ABSTRACT

Physicochemical study of mixed components plays a vital role in understanding the solute-solute or ion-ion, solute-solvent or ion-solvent and solvent-solvent interactions in solutions. In order to explore the strength and nature of the interactions, the studies on thermodynamic, transport properties of electrolytes, optical and spectroscopic properties involving one or more solutes in pure and mixed solvent systems are highly useful. The principal objective of research work is to explore these diverse interactions prevailing in many electrolytic and non-electrolytic systems where the solvents may be both aqueous and non-aqueous. Moreover, for the proper planning of industrial processes and theoretical and applied areas of research in Chemistry the knowledge of Physicochemical properties are very important.

Ionic liquids have gained worldwide attention as green solvents in the last decade. In general, an ionic liquid is a wholly composed of ions. There are several reasons that ionic liquids are considered as “green solvents”. The most important reason is that ionic liquid possess negligible vapour pressure and hence do not evaporate to environment. Ionic liquids can be recycled to offer comparable performance in chemical transformations. These have various applications, as in chemical industry, pharmaceuticals, gas handling, cellulose processing, solar thermal energy, nuclear fuel processing, waste recycling, batteries etc.

“Biologically active solutes” are extra nutritional constituents that is produced by or extracted from a biological source such as micro-organism, organs and tissues of plant or animal origin, cell or fluids of human or animal origin called biologically active. Biologically active compounds are being intensively studied to evaluate their effects on health. These will reduce the risk of many diseases, including cancer, cardiovascular disease. Amino acids serves as the building blocks proteins, peptides, polypeptides, essential for human body, they are used in nutrition supplements, fertilizers, food technology, include the production of biodegradable plastics, drugs and chiral catalysts.

Using mixed solvents in these studies enable the variation of properties such as dielectric constant or viscosity, and therefore the ion-ion and ion-solvent

interactions could be better studied. Consequently, a number of conductometric and related studies of different electrolytes in non-aqueous solvents, especially mixed organic solvents, have been made for their optimal use in high-energy batteries and for understanding organic reaction mechanisms. 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.

In supramolecular chemistry, host-guest chemistry describes complexes that are composed of two or more molecules or ions that are held together in unique structural relationships by forces other than those of full covalent bonds. Host-guest chemistry encompasses the thought of molecular recognition and interactions through noncovalent bonding. Common host molecules are cyclodextrins, calixarenes, pillararenes, porphyrins crown ethers, zeolites, cryptophanes etc. Host-guest chemistry is observed in inclusion compounds, intercalaton compounds, clathrates and molecular tweezers. Among the host molecules, cyclodextrin seems to be the most promising to form inclusion complexes, especially with various guest molecules with suitable polarity and dimensions. There are various applications of Host-guest chemistry such as host-guest systems have been used to remove hazardous substances from the environment. It improves the drug delivery methods in medical science.

Studies of transport properties of substances along with thermodynamic, optical and spectroscopic studies, give valuable information regarding molecular interactions in solution phase. The influence of these solute-solvents interactions may be sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in such diverse areas as organic and inorganic synthesis, studies of reaction mechanisms, non-aqueous battery technology and extractions.

CHOICE OF SOLVENTS AND SOLUTES USED

Industrially important solvents have been used for the research work. 1-Hexanol, 1-Heptanol, 1-Octanol, solution of ionic liquids, solution of uric acid, solution of α-cyclodextrin, solution of crown ether (18-Crown-6 and 15-Crown-5) along with water considered as universal solvents have been chosen as a main solvent in this research work because these solvents are industrially very important and by mixing these solvents we could obtain a wide variation of viscosities and dielectric constants.

Ionic liquids (1-methyl-3-octylimidazolium chloride, 1-ethyl-3-methylimidazolium tosylate and benzyltrimethylammonium chloride), Amino acids (glycine, L-alanine, L-isoleucine, L-serine, L-proline and L-histidine), Citric acid were considered as solutes.

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

METHODS OF INVESTIGATION

It is of interest to apply various experimental techniques to get a better insight into the phenomena of solvation and different interactions existing in solution systems. I have, therefore, employed important physicochemical methods, namely, Densitometry, Viscometric, Surface tension, Conductometric, Optical property Refractometric and Spectroscopic Property like UV-Visible and NMR methods to examine and explore various interactions prevailing in solution systems.

PHYSICOCHEMICAL PARAMETERS AND THEIR SIGNIFICANCE

Limiting apparent molar volume ($\text{¤}_{\mathrm{V}}^{0}$) is obtained from experimental density values. The sign and magnitude of limiting apparent molar volume ($\text{¤}_{\mathrm{V}}^{0}$) provides useful information about the ion-solvent interaction while the experimental slope (S_V^*) provides information about ion-ion interactions.

Viscosity B-coefficient is another important parameter gives the valuable information regarding ion-solvent interaction, estimated from experimental viscosity values.

Limiting molar conductance (Λ_0) obtained from specific conductance as well as molar conductance gives a central idea about the ion-solvent interaction in

solution. Another parameter obtained from conductance study i.e. association constant (K_A) provides an idea about solvation of the ions by the solvent molecules.

Surface tension (γ), refractive index (n_D) and spectroscopic properties provides supporting information to confirm the interaction occurring in the solution systems.

Spectroscopic techniques such as UV-Visible, NMR are very useful to quantify the host-guest chemistry. UV-Visible spectroscopy also helpful to understand the formation of inclusion complex, stoichiometry and association constant (using Benesi-Hildebrand method). In NMR technique, by measuring chemical shifts (most commonly, proton) of different nuclei (host and guest) the binding activity between host and guest has been recognized.

SUMMARY OF 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 investigations.

CHAPTER-II

This chapter includes the general introduction of the thesis and forms a background of the works embodied in the thesis. A brief review of notable works in the field of ion-solvent interaction has been given. Various derived parameters dependent on density, viscosity, ultrasonic speed of sound, refractive indices and conductance along their importance in solution chemistry have been discussed.

CHAPTER-III

This chapter covers 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 used for the study.

CHAPTER-IV

The density (ρ), viscosity (η) and refractive index (n_D) of some biologically active molecules (glycine, L-alanine, and L-isoleucine) have been determined in

different mass fractions (w₁ = 0.001, 0.003, 0.005) of aqueous 18-crown-6 (18C6) solutions at three different temperatures. The limiting apparent molar volumes ($¤_V^0$), experimental slopes (S_V^*) have been found out from the Masson equation. *A*- and *B*-coefficients have been obtained from the Jones–Dole equation. The Lorentz–Lorenz equation has been employed to measure molar refractions (R_M). The standard volumes of transfer and solvation number of the amino acids have been considered for rationalizing various molecular interactions in the ternary solutions. Group contribution from charged end groups (NH_3^+, COO^-), -CH_2 and the alkyl groups of amino acids has been determined using a group additive approach. The results have been discussed in terms of ion-dipolar, hydrophilic-hydrophobic and hydrophobic-hydrophobic group interactions as well as thermodynamic parameters.

CHAPTER-V

A suitable host-guest inclusion complex has been made with a guest molecule, 1-methyl-3-octylimidazolium chloride ([MOIm]Cl) and a host molecule, *α*-cyclodextrin in aqueous medium. Formation of the host-guest inclusion complex has been established by Surface tension and conductivity readings while ^1H NMR and ultraviolet spectroscopy reading confirms 1:1 host-guest stoichiometry. These results have implications for the formation of host-guest inclusion complex of studied ionic liquid as guest in aqueous *α*–cyclodextrin media.

CHAPTER-VI

Density (ρ), viscosity (η) measurements have been carried out on 0.1(M) citric acid in w_1= 0.00001, 0.00002 and 0.00003 mass fraction of aqueous uric acid binary mixtures at T= 298.15, 303.15 and 308.15K. These measurements have been performed to derive some important parameters, as apparent molar volume (φ_V), limiting apparent molar volume (φ_V^0) using Masson equation; viscosity *A* and *B*-coefficients of Jones-Dole equation. The measurement of refractive index (n_D) has been done on the same ternary mixtures at T=298.15K. The values of refractive index help to evaluate molar refractive index (R_M) using Lorentz-Lorenz equation and also limiting molar index (R_M^0). These parameters have been interpreted in terms of solute-solute and solute-solvent interactions.

CHAPTER-VII

Inclusion complexation between crown ethers (*viz.*, 15-crown-5, 18-crown-6) and an ionic liquid (*viz.,* 1-ethyl-3-methylimidazolium tosylate) in aqueous medium have been demonstrated by conductivity, surface tension and ^{1}H NMR study. The results show the formation of 1:1 complexes between crown ethers and the ionic liquid through electron-deficient imidazolium cation and electron pairs of oxygen atoms of the crown ethers. Hydrogen bonding is the key factor responsible for complexation, while, the ion–dipole interactions also contribute towards the complex formation. The formation constants have been derived from conductivity study and the complexes have been analysed by ^{1}H NMR study.

CHAPTER-VIII

van der Waals forces, H-bonding, electrostatic forces, and configurational theory on volumetric, transport properties, molar refraction of molecular interaction, association behaviour have been studied through the precise measurements of density, viscosity, refractive index of L-Serine, L-Proline, and L-Histidine, in w_1=0.001, 0.003, 0.005, mass fraction of aqueous 1-butyl-1-methylpyrrolidinium hexafluorophosphate binary mixtures at 298.15K. The density, viscosity, and refractive index data have been analysed using the Masson, Jones-Dole, and Lorentz-Lorenz equations respectively. The limiting molar volume, viscosity *B*-coefficient and limiting molar refraction, interpreted the ion-solvent or solute-solvent interactions have been calculated and discussed. The group contribution of zwitterionic, -CH_2 and other functional groups to limiting molar volume and viscosity *B*-coefficient, have been taken into account and discussed for the same.

CHAPTER-IX

Precise measurements of electrolytic conductivities (Λ), densities (ρ), viscosities (η) and refractive index (n_D) of an ionic liquid (IL) benzyltrimethyl ammonium chloride [BTMA]Cl in 1-Hexanol, 1-Heptanol and 1-Octanol have been done. Densities and viscosities measurements have been carried out at different temperatures (T=298.15, 303.15 and 308.15 K) and conductivities and refractive index measured at 298.15 K. The limiting molar conductivities (Λ_0), association constants (K_A) and the distance of closest approach of the ions (R) have been evaluated using Fuoss conductance equation (1978). The Walden product is obtained and discussed. However, the deviation of conductometric curves (Λ versus $\sqrt{c}$) from linearity for the electrolyte in 1-Heptanol and 1-Octanol and therefore, the corresponding conductance data have been analysed by the Fuoss-Kraus theory of triple-ions. The observed molar coductivities have been explained by the ion-pair ($M^+ + X^- \rightleftharpoons MX$) and triple-ion ($2M^+ + X^- \rightleftharpoons M_2X^+$; $M^+ + 2X^- \rightleftharpoons MX_2^-$) formation. The limiting apparent molar volume (φ_V^0) and the experimental slope (S_V^*), interpreted in terms of solute-solvent and solute-solute interactions respectively have been derived from the Masson equation. The viscosities data have been analysed using Jones-Dole equation to derive the viscosity B -and A-coefficient which also interpreted in terms of solute-solvent and solute-solute respectively. The molar refractive index (R_M) and limiting molar refractive index (R_M^0) have been evaluated from the values of refractive index using Lorentz-Lorenz equation.

CHAPTER-X

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