

CHAPTER – I

SCOPE AND OBJECT OF THE RESEARCH

Fundamental research on non-aqueous electrolyte solutions has catalysed 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.¹⁻² 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 electrochromic displays and smart windows, photoelectrochemical cells, electromachining, etching, polishing, and electrosynthesis. 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.³ 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.^{2(b),4}

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.⁵

1.1 CHOICE OF THE MAIN SOLVENT USED

Tetrahydrofuran(THF) has been chosen as main solvent in my research works. The study of THF, 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(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 technologies and has sound 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 hours and distilled over lithium aluminium hydride (LiAlH_4). The purified solvent had a boiling point of 66°C , a density of 0.88072 g/cc , a coefficient of viscosity of 0.00460 p and a specific conductance of $\text{Ca. } 0.81 \times 10^{-6} \text{ s cm}^{-1}$ at 25°C .

Even though THF has drawn much focuss in recent years as solvent for electro analytical investigations, still more studies on the electrolytic behaviour in these non-aqueous medium can be explored. Therefore, we have embarked on a series of investigations on THF to study the chemical nature of the structure of ions and solvent and its mutual and specific interactions with

solvent molecules by studying the transport and thermodynamic properties of some selected compounds in THF through the measurement of conductance, viscosities, densities and the velocities of sound.

1.2 SCOPE OF THE WORK

The object of the present work is therefore to elucidate the nature of various interactions of some common alkali metal chloride, sulphate salts and other important salts such as resorcinol, tetraalkylammonium salts (Bu_4NI , Pr_4NI , Et_4NBr , Me_4NCl) in non-aqueous solvents having low dielectric constant such as tetrahydrofuran (THF), $\epsilon = 7.58$ at 298.15K and 1,4 dioxane (DO), $\epsilon = 2.209$ at 298.15K from volumetric, viscometric, conductometric and interferometric measurements. The available data have been utilized to examine the solvation phenomena of ions and ion-pairs in the non-aqueous solvents. This type of ion-pairs interaction in non-aqueous solvent media are widely applied in the high energy battery technology and the assessment of ion pairing in these systems is important because of its effect on the ionic conductivity.

Our further objective is to study the interaction between the solvent-solvent of some polar and non-polar solvent of moderate dielectric constant. These type of interactions are also widely used for cosmetic products and other organic synthesis as manifested from the physico-chemical studies in these media.

1.3 METHODS 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 five important methods, namely, conductometry,

viscometry, densitometry, ultrasonic interferometry and spectrophotometry 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.¹⁷

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.

1.4A SUMMARY OF THE WORK DONE

Tetrahydrofuran(THF) has been chosen as main solvent in my research works. The study of THF, 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(THF) and 1,4-dioxane and their mixtures are the very important solvents widely used in various industries. They are good industrial

solvent and figure prominently in the high energy modern battery technologies and have found their applications in organic syntheses as manifested from the physico-chemical studies in these media.

Even though THF and 1,4-dioxane have drawn much focus in recent years as solvents for electroanalytical investigations, still more studies on the electrolytic behaviour in these non-aqueous medium can be explored. Therefore, we have embarked on a series of investigations on THF and 1,4-dioxane 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 1,4-dioxane through the measurements of conductances, viscosities, densities and the velocities of sound.

The present dissertation has been divided into eleven chapters.

Chapter I : This chapter involves the scope and object of the research work. This mainly contains the choice of the main solvent used and its industrial applications, scope of the work, methods of investigation and summary of the work done.

Chapter II : This chapter forms the introduction of review of the earlier works . This chapter is presenting a brief review of notable works of importance of solution chemistry, thermodynamics of ion-pair formation, division of B-coefficient into ionic values, thermodynamics of viscous flow, ion-size parameter and ionic association, Stokes' law and Walden's rule. The works are presenting the field of solute-solvent, solute-solute and solvent-solvent interactions, the discussion centres around the conductance, density, viscosity and adiabatic compressibility of different electrolytes in different solvent systems at different 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-coefficients of some alkali metal chlorides (LiCl, NaCl, KCl) in different mass% of THF + H₂O mixtures (20, 40, 60, 80) at (303, 308, 313 and 318)K. the limiting apparent molar volumes (V_{ϕ}°) 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 viscosity data have been analyzed using the Jones-Dole equation and the derived parameters B and A have also been interpreted in terms of solute-solvent and solute-solute interactions respectively. The structure making and breaking capacities of alkali metal chlorides investigated here have been discussed.

Chapter V : This chapter entails the studies on the conductance of some tetraalkylammonium and alkali metal bromides in tetrahydrofuran (THF) + 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 characteristics parameters, Λ° , 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 VI : This chapter describes the studies on thermodynamics and transport properties of two binary mixtures in which tetrahydrofuran (THF) plays the role of first component (x_1) at different temperatures (303.15, 308.15, 313.15, 318.15 and 323.15)K. From the experimental results the excess molar

volume (V^E), the deviation of viscosity from the mole fraction average ($\Delta\eta$) and Grunborg-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 VII : This chapter includes the volumetric and viscometric studies of some mineral salts [NH_4SO_4 , Na_2SO_4 , MgSO_4 and $\text{Al}_2(\text{SO}_4)_3$] in aqueous binary mixtures of tetrahydrofuran (THF) at different temperatures (303, 308, 313 and 318)K. Apparent molar volumes (V_ϕ) and viscosity B-coefficients of these electrolytes are derived from these data supplemented with their densities and viscosities respectively. The limiting apparent molar volume (V_ϕ°) and experimental slopes (S_v^*) obtained from the Masson equation have been discussed in terms of solute-solvent and solute-solute interactions respectively. The B-coefficient values analyzed using the Jones-Dole equation. The V_ϕ° values vary with temperatures as a power of series of temperature. The structure making/breaking capacities of the electrolyte studied here have been inferred from the Hepler's criterion.

Chapter VIII : This chapter entails the studies on density and viscosity of ternary liquid mixtures (n-hexane + tetrahydrofuran + benzene, n-hexane + tetrahydrofuran + isopropanol and n-hexane + isopropanol + benzene) at different temperatures (303, 313 and 323)K. Various excess thermodynamics functions viz. excess viscosity (η^E), excess volume (V^E) excess Gibbs free energy of activation of flow ($\Delta G^{\neq E}$) and the values of interaction parameter d in Grunberg and Nissan equation have been 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 IX : In this chapter density, viscosity and ultrasonic speeds data have been reported for resorcinol in 10, 20, 30 mass% of 1,4-dioxane + water mixtures and pure 1,4-dioxane (DO) at 303.15, 313.15 and 323.15K. The

limiting apparent molar volumes (V_{ϕ}°) and experimental slopes (S_v^*) derived from Masson equation have been interpreted in terms of ion-solvent and ion-ion 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 ion-solvent and ion-ion interactions respectively. The structure making/breaking capacities of resorcinol investigated here have been discussed. The compressibility obtained from the data supplemented with their ultrasonic speeds indicate the electrostriction of the solvent molecules around the ions.

Chapter X : This chapter contains the studies on electrical conductance of some ammonium halides e.g. ammonium fluoride, ammonium chloride and ammonium bromide; some tetraalkylammonium halides such as tetramethyl ammonium chloride (Me_4NCl) and tetrabutyl ammonium Iodide (Bu_4NI) and Sodium Iodide in different mass% (10, 20, 30) of tetrahydrofuran + water mixtures at 298.15K. The experimental data have been analyzed by the 1978 Fuoss conductance equation and the derived characteristics parameters Λ° , K_A and R have been calculated. The studies throw light on the effect of nature of the electrolytes, solvent composition on the solvation behaviour of ions in THF + water mixtures and the results have been explained in view of solute-solvent and solute-solute interactions. The ionic Walden products have also been determined and their variations with solvent composition have been discussed.

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