

CHAPTER - VIII

*** C O N C L U D I N G R E M A R K S ***

At the present work, we have tried to explore the different aspects of solution chemistry and some useful conclusions of them have been derived.

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 has come from studies on various thermodynamic properties e.g. apparent molal 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 (THF) and 1,2 dimethoxyethane (1,2DME) and their aqueous mixtures from the measurements of their viscosities, conductances, apparent molal volumes and adiabatic compressibilities.

The apparent molal volumes (ϕ_v) of the solutes and the apparent molal adiabatic compressibilities (ϕ_k) of the liquid solution were calculated from the following relations respectively

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

$$\phi_k = \frac{1000}{m\rho\rho_0} (\beta\rho_0 - \beta^0\rho) + \beta \frac{M}{\rho_0}$$

Where the symbols have their usual significances.

The determination of apparent molal 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 magnitudes of the limiting apparent molal volumes, $\phi_{V, \infty}^{\circ}$, and the limiting apparent molal adiabatic compressibilities $\phi_{K, \infty}^{\circ}$, would enable us to provide information about the strengths of interactions between ions and solvent molecules. Measurements of the apparent molal 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 provides an unequivocal method of obtaining single-ion values.

The conductance method primarily depends on the mobility of ions. So it can be suitably utilised to determine the dissociation constants 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 conductances of electrolytes. Proper evaluation of the limiting equivalent conductance, Λ° , the single-ion conductance, λ_{\pm}° , the ionic association constant, K_A and the single ion-size parameter a° 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_{\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 η of an electrolytic solution together with the thermodynamic property, \bar{V}_2 , the partial molal volume gives much information and insight regarding ion-solvent interactions and the structures of the electrolytic solutions.

Viscosity is a measure of the friction between adjacent, relatively moving, parallel planes of the liquid. Anything that increases or decreases the interaction between the planes will raise or lower the friction and therefore increase or decrease the viscosity.

The viscosity β -coefficients give us quantitative

values of the ion-solvent interactions, but still we have no unambiguous method of division of β -coefficients into ionic β -values in all solvents. The use of Bu_4NBBu_4 or Bu_4NBPh_4 appears to be sound, but we lack sufficient data measured in different solvents to arrive at a definite conclusion. It is desirable to use different methods of division of β -values to have reasonably consistent ionic β values.

Accurate β_{ion} values would give the solvation number of ions. It is known that

$$\beta_{\text{ion}} = \beta_{\text{ion}}^{\text{Einst}} + \beta_{\text{ion}}^{\text{Str.}} + \beta_{\text{ion}}^{\text{Disord}}$$

but it is not possible to calculate the individual constituents like $\beta_{\text{ion}}^{\text{Einst}}$ etc. so that the effect of charges on the nature of solvation can be properly explored. Efforts should be made to know at least $\beta_{\text{ion}}^{\text{Einst}}$ values experimentally.

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 phenomena 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 molal 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.