



CHAPTER – I

SCOPE AND OBJECT OF THE RESEARCH

Molecular interactions in solution phases can be better understood by studying various excess thermodynamic properties. 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.

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.

Rheology is the branch of science ^[1] that studies material deformation and flow, and is implicated in the mixing and flow of medicinal formulations and cosmetics and is increasingly applied in the analysis of the viscous behavior of many pharmaceutical products ^[2-6], 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 ^[7]. Synergy and antagonism gives the mutual enhancement or components for a given mixture. If the total viscosity of the system is equal to the sum of decrement of the physico-

chemical, biological or pharmaceutical activity between different the viscosities of each component considered separately, the system [8-9] is said to lack interaction. The study of the viscous behavior of pharmaceuticals, foodstuffs, cosmetics or industrial products etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the product.

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 [10], Meck [11], Popovych [12], Bates [13-15], Parker [16-17], Criss and Salomon [18], Mercus [19] and others [20-22]. The solute-solute and solute - solvent interactions has been subject of wide interest as apparent from recent *Faraday Trans. of the chemical society* [23].

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 [24].

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 [25-26]. 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 [27]. 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 [28-29].

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 [30].

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 behaviour to study the chemical nature of the structure of solutes and solvents and their mutual and specific interactions in solution.

I.1. Importance & scope of physico-chemical parameters

The study of physico-chemical properties involves the interpretation of the excess properties as a mean of unraveling the nature of intermolecular interaction 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 [31-32].

The phenomenon of ion-ion or solute-solute, ion-solvent or solute-solvent and solvent-solvent synergy, and antagonism, are intriguing. It is desirable to explore these interactions using different experimental techniques. We have, therefore, employed four important methods, viz. densitometry, viscometry, ultrasonic interferometry and conductometry in our research works.

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 [33-34] between the mixing components in the mixtures while its positive values suggest dominance of dispersion forces [33-34] 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 [33].

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 [35-36].

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 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.

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.

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 [37-38].

These facts therefore prompted us to undertake the study of binary or ternary solvent systems with some polar, weakly polar and non-polar solvents as well as with some solutes. Furthermore, the excess properties derived from experimental density, viscosity, 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.

1.2. Choice & importance of solvents and solutes used

Tetrahydrofuran, N,N-dimethylformamide, acrylonitrile, dimethylsulfoxide, some monoalkanols viz. methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-

butanol, amyl alcohol and *iso*-amyl alcohol, benzene, some aromatic aldehydes viz. cinnamaldehyde, anisaldehyde and benzaldehyde along with water, considered as a universal solvent, have been chosen as main solvents in this research work.

Resorcinol; amino acids, viz., glycine, alanine, valine, leucine; nicotinamide; citric acid monohydrate; ascorbic acid; tetraalkylammonium bromides, viz., tetra n-butylammonium bromide, tetra n-pentylammonium bromide, tetra n-hexylammonium bromide, tetra n-heptylammonium bromide; tetraalkylammonium iodides, viz., tetra n-butylammonium iodide, tetra n-pentylammonium iodide, tetra n-hexylammonium iodide, tetra n-heptylammonium iodide were considered as solutes.

The study of these solvents and solutes, in general, is of great interest because of their wide use as solvents and solubilizing agents in many industries ranging from pharmaceutical to cosmetics.

I.3. Methods of investigations

The existence of free ions, solvated ions, ion-pairs and triple-ions in aqueous and non-aqueous media depends upon the concentrations of the solvent systems. Hence, the study of various interactions and equilibrium of ions in different concentration regions are of immense importance to the technologist and theoretician as most of the chemical processes occurs in these systems.

It is of interest to employ different experimental techniques to get a better insight into the phenomena of solvation and different interactions prevailing in solution. We have, therefore, employed four important methods, namely, conductometric, viscometric, densitometry and interferometric, 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 sign and magnitude of limiting apparent molar volume (V_{ϕ}^0) also provides information about the nature and magnitude of ion-solvent interaction while the experimental slope S_V^* provides

information about ion-ion interactions [39]. 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.

Viscosity and density have been used to interpret the synergic and antagonic behavior in the solvent mixtures. The values of synergic and antagonic interaction indices determine the nature of the molecular package. The change in solvent viscosity by the addition of electrolytes is attributed to inter-ionic and ion-solvent effects. 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 the same, a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, preferential solvation, structure-breaking or structure-making, polarization, etc. may be given.

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.

I.4. Summary of the work done

The present dissertation has been divided into eight chapters.

Chapter I

Background, Object and Application of Research Work

This chapter contains the object and applications of the research work, the reasons for choosing the main solvents and solutes and methods of investigation. This also includes a summary of the works associated with the thesis.

Chapter II

General Introduction

This chapter contains the general introduction of the thesis and forms a background of the works embodied in the thesis. A brief review of notable works on the behavior of viscous synergy and antagonism, ion-ion, ion-solvent and solvent-solvent interaction has been made. Also an attempt has been made to define these interactions. Various derived parameters dependent on density, viscosity, ultrasonic speed of sound, refractive indices and conductance along with their importance in solution chemistry has been discussed. Several semi-empirical models to estimate dynamic viscosity of binary liquid mixtures have been discussed. Ionic association and its dependence on ion-size parameters as well as relation between solution viscosity and limiting conductance of an ion has been discussed using Stokes' law and Walden rule. Critical evaluations of different methods employed frequently for obtaining the single ion values (viscosity B -coefficient and limiting equivalent conductance) and their implications have been discussed.

Chapter III

Experimental section

This chapter contains the experimental section mainly involving 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

Study on Solid - Liquid systems by Density, Viscosity and Ultrasonic speed Measurements

Chapter IV-A

Apparent molar volumes V_{ϕ} , viscosities η , and apparent molal isentropic compressibility κ_{ϕ} , of glycine, L-alanine, L-valine and L-leucine in 0.05, 0.10, 0.15

mol·kg⁻¹ resorcinol solutions have been determined at 298.15 K by measuring the densities, viscosities and ultrasonic speed of the above solutions respectively. The apparent molar volumes at infinite dilution V_{ϕ}^0 , standard volumes of transfer $\Delta_{tr}V_{\phi}^0$, apparent molar isentropic compressibilities κ_{ϕ}^0 , transfer compressibilities $\Delta_{tr}\kappa_{\phi}^0$, hydration number N_w , of the amino acids have been calculated for investigating the various interactions in the ternary solutions. The linear correlation of partial molar volume and viscosity B -coefficients with increasing number of carbon atoms in the alkyl chain have been utilized to calculate the contributions of charged end groups (NH_3^+ , COO^-), CH_2 - groups and other alkyl chains of amino acids to V_{ϕ}^0 . The results have been interpreted in terms of ion-ion, ion-polar, hydrophilic-hydrophilic and hydrophobic-hydrophobic group interactions in the mixed ternary solutions.

Chapter IV-B

Apparent molar volumes V_{ϕ} and viscosity B -coefficients for tetra n-butyl ammonium bromide (TBAB) in (0.00, 0.05, 0.10 and 0.15) mol·dm⁻³ aqueous ascorbic acid solutions have been determined from solution density and viscosity measurements at temperatures over the range (298.15 to 318.15) K as function of concentration of ascorbic acid solutions. In the investigated temperature range, the relation: $V_{\phi}^0 = a_0 + a_1T + a_2T^2$, have been used to describe the partial molar volume V_{ϕ}^0 . These results, in conjunction with the results obtained in pure water, have been used to calculate the standard volumes of transfer ΔV_{ϕ}^0 and viscosity B -coefficients of transfer for TBAB from water to aqueous ascorbic acid solutions for rationalizing various interactions in the ternary solutions. The structure making or breaking ability of TBAB has been discussed in terms of the sign of $\left[\frac{\partial^2 V_{\phi}^0}{\partial T^2} \right]_P$. An increase in the transfer volume of TBAB with increasing ascorbic acid concentration has been explained by Friedman-Krishnan co-sphere model. The activation parameters of

viscous flow for the ternary solutions studied have also been calculated and explained by the application of transition state theory.

Chapter IV-C

Apparent molar volumes V_{ϕ} , viscosity B -coefficients for nicotinamide in (0.03, 0.05, 0.07 and 0.10) mol·dm⁻³ aqueous citric acid monohydrate solutions have been determined from solution density and viscosity measurements at (298.15, 308.15 and 318.15) K as function of concentration of nicotinamide. In the investigated temperature range, the relation: $V_{\phi}^0 = a_0 + a_1T + a_2T^2$, have been used to describe the temperature dependence of standard partial molar volume V_{ϕ}^0 . This results have, in conjunction with the results obtained in pure water, been used to calculate the standard volumes of transfer ΔV_{ϕ}^0 and viscosity B -coefficients of transfer for nicotinamide from water to aqueous citric acid monohydrate solutions for rationalizing various interactions in the ternary solutions. The structure making or breaking ability of nicotinamide has been discussed in terms of the sign of $\left[\frac{\partial^2 V_{\phi}^0}{\partial T^2} \right]_P$ and dB/dT . An increase in the transfer volume of nicotinamide with increasing citric acid monohydrate concentration has been explained by Friedman-Krishnan co-sphere model. The activation parameters of viscous flow for the ternary solutions studied have also been calculated and explained by the application of transition state theory.

Chapter V

Study on Liquid - Liquid systems by Density, Viscosity and Ultrasonic speed Measurements

Chapter V-A

This chapter includes the study on interaction between solvent-solvent occurring in binary mixtures of acrylonitrile with some aromatic aldehydes by volumetric, viscometric and acoustic measurements. The excess molar volume V^E ,

and viscosity deviations $\Delta\eta$, have been derived from density ρ , and viscosity η , measurements of the binary mixtures of acrylonitrile with anisaldehyde, cinnamaldehyde, and benzaldehyde measured at (298.15, 308.15, and 318.15) K. The data have been correlated with the Grunberg-Nissan equation. Moreover, deviations in isentropic compressibility $\Delta\kappa_s$, have been calculated from ultrasonic speed measurements of these binary mixtures at 298.15 K. The results have been discussed in terms of molecular interactions and structural effects.

Chapter V-B

The densities and viscosities of eight ternary mixtures of Tetrahydrofuran (THF), Dimethylsulphoxide (DMSO) and monoalkanols: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, amyl alcohol, *i*-amyl alcohol are determined over the entire range of composition at 298.15 K. From the experimental measurements excess molar volumes V^E , Viscosity deviation $\Delta\eta$, antagonism and antagonistic index I_A , are derived by the equations developed by Kalentunc-Gencer and Peleg and Howell, respectively. A power factor, F_η has also been introduced here. Also, the speeds of sound of these ternary mixtures have been measured over the whole composition range at the same temperature and thus, the isentropic compressibility κ_s and excess isentropic compressibility κ_s^E have been evaluated from the experimental data. The results are discussed in terms of molecular packing, specific interactions and nature of liquid mixtures. The systems studied here exhibit very strong cross association through hydrogen bonding.

Chapter VI

Study on Solid - Liquid systems by Electrical Conductance Measurements

Chapter VI-A

Conductivities of some tetraalkylammonium halides, viz. tetra *n*-butylammonium bromide (Bu_4NBr), tetra *n*-pentylammonium bromide (Pen_4NBr),

tetra n-hexylammonium bromide (Hex_4NBr) and tetra n-heptylammonium bromide (Hep_4NBr) were measured at 298.15 K in THF + C_6H_6 mixtures with 10, 20, 30 and 40 mass percent of C_6H_6 . A minimum in the conductometric curves (Λ versus \sqrt{c}) was observed at concentrations which dependent both on the salt and the solvent. The observed molar conductivities were explained by the formation of ion-pairs ($\text{M}^+ + \text{X}^- \leftrightarrow \text{MX}, K_p$) and triple-ions ($2\text{M}^+ + \text{X}^- \leftrightarrow \text{M}_2\text{X}^+$; $\text{M}^+ + 2\text{X}^- \leftrightarrow \text{MX}_2^-, K_T$). A linear relationship between the triple-ion formation constants [$\log (K_T/K_p)$] and the salt concentrations at the minimum conductivity ($\log C_{\min}$) was given for all salts in $\text{C}_6\text{H}_6 + \text{THF}$ mixtures. The formation of triple-ions might be attributed to the ion sizes in solutions in which coulombic interactions and covalent bonding forces act as the main forces between the ions ($\text{R}_4\text{N}^+ \cdots \text{X}^-$).

Chapter VI-B

Precise measurements on electrical conductances of tetraalkylammonium iodides, R_4NI ($\text{R} = \text{n-butyl to n-heptyl}$) in different mass % (0-100) of dichloromethane (DCM) + N,N-dimethylformamide (DMF) at 298.15 K have been performed. Limiting molar conductances Λ_0 , association constants K_A , and co-sphere diameter R , for ion-pair formation in the mixed solvent mixtures have been evaluated using the Fuoss conductance-concentration equation. However, the deviation of the conductometric curves (Λ versus \sqrt{c}) from linearity for the electrolytes in 100 mass % of DCM indicated triple ion formation, and therefore corresponding conductance data have been analyzed by the Fuoss-Kraus theory of triple ions. Limiting ionic molar conductances λ_0^\pm (have been calculated by the reference electrolyte method along with a numerical evaluation of ion pair and triple ion formation constants ($K_p \approx K_A$ and K_T). The results have been interpreted in terms of ion-solvent interactions and structural changes in the mixed solvents.

Chapter VII**Study on Solid - Liquid systems by Spectroscopy Measurements**

The FTIR spectra of tetra n-pentylammonium bromide (Pe_4NBr), tetra n-pentylammonium iodide (Pe_4NI), tetra n-hexylammonium bromide (He_4NBr), tetra n-hexylammonium iodide (He_4NI), tetra n-heptylammonium bromide (Hp_4NBr) and tetra n-heptylammonium iodide (Hp_4NI) in pure acrylonitrile were observed at 0.1(M), 0.08(M), 0.05(M) and 0.02(M) concentrations. The region of immobilized solvent resulting from the structure-making effects of electrostriction increases with increase in charge-surface ratio of the ions. Cation-anion interactions are thus, investigated by evaluating the frequency shifts of the solvent in the pure state upon complexation with the salt.

Chapter VIII**Concluding remarks**

The dissertation ends with some concluding remarks in this chapter.

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