

# **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 behaviour 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

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

the analysis of the viscous behaviour of many pharmaceutical products,<sup>12-16</sup> and to establish their stability and even bio-availability.

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.

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>17</sup>, Franks<sup>18</sup>, Popovych<sup>19</sup>, Bates<sup>20</sup>, Parker<sup>21</sup>, Criss and Salomon<sup>22</sup>, Marcus<sup>23</sup> and others.<sup>24-26</sup> The solute-solute and solute-solvent interactions have been subject of wide interest as apparent from Faraday Transactions of the chemical society.<sup>27</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>18,28</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

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

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>29</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>30-32</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>33,34</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>35</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

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

structured solvents like water, is substantially modified by the presence of solutes.<sup>36</sup>

A knowledge of ion-solvent interactions in non-aqueous solutions<sup>25</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 behaviour 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 behaviour of some physical properties such as density, volume, viscosity, compressibility, etc.<sup>37,38</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 ( $V_m^E$ ) suggest specific interactions<sup>39,40</sup> between the mixing components in the mixtures while its positive values suggest dominance of dispersion forces<sup>39,40</sup> between them. The negative  $V_m^E$  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

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

negative  $V_m^E$  values may also be due to the difference in the dielectric constants of the liquid components of the binary mixture.<sup>39</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>41,42</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.

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>43,44</sup> These facts therefore prompted us to

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

undertake the study of binary or ternary solvent systems with formamide, 1,2-dimethoxyethane, cyclohexane, cyclohexanone, glycerol and acetonitrile 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 and solutes used**

Formamide, 1,2-dimethoxyethane, 2-methoxyethanol, acetonitrile, acetophenone, dimethylsulfoxide, benzene, some benzene derivatives, viz., toluene, chlorobenzene, benzylchloride, benzaldehyde, nitrobenzene, aniline; cyclohexane, cyclohexanone, some alkyl acetates, viz., methyl acetate, ethyl acetate, propyl acetate; glycerol, monoalkanols; viz., methanol, n-amyl alcohol, iso-amyl alcohol along with water also considered as solvents and some alkali metal acetates, viz., lithium acetate, sodium acetate, potassium acetate; sodium bromide, sodium tetraphenylborate, tetrabutylammonium bromide, sodium molybdate, sodium tungstate, ammonium sulphate, some mineral sulphates, viz., sodium sulphate, potassium sulphate, magnesium sulphate, zinc sulphate, cadmium sulphate; nicotinamide, tetrabutylammonium bromide, nicotinic acid, and benzoic acid 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 pharmaceutical to cosmetics.

Formamide and its derivatives are good solvents for many organic and inorganic compounds and also used as a plasticizer. It is also chosen for the study as it is a simplest amide that contains a peptide linkage, the fundamental building block of proteins.<sup>45</sup>

1,2-Dimethoxyethane is used as an alternative to diethyl ether.<sup>46</sup> Acetonitrile is widely used for dissolving inorganic and organic compounds.

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

Cyclohexane is inflammable. It is used as a solvent for oils, fats and waxes; and also as a paint remover. Cyclohexanone has also an important role in the manufacture of caprolactum, nylon, adipic acid, celluloid, artificial leather and printing inks.<sup>46</sup>

Glycerol is an important polyhydroxy compound. It has bio-physical importance for being a primary bio-molecule in the intestine, a product of lipid hydrolysis and it also participates in the metabolism of glucose in lever.

The increasing use of formamide, 1,2-dimethoxyethane, cyclohexane, cyclohexanone, glycerol and acetonitrile; and their aqueous, binary or liquid mixtures in many industrial processes have greatly stimulated the need for extensive information on their various properties. Viscosity, density, ultrasonic speed of sound and conductivity 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>47,48</sup>

Acetophenone is a typical ketone, has been used in perfumery and as a hypnotic under the name "hypnone". It is also used as a solvent for cellulose ethers.

Dimethylsulphoxide is a powerful broad spectrum solvent for a wide variety of inorganic and organic reactants. Having low toxicity, it can be used in biology and medicine, especially for low-temperature preservation.<sup>46</sup>

Benzene is a good solvent for fats and lower m. w. aromatic compounds. The vapour is toxic when inhaled over long periods. Its principal industrial use is as a starting point for other chemicals like dyes, drugs, perfumes; and particularly ethyl benzene, cumene, cyclohexane, styrene, phenol and nylon precursors. Structurally benzene is the simplest stable compound having aromatic character.<sup>46</sup>

Aniline is used in the manufacture of antioxidants and vulcanization accelerators for the rubber industry, but it is also employed for the manufacture of dyes and pharmaceuticals. Toluene is used as a constituent of high-octane aviation and motor gasolines, as a solvent and as a raw material in the manufacture of benzene, caprolactam, phenol,

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

many dyestuffs and various other chemicals. Chlorobenzene is used as an intermediate in the manufacture of other chemicals; particularly phenol, DDT and aniline. Benzyl chloride is used for benzylating amines and for preparing benzyl alcohol and benzaldehyde.<sup>46</sup>

Benzaldehyde is used- (i) for flavouring purposes, in perfumery; (ii) in the manufacture of dyes; and (iii) as a starting material for the synthesis of several other organic compounds, e.g., cinnamaldehyde, cinnamic acid, benzoyl chloride, etc.<sup>46</sup>

Nitrobenzene is used- (i) mainly for the manufacture of aniline and aniline dyes; (ii) as high-boiling industrial solvent; (iii) for the preparation of benzidine; and (iv) as an oxidising agent in organic synthesis.<sup>49</sup>

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 behaviour 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.

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>50</sup>

2-Methoxyethanol finds a wide range of applications of technological importance, namely, as solvents and solubilizing agents in organic synthesis, reaction kinetics and electrochemical studies.<sup>51</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

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

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.

Ammonium sulphate is used as fertilizer, although tending to be replaced by fertilizers with higher nitrogen contents. Sodium sulphate is used in wood pulp production, glass, detergent and chemical manufacture. Potassium sulphate is used as fertilizer especially where Cl<sup>-</sup> content must be kept down in irrigated soils. Magnesium sulphate occurs naturally as kieserite; and is used as apurgative, as a dressing for cotton goods and in dying. Zinc sulphate is used in the textile industry and in arsenical sprays in agriculture.<sup>46</sup>

Sodium molybdate, sodium tungstate, sodium bromide, sodium tetraphenylborate, cadmium sulphate, lithium acetate, sodium acetate and potassium acetate are the electrolytes with important roles in the study of ion-sovent interactions in pure or mixed solvent systems.

Nicotinamide is commonly known as vitamin B<sub>3</sub>,<sup>52</sup> is a water-soluble vitamin, an essential micronutrient and a reactive moiety of the coenzyme nicotinamide adenine dinucleotide (NAD). It is also an interesting molecule for its two nitrogen atoms- one in the heterocyclic ring and the other as the amide group.

Tetraalkylammonium salts are bulky in nature and are known to orient water molecules around them depending on their alkyl chain.<sup>53,54</sup> Salts like tetrabutylammonium bromide can give a better insight into the effect of electrostatic and hydrophobic interactions on the stability of vitamins as these salts are known to influence macromolecular conformations by weakening attraction or repulsion inter- and intra-charge-charge interactions and by affecting hydrophobic interactions through the side chain of the alkyl groups.

Nicotinic acid is an essential micro-nutrient. Sometimes it is referred to as nothing more than vitamin PP (Pellagra Preventive),<sup>55,56,57</sup> since its deficiency in human diet causes pellagra.

Benzoic acid is a good adsorbing reagent for insulin<sup>58</sup> and is used in medicine as a urinary antiseptic and in the vapour form for disinfecting

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

bronchial tubes. This acid also finds many important applications in the manufacture of alkyl resins, plasticizers, dyestuffs and pharmaceuticals.<sup>48</sup>

The knowledge of the type and structure of the complex species in solution is essential for the optimal choice of solvents as well as solutes. 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 solute-solute/ion-ion, solute-solvent/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.

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 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

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

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 solvents and solutes as well as the methods of investigation. This also includes a summary of the works embodied in the thesis.

#### **Chapter II**

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 solute-solute/ion-ion, solute-solvent/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 and ternary 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**

This chapter contains the experimental section mainly involving the source and purification of the solvents and solutes used and the details of

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

the experimental methods employed for measurement of the thermodynamic, transport and acoustic properties.

### **Chapter IV**

In this chapter, the densities and viscosities of binary liquid mixtures of formamide with 2-methoxyethanol, acetophenone, acetonitrile, 1,2-dimethoxyethane and dimethylsulfoxide have been measured at 298.15, 308.15, and 318.15 K and over the entire composition range at  $p = 0.1$  MPa. Ultrasonic speeds of these binary liquid mixtures have also been measured at 298.15 K and the same pressure. From the experimental data, values of excess molar volume ( $V_m^E$ ), viscosity deviation ( $\Delta\eta$ ) and deviation in isentropic compressibility ( $\Delta\kappa_s$ ) have been determined. These results were fitted to the Redlich-Kister-type polynomial equation. The density and viscosity data have been analyzed in terms of some semi-empirical viscosity models.

### **Chapter V**

In this chapter, the densities, viscosities and ultrasonic speeds of sound for the binary mixtures of 1, 2-dimethoxyethane + benzene, + toluene, + chlorobenzene, + benzyl chloride, + benzaldehyde, + nitrobenzene, and + aniline have been measured over the entire range of composition at 298.15 K and at atmospheric pressure. From the experimental density, viscosity and ultrasonic speed data, excess molar volumes ( $V_m^E$ ), viscosity deviations ( $\Delta\eta$ ) and deviation in isentropic compressibility ( $\Delta\kappa_s$ ) have been calculated. The excess or deviation properties were fitted to Redlich-Kister smoothing equation. From excess molar volumes ( $V_m^E$ ), partial molar volumes ( $\bar{V}_{m,1}^0$  and  $\bar{V}_{m,2}^0$ ) and excess partial molar volumes ( $\bar{V}_{m,1}^{0,E}$  and  $\bar{V}_{m,2}^{0,E}$ ) at infinite dilution were calculated. Along with various acoustic parameters, theoretical speeds of sound for the mixtures from different equations have also been calculated with the experimental density and ultrasonic speed data for comparison. McAllister's three-body and Heric-Brewer model have been used to correlate mixture viscosities.

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

### **Chapter VI**

In this chapter, the excess molar volumes ( $V_m^E$ ) and viscosity deviations ( $\Delta\eta$ ) were calculated from the measured density and viscosity data over the whole composition range for the ternary systems of cyclohexane + cyclohexanone + methyl acetate, + ethyl acetate, + propyl acetate and the constituent binary mixtures of cyclohexane or cyclohexanone + methyl acetate, + ethyl acetate, + propyl acetate and cyclohexane + cyclohexanone at 298.15 K under atmospheric pressure. The excess or deviation properties of the binary and ternary systems were fitted to Redlich-Kister and Cibulka equations, respectively. The excess or deviation properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures.

### **Chapter VII**

In this chapter, the molar conductances of lithium acetate, sodium acetate, potassium acetate, sodium bromide, sodium tetraphenylborate and tetrabutylammonium bromide in a series of glycerol + water mixtures at temperatures from 298.15 K to 318.15 K has been reported. The limiting polar conductances ( $\Lambda_0$ ), association constants ( $K_{A,c}$ ) and cosphere diameter ( $R$ ) have been derived from the Lee-Wheaton conductivity equation. The limiting ionic conductivities ( $\lambda_0^\pm$ ) have been calculated by reference electrolyte method. Ionic conductivities of cations and anions are discussed in terms of solvent viscosity, the Stokes radii and ion-ion and ion-solvent interactions. The small values of  $K_{A,c}$  for all the electrolytes studied indicate their weak association in aqueous glycerol mixtures, which is in line with the high dielectric constants of the solvent media.

### **Chapter VIII**

In this chapter, the apparent molar volumes ( $\phi_V$ ) and viscosity  $B$ -coefficients of sodium molybdate and sodium tungstate in aqueous binary mixtures of acetonitrile were determined from solution density and viscosity measurements at 298.15, 308.15 and 318.15 K and various electrolytic concentrations. The experimental density and viscosity data

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

were evaluated by Masson equation and Jones-Dole equation, respectively; and the derived parameters were interpreted in terms of ion-solvent and ion-ion interactions. The activation parameters of viscous flow were also determined and discussed using transition state theory.

### **Chapter IX**

In this chapter, the densities and viscosities of several sulphates, viz., ammonium sulphate, sodium sulphate, potassium sulphate, magnesium sulphate, zinc sulphate and cadmium sulphate in aqueous binary mixtures of formamide have been determined at 298.15, 308.15 and 318.15 K and at atmospheric pressure. The ultrasonic speeds of the electrolytic solutions have also been measured at 298.15 K. Apparent molar volumes ( $\phi_V$ ), viscosity  $B$ -coefficients and adiabatic compressibilities ( $\kappa_s$ ) of these electrolytic solutions were calculated from the experimental density, viscosity and acoustic data. The density and viscosity data were evaluated by using Masson and Jones-Dole equation, respectively; the derived parameters have been analyzed in terms of ion-ion and ion-solvent interactions. The structure making/breaking capacities of the electrolytes have been inferred from the sign of  $\left(\frac{\delta^2 \phi_V^0}{\delta T^2}\right)_P$ . The results showed that all the electrolytes act as structure-makers in these media. Also, the compressibility data indicated electrostriction of the solvent molecules around the cations. The activation parameters of viscous flow were also determined and discussed by the application of transition state theory.

### **Chapter X**

In this chapter, 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 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:  $\phi_V^0 = a_0 + a_1T + a_2T^2$ , have been used to describe the temperature dependence of the standard partial molar volumes ( $\phi_V^0$ ). These results have, in conjunction with the results

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

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  $(\delta^2\phi_V^0 / \delta T^2)_p$ . 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 XI**

In this chapter, the apparent molar volumes ( $\phi_V$ ) and viscosity  $B$ -coefficients ( $B$ ) for nicotinic acid and benzoic acid in mixed solvents containing 10, 20 and 30 mass % of n-amyl alcohol (n-AmOH) or iso-amyl alcohol (i-AmOH) in methanol and in pure methanol (MeOH) were determined from the solution density and viscosity measurements at 298.15 K as a function of concentrations of nicotinic acid and benzoic acid. These results were, in conjunction with the results obtained in pure methanol, used to deduce the partial molar volumes of transfer ( $\Delta\phi_V^0$ ) and viscosity  $B$ -coefficients of transfer ( $\Delta B$ ) for nicotinic acid and benzoic acid from methanol to different mixed methanol solvents, in order to rationalize various interactions in the ternary solutions. An increase in the transfer properties of nicotinic acid and benzoic acid with increasing mass % of n-AmOH and i-AmOH in methanol was observed and explained by the effect of structural changes and preferential solvation. Also, the free energies of viscous flow,  $\Delta\mu_1^{0\neq}$  and  $\Delta\mu_2^{0\neq}$ , per mole of solvent and solute, respectively, were calculated and analyzed on the basis of transition state theory of relative viscosity.

### **Chapter XII**

This chapter contains the concluding remarks on the works embodied in the thesis.

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

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

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

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