ABSTRACT

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.

A material is said to be biologically-active if it has an interaction or effect on living organism. "Biologically-active compounds" are extra nutritional constituents that typically occur in small quantities in foods. They are being intensively studied to evaluate their effects on health. Biologically-active solutes find great application in pharmaceutical and cosmetic products including medicinal industries. The word "salt" is a general chemical term that refers to ionic compounds formed when an acid reacts with a base. Today, salt continues to be of major economic importance, with thousands of uses in addition to flavoring and preserving food. An ionic liquid (IL) is a salt in the liquid state whose melting point is below some arbitrary temperature, such as 100 °C (212 °F). Ionic liquids have wide range of industrial applications. They used in chemical industry, pharmaceuticals, cellulose processing, gas handling, gas treatment, solar thermal energy, nuclear fuel processing, food and bi-products, waste recycling, batteries etc.

Solution chemistry is an important branch of physical chemistry that studies the change in properties that arise when one substance dissolves in another substance. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. The mixing of different solute or solvent with another solvent/solvent mixtures gives rise to solutions that generally do not behave ideally.

In 'Solution Chemistry' broadly three types of approaches have been made to estimate the extent of solvation. The approaches involves the studies of viscosity, conductance, etc., of electrolytic solutions and the derivation of various factors associated with ionic solvation, the second is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated with solvation can be elucidated, and the third is spectroscopic measurements where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature.

In recent years there have been increasing interests in the behavior of electrolytes in non- aqueous and mixed solvents with a view to investigating solute-solute/ion-ion and solute–solvent/ion-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 open vistas for physical chemists and interests in these organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry .

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 biologically active solutes and ionic salts in pure and mixed solvent systems.

- To investigate the physico-chemical properties of biologically-active solutes and ionic salts in pure and mixed solvent systems.
- To study the transport properties of ionic salts along with thermodynamic and acoustic ones to characterize molecular interactions in solutions.

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.

CHOICE OF SOLVENTS, SOLUTES AND ELECTROLYTES USED

Nitromethane, formamide, N-methylformamide, 1,3-dioxolane, methanol, acetonitrile, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulphoxide along with water, considered as a universal solvent, have been chosen as 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 giving us an optimum environment for the study.

Amino acids (glycine, L-alanine, L-valine,), carbohydrates (D-glucose, D-mannitol, D-sucrose), ascorbic acid (vitamin C), Nicotinic acid (vitamin B_3) were considered as solutes. The study of these solutes is of great interest because of their wide use as solvents solubilizing agents in pharmaceutical, cosmetics and medicinal industries.

The electrolytes used are tetrabutylammonium tetrafluoroborate, tetrabutylammonium perchlorate, tetrabutyphosphonium tetrafluoroborate, tetrabutyphosphonium methanesulfonate. These electrolytes are used as reference and supporting electrolytes and are used as non-aqueous electrolytes in electrochemical applications.

METHODS OF INVESTIGATION

The existence of free ions, solvated ions, ion-pairs and triple-ions in aqueous and non-aqueous media depends upon the concentrations of the solvent systems. Hence the study of various interactions and equilibrium of ions in different concentration regions are of immense importance to the technologist and theoretician as most of the chemical processes occurs in these systems.

It is of interest to employ different experimental techniques to get a better insight into the phenomena of solvation and different interactions prevailing in solution. We have, therefore, employed five important methods, namely conductometry, viscometry, densitometry, Ultrasonic Interferometry and Refractometry to probe the problem of solvation phenomena.

PHYSICO-CHEMICAL PARAMETERS AND THEIR SIGNIFICANCE

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent/ion-solvent ad solute-solute/ion-ion interactions in solution. The sign and magnitude of partial molar volume (ϕ_V^0) also provides information about the nature and magnitude of ion-solvent interaction while the experimental slope (S_v^*) provides information about ion-ion interactions. Viscosity B-coefficient obtained from the viscosity values indicates the extent of ion-solvent interaction in a solution. From experimental speed of sound values, limiting apparent molar adiabatic compressibility (ϕ°_K) and the experimental slope (S_k^*) can be estimated. These parameters also give an idea about the ion-solvent and ion-ion interaction in the solution.

The transport properties in most cases are studied using the conductance data, especially conductance at infinite dilution. Limiting molar conductance (Λ_0) gives an idea about the ion-solvent interaction in the solution. Association constant (K_A) obtained from the conductance study gives an idea about the solvation of the ions.

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 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. 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 apparent molar volume (ϕ_V), viscosity B-coefficient, molal refraction (R) and adiabatic compressibility (ϕ_K) of L-Glycine, L-Alanine, and L-Valine have been determined in 0.010, 0.03, 0.05 mol·dm^{-3} aqueous ascorbic acid solutions at 298.15 K from density (ρ), viscosity (η), refractive index (n_D) and speed of sound (u) respectively. The limiting apparent molar volumes (ϕ_V^0) and experimental slopes (S_V^*), derived from the Masson equation, have been interpreted in terms of solute-solvent and solute-solute interactions respectively. The viscosity data were 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 in the solutions. Molal refractions (R) have been calculated using the Lorentz-Lorenz equation. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) of these amino acids at infinite dilution were evaluated and discussed.

CHAPTER V

Density (ρ) and viscosity (η) measurements of bio-active solutes (D-glucose, D-mannitol and D-sucrose) in aqueous nicotinic acid, (Vitamin B_3) at 298.15, 308.15 and 318.15 K have been carried out. Using these properties, the apparent molar volume (ϕ_V), the partial molar volume (ϕ_V^0), the partial molar volume of transfer ($\Delta\phi_V^0$) of carbohydrates from water to aqueous nicotinic acid solution were calculated. A plausible mechanism for the reaction of carbohydrates in aqueous nicotinic acid is also suggested along with the interaction of the product with water. The viscosity *B*-coefficients of Jones-Dole equation and the molar refraction (R) of the solutions have been computed for the interpretation of solute-solvent interactions. The structure-making or breaking capacity of carbohydrates in the solution has been discussed. All these parameters are used to study solute-solvent and solute-solute interactions in the aforementioned mixtures.

CHAPTER VI

In this chapter electrolytic conductivities (Λ), densities (ρ), viscosities (η) and ultrasonic speed (u) of an ionic liquid (IL) Tetrabutylphosphonium Tetrafluoroborate [Bu_4PBF_4] have been studied in dimethylsulfoxide (DMSO), dimethylacetamide (DMA), and dimethylformamide (DMF) at 298.15 K. The limiting molar conductivity (Λ_0), the association constant (K_A), and the distance of closest approach of ions (R) have been evaluated using the Fuoss conductance equation (1978). The molar conductivities observed were explained by the formation of ion-pairs ($M^+ + X^- \leftrightarrow MX$). The Walden product is obtained and discussed. Ion-solvent interactions have been interpreted in terms of apparent molar volumes (ϕ_V) and viscosity *B*-coefficients which are obtained from the results supplemented with densities and viscosities, respectively. 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. The adiabatic compressibility (β) has been evaluated using the ultrasonic speed (u) values. Finally values of the limiting partial molar adiabatic compressibility (ϕ_K^0) are calculated and discussed.

CHAPTER VII

This chapter entails the qualitative and quantitative analyses of molecular interaction prevailing in ionic liquid tetrabutylphosphonium methanesulfonate [Bu_4PMS] in dimethyl sulfoxide (DMSO), N,N- dimethyl formamide (DMF) and N,N-dimethyl acetamide (DMA) probed by electrical conductances and Fourier transform infrared (FT-IR) measurements have been reported at 298.15 K. Corresponding conductance data have been analysed using the Fuoss conductance-concentration equation (1978) for ion pair formation. The limiting ionic conductances ($\lambda_0^\pm$) have been estimated from the appropriate division of the limiting molar conductivity value of tetrabutylammonium tetraphenylborate [Bu_4NBPh_4] as the "reference electrolyte". The diffusion coefficient (D) has been obtained from Stokes-Einstein relation and the ionic mobility (i) for [Bu_4P]$^+$ and MS$^-$ using appropriate equation. The results have been discussed in terms of dipole-dipole interactions, hydrogen bond formation and structural aspect of the solvents and configurational theory. The FT-IR spectra have also been studied to predict the interactions occurring in the system.

CHAPTER VIII

In this chapter qualitative and quantitative analyses of molecular interaction prevailing in ionic salt-organic solvent media, probed by electrical conductances have been reported. Tetrabutylammonium tetrafluoroborate [Bu_4NBF_4] in acetonitrile (CH_3CN), methanol (CH_3OH), dimethylsulfoxide (DMSO) and 1,3-dioxolane (1,3-DO) have been studied at 298.15 K. The extent of interaction is expressed in terms of the association constant (KA) and shows the interaction to be a function of viscosity. Limiting molar conductances (Λ_0), association constants (K_A), and the association diameter (R) for ion-pair formation have been analyzed using the Fuoss conductance-concentration equation (1978). The observed molar conductivities were explained by the formation of ion-pairs ($M^+ + X^- \leftrightarrow MX$, K_P) and

triple-ions ($2M^+ + X^- \leftrightarrow M_2X^+$; $M^+ + 2X^- \leftrightarrow MX_2^-$, K_T). The Walden product is obtained and discussed. The deviation of the conductometric curves (Λ vs $\sqrt{c}$) from linearity for the electrolyte in 1, 3-dioxolane indicates triple-ion formation, and therefore the corresponding conductance data have been analyzed by using the Fuoss-Kraus theory of triple-ions. The limiting ionic conductances ($\lambda_o^{\pm}$) have been calculated from the appropriate division of the limiting molar conductivity value of tetrabutylammonium tetraphenylborate [Bu_4NBPh_4] as the "reference electrolyte" method along with a numerical evaluation of ion-pair and triple-ion formation constants ($K_P \approx K_A$ and K_T). The results have been interpreted in terms of solvent properties and configurational theory.

CHAPTER IX

In these chapter Molecular interactions of tetrabutylammonium salts prevailing in organic solvent media have been analyzed, both qualitatively and quantitatively, using conductometric studies and validating the results with Fourier transform infrared (FT-IR) measurements. From conductometric studies of tetrabutylammonium tetrafluoroborate [Bu_4NBF_4] and tetrabutylammonium perchlorate [Bu_4NClO_4] in nitromethane (NM), N-methyl formamide (NMF), and formamide (FA) at 298.15 K, it is revealed that high molecular interaction is mainly because of ion-dipole interactions, which is evidenced from the FT-IR measurements. The 1978 Fuoss conductance-concentration equation in terms of the limiting molar conductance (Λ_o), the association constant (K_A), and the association diameter (R) was used to interpret the conductance data. Tetrabutylammonium tetraphenylborate [Bu_4NBPh_4] as the "reference electrolyte" was used to estimate the ionic contributions to the limiting molar conductance. The degree of interaction is articulated in terms of the association constant (K_A), which illustrates that viscosity of the solvent plays an important role in the ion-dipole interaction. The ionic interaction obtained is highest in the case of [Bu_4NBF_4] and FA in comparison to the other systems. The consequences have been considered in terms of dipole-dipole interactions, hydrogen bond formation, structural feature, and configurational theory. The FT-IR spectroscopic studies of the variational intensity of characteristic bands of the solvents have been undertaken, and the solvation phenomenon is evidenced by the change of band intensities owing to the occurrence of the electrolytes.

CHAPTER X

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