

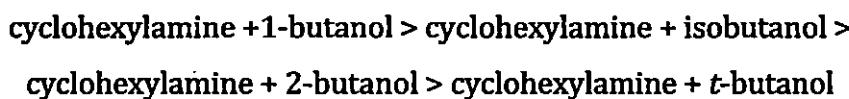
CHAPTER XII

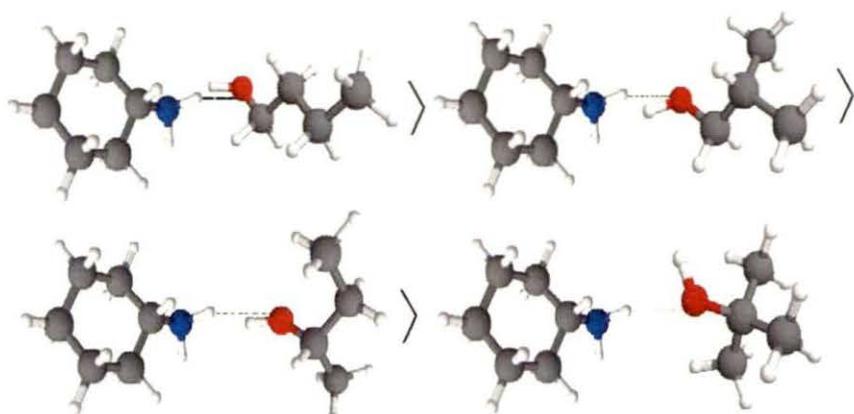
Concluding Remarks

Thermodynamic and transport properties for solutions can reveal the existence of molecular interactions. Therefore, the systematic study of these properties has great importance in gaining a better knowledge of these interactions. Such a study would have an impact in chemical engineering areas especially to understand the mixing behaviour of different components in the mixture.

The aim of the works embodied in this thesis was to investigate the physico-chemical properties of some solvent-solvent and solute-solvent systems. In the present study, we have tried to investigate the various interactions of ions/solutes in aqueous, non-aqueous and mixed solvent media in different concentration regions and some useful conclusions of them have been derived.

The compounds – 1-butanol, 2-butanol, isobutanol and *t*-butanol are extensively used in different industries viz., pharmaceuticals, plastics, paper, rubber, petroleum and some synthetic sweeteners, in organic synthesis, in production of fruit essences, as a flavouring in food, as a solvent, in production of agriculture etc. In chapter IV the study of excess molar volume, deviation in viscosity, viscous synergy and antagonism, deviation in isentropic compressibility and refractive index, of the binary systems of cyclohexylamine with 1-butanol, 2-butanol, isobutanol and *t*-butanol at 298.15 K over the entire composition range lead to the conclusion that the strength of interaction follows the order:





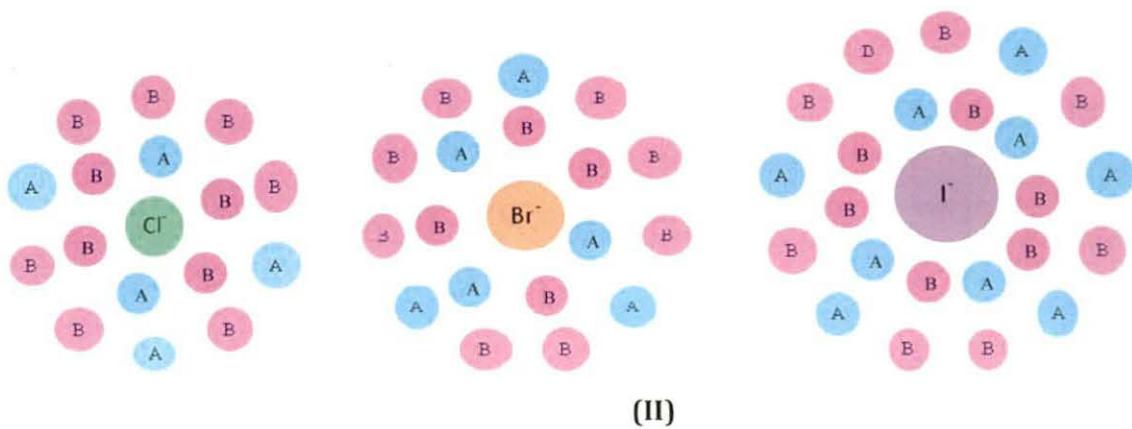
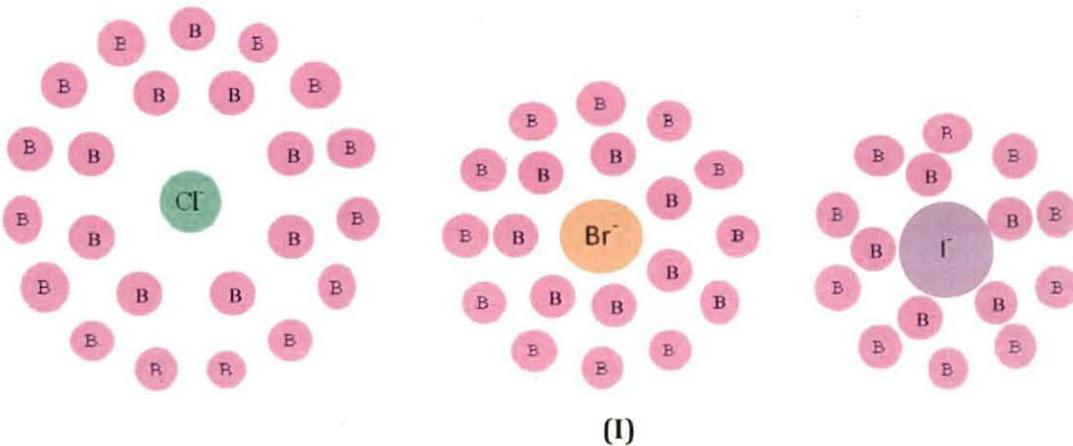
and in case of isomers, the monoalkanols with the -OH group positioned at the first carbon atom interacts with cyclohexylamine to a greater extent than those with the hydroxyl group at secondary or tertiary alcohols.

The behaviour of nicotinic acid (pyridine-3-carboxylic acid) and benzoic acid in the binary mixtures of methanol with n-amyl (n-AmOH) and iso-amyl alcohol (i-AmOH) was investigated at 298.15 K in chapter V. The study reveals the presence of strong solute-solvent interactions and these interactions are further strengthened at higher amount of the isomeric n-amyl or iso-amyl alcohol in methanol binary mixtures. Also, the nicotinic acid and benzoic acid are found to act as methanol-structure promoters due to the preferential solvation of these solutes by n-AmOH / i-AmOH; and the branched structure of i-AmOH renders it a more efficient solvent. This fact may also be due to the +I-effect of studied alcohols and the polarity of the alcoholic O-H bonds. The solvation behaviour of nicotinic acid and benzoic acid towards the mixed alcohols are more or less similar in nature.

In high energy battery industries the use of mixed solvents are being increased. In this regard, lithium batteries are widely used in various electronic products. Conductance measurement is one of the most accurate and widely used physical methods for investigation of electrolyte solutions. The conductance study of some alkali halides (LiCl , LiBr , LiI) in mass fraction (0.10, 0.20 and 0.30) of ethylene glycol monomethyl ether + methyl alcohol mixtures at 303.15 K reveals that all the electrolytes mentioned in chapter VI are highly associated in these media. The association constant (K_A) increases with an increase in the amount of ethylene glycol monomethyl ether as well as the size of the halide ion of the alkali halides in the solvent mixtures for all the

electrolytes leading to decrease in limiting molar conductance. The values of ϕ_V , viscosity B -coefficient also indicate the presence of strong ion-solvent interactions and these interactions are further strengthened at higher molarity and size of lithium halides in the solutions. Consequently, the refractive index was also found to be increased with molecular polarizability.

- (I) The conductance of lithium halides in methyl alcohol is enhanced by the following order: LiCl < LiBr < LiI.
- (II) But in methyl alcohol + ethylene glycol monomethyl ether mixture the case is reversed: LiCl > LiBr > LiI,
as shown by the following diagram:-



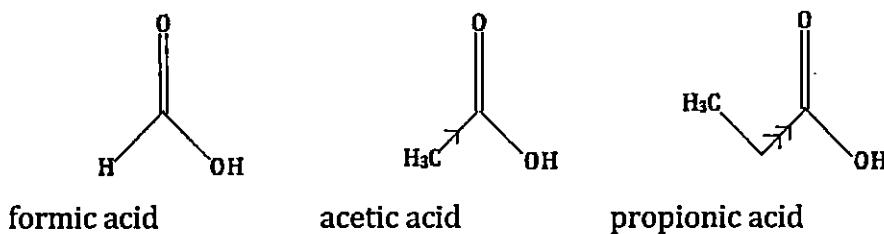
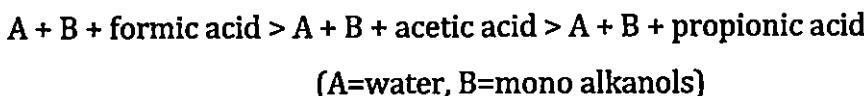
The study in chapter VII reveals that proteins are complex molecules and their behaviour in solutions is governed by a combination of many specific interactions. To study the interactions in systems containing smaller biomolecules, such as amino acids, reveals that although for aqueous catechol solution of glycine, L-alanine and L-valine the ion-hydrophilic interaction between the hydrophilic part of the amino acids and catechol predominates over hydrophobic interaction, in case of L-leucine in aqueous catechol solutions the hydrophobic interactions develop. The size and number of carbon atoms of the alkyl chain groups of the amino acids also play a pivotal role in determining the nature and strength of the interactions in these solvent media.

The studies for the binary systems consisting of 1,3-dioxolane with 2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol, 2-propylamine and cyclohexylamine at 298.15 K in chapter VIII exposes that the derived thermodynamic functions such as excess molar volume, viscosity deviation, deviation in isentropic compressibility and molar refraction are quite systematic and functions of the composition of the binary and ternary mixtures. It was found that with the increases in +I effect of the alkyl group the disruption forces becomes more effective in characterising these binary systems. Also for the amines, the H-bonding and steric effects play a vital role in the solvent mixtures.

The comparative study in chapter IX done on binary mixtures of ethyl acetoacetate with dichloromethane, chloroform, carbontetrachloride, nitromethane, methyl acetate, acetonitrile and acetic acid gives a clear distinction between the excess or deviation properties. The explanation of the interactions is based on the known phenomenon- intermolecular hydrogen bonding between the component liquids, dipole-dipole or dipole-induced dipole interaction and also the interstitial accommodation of the mixing components.

Wide use of aqueous alcohol and acid solutions in many industrial processes like pharmaceutical and cosmetics, has enhanced the need for extensive study on their properties. The results supplemented with the

viscosity data in chapter X, show the viscous synergy interaction index, I_S , as a function of mass% of H_2O and the number of carbon atoms corresponding to the monoalkanols with the position of the hydroxyl group. The results also indicate that the synergic indices of the monoalkanoic acids in aqueous monoalkanols follow the order:



The gradual decrement of synergy interaction values from formic acid to propionic acid can be explained in view of +I-effect. $-\text{C}_2\text{H}_5$ has more +I-effect than $-\text{CH}_3$ which has in turn than $-\text{H}$. This facilitates more interactions of formic acid with unlike molecules than acetic acid and propionic acid rendering to higher values of synergy interaction parameters.

Having wide usage in flavouring, perfumery, artificial essences, and cosmetics, esters become one of the industrially important classes of liquids. Esters are also used as solvents in pharmaceutical, paint industries and as plasticizers in plastic industries. The measurement of viscosities, densities, speeds of sound and refractive index in chapter XI for the ternary systems of 1,3-dioxolane, dichloromethane + methyl acetate, ethyl acetate, propyl acetate, butyl acetate and isoamyl acetate demonstrates that the strength of interaction of alkyl acetates with 1,3-dioxolane+dichloromethane mixtures increase with the chain length of the alkyl acetates. Moreover, usual discrepancy in size, polarity of the solvents and donor-acceptor interaction of the components characterize the molecular interactions among the components of the mixtures.

Thus the proper understanding of the ion-solvent interactions would form the basis of explaining quantitatively the influence of the solvent and the extent

of interactions of the ions in solvents and have the way for the real understanding of the different phenomenon associated with the solution chemistry.

More extensive studies of the different thermodynamic and transport properties of the electrolytes will be of sufficient help in understanding the nature of the ion-solvent interactions and the role of solvents in different chemical processes.

Studies on viscosities, densities, ultrasonic velocities, refractive indices and conductance of solutions containing ions assist in characterizing the structure and properties of the components. Various types of interactions exist between the ions in solutions, and of these, ion-ion and ion-solvent interactions are of current interest in all branches of chemistry. These interactions help in better understanding the nature of solute and solvent, that is, whether the solute modifies or distorts the structure of the solvent.

Excess and bulk properties are fundamentally important in understanding the intermolecular interactions between dissimilar molecules and in developing the thermodynamic models. Moreover, knowledge of excess properties lets us develop an understanding of the interactions that determine the physical properties, making it easier to search for an optimal ionic liquid for a determined application.

Furthermore, thermodynamic properties of solvent mixtures, containing components capable of undergoing specific interactions, exhibit significant deviation from ideality arising not only from difference in molecular size and shape but also due to structural changes.

The volumetric behaviour of solutes has been proven to be very useful in elucidating the various interactions occurring in aqueous and nonaqueous solutions. Studies on the apparent and partial molar volumes of electrolytes and the dependence of viscosity on concentration of solutes and temperature of solutions have been employed as a function of studying ion-ion and ion-solvent interactions. It has been found that the addition of electrolyte could either break or make the structure of a liquid. Because a liquid's viscosity depends on

the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at different concentrations and temperatures.

Mixed solvents enable the variation of properties such as use dielectric constant or viscosity, and therefore the ion-ion and ion-solvent interactions can be better studied. Moreover, different quantities strongly influenced by solvent properties can be derived from concentration dependence of the electrolyte conductivity. Consequently, a number of conductometric and related studies of different electrolytes in nonaqueous solvents, especially mixed organic solvents, have been made for their optimal use in high-energy batteries and for understanding organic reaction mechanisms. Ionic association of electrolytes in solution depends upon the mode of solvation of its ions, which in turn depends on the nature of the solvent or solvent mixtures. Such solvent properties as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent-solvent interactions. Thus, extensive studies on electrical conductance in mixed organic solvents have been performed to examine the nature and magnitude of ion-ion and ion-solvent interactions.

Thus excess thermodynamic properties, deviations of properties and transport properties for mixtures of liquids have both practical and theoretical interest. They have to be known to design industrial processes properly. They can be used to develop models that allow us to predict other properties. Finally, they can also reveal the existence of specific molecular interactions.