

Chapter - XI

Concluding Remarks

At the present work, we have tried to investigate the various interactions of some metal and tetraalkylammonium salts in different solvent media and some useful conclusions of them have been derived.

Alcohols and their mixtures are the very important solvents widely used in various industries including the manufacture of pharmaceuticals and cosmetic products and tetrahydrofuran and its aqueous and non-aqueous mixtures are widely used in modern battery technology. Viscous antagonism is the term used in application to the interaction between the components of a system that causes the total viscosity of the latter to be less than the sum of the viscosities of each components considered separately.

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 present investigation quantifies the viscous antagonism established in two ternary mixtures studied here at different temperatures. Since these systems exhibit volume contraction, an analysis has also been made of the density of the mixtures at various temperatures.

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.

Viscous synergy is the term used in application to the interaction 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 component 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 of interaction.

The method most widely used to analyse the antagonism and synergic behavior of various solvent mixtures is that developed by Koletunc-Gencer and Peleg allowing quantification of the antagonic interactions taking place in mixtures involving variable proportions of the constituent components. The method, compares the viscosity of the system, determined experimentally, η_{exp} , with the viscosity expected in the absence of interaction, η_{mix} , defined as,

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

where X_A , X_B are the fraction by weight of the system A and B, η_A and η_B are the viscosities measured experimentally of the systems A and B respectively. Accordingly, when $\eta_{exp} < \eta_{mix}$, viscous antagonism exists, when $\eta_{exp} > \eta_{mix}$, 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 antagonic index (I_n), introduced by Howell, is also taken into account.

$$I_n = (\eta_{mix} - \eta_{exp}) / \eta_{mix} = \Delta \eta / \eta_{mix}.$$

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, ρ_{exp} and a calculation is made of its theoretical value, ρ_{mix} in the supposition that volume contraction exists, based on the following expression.

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

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

Alkali metal 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) + CH₃OH and CH₃OH + H₂O and among the ternary mixtures tetrahydrofuran + methanol + benzene and isopropanol + benzene + n-hexane at different mixtures.

The apparent molar volumes (ϕ_v) of the solutes and the apparent molal adiabatic compressibilities (ϕ_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 ion-solvent, ion-ion and solvent-solvent interactions. The concentration dependence of these properties can be used to study ion-ion interactions. The relative magnitude of the limiting apparent molar volumes, ϕ_v^0 and the limiting apparent molal adiabatic compressibilities ϕ_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 ion-ion and ion-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, Λ^0 , the single ion conductance, λ^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 ion-ion and ion-solvent interactions. However, the variation of λ^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 ion-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 ion-solvent interactions.

The proper understanding of the ion-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 ion-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.

More extensive studies of the different thermodynamic and transport properties of the electrolytes will be of sufficient help in understanding the nature of the ion-solvent interactions and the role of solvents in different chemical processes.