

## **CHAPTER – I**

### **Scope and Object of the Research**

Physico-chemical studies of electrolytes play a very important role in understanding the ion-ion, ion-solvent and solvent-solvent interactions in solutions. In order to explore the strength and nature of the interactions, transport properties of electrolytes, along with thermodynamic and acoustic studies involving binary and ternary molecular liquids and of one or more solutes in pure and mixed molecular liquids are very useful.

The importance and uses of the chemistry of electrolytes in non-aqueous and mixed solvents are well organized. The applications and implications of the studies of reactions in non-aqueous and mixed solvents have been summarized by Franks <sup>(1)</sup>, Meck <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 solute-solute and solute – solvent interactions have been subject of wide interest as apparent from recent Faraday Trans. of the chemical society <sup>(13)</sup>.

The proper understanding of the solute-solvent interactions would form the basis of explaining quantitatively the influence of the solvent and the extent of interaction of ions in solvents and thus pave the way for real understanding of the different phenomena associated with solution chemistry. Estimate of solute- solvent interactions can be obtained thermodynamically and also from the measurement of partial molar volumes, viscosity *B*-coefficient and conductivity studies.

In recent years there have been increasing interests in the behavior of electrolytes in non- aqueous and mixed solvents with a view to investigating solute-solute and solute-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 interests in these organic solvents transcends the traditional boundaries of inorganic, physical organic analytical and electrochemistry<sup>(14)</sup>.

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, especially 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 supercapacitors, electrodeposition and electroplating are some devices and processes for which the use of non-aqueous electrolyte solutions has brought the biggest success<sup>(15-16)</sup>. Other fields where non-aqueous electrolyte solutions are some devices and processes for which the use of non-aqueous electrolyte solutions are broadly used include electro-chromic displays and smart windows, photo-electrochemical cells, electro-machining, etching, polishing, and electro-synthesis. In spite of wide technical applications, our understanding 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>(17)</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>(18-19)</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 are significantly modified by all solvents. Conversely, the nature of strongly structured solvents, like water, is substantially modified by the presence of solutes<sup>(20)</sup>.

### 1.1. Choice of the Main Solvent Used

1, 2-Dimethoxyethane, 2-methoxyethanol, tetrahydrofuran, benzene, ethane-1, 2-diol, and glycerol have been chosen as main solvents in my research works. The study of these solvents, in general, are of interest because of their wide use as solvents and so in general, is of interest because of its wide use as solvent and solubilizing agent in many industries with interests ranging from pharmaceutical to cosmetic products.

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<sup>(21-22)</sup>.

Tetrahydrofuran (Merck, India), was kept several days over potassium hydroxide (KOH), refluxed for 24 hours and distilled over lithium aluminium hydride ( $\text{LiAlH}_4$ ). The purified solvent had a boiling point of  $66^\circ\text{C}$ , a density of  $0.88072 \text{ g}\cdot\text{cm}^{-3}$ , a coefficient of viscosity of  $0.46300 \text{ mPa}\cdot\text{s}$  and a specific conductance of  $\text{Ca. } 0.81 \times 10^{-6} \text{ } \Omega^{-1} \text{ cm}^{-1}$  at  $25^\circ\text{C}$ <sup>(14)</sup>.

1,2-dimethoxyethane (dielectric constant,  $\epsilon = 7.03$ )<sup>(23)</sup> and 2 methoxy-ethanol find a wide range of application of technological importance and these solvents are relevant to battery construction using suitable electrodes<sup>(23)</sup>.

1, 2-Dimethoxyethane (Fluka, Purrum) was shaken with  $\text{FeSO}_4$  (AR, BDH) for 1-2 h, decanted and distilled. The distillate was refluxed for 12 h and

redistilled over metallic sodium<sup>(23)</sup> and the middle fraction was collected. The purity of the solvent as checked by gas chromatography was found to be >99.8%. Its boiling point (84.5<sup>0</sup>C), density (0.86109 g.cm<sup>-3</sup>) and viscosity (0.4089 mPa.s) compared well with literature values<sup>(23-24)</sup> at 25<sup>0</sup>C.

2-Methoxyethanol was allowed to stand overnight with CaSO<sub>4</sub> and distilled from Sodium. Before fractional distillation the solvent was treated with 2, 4-dinitrophenylhydrazine<sup>(26)</sup>. The purity of the solvent as checked by gas chromatography was found to be >99.9%. The density (0.95772 g.cm<sup>-3</sup> at 30<sup>0</sup>C), boiling point (124.4<sup>0</sup>C), and viscosity (1.39329 mPa.s at 30<sup>0</sup>C) compared well with literature values<sup>(25,26)</sup>.

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<sup>(27)</sup>, food, textiles fields<sup>(28)</sup>.

Ethane-1, 2-diol (A.R. S.D. Fine) was first dried over fused CaO overnight and then distilled twice under vacuum. The middle fraction was further dried using 4A<sup>0</sup> molecular sieves (Linde) and stored and protected against moisture and CO<sub>2</sub><sup>(29)</sup>.

Benzene is used as solvents for fats and oils, dry-cleaner of woolen clothes, anti-knock gasoline and in manufacture of detergents, insecticides, etc.

Aldrich gold label grade glycerol, quoted as 99.5 + % pure, was further distilled under reduced pressure, the temperature at the top of the fractionating column being 140<sup>0</sup>C and the pressure, measured near the receiving flask, being about 0.034 k Pa. The central fraction was used and found to have an electrical conductivity of  $7.4 \times 10^{-9} \Omega^{-1} \text{ cm}^{-1}$  at 23.9<sup>0</sup>C, this value not being significantly altered by further distillation<sup>(30)</sup>.

In recent years, attention has been focused on the solubility of polyethylene glycol and glycerol in both water and organic solvents, a valuable property in the development of more environmental friendly processes, like the

design of water-soluble catalysts, and in the extraction, separation, and purification of biological substances<sup>(31-32)</sup>. Thus, evaluation of thermodynamics and bulk properties of these solvents and their mixtures with organic solvents may prove quite relevant to the design and implementation of the above-mentioned processes, especially for the establishment of reliable correlations and predictions.

Moreover, in recent years, the above-mentioned solvents have drawn much focused in electro-analytical investigation, still more studies on the electrolytic behavior in these non-aqueous medium can be explore.

## 1.2. Methods of Investigations

The interactions and equilibria of ions in aqueous and non-aqueous media in different concentration regions are of immense importance to the technologist and theoretician as most of the chemical processes occur in these systems. The structures and existence of free ions, solvated ions, and ion pairs depend on concentration regions<sup>(9)</sup>.

Various techniques<sup>(5a, 33)</sup> have been employed to study the solvation structure, ion-solvent interactions and dynamics of ions in aqueous and non-aqueous media.

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 five important methods, namely, conductometric, viscometric, densitometry, ultrasonic interferometer and spectrophotometer 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 to 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 viscosity by the addition of electrolyte solutions is attributed to interionic and ion-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, polarization, etc. may be given<sup>(34)</sup>.

The transport properties in most cases are studied using the conductance data, especially 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.

### 1.3. Summary of the Work Done

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**The present dissertation has been divided into eleven chapters.**

**Chapter I:** This chapter involves the object and scope of the research work. This mainly comprised the choice of the main solvent used and its applications in different fields, methods of investigation and summary of the work done.

**Chapter II:** This chapter contains the general introduction of the thesis and the background of the present work. After presenting a brief review of notable works in the field of solute-solvent, solute-solute and solvent-solvent interactions, the discussion centers on the conductance, density, viscosity and adiabatic compressibility of different electrolytes in different solvent systems at different temperatures. 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 study of densities, viscosities and ultrasonic speeds of binary mixtures containing 1, 2 - dimethoxyethane and some alkan-1-ol at 298.15 K. This study involves seven binary mixtures in which 1, 2-dimethoxyethane plays the role of first component ( $x_1$ ). The viscosity deviation ( $\Delta\eta$ ), the excess molar volume ( $V^E$ ) and excess isentropic compressibility ( $K_s^E$ ), excess acoustic impedance ( $Z^E$ ), excess intermolecular free length and deviation of sound speeds ( $\Delta u$ ) are calculated from the experimental values of viscosity ( $\eta$ ), density ( $\rho$ ) and speed of sound ( $u$ ) for binary liquid mixture of 1,2 -dimethoxyethane with methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol and octan-1-ol over the entire range of composition at 298.15 K. Various interaction parameters and excess functions have been discussed on the basis of molecular interactions between the components of the mixture.

**Chapter V:** This chapter entails the studies on the conductance of some alkali metal halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) in glycerol + water mixtures (10, 20, 30 mass% of glycerol) at (298.15, 308.15 and 318.15) K. The conductance data have been analyzed by the Fuoss-conductance-concentration equation in terms of the limiting molar conductance ( $\Lambda^0$ ), the association constant ( $K_A$ ), and the distance of closest approach of ion ( $R$ ). Thermodynamic parameters  $\Delta H^0$ ,  $\Delta G^0$ , and  $\Delta S^0$  are obtained and discussed. Also, Walden products ( $\Lambda^0\eta^0$ ) are reported. The results have been interpreted in terms of ion-solvent interactions and structural changes in the mixed solvents.

**Chapter VI:** This chapter describe the study of densities, viscosity deviations, and isentropic compressibilities of ternary liquid mixtures (water + ethane-1, 2-diol + methanol, water + ethane-1, 2-diol + propanol) at various temperatures (298.15, 308.15 and 318.15) K. Various excess thermodynamics functions viz. viscosity deviations ( $\Delta\eta$ ), excess volumes ( $V^E$ ) excess Gibbs free

energy of activation of flow ( $\Delta G^{\ddagger E}$ ) and the values of interaction parameter  $d$  in Grunberg and Nissan equation are calculated as a function of composition of ternary mixtures. The results have been interpreted in terms of molecular interactions existing between the components of these mixtures.

**Chapter VII:** This chapter involves the studies on the solute-solvent interactions and ultrasonic speed of resorcinol in 2-methoxyethanol and tetrahydrofuran at different temperatures. In this chapter, the densities, viscosities and ultrasonic speeds of resorcinol in pure 2-methoxyethanol and pure tetrahydrofuran are determined experimentally at 303.15 K, 313.15 K and 323.15 K. Apparent molar volumes ( $V_\phi$ ), viscosity parameters of these solutions are obtained from these data supplemented with their densities and viscosities respectively. The limiting apparent molar volumes ( $V_\phi^0$ ) and experimental slopes ( $S_v^*$ ) derived from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The viscosity data have been analyzed using Jones-Dole equation and the derived parameters  $B$  and  $A$  have also been interpreted in terms of solute-solvent and solute-solute interaction respectively. The structure making/breaking capacity of this solute investigated here has been discussed. The compressibility data also indicate the electrostriction of the solvent molecules around the solute particles.

**Chapter VIII:** This chapter describes the electrical conductance of some tetraalkylammonium bromides ((Me<sub>4</sub>NBr, Et<sub>4</sub>NBr, Pr<sub>4</sub>NBr, Bu<sub>4</sub>NBr), alkali metal bromides (LiBr, NaBr, and KBr), and sodium tetraphenylborate (NaBPh<sub>4</sub>) in ethane-1, 2- diol and formamide at 298.15 K. The conductance data have been analyzed by the 1978 Fuoss conductance- concentration equation in terms of limiting molar conductance ( $\Lambda^0$ ), the association constant ( $K_A$ ), and the association diameter ( $R$ ). The limiting molar conductances of studied electrolytes in ethane-1, 2-diol have been compared well with the same electrolytes in formamide. The limiting ionic conductance have been estimated from the appropriate division of the limiting molar conductivity value of the

“reference electrolyte”  $\text{Bu}_4\text{NBPh}_4$ . The results have been analyzed in terms of ion-ion and ion-solvent interactions.

**Chapter IX:** This chapter describes the studies on thermodynamics and transport properties of two binary mixtures in which benzene plays the role of first component ( $x_1$ ) at different temperatures (298.15, 308.15, and 318.15) K. From the experimental results the excess molar volume ( $V^E$ ), the deviation of viscosity ( $\Delta\eta$ ), excess free energy of activation of viscous flow ( $G^{*E}$ ), and Grunberg-Nissan parameter ( $d$ ) have been determined. These excess functions have been discussed on the basis of molecular interactions between the components of the mixture.

**Chapter X:** This chapter includes the volumetric, viscometric, and ultrasonic studies of some mineral salts [ $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Ca}(\text{NO}_3)_2$ ] in aqueous binary mixtures of ethane-1, 2-diol (10, 20 and 30 mass % ethane-1, 2-diol) at different temperatures (298.15, 308.15, and 318.15) K. The experimental values  $\rho$  was used to calculate the values of the apparent molar volume ( $\Phi_v$ ). The limiting apparent molar volume ( $\Phi_v^0$ ) and the experimental slope ( $S_v^*$ ) have been interpreted in terms of ion-solvent and ion-ion interactions respectively. Various acoustic parameters like isentropic compressibility ( $K_s$ ), specific acoustic impedance ( $Z$ ), intermolecular free length ( $L_f$ ), molar sound speed ( $R_m$ ) and relative association ( $R_A$ ) is also calculated at 298.15 K. The behavior of these parameters suggests strong ion-solvent interactions in these systems. The structure-making/breaking capacities of the salts investigated have also been discussed.

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

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