

CHAPTER - 1

1.1. Scope and utility of the research work

The importance and uses of chemistry in the study of aqueous and non-aqueous solvent systems are well-recognized. In recent years there has been an increasing interest in the study of physico-chemical properties of solvent-solvent¹⁻³ and solute-solvent⁴⁻⁶ systems. The physico-chemical properties play a important role in interpreting the intermolecular interactions among mixed components and efforts in recent years 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. The excess thermodynamic properties of the mixtures correspond to the difference between actual property and the property if the system behaves ideally. So these properties provide important information about the nature and strength of intermolecular forces operating among mixed components. The 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.

Rheology is the branch of science⁷ that studies material deformation and flow, and is implicated in the mixing and flow of medicinal formulations and cosmetics and is increasingly applied to the analysis of the viscous behavior of many pharmaceutical products,⁸⁻¹² and to establish their stability and even bio-availability.

Considering the rheological behavior, thermodynamic investigation is very important, since many products are formulated with more than one component in order to yield the desired physical structure and properties.¹³ Synergy and antagonism gives the mutual enhancement or decrement of the physico-chemical, biological or pharmaceutical activity between different components for a given mixture. If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system^{14,15} is said to lack interaction. The study of the viscous

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behavior of pharmaceuticals, foodstuffs, cosmetics or industrial products etc., is essential for confirming that their viscosity is appropriate for the product.

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.

The importance and uses of the chemistry of electrolytes in non-aqueous and mixed solvents are now well recognized. The applications and implications of the studies of reaction in non-aqueous and mixed solvents have been summarized by Meck¹⁶, Franks¹⁷, Popovych¹⁸, Bates¹⁹, Parker²⁰, Criss and Salomon²¹, Marcus²² and others.²³⁻²⁵ The solute-solute and solute-solvent interactions have been subject of wide interest as apparent from Faraday Transactions of the chemical society.²⁶

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. But, 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 along with a host of other properties.^{17,27}

In recent years, there has been increasing interest in the study of behavior of electrolytes or solutes 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 opened vistas for physical chemists and interest in these organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry.²⁸

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Fundamental research on non-aqueous electrolyte solutions has catalyzed their wide technical applications in many fields. Non-aqueous electrolyte solutions are 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.²⁹⁻³¹ Other fields where non-aqueous electrolyte solutions are 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.

The influence of these solute-solvent interactions is large enough 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.^{32,33,34}

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become evident that the majority of the solutes are significantly influenced by the solvents. Conversely, the nature of strongly structured solvents like water, is substantially modified by the presence of solutes.³⁵

Knowledge of ion-solvent interactions in non-aqueous solutions²⁴ 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 theories.

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, spectrometric and conductometric behavior to study the chemical nature of the

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structure of solutes and solvents and their mutual and specific interactions in solution.

1.2. Importance and scope of Physico-chemical parameters

The rheological and thermodynamic study of physico-chemical properties involves the interpretation of the excess properties as a mean of unraveling the nature of intermolecular interactions among the mixed components. The interactions between molecules can be established from a study of characteristic departure from ideal behavior of some physical properties such as density, volume, viscosity, compressibility etc.^{36,37}

Density of solvent mixtures and related volumetric properties like excess molar volume are essential for theoretical as well as practical aspects. The sign and magnitude of excess molar volume imparts estimate of strength of unlike interactions in the binaries. The negative values of excess molar volume (V^E) suggest specific interactions^{38,39} between the mixing components in the mixtures while its positive values suggest dominance of dispersion forces^{38,39} between them. The negative V^E values indicate the specific interactions such as intermolecular hydrogen bonding between the mixing components and also the interstitial accommodation of the mixing components because of the difference in molar volume. The negative V^E values may also be due to the difference in the dielectric constants of the liquid components of the binary mixture.³⁸

Viscosity data provides valuable information about the nature and strength of forces operating within and between the unlike molecules. Recently the employment of computer simulation of molecular dynamics has led to significant improvement towards a successful molecular theory of transport properties in fluids and a proper understanding of molecular motions and interaction patterns in non-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents.^{40,41} The study of physico-chemical behaviors like dissociation or association from acoustic measurements and from the calculation of isentropic compressibility has gained much importance. Excess isentropic compressibility, intermolecular free

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length etc impart valuable information about the structure and molecular interactions in pure and mixed solvents. The acoustic measurements can also be used for the test of various solvent theories and statistical models and are quite sensitive to changes in ionic concentrations as well as useful in elucidating the solute-solvent interactions.

Drug transport across biological cells and membranes is dependent on physico-chemical properties of drugs. But direct study of the physico-chemical properties in physiological media such as blood, intracellular fluids is difficult to accomplish. One of the well-organized approaches is the study of molecular interactions in fluids by thermodynamic methods as thermodynamic parameters are convenient for interpreting intermolecular interactions in solution phase. Also the study of thermodynamic properties of drug in a suitable medium can be correlated to its therapeutic effects.^{42,43} These facts therefore prompted us to undertake the study of binary or ternary solvent systems with 1,4-dioxane and 1,3-dioxolane or tetrahydrofuran as primary solvents with some polar, weakly polar and non-polar solvents as well as with some solutes. Furthermore, the excess properties derived from experimental density, viscosity and speeds of sound data and subsequent interpretation of the nature and strength of intermolecular interactions help in testing and development of various theories of solution.

1.3. Importance of solvents used:

Acetonitrile, Benzene, N, N-Dimethylformamide, Dimethylsulfoxide, monoalkanols viz. methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol and some cyclic as well as acyclic ethers viz. 1,3 dioxolane, 1,4 dioxane, tetrahydrofuran, diethyl ether, di-isopropyl ether, 1,2 dimethoxy ethane, 2-methoxy ethanol, 2-ethoxy ethanol along with water considered as a universal solvent have been chosen as main 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.

1,4-dioxane is very hygroscopic and miscible in all proportions with water. Its dielectric constant and dipole moment are 2.209 and 0.45D respectively at 25⁰C.

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However, its dipole moment rises with increase in temperature suggesting formation of boat form.²⁸

1,4-dioxane and 1,3-dioxolane are all cyclic diethers and they figure prominently in the high-energy battery technology⁴⁸ 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 differ in one methylene group and thus they differ in quadrupolar and dipolar order.⁴⁴

N, N-dimethylformamide is a non-associative aprotic protophilic solvent with a liquid range of -60 to 153°C , low vapour pressure and good solubility for a wide range of substances. It is also used in the separation of saturated and unsaturated hydrocarbons and serves as solvents for vinyl resins, acid gases, polyacrylic fibres and catalyst in carbonylation reaction as well as in organic synthesis. It has also been used as the model of peptide linkage in studies aimed at understanding of protein denaturation studies.^{45,46}

Dimethyl sulfoxide is one of the most widely used members of the class of dipolar aprotic solvent and has an extensive dissolving power. It is highly associated liquid.

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^{47,48}.

1,2-dimethoxyethane (dielectric constant, $\epsilon = 7.03$)⁴⁹ and 2 methoxy-ethanol find a wide range of application of technological importance and these solvents are relevant to battery construction using suitable electrodes.⁴⁹

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

Alcohols and their 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

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alternative energy source.⁵⁰ A knowledge of their physico-chemical characteristics helps to understand their behavior in a better way.

Methanol is used as solvent for paints and varnishes, antifreeze for automobile radiators, motor fuel, denaturant for ethanol, etc. It is obtainable commercially in adequate purity for most purposes, the principle impurity being up to 0.05% water usually be removed by distillation, or by use of molecular sieves and calcium hydride.

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.

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 explored.

1.4. Method 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 regions⁵¹.

Various techniques^{52,53} 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 viscometry, conductometry, densitometry, ultrasonic interferometry and spectrophotometry in the research work.

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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.⁵⁴

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.

1.5 Summary of the work done

Chapter 1 This chapter involves the scope and utility of the research work. This mainly comprised the choice of the main solvents used and its applications in different fields, methods of investigation and summary of the works associated with the thesis.

Chapter 2 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 3 This chapter includes the experimental section, which mainly contains the sources, and purification of the solvents and solutes used and the various techniques of the experiments applied for measurement of the thermodynamic, transport and acoustic properties.

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Chapter 4 This chapter describes the study of densities, viscosities and ultrasonic speeds of binary mixtures containing 2-methoxy ethanol and some alkan-1-ol at 298.15 K. This study involves seven binary mixtures in which 2-methoxy ethanol 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 (Δu) are calculated from the experimental values of viscosity (η), density (ρ) and speed of sound (u) for binary liquid mixture of 2-methoxy ethanol with methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol and heptan-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 5 This chapter entails the studies on the conductance of some Tetraalkylammonium Halides in 1,4-dioxane + Methanol mixtures at 298.15 K. The tendency of the ion-pair and triple-ion formation of R_4NX have been analyzed by using Fuoss and Kraus conductance equation. The various derived parameters like limiting molar conductivity (Λ_0), the association constant (K_A) and association distance (R) in the solvent mixtures have also been evaluated. The formation of ion-pair and triple-ions might be attributed to the ion sizes in solutions and bonding forces like coulombic forces and covalent interactions between the ions.

Chapter 6 In this chapter studies on apparent molar volume, viscosity B-coefficient and adiabatic compressibility of some thiocyanate salts in aqueous binary mixtures of 1,3-dioxolane at different temperatures have been made from density, viscosity and ultrasonic speed data. The structure making / breaking capacities of the electrolytes have been inferred from the sign of $(\delta^2 V_\phi^0 / \delta T^2)_p$ and dB/dT . The activation parameters of viscous flow for the ternary solutions studied were also calculated and explained by the application of transition state theory.

Chapter 7 This chapter involves the studies on the interaction by hydrogen bond formation of the primary alcohols, (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol) in (20, 40, 60, 80) mass % of cyclic ethers, (tetrahydrofuran and 1,3-dioxolane) using the FTIR spectroscopic method

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at 298.15K. Formation constant (K) and free energy changes (ΔG^0) of complex formation are determined. The solvent effects on the hydrogen bond formation is discussed in terms of specific interaction and mutual association between the solvents.

Chapter 8 This chapter includes the volumetric, viscometric, and ultrasonic studies of some acetate salts [$\text{CH}_3\text{COONH}_4$, CH_3COOLi , CH_3COONa , CH_3COOK] in aqueous binary mixtures of tetrahydrofuran (10, 20 and 30 mass % tetrahydrofuran) at different temperatures (303.15, 313.15, and 323.15) K. The experimental values of ρ was used to calculate the values of the apparent molar volume (Φ_v). The limiting apparent molar volume (Φ_v^0) and the experimental slope (S_v^*) have been interpreted in terms of ion-solvent and ion-ion interactions respectively. The structure making / breaking capacities of the electrolytes have been inferred from the sign of $(\delta^2 V_\phi^0 / \delta T^2)_p$ and dB/dT . The compressibilities obtained from the data supplemented with their ultrasonic speeds indicate the electrostriction of the solvent-mixture molecule around the ammonium and metal ions.

Chapter 9 In this chapter the densities(ρ) and viscosities(η) for the ternary liquid mixtures of N,N-dimethylformamide + benzene + ethers, have been measured over the entire range of composition at 298.15 K. From the experimental measurements excess molar volumes (V^E), viscosity deviation($\Delta\eta$) and antagonic index (I_A) have been evaluated. The speeds of sound have also been measured and excess isentropic compressibilities (K_S^E) are calculated at the experimental temperature. The results are discussed and interpreted in terms of molecular package and specific interaction predominated by hydrogen bonding.

Chapter 10 This chapter describes the electrical conductance of some alkali metal halides in 20, 40 and 60 mass% of dimethyl sulfoxide (DMSO) in DMSO + Acetonitrile mixtures at 298.15 K. The conductance data have been analyzed by the 1978 Fuoss conductance- concentration equation in terms of limiting molar conductance (Λ^0), the association constant (K_A), and the association diameter (R). The limiting ionic conductance have been estimated from the appropriate division of the limiting molar conductivity value of the "reference electrolyte" Bu_4NBPh_4 . The results have been analyzed in terms of ion-ion and ion-solvent interactions.

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Chapter 11 In this chapter partial molar volumes (ϕ_v°) and viscosity B -coefficients for nicotinamide in different aqueous resorcinol solutions have been determined from solution density and viscosity measurements at 298.15, 308.15 and 318.15 K. 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 in the ternary solutions. The structure making or breaking ability of nicotinamide has been discussed in terms of the sign of $(\delta^2 \phi_v^\circ / \delta T^2)_p$. The activation parameters of viscous flow for the ternary solutions studied were also calculated and explained by the application of transition state theory.

Chapter 12 This chapter contains the concluding remarks on the works related to the thesis.

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