

# Chapter - I

## Necessity of the Research Work

### 1.1. Object and application of the work

The importance and uses of the chemistry of electrolytes in non-aqueous and mixed solvents are well-recognized. The applications and implications of the studies of reaction in non-aqueous and mixed solvents have been summarized by Meck<sup>1</sup>, Franks<sup>2</sup>, Popovych<sup>3</sup>, Bates<sup>4-5</sup>, Parker<sup>6,7</sup>, Criss and Salomon<sup>8</sup>, Mercus<sup>9</sup> and others<sup>10-12</sup>. The ion-ion and ion-solvent interactions have been subject of wide interest as apparent from recent Faraday Transactions of the chemical society.<sup>13</sup>

In spite of vast collections of data on the different electrolytic and non-electrolytic solutions in water, the structure of water and the different types of interactions that water undergoes with electrolytes are yet to be properly understood. However, the studies on properties of aqueous solutions have provided sufficient information on the thermodynamic properties of different electrolytes and non-electrolytes, the effects of variation in ionic-structure, ionic mobility and common ions on the properties of aqueous solutions and a host of other properties.<sup>14,15</sup>

In recent years there have been an increasing interest in the behaviour of electrolytes in non-aqueous and mixed solvents with a view to investigating ion-ion and ion-solvent interactions under varied conditions. However, different sequence of solubility, difference in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have open vistas for physical chemists and interest in these organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry.<sup>16</sup>

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 ions in solvents and thus pave the way for real understanding of the different phenomena associated with solution chemistry. Estimate of ion-solvent interactions can be obtained thermodynamically and also from the measurements of partial molar volumes, viscosity B-coefficients and conductivity studies.

Estimates of single-ion values enable us to refine our model of ion-solvent interactions. Acceptable values of ion-solvent interactions would enable the chemists to choose solvents that will enhance (i) the rates of chemical reactions, (ii) the solubility of minerals in leaching operations or reverse the direction of equilibrium reactions.

It is thus apparent that the real understanding of the ion-solvent interactions is a difficult task. The aspect embraces a wide range of topics but we concentrated on the measurements of transport properties like viscosity and conductivity as well as of thermodynamic properties such as apparent molar volume and apparent molal adiabatic compressibility studies.

Fundamental research on non-aqueous electrolyte solutions has catalyzed their wide technical applications in many fields. Non-aqueous electrolyte solutions are actually competing with other ion conductors, specially at ambient and at low temperatures, due to their high flexibility based on the choice of numerous solvents, additives and electrolytes with widely varying properties. High-energy primary and secondary batteries, wet double-layer capacitors and super capacitors, electro-deposition and electroplating are some devices and processes for which the use of non-aqueous electrolyte solutions had brought the biggest successes.<sup>17-18</sup> Other fields where non-aqueous electrolyte solutions are broadly used include electrochromic displays and smart windows, photoelectrochemical cells, electromachining, etching, polishing and electrosynthesis. In spite of wide technical applications, our outstanding of these systems at a quantitative level is still not clear. The main reason for this is the absence of detailed information about the nature and strength of ion-molecular interactions and their influence on structural and dynamic properties of non-aqueous electrolyte solutions.

Studies of transport properties of electrolytes along with thermodynamic and compressibility studies, give very valuable information about ion-ion and ion-solvent interactions in solutions.<sup>19</sup> The influence of these ion-solvent interactions is sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in such diverse areas as organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extraction.<sup>18(b), 20</sup>

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become increasingly clear that the majority of the solutes is significantly modified by all solvents. Conversely, the nature of strongly structured solvents like water, is substantially modified by the presence of solutes.<sup>21</sup>

## 1.2. Choice of the main solvents used

Tetrahydrofuran (THF) and methanol have been chosen as main solvents in my research works. The study of THF and methanol, in general, are of interest because of their wide use as solvents and solubilizing agents in many industries with interests ranging from pharmaceutical to cosmetic products.

Tetrahydrofuran (THF) and its mixtures are the very important solvents widely used in various industries. THF is a good industrial solvent and figures prominently in the high energy battery technology and has found its application in organic syntheses as manifested from the physico-chemical studies in this medium.

Tetrahydrofuran (THF), Merck, India, was kept several days over potassium hydroxide (KOH), refluxed for 24 h and distilled over lithium aluminium hydride ( $\text{LiAlH}_4$ ). The purified solvent had a boiling point of  $66^\circ\text{C}$ , a density of  $0.88072 \text{ g cm}^{-3}$ , a coefficient of viscosity of  $0.00460 \text{ p}$  and a specific conductance of  $\text{Ca. } 0.81 \times 10^{-6} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ .

Methanol and its mixtures are the very important solvents widely used in various industries including the manufacturing of pharmaceuticals and cosmetic products in enology and as an energy source.

Methanol, E. Merck, was dried over  $3\text{\AA}$  molecular sieves and distilled fractionally, the middle fraction was collected and redistilled. The purified solvent had a density of  $0.78654 \text{ g cm}^{-3}$  and coefficient of  $0.545 \times 10^2 \text{ m Pa's}$  at  $25^\circ\text{C}$ .

Even though THF and methanol have drawn much focus in recent years as solvents for electroanalytical investigations, still more studies on the electrolytic behavior in these non-aqueous medium can be explored. Therefore, we have embarked on a series of investigations on THF and *methanol* to study the chemical nature of the structure of ions and solvents and their mutual and specific interactions with solvent molecules by studying the transport and thermodynamic properties of some selected

compounds in THF and *methanol* through the measurements of conductances, viscosities, densities and the velocities of sound.

### 1.3. Method of Investigations

The phenomenon of ion-solvent interactions and solvation is intriguing. It is desirable to attack this problem using different experimental techniques. We have, therefore, employed four important methods, namely, Conductometry, Viscometry, Densitometry and Ultrasonic Interferometry to probe the problem of solvation phenomena.

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution. The compressibility, a second derivative of Gibbs energy, is also a sensitive indicator of molecular interactions and can provide useful information in such cases where partial molar volume data alone cannot provide an unequivocal interpretation of these interactions.

The change in solvent viscosity by the addition of electrolyte solutions is attributed to interionic and non-solvent effects. The B-coefficients are also separated into ionic components by the "reference electrolyte" method and from the temperature dependence of ionic values, a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, structure-breaking or structure-making, polarisation, etc. may be given.<sup>22</sup>

The transport properties in most cases are studied using the conductance data, specially the conductance at infinite dilution. Conductance data obtained as a function of concentration can be used to study the ion-association with the help of appropriate equations.

### 1.4. Summary of the Work Done

#### Chapter I

This chapter involves the necessity of the research work. This mainly contains the object and applications of the research work, the reasons for choosing the main solvents used, methods of investigations and the gist of the work done.

## Chapter II

This chapter forms the background of the present work. After presenting a brief review of notable works in the field of ion-solvent interactions, the discussion centres around the density, conductance, viscosity and adiabatic compressibility of different electrolytes in different solvent media at various temperatures. Critical evaluations of different methods on the relative merits and demerits on the basis of various assumptions employed from time to time of obtaining the single ion values and their implications have been made. The solvent properties are then discussed, stressing the importance of the work.

## Chapter III

This chapter includes the experimental section which mainly contains the sources and purification of the solvents and electrolytes used and the various techniques of the experiments applied.

## Chapter IV

This chapter describes the determination of the apparent and partial molar volumes and the viscosity B-co-efficients of some alkali metal chlorides in different mass % of THF + H<sub>2</sub>O mixtures (20, 40, 60, 80) at (303, 308, 313 and 318)K. The limiting apparent molar volumes ( $V_{\phi}^0$ ) and experimental slopes ( $S_v^*$ ) obtained by using the Masson equation have been interpreted in terms of ion-solvent and ion-ion interactions respectively. The experimental results for viscosity have been analyzed using the Jones-Dole equation and the B-co-efficient values have been discussed with changes in the solvent structures.

## Chapter V

This chapter entails the studies on thermodynamic and transport properties of binary mixtures at different temperatures. From the experimental results, the excess molar volume ( $V^E$ ), the deviation of viscosity from the mole fraction average ( $\Delta\eta$ ) and Grunberg-Nissan parameters ( $d$ ) have been determined. These excess functions have been discussed on the basis of molecular interactions between the components of the mixture.

## Chapter VI

This chapter describes the volumetric, viscometric and ultrasonic studies of some nitrate compounds in aqueous binary mixture of tetrahydrofuran (THF) at different temperatures. The limiting apparent molar volume ( $V_{\phi}^0$ ) and the experimental slopes ( $S_v^*$ ) obtained from the Masson

equation have been discussed in terms of solute-solvent and solute-solute interactions respectively. The B-co-efficient values analyzed using the Jones-Dole equation show that the electrolytes studied here have structure breaking capacities in this mixed solvent system.

### **Chapter VII**

This chapter describes the studies on the conductance of some tetraalkylammonium and alkali metal bromides in tetrahydrofuran + water mixtures (20, 40, 60, 80 mass % of THF) at (303, 313 and 318)K. The experimental data have been analyzed by the 1978 Fuoss conductance equation and the derived characteristic parameters,  $\Lambda^0$ ,  $K_A$  and  $R$  have been evaluated. The ionic Walden products have been determined and their variations with solvent composition and temperature have been discussed.

### **Chapter VIII**

In this chapter density, viscosity and adiabatic compressibility data have been reported for some mineral salts ( $\text{NH}_4\text{NO}_3$ ,  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Ca}(\text{NO}_3)_2$ ) in water and various temperatures. Apparent molar volume ( $V_\phi$ ) and viscosity B-co-efficient of the mineral salts are determined from these data supplemented with their density and viscosity respectively. The ion-solvent and ion-ion interactions have been discussed on the basis of the values of limiting apparent molar volume ( $V_\phi^0$ ) and experimental slopes ( $S_v^*$ ) respectively. The viscosity data have been analyzed using the Jones-Dole equation and the derived parameters  $B$  and  $A$  have also been interpreted in terms of ion-solvent and ion-ion interactions respectively. The structure making and breaking capacities of these salts investigated here have been discussed.

### **Chapter IX**

This chapter entails the studies on viscous antagonism of some ternary liquid mixtures (tetrahydrofuran + methanol + benzene and isopropanol + benzene + n-Hexane) at different temperatures (303, 313 and 323) K. 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. In order to secure more comparable viscous antagonism results, the so called antagonistic Index ( $I_\eta$ ) introduced by Howell, is also taken into account, where

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

The symbols have their usual significance. The explanation of antagonistic behavior of these ternary mixtures is based on the known phenomenon of molecular dissociation and the molecular package.

### Chapter X

This chapter illustrates the partial molar volumes, transport properties and ultrasonic speeds of some acetate compounds ( $\text{CH}_3\text{COONH}_4$ ,  $\text{CH}_3\text{COOLi}$ ,  $\text{CH}_3\text{COONa}$  and  $\text{CH}_3\text{COOK}$ ) in aqueous mixture of THF at various temperatures (303.15, 313.15 and 323.15) K. The limiting apparent molar volume ( $V_{\phi}^0$ ) and experimental slopes ( $S_v^*$ ) have been explained in terms of ion-solvent and ion-ion interactions. Structure making/structure breaking capacities of various salts studied here have been inferred from the sign of  $(\delta^2 V_{\phi}^0 / \delta T^2)_P$ ,  $dB/dT$  and the B-co-efficients for all electrolytes. The compressibility obtained from the data supplemented with their ultrasonic speeds indicates the electrostriction of the solvent mixtures around the ammonium and the metal ions.

### Chapter XI

The dissertation ends with some concluding remarks in this *Chapter*.

## References

1. D.K. Meck. In the chemistry of non-aqueous solvents, Ed., J.J. Logowski, Academic Press, New York, London, 1966, Part I, Chapter I.
2. F. Franks. In physico-chemical processes in Mixed Aqueous Solvents. Ed. F. Franks, Heinemann Educational Books Ltd., 1967, pp. 141-151.
3. O. Popovych. *Crit. Rev. Anal. Chem.* **1**, 73, 1970.
4. R.G. Bates, Determination of pH theory and practice, Second Ed., John Wiley and Sons. N.Y. 1973, Chapter 8.
5. (a) R.G. Bates. Solute-solvent interactions. Eds., J.J. Coetzee and C.D. Ritchie, Marcel Dekker, New York and London, 1969.  
(b) R.G. Bates and A.J. Parker. Chemical Physics of ionic solutions. Eds., B.E. Conway and R.G. Barradas. John Wiley and Sons. Inc. New York, 1966, pp. 211-233.
6. J.H. Sharp and A.J. Parker. Proceedings of the Royal Australian Chemical Institute. 1972. p. 89.
7. A.J. Parker. *Electrochim. Acta.* **21**, 671, 1976.

8. C.M. Cris and M. Salomon. *J. Chem. Educ.* **53**, 763, 1976.
9. Y. Marcus. In *ion Solvation*. Wiley. Chinchester. 1986.
10. R.R. Dogonadze, E. Kalman, A.A. Kornyshev and J. Ulstrup. In *The chemical physics of salvation, part C*, Elsevier, Amsterdam. 1988.
11. O. Popovych and R.P.T. Tomkins. In *Non-aqueous solution chemistry*. John Wiley and Sons, New York, 1981.
12. E.J. King. *Acid-base equilibria*. Pergamon Press, Oxford, 1965.
13. Faraday Discussions of the chemical society. No. 67, 1977.
14. G.S. Kell, C.M. Davies and J. Jaszynski. In *water and aqueous solutions, structure, thermodynamics and transport process*. Ed. R.A. Horne, Wiley Interscience, 1972, Chapter 9&10.
15. T. Franks. *Physico-chemical processes in mixed aqueous solvents*. Ed. F. Franks. Heinemann Educational Books Ltd., 1967, pp. 141-151.
16. A.K. Covington and T. Dickenson. In *physical chemistry of organic solvent systems*. Eds. A.K. Covington and T. Dickenson, Plenum Press, London and New York, 1973.
17. (a) Y. Marcus. *Ion-solvation*, Wiley Interscience, Chichester, 1986.  
(b) Y. Marcus. *Ion Properties*, Dekker, New York, 1997.
18. (a) A. Masquez, A Vargas and P.B. Balbuena. *J. Electron. Soc.* **45**, 3328, 1998.  
(b) A.F.D. Namor, M.A.L. Tanco, M. Solomon and J.C.Y. Ng. *J. Phys. Chem.* **98**, 11796, 1994.  
(c) Y. Matsuda and H. Satake. *J. Electronal. Chem.* **127**, 877, 1980.
19. (a) O. Popovych and R.P.T. Tomkins. *Non-aqueous solution chemistry*. Wiley Intersciences, New York, 1981.  
(b) A. Chandra and B. Bagchi. *J. Phys. Chem. B.* **104**, 9067, 2000.  
(c) G. Atkinson, R. Garnrey and M.J. Taft. In *Hydrogen Bonded Solvent Systems*. Eds. A.K. Covington and P. Jones, Taylor and Francis Ltd., London, 1968.
20. W.E. Waghorne. *Chem. Soc. Rev.* 285, 1993.
21. (a) R.G. Bates. *J. Electronal. Chem.* **29**, 1, 1971.  
(b) K. Gunaseelau, S. Dev and K. Ismail. *Ind. J. Chem.*, **39A**, 761, 2000.
22. B. Das and D.K. Hazra. *Bull. Chem. Soc. Jpn.* **64**, 3470, 1992.