

## Chapter - XI

### Concluding Remarks

In the present work described in my thesis, we have tried to investigate the different interactions such as solute-solute, solute-solvent and solvent-solvent of some ammonium and tetraalkylammonium salts, mineral salts etc. in different solvent systems and some useful conclusions of them have been derived.

Some monoalcohols and their mixtures are the very important solvents widely used in various industries including the manufacture of pharmaceuticals and cosmetic products and dimethylsulfoxide, 1,4 dioxane and tetrahydrofuran and their aqueous and non-aqueous mixtures are widely used in modern battery industry.

The method used to analyse volume contraction and dilation is similar to that applied to viscosity, *i.e.*, density of the mixture is determined experimentally,  $\rho_{\text{exp}}$  and a calculation is made of its theoretical value,  $\rho_{\text{mix}}$  in the supposition that volume contraction exists, based on the following expression.

$$\rho_{\text{mix}} = X_A \rho_A + X_B \rho_B.$$

where  $X_A$ ,  $X_B$  are the fraction by weight of the system A and B and  $\rho_A$  and  $\rho_B$  are the densities, measured experimentally of the systems A and B respectively. Accordingly, when  $\rho_{\text{exp}} > \rho_{\text{mix}}$ , volume contraction occurs.

Viscous antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each components considered separately. In turn, if the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction.

Peleg allowing quantification of the antagonistic interactions taking place in mixtures involving variable proportions of the constituent components. The method, compares the viscosity of the system, determined experimentally,  $\eta_{\text{exp}}$ , with the viscosity expected in the absence of interaction,  $\eta_{\text{mix}}$ , defined as,

$$\eta_{\text{mix}} = X_A \eta_A + X_B \eta_B.$$

where  $X_A$ ,  $X_B$  are the fraction by weight of the system A and B,  $\eta_A$  and  $\eta_B$  are the viscosities measured experimentally of the systems A and B respectively. Accordingly, when  $\eta_{\text{exp}} < \eta_{\text{mix}}$ , viscous antagonism exists, when  $\eta_{\text{exp}} > \eta_{\text{mix}}$ , the system is considered to exhibit viscous synergy.

This procedure is used when Newtonian fluids are involved since in Non-Newtonian systems shear rate must be taken into account and other antagonism indices are defined in consequence. In order to secure more comparable viscous antagonism results, the so called antagonistic Index ( $A_\eta$ ) introduced by Howell, is also taken into account, where

$$A_\eta = (\eta_{\text{mix}} - \eta_{\text{exp}}) / \eta_{\text{mix}} = \Delta\eta / \eta_{\text{mix}}$$

The symbols have their usual significance.

The explanation of antagonistic behavior of these binary mixtures is based on the known phenomenon of molecular dissociation.

Viscous synergy is the term used in application to the interactions between the components of a system that causes the total viscosity of the latter to be greater than the sum of the viscosities of each components considered separately. In turn, if the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction. In order to secure more comparable viscous synergy results, the so called synergic Index ( $S_\eta$ ) introduced by Howell, is also taken into account, where

$$S_\eta = (\eta_{\text{exp}} - \eta_{\text{mix}}) / \eta_{\text{mix}} = \Delta\eta / \eta_{\text{mix}}$$

The symbols have their usual significance.

The explanation of synergy behavior of these liquid mixtures is based on the known phenomenon of solvation, as a consequence of the hydrogen bonds formed between the molecules of the components of the mixtures – producing molecular package, which logically implies a rise viscosity and density.

Rheology is the branch of science that studies material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products and to establish their stability and even bioavailability since it has been firmly established that viscosity influences drug absorption rate in the body.

The study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics or industrial products etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the products.

Some mineral salts and symmetrical tetraalkylammonium salts show numerous interesting properties that are now being actively investigated in many laboratories. Most of the present day knowledge on non-aqueous solutions have come from studies on various thermodynamic properties, *e.g.*, apparent molar volumes, adiabatic compressibilities, heat capacities etc. as well as on transport properties, *e.g.*, conductance, viscosity, and transference numbers. So, we determined the thermodynamic and transport properties of some alkali metal and tetraalkylammonium salts in tetrahydrofuran and water mixtures from the measurements of their viscosities, conductances, apparent molar volumes and adiabatic compressibilities. In addition to this, we also investigated the interactions between the binary mixtures tetrahydrofuran (THF) + CH<sub>3</sub>OH and CH<sub>3</sub>OH + H<sub>2</sub>O and among the ternary mixtures tetrahydrofuran + methanol + benzene and isopropanol + benzene + n-hexane at different mixtures.

The apparent molar volumes ( $\phi_v$ ) of the solutes and the apparent molal adiabatic compressibilities ( $\phi_K$ ) of the liquid solution were calculated from the following relations.

$$\phi_v = M/\rho_0 - 1000 (\rho - \rho_0)/c \rho_0.$$

$$\phi_K = \beta.M/\rho_0 + 1000 (\beta\rho - \beta^0\rho)/m\rho\rho_0.$$

where the symbols have their usual significances.

The determination of apparent molar volumes and apparent molal adiabatic compressibilities of electrolyte solutions is useful as a guide to the structural properties of solutions, particularly in the study of solute-solvent, solute-solute and solvent-solvent interactions. The concentration dependence of these properties can be used to study solute-solute interactions. The relative magnitude of the limiting apparent molar volumes,  $\phi_v^0$  and the limiting apparent molal adiabatic compressibilities  $\phi_K^0$ , would enable us to provide information about the strengths of interactions between ions and solvent molecules. Measurements of the apparent molar volumes as a function of temperature can give an indication of electrostriction or contraction of solvent molecules around an ion.

Conductance measurement is one of the most accurate and widely used physical methods for investigation of electrolytic solutions. The

measurements can be made in a variety of solvents over wide ranges of temperature and pressure and in dilute solutions where interionic interaction theories are not applicable. Recent development of experimental techniques provides an accuracy to the extent of 0.01% or even more. Conductance measurements together with transference number determinations provide an unequivocal method of obtaining single ion values.

The conductance method primarily depends on the mobility of ion so, it can be suitably utilized to determine the dissociation constant of weak acids and association constants of electrolytes in aqueous and non-aqueous solvents. This method in conjunction with the viscosity measurements gives us much information regarding the solute-solute and solute-solvent interactions.

Different methods are to be used to find out the limiting conductance of the ions from the limiting equivalent conductance of electrolytes. Proper evaluation of the limiting equivalent conductance,  $\Lambda^0$ , the single ion conductance,  $\lambda^0_{\pm}$ , the ionic association constant  $K_A$  and the single ion-size parameter  $a^0$  and their dependence on the dielectric constant would be of great help in determining solute-solute and solute-solvent interactions. However, the variation of  $\lambda^0_{\pm}$  values for ions depends not only on their solvodynamic entity but also on their movement through different solvents. This aspect needs consideration and further study.

Viscosity is one of the most important transport properties used for the determination of solute-solvent interactions. It is not a thermodynamic quantity, but viscosity of an electrolytic solution together with the thermodynamic property,  $\bar{V}_2$ , the partial molar volume gives much information and insight regarding ion-solvent interactions and the structures of the electrolytic solutions. The viscosity B-coefficients give us quantitative values of the solute-solvent interactions.

The proper understanding of the solute-solvent interactions would form the basis of explaining quantitatively the influence of the solvent and the extent of interactions of the ions in solvents and pave the way for the real understanding of the different phenomenon associated with the solution chemistry.

However, it is necessary to remember that solute-solvent interactions are very complex in nature. There are strong electrical forces between the

ions and between the ions and solvents, and it is not really possible to separate them all. Nevertheless, if careful judgement is used, valid conclusions can be drawn in many cases from viscosity, conductivity, apparent molar volume and apparent molal adiabatic compressibility measurements relating to degree of structure and order of the system.

Extensive studies of the different physico-chemical studies on various thermodynamic and transport properties of the electrolytes will be of sufficient help in understanding the nature of the different interactions, *viz.*, solute-solute, solute-solvent and solvent-solvent prevailing in the electrolyte solutions.