

CHAPTER XI

Concluding Remarks

In the present work described in my thesis, we have tried to investigate the viscous synergy and antagonism of some liquid mixtures along with the different interactions such as solute-solute, solute-solvent and solvent-solvent of some compounds in various solvent systems.

The study of synergy and antagonism in the ternary mixture of 1,3-dioxolane, water and the monoalkanols lead to the conclusion that synergy prevails in lower monoalkanols viz. methanol and ethanol and as the chain length increases the interaction between the unlike solvent molecules decreases and finally the repulsion factor i.e. antagonism comes into play. In case of isomers, the monoalkanols with -OH group at a position other than primary C-atom, attracts more unlike molecules. This favors easy breakage during mixing process.

The behavior of resorcinol in different mass % of aqueous 1,4-dioxane mixtures and pure 1,4-dioxane was observed at different temperatures. This indicates the presence of strong solute-solvent interactions that strengthens with a rise in temperature and weakens with an increase in the amount of 1,4-dioxane in the mixed solvent under investigation. The results also indicates the presence of weak solute-solute interactions that decrease with a rise in temperature and increase with an increase in the amount of 1,4-dioxane in the mixture. Further, resorcinol acts as a structure breaker in these solvent mixtures.

The measurement of viscosities and densities of binary liquid mixtures, ethylene glycol + tetrahydrofuran and ethylene glycol + 1,4-dioxane mixtures along with the ternary liquid mixtures, tetrahydrofuran + methanol + benzene and i-propanol + benzene + n-hexane at 303.15 K, 313.15 K and 323.15 K demonstrates the presence of viscous antagonism and volume contraction in these solvent mixtures. The rise in temperature, implies a decrease in the antagonistic interaction index, I_A as the molecular package increases gradually.

The excess properties of the binary mixtures of 1,3-dioxolane and a series of monoalcohols lead to numerous conclusions. MeOH having the highest polarity achieves the most favorable intermolecular H-bonded interactions with the cyclic diether molecules. Moreover, its simple structure and smaller size leads to interstitial accommodation with 1,3-dioxolane molecules more easily compared to the higher monoalcohols that have greater structural complexity. Alcohol molecules self-associate very strongly (OH---OH interaction), whereas the cyclic diether molecules self associate rather marginally (O---O interaction).

The examination of the ion-solvent and ion-ion interactions of some tetraalkylammonium, alkali metals and ammonium halides in pure *i*-amyl alcohol reveals that all the electrolytes are highly associated in this solvent. The most outstanding feature is that the electrolytes containing smaller cations show considerable amount of association. Furthermore, the process of ionic association of these electrolytes does not exhibit the simple dependence upon ionic size as predicted by electrostatic theory.

The comparative study done on ethylene glycol, water, tetrahydrofuran/1,4-dioxane/*N,N*-dimethylformamide/dimethyl sulphoxide gives a clear distinction between the excess properties and antagonistic behavior of these aqueous mixed solvent systems. 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.

We have investigated the molecular interactions of four acetate salts i.e. ammonium acetate, potassium acetate, sodium acetate and lithium acetate in different mass % of tetrahydrofuran and methanol binary solvent mixtures at different temperatures. The study indicates the presence of strong ion-solvent interactions between NH_4^+ ion and THF + MeOH molecules. The interactions become weaker with the decrease in the size of the cations and also with rise in temperature. The electrostrictive solvation is observed to be greater for smaller cations and at higher temperatures along with the increase in amount of THF in the solution. In other words, there are strong ion-ion interactions between Li^+ ion and THF + MeOH molecules.

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.

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.

Extensive studies of the different physico-chemical, biological or pharmaceutical activity between different components of a given mixture will be of sufficient help in understanding the nature of the different interactions prevailing in systems.

