

CHAPTER: XII

Concluding Remarks

In our thesis, we have tried to investigate the various interactions such as solute-solute, solute-solvent and solvent-solvent prevailing in aqueous, non-aqueous and mixed solvent systems 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. Formamide and its derivatives are good solvents for many organic and inorganic compounds and also used as a plasticizer. It is also chosen for the study as it is a simplest amide that contains a peptide linkage, the fundamental building block of proteins.

1,3-dioxolane is cyclic diether and it figure prominently in the high energy battery technology and have also found application in organic synthesis as manifested from the physico-chemical studies in this media.

Some monoalcohols and their mixtures are the important solvents widely used in various industries including the manufacture of pharmaceuticals and cosmetics products. Besides, many other industrially important solvents have been used for this research work.

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 and acetates, sodium tetraphenylborate 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 thermodynamics properties e.g. apparent molar volumes,

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adiabatic compressibilities, heat capacities etc. as well as on transport properties, e.g. conductance, viscosity and transference numbers. So, we determined the thermodynamics, acoustic and transport 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 (K_ϕ) of the solution were determined using the following equations.

$$V_\phi = M/\rho_0 - 1000(\rho - \rho_0)c/\rho_0$$

$$K_\phi = [(1000/m\rho\rho_0)(K_S\rho_0 - K_S^0\rho)] + K_S M/\rho_0$$

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^0 and the limiting apparent molal isentropic compressibilities K_ϕ , 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.

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

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

$$L_f^E = L_f - \sum_{i=1}^n x_i L_{f,i}$$

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

$$\Delta u = u - \sum_{i=1}^n x_i u_i$$

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

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

(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^0) 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

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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 A° .

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

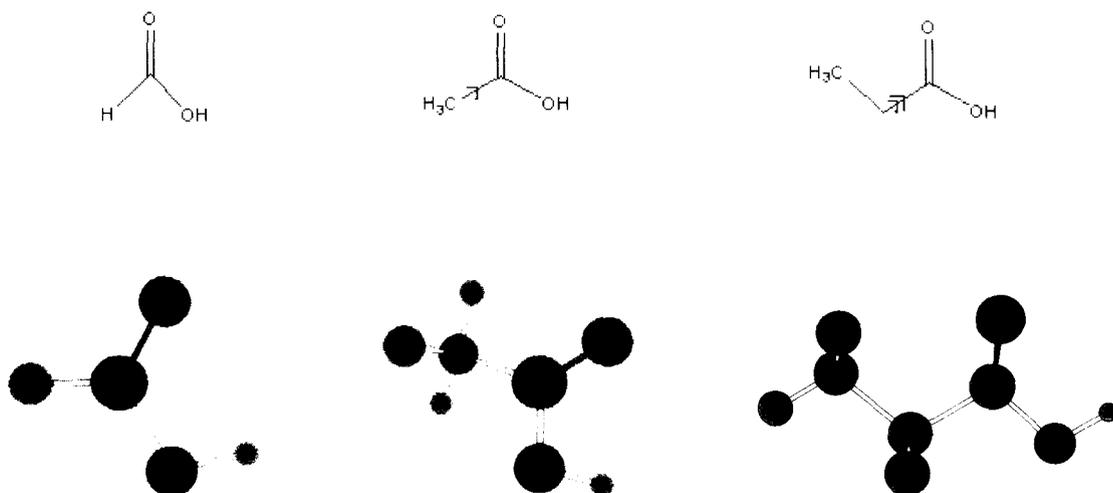
The proper understanding of the ion-solvent interactions would form the basis of explaining quantitatively the influence of the solvent and the extent of interactions of the ions in solvents and have the way for the real understanding of the different phenomenon associated with the solution chemistry.

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.

The results supplemented with the viscosity data show the viscous synergy interaction index, I_S , as a function of mass% of H_2O and the number of carbon atoms corresponding to the monoalkanols with the hydroxyl group at the end of the molecular chain and the second carbon atom respectively. These results also indicate that the synergic indices of the monoalkanoic acids in aqueous monoalkanols follow the order:



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The gradual decrement of synergy interaction values from HCOOH to CH₃CH₂COOH can be explained in view of +I-effect. -C₂H₅ has more +I-effect than -CH₃ which has in turn than -H. This facilitates more interactions of HCOOH with unlike molecules than CH₃COOH and CH₃CH₂COOH rendering to higher values of synergy interaction parameters.

More extensive studies of the different thermodynamic, transport, spectroscopic and acoustic properties of the electrolytes will be of sufficient help in understanding the nature of the various molecular interactions and the role of solvents in different physico-chemical processes.