CHAPTER XI

Concluding Remarks

In the present study, we have tried to investigate the various interactions and equilibria of ions in aqueous, non-aqueous and mixed solvents media in different concentration regions and some useful conclusions of them have been derived.

Tetrahydrofuran and its mixtures are the very important solvents widely used in various industries. This is a good industrial solvent and figures prominently in the high-energy battery technologies and has sound its application in organic syntheses as manifested from the physico-chemical studies in this medium. 1,2-dimethoxyethane and 2-methoxyethanol find a wide range of application of technological importance and these solvents are relevant to battery construction using suitable electrodes. Glycerol and ethane-1, 2-diol have received increasing attention as a class of substances widely used in different applications. These are important liquids, which find a variety of applications such as pharmaceutical, cosmetics, food, textiles fields. Some monoalcohols and their mixtures are the important solvents widely used in various industries including the manufacture of pharmaceuticals and cosmetics products.

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 bio-availability, since it has been firmly established that viscosity influences the drug absorption rate in the body.

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

Some alkali metal halides, nitrate salts, sodium tetraphenylborate and sy mmetrical 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 thermodynamics properties e.g. apparent molar volumes, isentropic compressibilities, heat capacities etc. as well as on transport properties, e.g. conductance, viscosity and transference numbers. So, we determined the thermodynamics, acoustic and transpsort properties of some alkali metal halides, nitrate salts, sodium tetraphenylborate and tetraalkylammonium salts in pure and mixed solvent systems from the various techniques such as volumetric, viscometric, ultrasonic and conductometric. In addition to this, we also investigated the interactions between the binary mixtures 1,2-dimethoxyethane + some monoalcohols at 298.15 K, benzene + carbontetrachloride, benzene + chloroform and among the ternary mixtures water + ethane-1, 2-diol + some monoalcohols at different temperatures.

The apparent molar volumes (V_ϕ) and the apparent molal isentropic compressibilities (ϕ_k) of the solution were determined using the following equations.

$$V_\phi = M/\rho_o - 1000(\rho - \rho_o)c\,\rho_o$$

$$\phi_K = [(1000/m\,\rho\rho_o)(K_S\rho_o - K_S^o\,\rho)] + K_S M/\rho_o$$

where the symbols have their usual significances.

The study of apparent molar volumes and apparent molal isentropic compressibilities of electrolyte solutions is very useful to obtain information on ion-ion, ion-solvent and solvent-solvent interactions. The relative magnitude of the limiting apparent molar volumes, V_ϕ^o and the limiting apparent molal isentropic compressibilities ϕ_K, 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 concentration of solvent molecules around an ion.

The excess molar volumes, excess viscosity, excess free energy of activation of viscous flow, excess acoustic impedance, excess isentropic compressibility and excess intermolecular free length are the thermodynamics properties sensitive to different kinds of association in pure liquids and in the mixtures. These thermodynamic properties are based on following equations.

$$V^E = V - \sum_{i=1}^{n} x_i V_i$$

$$\Delta\eta = \eta - \sum_{i=1}^{n} x_i \eta_i$$

$$L^E_f = L_f - \sum_{i=1}^{n} x_i L_{fi}$$

$$Z^E = Z - \sum_{i=1}^{n} x_i Z_i$$

$$\Delta u = u - \Sigma_{i=1}^{n} x_1 u_1$$

$$\Delta G^{*E} = RT \ln(\eta M/\rho) - RT \sum_{i=1}^{n} x_i \ln(\eta_i M_i/\rho_i)$$

$$K_S^E = K_S - \sum_{i=1}^{n} x_i K_{S,i}$$

(Symbols have their usual significance)

The conductometric method is well suited to investigate ion-solvent and ion-ion interactions in 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 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 limiting equivalent conductance (Λ^{o}) and the ion-association constant (K_A) will be evaluated using Shedlovsky equation. The results will be discussed in terms of ion-ion, ion-solvent and solvent-solvent interactions. Thermodynamics parameters will be evaluated to understand the change of the association constants with solvent composition. The conductance data can also be analyzed with Fuoss 1978 equation and Fuoss Kraus equation that is still one of widely used equations for the simultaneous evaluation of K_A and Λ^{o}.

Viscosity, one of the most important transport properties is used for the determination of ion-solvent interactions and studies extensively. Viscosity is not a thermodynamic property but viscosity of an electrolyte solution along with the thermodynamic property, partial molar volume, gives much information and insight regarding the ion-solvent interactions, structures of electrolytic solutions and solvation. 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 have 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 judgment is used, valid conclusions can be drawn in many cases from viscosity, conductivity, apparent molar volume and apparent molal isentropic 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 rôle of solvents in different chemical processes.