chain length of the alkyl group increases.

The study in chapter XII revealed from a rudimentary standpoint the ion-pair is formed with only the action of the Coulombic force in a continuum medium, the values of ΔH^0 and ΔS^0 of the ion-pair formation will be negative. Therefore, all the experimental values of ΔH^0 and ΔS^0 are negative for all potassium salts studied. The negative sign of ΔH^0 means that

the association processes are exothermic. The study also justified that potassium halides with Cl^- is most solvated and those with having I^- are the least solvated one in all nearly compositions of glycerol + H_2O mixtures.

1,4-dioxane has been found to differ from the alcohols in their behavior towards water. While alcohols are usually structure makers, 1,4-dioxane is a net structure breaker. 1,4-dioxane can be considered as a non-polar fluid in contrast with 1,3-dioxolane, considered as a polar fluid. Also 1,3-dioxolane has more structure making character than 1,4-dioxane. The reason is probably the lower quadrupolar order and smaller electron donor strength of 1,3-dioxolane with respect to those of 1,4-dioxane.

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 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.