

## CHAPTER I

### **Necessity of the Research Work**

#### **1.1. Object and Application of the Research Work:**

Thermo-physical and bulk properties of solutions are very useful to obtain information on the intermolecular interactions and geometrical effects in the systems. Moreover, knowledge of the thermodynamic properties is essential for the proper design of industrial processes. Accurate knowledge of thermodynamic properties of solution mixtures has great relevance in theoretical and applied areas of research.

Measurements of the bulk properties, such as viscosities and densities of liquids, measurements of excess molar enthalpies, measurements of refractive indices and measurements of isentropic compressibilities provide insight into the molecular arrangement in liquids and help one to understand the thermodynamic properties of liquid mixtures.

Proper understanding of these properties is very imperative in many practical problems regarding energy transport, heat transport, mass transport, and fluid flow. Acoustic properties have been the subject of extensive research activity to study the intermolecular interactions in ion-solvent systems. Besides finding applications in the engineering branch, the study is important from practical and theoretical points of view in understanding liquid theory. The nonaqueous systems have been of immense importance to the technologist and theoretician as many chemical processes occur in these systems.

The physico-chemical properties play a pivotal 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, acoustic and optical studies on binary and ternary solvent systems are highly useful. Young<sup>1</sup> made the first systematic

attempt in these directions by collecting a number of data on the thermodynamic and mechanical properties of liquid mixtures.

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.

The refractive index,  $n_D$ , is defined as the ratio of velocity of light in the vacuum to the velocity of light in the medium and, therefore, for a fluid it is greater than unity. The refractive index is a thermodynamic property and is a state function, which for a pure fluid depends on temperature and pressure. For gases, the refractive index is very close to unity, but for liquids, it is greater than 1. The refractive index or refractivity ( $n_D$ ) can be easily measured by the sodium D line of a simple refractometer at a temperature of interest. The refractive index, is easily measurable, and used to estimate the thermo-physical properties of solvent/solution mixtures. Properties such as critical constants, heat capacity, and transport properties are related to the refractive index.

The rheological and molecular behaviour of a formulation <sup>1</sup> can influence aspects such as, patient acceptability, since it has been well demonstrated that viscosity and density both influence the absorption rate of such products in the body. <sup>2, 3</sup> Rheology is the branch of Science <sup>4</sup> 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 behaviour of many pharmaceutical products, <sup>5-9</sup> and to establish their stability and even bio-availability.

Considering the rheological perspective, the study of viscous synergy and antagonism is important, since many products are formulated with more than one component in order to yield the desired physical structure and properties. <sup>10</sup> Synergy and antagonism give the mutual enhancement or decrement of the physico-chemical, biological or pharmaceutical activity between different components of a given mixture.

The study of the viscous behaviour of pharmaceuticals, foodstuffs, cosmetics or industrial products, etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the products. If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system <sup>11,12</sup> is said to lack interaction.

In solution chemistry, the way for proper understanding of the different phenomena regarding the molecular interactions forms the basis of explaining quantitatively the influence of the solvent and the extent of interactions of ions in solvents. Estimates of ion-solvent interactions can be known thermodynamically and also from the measurement of partial molar volumes, viscosity *B*-coefficient and limiting ionic conductivity studies. Estimates of single-ion values enable us to refine our model of ion solvent interactions. Acceptable values of ion-solvent interactions would enable the chemists to choose solvents that will enhance (i) the rates of chemical reactions, (ii) the solubility of minerals in leaching operations or (iii) reverse the direction of equilibrium reactions. 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 Meck, <sup>13</sup> Franks, <sup>14</sup> Popovych, <sup>15</sup> Bates, <sup>16</sup> Parker, <sup>17</sup> Criss and Salomon, <sup>18</sup> Marcus <sup>19</sup> and others. <sup>20-22</sup> In spite of vast collections of data on the different electrolyte and non-electrolyte solutions in water, the structure of water and the different types of interactions that water undergoes with electrolytes are yet to be properly understood.

However, 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.<sup>23</sup>

In recent years, there has been increasing interest in the behaviour 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 the organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry.<sup>24</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 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.<sup>25-27</sup> 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.<sup>28,29</sup> 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.<sup>30</sup>

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.<sup>31</sup> A knowledge of ion-solvent interactions in non-aqueous solutions 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. 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, refractometric and conductometric behaviours to study the chemical nature of the structure of solutes and solvents and their mutual and specific interactions in solution.

## **1.2. Importance and Scope of Physico-Chemical Parameters:**

The study of physico-chemical properties involves the interpretation of the excess properties as a mean of unravelling the nature of intermolecular interactions among the mixed components. The interactions between molecules can be established from a study of characteristic departure from ideal behaviour of some physical properties such as density, volume, viscosity, speeds of sound, refractive index etc.<sup>32, 33</sup> 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 solvent mixtures. The negative values of excess molar volume ( $V^E$ ) suggest specific

interactions<sup>35, 36</sup> between the mixing components in the mixtures while its positive values suggest dominance of dispersion forces<sup>34, 35</sup> 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 volumes. The negative ( $V^E$ ) values may also be due to the difference in the dielectric constants of the components of the liquid mixtures.<sup>34</sup>

Understanding of fluid's viscosity is required in most engineering calculations where fluid flow, mass transport and heat transport are important factors. 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 electrolyte solvent mixtures involving both hydrogen bonding and non hydrogen bonding solvents.<sup>36, 37</sup> The study of physico-chemical behaviours 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.

Deviations in refractive index and molar refractivity also provide valuable information about molecular interactions prevailing in solution. Positive and negative values of  $\Delta n_D$  or  $\Delta R$  have immense significance to understand the molecular interactions.

The study of bio-molecules plays a key role in the elucidation of thermodynamic properties of bio-chemical processes in living cells. The process of drug transport, protein binding, anaesthesia, etc. are few examples

where drug and bio-macromolecules appear to interact in an important and vitally significant way. 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.<sup>38,39</sup>

These facts therefore prompted us to undertake the study of different binary or ternary systems. Furthermore, the excess properties derived from experimental density, viscosity, speeds of sound and refractive index data and subsequent interpretation of the nature and strength of intermolecular interactions help in testing and development of various theories of solution.

### **1.3. Solvents and Solutes Used:**

1,3-dioxolane, acetonitrile, dichloromethane, nitromethane, chloroform, carbontetrachloride, some organic acids viz., formic acid, acetic acid, propionic acid; some amines viz., iso-propyl amine, cyclohexylamine, some alkyl acetates, viz., methyl acetate, ethyl acetate, propyl acetate; butyl acetate, iso-amyl acetate, monoalkanols; viz., methanol, 1-propanol, 2-propanol, n-amyl alcohol, iso-amyl alcohol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 2-methoxy ethanol, 2-ethoxy ethanol, 2-butoxy ethanol along with water are considered as solvents.

Some alkali metal halides, viz., lithium chloride, lithium bromide, lithium iodide, some amino acids viz., glycine, l-alanine, l-valine, , l-leucine; nicotinic acid, benzoic acid, and also catechol which are considered as solutes, have been chosen in this research work.

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

#### 1.4. Methods of Investigations:

The phenomenon of viscous synergy and antagonism and ion-solvent interactions is intriguing. It is desirable to attack this problem using different experimental techniques. We have, therefore, employed five important methods, namely, **Densitometry, Viscometry, Ultrasonic Interferometry, Refractometry** and **Conductometry** to probe the problem of solvation phenomena.

Viscosity and density have been used to interpret the viscous synergic and antagonistic behaviour in the solvent mixtures. The values of viscous synergic index and antagonistic interaction index determine the nature of the molecular package.

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 electrolyte solutions is attributed to interionic and non-solvent effects. The *B*-coefficients give a satisfactory interpretation of ion-solvent interactions such as the effects of 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 deviation and excess isentropic compressibility along with the correlating equations explain molecular interactions more effectively.

To investigate thermodynamic properties- refractive index, molar refractivity and deviation in both these parameters are also very important to interpret the molecular interactions.

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

## **1.5. Summary of the Works Done**

### **CHAPTER I**

This chapter contains the object and applications of the research work, the solvents and solutes used and methods of investigations. This also involves the summary of the works done associated with the thesis.

### **CHAPTER II**

This chapter contains the general introduction of the thesis and forms the background of the present work. Viscous synergy and antagonism have been defined along with the interaction index. 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, refractive index and conductance. 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 molecular interactions are interpreted based on various equations.

### **CHAPTER III**

This chapter contains the experimental section which mainly involves the structure, source, purification and application of the solvents and solutes used

in the research work and the details of the instruments that are employed to understand the thermodynamic, transport, acoustic and optical properties.

## CHAPTER IV

This chapter quantifies the viscous synergism and antagonism established in four binary liquid mixtures of cyclohexylamine with 1-butanol, 2-butanol, iso-butanol and *t*-butanol at 298.25 K. By volumetric, viscometric, refractometric and interferometric measurements the nature of interactions between the liquids has been investigated. From the experimental results, the excess molar volumes,  $V^E$ , the deviations in viscosity,  $\Delta\eta$  and synergic index,  $I_s$ , are derived by the equation developed by Kalentunc – Gencer and Peleg and Howell, respectively. Deviation in isentropic compressibilities,  $K_S^E$ , and refractive indices,  $\Delta n_D$ , are also considered. Through the experiment it can be interpreted that the strength of hydrogen bond interaction between the alcoholic oxygen and hydrogen of  $-\text{NH}_2$  group in the cyclohexylamine molecule are different for different alcohols.

## CHAPTER V

This chapter demonstrates the apparent molar volumes,  $\phi_v$ , and viscosity  $B$  coefficients for nicotinamide in 0.00, 0.05, 0.10 and 0.15 mol·dm<sup>-3</sup> aqueous tetrabutylammonium bromide (TBAB) solutions. The studies have been determined from solution density and viscosity measurements at temperatures from 298.15 K to 318.15 K as function of concentration of nicotinamide. In the investigated temperature range, the relation:  $\phi_v^0 = a_0 + a_1T + a_2T^2$ , has been used to describe the temperature dependence of the standard partial molar volumes,  $\phi_v^0$ . These results have, in conjunction with the results obtained in pure water, been used to deduce the standard volumes of transfer,  $\Delta\phi_v^0$ , and viscosity  $B$ -coefficients of transfer for nicotinamide from water to aqueous TBAB 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  $(\delta^2 \rho^0_v / \delta T^2)_p$ . An increase in the transfer volume of nicotinamide with increasing TBAB concentration has been explained by Friedman-Krishnan co-sphere model. The activation parameters of viscous flow for the ternary solutions investigated, were also determined and discussed by the application of transition state theory.

## CHAPTER VI

In this chapter electrolytic conductivities, densities, viscosities and refractive indices of some lithium halides (LiCl, LiBr, LiI) have been studied in mass fraction (0.10, 0.20 and 0.30) of methyl alcohol + ethylene glycol monomethyl ether mixtures at 303.15 K. Also the limiting molar conductivities,  $\Lambda^0$ , association constants,  $K_A$  and the distance of closest approach of the ions,  $R$ , have been evaluated using the Fuoss conductance equation (1978). Accordingly the Walden product is obtained and discussed too. Through the study of limiting apparent molar volumes,  $\rho^0_v$ , experimental slopes,  $S_V^*$ , derived from the Masson equation and viscosity  $A$  and  $B$ -coefficients using the Jones-Dole equation the ion-ion and ion-solvent interactions have been illustrated. It can be seen that the electrolytes remain largely associated in the mixture and conductance values are varied with the size of the halides as well as the amount of ethylene glycol monomethyl ether.

## CHAPTER VII

Proteins are complex molecules and their behaviour in solutions is governed by a combination of many specific interactions. One approach that reduces the degree of complexity and requires less complex measurement techniques is to study the interactions in systems containing smaller bimolecular, such as amino acids and peptides. Some studies have revealed that the presence of an electrolyte drastically affects the behaviours of amino acids in solutions and this fact can be used for their separation and purification. Therefore, in this chapter an attempt has been made to unravel the various

interactions prevailing in some amino acids- glycine, l-alanine, l-valine and l-leucine in aqueous catechol solutions by volumetric, viscometric and interferometric study at 298.15 K.

## CHAPTER VIII

In this chapter the binary mixtures of 1,3-dioxolane with 2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol, 2-propylamine and cyclohexylamine have been studied at 298.15 K. Excess molar volume,  $V^E$ , deviations in viscosity,  $\Delta\eta$ , deviations in isentropic compressibility,  $K_S^E$ , and deviations in molar refraction,  $\Delta R$ , have been evaluated from density,  $\rho$ , viscosity,  $\eta$ , ultrasonic speeds of sound,  $u$  and refractive indices,  $n_D$  of the mixtures respectively. The excess or deviation properties have been fitted to the Redlich-Kister polynomial equation to derive the adjustable parameters,  $A_k$ , and corresponding standard deviations,  $\sigma$ . The excess properties are found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures and it has been a recent upsurge of interest in the study of thermodynamic properties of binary liquid mixtures which is extensively used to obtain information on intermolecular interactions and stereo chemical effects in these systems.

## CHAPTER IX

This chapter contains the volumetric, viscometric, interferometric and refractometric properties of binary liquid mixtures of ethyl acetoacetate with dichloromethane, chloroform, carbontetrachloride, nitromethane, methyl acetate, acetonitrile and acetic acid at 298.15 K over the entire composition range. The density and viscosity data are examined in terms of molecular interactions and structural effects. The excess properties are found to be dependent on the molecular interactions along with the nature of liquid mixtures. Several thermodynamic parameters like intermolecular free length,

specific acoustic impedance, etc. have also been derived from the density and ultrasonic speed data to inspect the nature of the interactions.

## CHAPTER X

This chapter illustrates the study of the densities and viscosities of six ternary mixtures of the water, monoalkanols (1-propanol, 2-propanol) and monoalkanoic acids (formic acid, acetic acid and propionic acid) determined over the entire range of composition at 298.15, 308.15 and 318.15 K. From the experimental observations the excess molar volumes,  $V^E$  and viscosity deviations,  $\Delta\eta$ , were calculated, and then the viscous synergy and synergy interaction index are derived by the equations developed by Kalentunc -Gencer and Peleg and Howell, respectively. The speeds of sound of these ternary mixtures have been measured over the whole composition range at the same temperatures (298.15 K) and also, the isentropic compressibilities,  $K_S$  and excess isentropic compressibilities,  $K_S^E$ , have been evaluated from the experimental data. The variation of  $\eta_{max}$  and  $I_S$  with the number of carbon atoms are also shown. The results thus obtained indicate that monoalkanoic acids containing up to three carbon atoms mix with water and monoalkanol mixtures in any proportion but the synergic interactions tend to decrease with the increase of C atoms in the chain due to increasing +I-effect and the monoalkanols with the hydroxyl group positioned at the second carbon atom accept more water and acids than those with the terminal hydroxyl group.

## CHAPTER XI

In this chapter we have considered five ternary mixtures of the cyclic diether (1,3-dioxolane), dichloromethane and alkyl acetates viz; methyl acetate, ethyl acetate, propyl acetate, butyl acetate and iso-amyl acetate at 298.15 K. From the experimental observations, the excess molar volumes,  $V^E$ , viscosity deviations,  $\Delta\eta$ , excess isentropic compressibilities,  $K_S^E$  and deviation in molar refraction have been calculated from the density,  $\rho$ , viscosity,  $\eta$ , speed of sound,

$u$  and refractive index,  $n_D$ , respectively. The excess or deviation properties were found to be either negative or positive depending on the molecular interactions and the nature of the liquid mixtures.

## **CHAPTER XII**

This chapter contains the concluding remarks of the works related to the thesis.

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