

## CHAPTER I

### **1.1. Object and application of the research work**

In recent years there has been an increasing interest in the study of physico-chemical properties of solvent-solvent<sup>1-3</sup> and solute-solvent<sup>4-6</sup> 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 and acoustic studies on binary and ternary solvent systems are highly useful. Young<sup>7</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.

Molecular behavior of a formulation<sup>8</sup> can influence aspects such as, patient acceptability, since it has been well demonstrated that density and viscosity both influence the absorption rate of such products in the body.<sup>9, 10</sup> The rheological behavior of such products is also a matter of major concern in this regards. Rheology is the branch of science<sup>11</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 behavior of many pharmaceutical products,<sup>12-16</sup> and to establish their stability and even bio-availability.

Considering the rheological behavior, the study of viscous synergy and antagonism is important, since many products are formulated with

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more than one component in order to yield the desired physical structure and properties.<sup>17</sup> Synergy and antagonism gives the mutual enhancement or decrement of the physico-chemical, biological or pharmaceutical activity between different components of 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<sup>18, 19</sup> 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 products.

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 had 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>20</sup>, Franks<sup>21</sup>, Popovych<sup>22</sup>, Bates<sup>23</sup>, Parker<sup>24</sup>, Criss and Salomon<sup>25</sup>, Marcus<sup>26</sup> and others.<sup>27-29</sup> The solute-solute and solute-solvent interactions have been subject of wide interest as apparent from Faraday Transactions of the chemical society.<sup>30</sup>

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. 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>21,31</sup>

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In recent years, there has been increasing interest in the 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.<sup>32</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>33-35</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>36,37</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>38</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

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significantly influenced by the solvents. Conversely, the nature of strongly structured solvents like water, is substantially modified by the presence of solutes.<sup>39</sup>

A knowledge of ion-solvent interactions in non-aqueous solutions<sup>28</sup> 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 and conductometric behavior 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 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.<sup>40, 41</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 binaries. The negative values of excess molar volume ( $V^E$ ) suggest specific interactions<sup>42,43</sup> between the mixing components in the mixtures while its positive values suggest dominance of dispersion forces<sup>42,43</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 volume. The negative

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$V^E$  values may also be due to the difference in the dielectric constants of the liquid components of the binary mixture.<sup>42</sup>

A knowledge of viscosity of fluids 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-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents.<sup>44,45</sup> 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.

Drugs are basically composed of organic molecules and 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, anesthesia, 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>46, 47</sup> These facts therefore prompted us to undertake the study of binary or ternary solvent systems with 1,4-dioxane and 1,3-dioxolane or

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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:

1,4-Dioxane, 1,3-Dioxolane, Tetrahydrofuran, Benzene, n-Hexane, N, N-Dimethylformamide, Butyric acid, Butylamine, 2-butanone, Monoalkanols viz. Methanol, Ethanol, 1-Propanol, 2-Propanol, 1-Butanol, 2-Butanol, t-Butanol, i-Amyl alcohol some alkyl acetates viz. Methyl acetate, Ethyl acetate, i-amyl acetate, Butyl acetate 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 25°C. However, its dipole moment rises with increase in temperature suggesting formation of boat form.<sup>32</sup>

Tetrahydrofuran is moderately toxic and has been widely used as a solvent for organometallics and forms blue solutions with alkali metals and most inorganic salts except lithium and sodium perchlorates are insoluble.

1,4-dioxane, 1,3-dioxolane and tetrahydrofuran are all cyclic ethers and they figure prominently in the high-energy battery technology<sup>48</sup> 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.<sup>49</sup>

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 slightly basic and a popular solvent in visible and near u. v. spectrometry (>270 nm) and for polarographic work. It is also used in the separation of saturated and

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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.<sup>50, 51</sup>

The increasing use of 1,4-dioxane, 1,3-dioxolane, tetrahydrofuran, N, N-dimethylformamide, 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.<sup>52, 53</sup>

The hydrocarbons, both aromatic and aliphatic have varied applications. Benzene is used as solvents for fats and oils, dry-cleaner of woolen clothes, anti-knock gasoline and in manufacture of detergents, insecticides, etc. whereas n-hexane, which is familiar in the laboratory as the principle component of petroleum ether, is used as solvent, dry-cleaner and motor fuel.

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 alternative energy source.<sup>8</sup> 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. Ethanol has been used as a solvent in quantitative studies and 'Absolute' alcohol usually contains 0.01% water. The importance of iso-amyl alcohol in research field is implied for its usefulness in gas chromatography. It can isolate high quality RNA from even the hardest to isolate samples for immediate use in micro array application and it is also useful in most DNA applications.<sup>54</sup>

However, it is worth mentioning that 1,4-dioxane differs from alcohols in its behaviour towards water. Alcohols are usually structure makers

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whereas 1,4-dioxane acts as a net structure breaker.<sup>55</sup> Aqueous 1,4-dioxane mixtures have been found to be more basic than water and the basicity has been found to be maximum in the region 45-50 mass% of 1,4-dioxane.<sup>56</sup>

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.

### 1.4. Method of Investigations

The phenomenon of synergy, antagonism, ion-ion, ion-solvent and solvent-solvent interactions 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.

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.

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 volume, partial molar expansibility, etc. obtained from density measurements, are generally convenient parameters for interpreting solute-solute and solute-solvent 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

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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 investigations.

The excess properties such as excess molar volume, viscosity deviations and deviation in isentropic compressibility along with the correlating equations explain 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.

### **1.5. Summary of the works done**

#### **Chapter I**

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**

This chapter contains the general introduction of the thesis and forms a background of the works embodied in the thesis. Viscous synergy and antagonism have been defined along with their interaction indices. A brief review of notable works on 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 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

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(viscosity  $B$ -coefficient and limiting equivalent conductance) and their implications have been discussed.

### Chapter III

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

This chapter presents a study on viscous synergy and isentropic compressibility in the systems comprising some monoalkanols ( $C_1$ - $C_4$ ) and cyclic ethers (1,4-dioxane and tetrahydrofuran) in the proportion  $w/w = 1:1$ , in water at different concentrations ( $w/w$ ) at 298.15 K to determine the proportion of monoalkanol + cyclic ether + water, at which maximum synergy occurs. The density and viscosity data have been analyzed using the equation developed by Kaletunc-Gencer and Peleg. Also a correlation between the density and viscosity increment for all the systems has been attempted. The ratio between maximum viscosity reached by the mixtures and pure state viscosity is expressed by the enhancement index defined as:

$$E_n = \eta_{max} / \eta_0$$

### Chapter V

In this chapter the densities, viscosities, and ultrasonic speeds of resorcinol in 1,4-dioxane + water mixtures and in pure 1,4-dioxane have been measured at 303.15, 313.15 and 323.15 K. Apparent molar volumes ( $V_\phi$ ) and viscosity  $B$ -coefficients were obtained from the experimental data. The limiting apparent molar volumes ( $V_\phi^0$ ) and experimental slopes ( $S_\phi^*$ ) 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 the Jones-Dole equation, and the derived parameters  $A$  and  $B$  have also been interpreted in terms of solute-solute and solute-solvent interactions, respectively. The structure making/breaking capacities of resorcinol in the studied solvent systems have been discussed.

### Chapter VI

In this chapter electrical conductances of some ammonium and tetraalkylammonium halides have been measured in different mass% of 1,4-dioxane + water mixtures (20%, 40%, 60% and 80%) at 298.15 K. The limiting molar conductivity ( $\Lambda_0$ ), the association constant ( $K_A$ ) and association distance ( $R$ ) in the solvent mixtures have been evaluated using Fuoss conductance equation (1978). 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 VII

In this chapter the densities and viscosities of ternary mixtures of tetrahydrofuran + methanol + benzene and isopropanol + benzene + n-hexane have been measured at 303.15, 313.15 and 323.15 K over the entire range of composition. The data have been analyzed using the equation developed by Kaletune-Gencer and Peleg. The experimental results have been discussed and explained in terms of molecular package and electrostriction.

### Chapter VIII

In this chapter the excess molar volume ( $V^E$ ), viscosity deviations ( $\Delta\eta$ ) and Gibbs excess free energy of activation for viscous flow ( $G^{\ddagger E}$ ) have been investigated from the density ( $\rho$ ) and viscosity ( $\eta$ ) measurements of eight binary mixtures of 1,3-dioxolane with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, t-butanol and iso-amyl alcohol over the entire range of mole fractions at 303.15 K. The viscosity data have been correlated with Grunberg-Nissan equation. The excess or deviation properties have been fitted to Redlich-Kister polynomial equation and the results have been discussed in terms of molecular interactions and structural effects.

### Chapter IX

In this chapter apparent molar volumes ( $V_\phi$ ) and viscosity  $B$ -coefficients of sodium molybdate in aqueous binary mixtures of 1,4-dioxane have been determined from density and viscosity measurements at 303.15, 313.15 and 323.15 K and at various electrolyte concentrations. Adiabatic compressibility ( $\beta$ ) of different solutions have been determined from the measurement of ultrasonic speeds of sound at 303.15 K. Experimental density data were evaluated using the Masson equation and the derived parameters interpreted in terms of ion-solvent and ion-ion interactions. Partial molar volumes ( $\Delta V_\phi^0$ ) and viscosity  $B$ -coefficients ( $\Delta B$ ) of transfer from water to aqueous 1,4-dioxane mixtures have also been calculated and discussed. The structure-making or breaking capacity of the electrolyte under investigation has been discussed in terms of the sign of  $(\delta^2 V_\phi^0 / \delta T^2)_p$ .

### Chapter X

In this chapter the densities and viscosities have been measured for the binary mixtures of butylamine and N, N- dimethylformamide with methyl acetate, ethyl acetate, butyl acetate and iso-amyl acetate at 298.15 K over the entire range of composition. From density and viscosity data, the values of excess molar volume ( $V^E$ ) and viscosity deviation ( $\Delta\eta$ ) have been determined. These results have been fitted to Redlich-Kister polynomial equation to estimate the binary coefficients and standard errors between the experimental and the computed values. The density and viscosity data have been analyzed in terms of some semiempirical viscosity models and the results have been discussed in terms of molecular interactions and structural effects.

### Chapter XI

In this chapter the densities and viscosities were measured for the binary mixtures of 1,4-dioxane and 1,3-dioxolane with butyl acetate, butyric acid, butylamine and 2-butanone at 298.15 K over the entire range of composition. From density and viscosity data, the values of excess molar volumes ( $V^E$ ) and viscosity deviations ( $\Delta\eta$ ) have been determined. These results were fitted to Redlich-Kister polynomial equation. The density and

viscosity data have also been analyzed in term of some semi empirical viscosity models.

### Chapter XII

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

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