ABSTRACT

Any compound which is very much important and essential to our environment systems is called the vital compound. Vitamins, Amino acids and Ionic liquids are considered as vital compounds. A vitamin is an organic compound required by an organism as a vital nutrient in restricted amounts. It is vital for life and can't live without them. An organic chemical compound (or related set of compounds) is called a vitamin when it cannot be synthesized in sufficient quantities by an organism, and must be obtained from the diet. Thus, the term is conditional both on the circumstances and on the particular organism. For example, ascorbic acid (vitamin C) is a vitamin for humans, but not for most other animals, and biotin (vitamin H) and vitamin D are required in the human diet only in certain circumstances. Vitamins are necessary precursors for various coenzymes. These coenzymes are therefore required in almost all metabolic pathways.

An ionic liquid (IL) is a salt in the liquid state/phase. The term has been classified to salts whose melting point is below some arbitrary temperature as 100°C (212°F). The chemical and physical properties of ILs, as insignificant low melting points, vapour pressures, good solvent characteristics for organic, inorganic and polymeric materials, low viscosity, adjustable polarity, selective catalytic effects, stable over a wide range of potentials, non-flammability, high ionic conductivity and catalytic activity, they have wide range of industrial applications. The search for efficient and environmentally safe chemical processes led in the past few years to a growing interest in the study of Ionic Liquids (ILs) as "green" alternatives to harmful organic solvents. Since efforts have been mainly focused on the investigation of their application, the characterization of ILs properties and the structure-property relationships of ILs are still lacking. Studies on the relationship between the physicochemical properties of various ILs and their binary mixtures with water and several vital/important solvents (alcohols, organic solvents) have been conducted.

Amino acids are important in nutrition and are commonly used in nutrition supplements, fertilizers, food technology, industry, include the production of bio-degradable plastics, drugs, and chiral catalysts.Physico-chemical studies of electrolytes play a very important role in understanding the solute-solute/ion-ion, solute-solvent/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, acoustic and optical properties

involving in one or more solutes in pure and mixed solvent systems are highly useful. The main objective of the research work is to explore these interactions prevailing in many electrolytic and in many other solution systems where the solvents may be both aqueous and non aqueous. Moreover, knowledge of the Physico-chemical and thermodynamic properties are very important for the proper planning of industrial processes and has great relevance in theoretical and applied areas of research in Chemistry.

'Solution Chemistry' is an imperative branch of the physical chemistry, which deals the change in properties that arise when one substance dissolves in another substance. The investigation have been done for the solubility of substances and studied how it is affected in both the physical and chemical nature for the solute and solvent. There are three types of approach have been made to estimate the extent of salvation in physical chemistry. The first one involves the studies of transport properties as viscosity, conductance, diffusion coefficient, ionic mobility etc., of the electrolytes in aqueous and non-aqueous solvents and the derivation of various factors associated with ionic salvation; the second one is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated with solvation can be explain; and the third one is to use spectroscopic study where the spectral line shifts or the chemical shifts of the functional group of electrolytes or non-electrolytes in solvents has been resolved qualitatively and quantitatively with their nature/mode of interactions.

The studies on supra-molecular chemistry give a broad idea of intermolecular interactions where covalent bonds are not likely to form between the interacting species. Thus, most of this interaction has been performed by host-guest interaction. 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. In host-guest chemistry, an inclusion compound is a complex in which one chemical compound (the "host") forms a cavity in which molecules of a second "guest" compound are located. The definition of inclusion compounds is very broad, extending to channels formed between molecules in a crystal lattice in which guest molecules can fit. If the spaces in the host lattice are enclosed on all sides so that the guest species is 'trapped' as in a cage, the compound is known as a clathrate.

In molecular encapsulation, a guest molecule is actually trapped inside another molecule.

Studies of transport properties of electrolytes, along with thermodynamic and acoustic studies, give very valuable information regarding molecular interactions in solutions. The influence of these 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 extraction. Knowledge of ion-solvent interactions in aqueous, non-aqueous solutions and mixed solvents is very important in many practical problems concerning energy transport, heat transport, mass transport and fluid flow. The proper understanding of the solute-solvent interactions would form the origin of explaining quantitatively the influence of the solvent and the degree of interaction of ions in solvents and thus pave the way for real understanding of the different phenomena related with solution chemistry.

The major aims of the research work are:

- To understand the nature and strength of various interactions, their influence on structural and dynamic properties of vital/important compounds in pure and mixed solvent systems.
- To investigate the physico-chemical properties of ionic liquids, amino acids and vitamin molecules in pure and mixed solvent systems.
- To study the transport properties of ionic liquids along with thermodynamic and acoustic ones to characterize molecular interactions in solutions.
- To understand the physicochemical properties of inclusion complexes form in diverse solvent 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 embraced 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 interactions in solution. Therefore, a number of conductometric and related studies of different electrolytes in non-aqueous

solvents, have been made for their optimal use in high-energy batteries and for understanding organic reaction mechanisms.

SUMMARY OF WORKS DONE

CHAPTER I

This chapter includes the object and applications of the research work, the reasons for choosing the main solvents and solutes and methods of investigation.

CHAPTER II

This chapter covers 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 with their importance in solution chemistry has been discussed.

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 used for the study.

CHAPTER IV

This chapter includes the qualitative and quantitative analysis of molecular interaction prevailing in ionic liquid and organic solvent media, probed by electrical conductance have been reported. Conductometric studies of an Ionic Liquid {1-ethyl-3-methylimidazolium methanesulfonate [emim]CH_3SO_3} in n-propanol, n-butanol, and n-pentanol at 298.15 K reveals high molecular interaction contributed mainly by ion–dipole interaction. Association constants (K_A), Limiting molar conductance (Λ_0), and the distance of closest approach of ions (R) for ion-pair formation have been analyzed using Fuoss conductance equation (1978). The molar conductivities observed were explained by the formation of ion-pairs ($M^+ + X^- \rightarrow MX$). The Walden product is obtained and discussed. Molar refraction (R_M) has been calculated using the Lorentz-Lorenz equation. The results show more association of

the ions in n-pentanol than in n-propanol and results have been interpreted in terms of ion–solvent and solvent–solvent interaction. The extent of interaction has also been expressed in terms of the association constant (K_A) and shows the ion–dipole interaction to be a function of viscosity.

CHAPTER V

Qualitative and quantitative analysis of molecular interaction prevailing in glycine, L-alanine, L-valine and aqueous solution of Ionic Liquid [1-ethylpyridinium tetrafluoroborate ($EPyBF_4$)] have been investigated by thermophysical properties. The apparent molar volume (ϕ_V), viscosity *B*-coefficient, molal refraction (R_M) and adiabatic compressibility (ϕ_K) of glycine, L-alanine, and L-valine have been studied in 0.001, 0.003, 0.005 mol dm^{-3} aqueous 1-ethylpyridinium tetrafluoroborate [$EPyBF_4$] solutions at 298.15 K from the values of densities (ρ), viscosities (η), refractive index (n_D) and speed of sound (u), respectively. The extent of interaction i.e. the solute–solvent interaction is expressed in terms of the limiting apparent molar volume (ϕ_V^0), viscosity *B*-coefficient and limiting apparent molar adiabatic compressibility (ϕ_K^0).The limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) derived from the Masson equation and viscosity *A* and *B*-coefficients using the Jones-Dole equation have been interpreted in terms of ion-ion and ion-solvent interactions, respectively. Molal refractions (R_M) have been calculated with the help of Lorentz–Lorenz equation. The role of the solvent (aqueous ionic liquid solution) and the contribution of solute–solute and solute–solvent interactions to the solution complexes have also been analyzed through the derived properties.

CHAPTER VI

This chapter entails the physicochemical, such as volumetric, viscometric, refractometric and acoustic study of solute-solvent interactions of nicotinic acid and ascorbic acid prevailing in aqueous solution of 1-ethyl pyridinium tetrafluoroborate ($[EPy]BF_4$), have been reported at different temperatures. Using the density data, Masson equation has been employed to obtain the limiting values at infinite dilution by the extrapolated to zero concentration of the apparent molar volumes (ϕ_V^0) and

experimental slopes (S_V^*), which interpreted the solute-solvent and solute-solute interactions, respectively. Using the Jones-Dole equation the viscosity data were analyzed to determine the viscosity *A* and *B*- coefficient, which have also been interpreted the solute-solute and solute-solvent interaction respectively in the solutions. The Lorentz-Lorenz equation has been employed to determine the molar refractions (R_M). The temperature dependence behaviour of partial molar quantities has been determined for the vitamins. At infinite dilution, limiting apparent molar adiabatic compressibilities (ϕ_K^0) of these vitamins were evaluated and discussed. The role of the solvent (aqueous ionic liquid mixture), and the extent of solute-solute and solute-solvent interactions to the solution complexes, have also been analyzed and discussed through the derived properties.

CHAPTER VII

In this chapter the molecular interactions existing in ionic liquid-organic solvent have been done, both qualitatively and quantitatively, by means of electrical conductance, molar refraction and FT-IR measurements. Conductometric studies of 1-ethyl-3-methylimidazolium nitrate, 1-ethyl-3-methylimidazolium methanesulfonate and 1-ethyl-3-methylimidazolium tosylate in N, N-dimethyl formamide, N, N-dimethyl acetamide and dimethyl sulphoxide at 298.15K reveals high molecular interaction between the solute and the solvent which is mainly contributed by ion-dipole interaction as manifested from the FT-IR measurements. The interaction is highest in case of 1-ethyl-3-methylimidazolium tosylate and dimethyl sulphoxide than others. The larger share of the conductance of imidazolium based ionic liquid in unlike solvents comes from anion than cation as evident from their individual ionic conductance values which is estimated from the suitable allotment of the limiting molar conductivity value of tetrabutylammonium tetraphenylborate as “reference electrolyte” method. The molecular polarizability also observed to be highest in case of dimethyl sulphoxide as visible from refractive index information.

CHAPTER VIII

In this section physico-chemical investigation of solute-solvent interactions in phenyl alanine, histidin and aqueous solution of nicotinic acid (vitamin) has been investigated by thermophysical properties. The apparent molar volume (ϕ_V), viscosity *B*-coefficient and molal refraction (R_M) of phenyl alanine and histidin have been studied in 0.01, 0.03, 0.05 mol dm^{-3} aqueous vitamin solutions at different temperatures. Using the density data, Masson equation has been employed to obtain the limiting values at infinite dilution by the extrapolated to zero concentration of the apparent molar volumes (ϕ_V^0) and experimental slopes (S_V^*), which deduced the solute-solvent and solute-solute interactions, respectively. Using the Jones-Dole equation the viscosity data were examined to determine the viscosity *A* and *B*-coefficient, which have also been deduced the solute-solute and solute-solvent interaction respectively in the solutions. The Lorentz-Lorenz equation has been employed to determine the molar refractions (R_M). The overall results established the strong solute-solvent interactions between the studied amino acids and vitamin mixture in the ternary solutions. UV-Visible absorption spectra of the ternary solutions also stand in support of the results obtained.

CHAPTER IX

In this chapter I have investigated the inclusion behavior of a guest ionic liquid (IL) 1-methyl-3-octylimidazolium tetrafluoroborate into the host cavity of *β*-cylodextrin in aqueous solution. Surface tension and Conductivity measurements results showed that 1:1 hosts-guest inclusion complexes are formed and favourable with the above system. Density, viscosity and refractivity measurements were also employed to study the same. The limiting apparent molar volume, viscosity B-coefficient, and molar refraction data have been used to characterize the solute-solvent interaction between IL and cyclodextrin in the experimental ternary solution systems.

CHAPTER X

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