CHAPTER I

Scope and Object of the Research

1.1. *Object and application of the work*

The physico-chemical properties play a pivotal role in interpreting the intermolecular interactions among mixed components and efforts have been directed at an understanding of such properties at microscopic and macroscopic levels. In order to gain insight into the mechanism of such interactions thermodynamic, transport and acoustic studies on binary and ternary solvent systems are highly useful. Young[1] made the first systematic attempt in these directions by collecting a number of data on the thermodynamic and mechanical properties of liquid mixtures. The proper understanding of the molecular interactions form the basis of explaining the influence of the solvent and the extent of interactions of ions in solvents and paves the way for real understanding of the different phenomena associated with Solution Chemistry.

In recent years, there has been an increasing interest in the behavior of electrolytes in non-aqueous and mixed solvents with a view to investigate 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 interest in organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry [2].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 [3], Meck [4], Popovych [5], Bates [6,7], Parker [8,9], Criss and Salomon [10], Mercus[11] and others[12-14] . The solute-solute and solute - solvent interactions has been subject of wide interest as apparent from recent Faraday Trans. of the chemical society [15].

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 ionic 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 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.[16-18] Other fields where non-aqueous electrolyte solutions are broadly used include electrochromic displays and smart windows, photoelectrochemical cells, electromachining, 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 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 acoustic studies, give very valuable information about molecular interactions in solutions.[19,20] The influence of these solute-solvent interactions is sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in diverse areas such as organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extraction.[21]

Excess thermodynamic properties are important parameters for understanding molecular interactions in the solution phase. The excess thermodynamic properties of the mixtures correspond to the difference between actual property and the property if the system behaves ideally. Thus these properties provide important information about the nature and strength of intermolecular forces operating among mixed components. Also physico-chemical properties involving excess thermodynamic functions have relevance in carrying out engineering applications in the process industries and in the design of industrial separation processes. Information of these excess thermodynamic functions can also be used for the development of empirical correlations and improvement of new theoretical models.

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become evident that the solvents significantly influence the majority of the solutes. Conversely, the nature of strongly structured solvents like water, is substantially modified by the presence of solutes.[22]

A knowledge of ion-solvent interactions in non-aqueous solutions[23] is very important in many practical problems concerning energy transport, heat transport, mass transport and fluid flow. Besides finding applications in engineering branch, the study is important from practical and theoretical point of view in understanding liquid theory. The non-aqueous systems have been of immense importance to the technologist and theoretician as many chemical processes occur in these systems.

It is thus, apparent that the real understanding of the molecular interactions is a difficult task. The aspect embraces a wide range of topics but we have embarked on a series of investigations based on the volumetric, viscometric, interferometric and conductometric behavior to study the chemical nature of the structure of solutes and solvents and their mutual and specific interactions.

1.2. *Importance of solvents used:*

Acetonitrile, 1,4-Dioxane, 1,3-Dioxolane, Tetrahydrofuran, 2-ethoxyethanol, Alchohols (Methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1- octanol, t-butyl alchohol), Hydrocarbons- (n-pentane, n-hexane, n-heptane), Dimethylsulfoxide, butyl acetate, 2-butanone, butylamine, 2-Methoxyethanol, Carbon Tetrachloride, along with water which is a universal solvent have been chosen as solvents in this research work. The study of these solvents, in general, is of great interest because of their wide use as solvents and solubilizing agents in many industries ranging from pharmaceutical to cosmetics.

Acetronitrile is a dipolar aprotic solvent lacking strong specific intermolecular forces, where dipole-dipole forces predominate. It has a wide range of technological applications, namely, in battery systems and plating techniques.[24,25]

1,4-dioxane, 1,3-dioxolane and tetrahydrofuran are all cyclic ethers and they figure prominently in the high-energy battery technology[24] and have also found application in organic synthesis as manifested from the physico-chemical studies in these media. 1,4-dioxane and 1,3-dioxolane are cyclic diethers differing in one methylene group and thus they differ in quadrupolar and dipolar order.[26]

The increasing use of 1,4-dioxane, 1,3-dioxolane, tetrahydrofuran and their aqueous or binary liquid mixtures in many industrial processes have greatly stimulated the need for extensive information on their various properties. Viscosity and density of these liquid mixtures are used to understand molecular interactions between the components of the mixture to develop new theoretical models and also for engineering applications.[27,28]

The alkoxyethanols (2-ethoxyethanol and 2-Methoxyethanol) occupiers an important place in many industrial processes such as pharmaceutical and cosmetics industry and have greatly stimulated the need for extensive information on the thermodynamic, acoustic and transport properties of these solvents and their mixtures.

Alcohols and its aqueous and non-aqueous mixtures are widely used in pharmaceutical industry as excipients in different formulations or as solvents. Alcohols have varied applications in chemical and cosmetic industries. These are useful in enology and as an alternative energy source.[29,30] Methanol is used as solvent for paints and varnishes, antifreeze for automobile radiators, motor fuel, denaturant for ethanol, etc. A knowledge of their physico-chemical characteristics helps to understand their behavior in concrete manner.

Carbon tetrachloride is used to make compounds such as Chlorofluoromethanes, used as refrigerants and aerosol-spray propellants, in fire extinguishers and for dry cleaning of fabrics.

The hydrocarbons, both aromatic and aliphatic have varied applications. n-hexane, which is familiar in the laboratory as the principle component of petroleum ether, is used as solvent, dry-cleaner and motor fuel.

Dimethyl sulfoxide (DMSO), a typical aprotic solvent having both polar and nonpolar groups, is an important solvent in chemistry, biotechnology, and medicine for the dissolution of various substances and as an antifreeze agent of living cells.[31] This solvent has wide range of applicability as a solvent in chemical and biological processes.

Water is the most widely used solvent in the chemical industries, since it is the most physiological and best tolerated excipient. However, in some cases, water cannot be used as a solvent because the active substance or solute is insoluble or slightly soluble in it. The non-aqueous solvents with common characteristics of being soluble or miscible in water are thus used. Such solvents can be used to prepare binary or ternary mixtures and they can serve different purposes such as increasing water solubility, modifying the viscosity, absorption of the dissolved substance.

The knowledge of the type and structure of the complex species in solution is essential for the optimal choice of solvents. Even though these solvents have drawn much focus in recent years as solvents for physico-chemical investigations, still a lot remains to be explored.

1.3. *Methods of Investigation*

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 [32].

Various techniques [33,34] 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 and ultrasonic interferometer to probe the problem of solvation phenomena.

Thermodynamic properties of solutions are not only useful for estimation of feasibility of chemical reactions in solution, but they also offer one of the better methods of investigating the theoretical aspects of solution structure. Thermodynamic properties, like apparent molar volumes, partial molar expansibility, etc. obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution.

The change in solvent viscosity by the addition of electrolytes is attributed to inter-ionic and ion-solvent effects. The B-coefficients gives a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, preferential solvation and structure-breaking or structure-making capacity of the solutes.

The compressibility, a second derivative of Gibbs energy, is also a sensitive indicator of molecular interactions and provides useful information in such cases where partial molar volume data alone cannot provide an unequivocal interpretation of these interactions. Various acoustical parameters have been derived in carrying out the investigation.

The excess properties such as excess molar volume, viscosity deviations, excess isentropic compressibility along with the correlating equations explains molecular interactions in a more effective way.

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

1.4. *Summary of the works done*

The volume of work covered under this dissertation has been divided into twelve chapters. Brief summaries of each of the chapters are given below.

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. A brief review of notable works in the field of ion-solvent interaction has been given. The discussion includes solute-solvent, solute-solute and solvent-solvent interactions of mixed solvent systems and of electrolytes in pure, aqueous, non-aqueous solvent systems at various temperatures in terms of various derived parameters of density, viscosity, ultrasonic speed and conductance. Critical evaluations on the relative merits and demerits of the different methods used on the basis of various assumptions employed from time to time of obtaining the single ion values and their implications have been made. The molecular interactions are interpreted based on various equations. The trends in solvation models stress the importance of the work.

Chapter III

This chapter contains the experimental section that mainly involves the source and purification of the solvents and solutes used and the details of the experimental methods employed for measurement of the thermodynamic, transport and acoustic properties.

Chapter IV

This fourth chapter deals with the study of excess properties of binary mixtures of acetonitrile with some cyclic ethers (1,4-dioxane, 1,3-dioxolane, tetrahydrofuran) at 298.15 K, 308.15 K and 318.15 K. Densities and viscosities of the binary mixtures of acetonitrile with tetrahydrofuran, 1,3-dioxolane, and 1,4-dioxane were measured over the entire range of composition atall the experimental temperatures. Ultrasonic speeds of these binary mixtures have also been measured at 298.15 K. From the experimental data, values of excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), and deviations in isentropic compressibility (ΔK_S) have been calculated. These results were fitted to Redlich-Kister polynomial equation. The density and viscosity data were analyzed by some semi empirical viscosity models, and the results have been discussed in terms of molecular interactions and structural effects. To explore the nature of the interactions, various thermodynamic parameters (e.g., intermolecular free length, specific acoustic impedance, etc.) have also been derived from the density and ultrasonic speed data.

Chapter V

In this chapter the densities, viscosities, and ultrasonic speeds of binary mixtures of 2-ethoxyethanol with 1-alkanols (methanol to 1-octanol) have been measured at 298.15 K. The excess molar volume (V^E), viscosity deviations ($\Delta\eta$) and Gibbs excess free energy of activation for viscous flow (G^{*E}) have been investigated from the experimentally measured density (ρ) and viscosity (η) values. The viscosity data have been correlated by Grunberg and Nissan, Tamura-Kurata and Hind correlation equation. The deviations in isentropic compressibility (ΔK_S) were also calculated using the measured speeds of sound. The results are discussed and interpreted in terms of molecular package and specific interaction predominated by hydrogen bonding. The sound speeds were predicted by using Free length and Collision factor theoretical formulations, by Nomotto equation, by Vandeal Vangael ideal mixing relation and the impedance dependence relation. The deviations have been fitted to a Redlich-Kister equation and the results are discussed in terms of molecular interactions and structural effects.

Chapter VI

The measured densities and viscosities of binary mixtures of tetrahydrofuran + n-pentane, tetrahydrofuran +n-hexane and tetrahydrofuran +n-heptane at 288.15, 293.15 and 298.15 K. have been used to calculate the excess molar volume, excess free energy, deviation in viscosity of the composition and the interaction parameter of Grünberg and Nissan over the entire composition range. 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_ϕ), viscosity parameters of these solutions are obtained from these data supplemented with their densities and viscosities respectively. The limiting apparent molar volumes (V_ϕ^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

In this chapter, Conductance measurements for selected alkali chlorides, MCl (M^+ = Li, Na, K) are performed in the binary mixtures of methanol with carbon tetrachloride and 1,4-dioxane at 298.15 K. The limiting equivalent conductance (Λ_0), the association constant (K_A), and the Walden products ($\Lambda_0\eta_0$) for the three salts are evaluated at all the mole fractions of the solvent mixtures using the 1978 Fuoss conductance equation. Based on the composition dependence of walden product ($\Lambda_0\eta_0$) the influence of the mixed solvent composition on the solvation of ions has also been discussed. The results have been discussed in terms of ion-solvent and ion-ion interactions and the structural changes in the mixed solvent systems.

Chapter IX

The densities, viscosities and ultrasonic speeds of some monobasic acetate salts, viz. ammonium acetate (CH_3COONH_4), lithium acetate (CH_3COOLi), sodium acetate (CH_3COONa) and potassium acetate (CH_3COOK) in methanol water mixtures (10%, 20%, 30%) have been measured at (298.15, 308.15, 318.15) K. The limiting apparent molar volumes (V_ϕ^0), the experimental slope (S_v^*), supplemented with the measured density data have been interpreted in terms of solute-solvent and solute- solute interactions respectively. The parameters B and A obtained from viscosity data analyzed using Jones-Dole equation have also been interpreted in terms of solute-solute and solute-solvent interactions respectively. The structure making or structure breaking nature of the acetates in the solvent-mixtures studied here has been discussed. The compressibility data supplemented with the ultrasonic speeds explain the electrostriction of the solvent molecules around the positive ions.

Chapter X

Apparent molar volumes, Viscosity B-Coefficients, and apparent molar Isentropic compressibilities of Glycine, L-Alanine, L-Valine and L-Leucine in aqueous tetra butyl ammonium bromide (TBAB) Solution of three different concentrations (0.062, 0.125and 0.256 mol·kg $^{-1}$) have been determined at 298.15 K from the experimental density, flow time and sound speed measurements respectively. The standard partial molar volumes and compressibilities are used to calculate the corresponding volume of transfer at infinite dilution, from water to aqueous TBAB solutions. The linear correlation of partial molar volumes for a homologous series of amino acids has been utilized to calculate the contribution of charged end groups and other alkyl chains of the amino acids to partial molar volumes. The hydration numbers of amino acids have also been determined. Viscosity B coefficients have been calculated using the Jones-Dole equation. The values of the charged end-groups contribution to the viscosity B-coefficients of the amino acids are also calculated.

Chapter XI

Densities and viscosities of binary mixtures of Dimethyl sulfoxide (DMSO) with tert-butyl alcohol, butyl acetate, 2-butanone and butyl amine were determined over the entire range of mole fractions at the temperatures of 298.15 K, 308.15 K and 318.15 K. At each temperature, the excess molar volume (V^E), viscosity deviations ($\Delta\eta$)· Gibbs excess free energy of activation for viscous flow (G^{*E}) have been investigated from these measured density and viscosity values. The experimental viscosity data were correlated by means of the equations of Grunberg-Nissan, Tamura and Kurata and Hind. The deviations have been fitted to a Redlich-Kister equation and the results are discussed in terms of molecular interactions and structural effects.

Chapter XII

The dissertation ends with some concluding remarks in this chapter.

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