Theoretical 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

Methanol, Acetonitrile, Benzonitrile 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.

Cyclodextrins, Crown ethers, Amino acids and its derivatives, ascorbic acid (vitamin C), (vitamin B_3, B_6) etc. 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 pyrolidinium based ionic liquids, Lithium Iodide etc. These electrolytes are used as reference and supporting electrolytes and are used as aqueous electrolytes in electrochemical applications.

METHODS OF INVESTIGATION

The existence of free ions, solvated ions, in aqueous and non-aqueous media depends upon the concentrations of the solvent systems. Hence the study of an assortment of 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 diverse experimental techniques to get a better insight into the phenomena of solvation and different interactions prevailing in solution. We have, therefore, employed vital methods which are experimental, spectrometric and theoretical namely to probe the dilemma 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. 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.

Surface tension, Steady State fluorescence, association constants with the help of fluorescence, UV, NMR Study (1H, 13C, 2D ROESY, NMR titration) were performed along with SEM, HRTEM, XRD and Ab-initio methods were applied to prove the existence of assorted interactions in the diverse systems.

SUMMARY OF WORKS DONE

CHAPTER-I

This chapter contains the *objective, novelty and applications of the research work*, the imperative compounds i.e., electrolytes/solutes and solvents used and methods of investigation. Moreover this also occupies the summary of the works done allied with the dissertation.

CHAPTER-II

The chapter encloses *general introduction (Review of the Earlier works)* of the thesis and forms the strong background of the work embodied in the

thesis. A brief review of noteworthy mechanism in the field of molecular as well as ionic interaction has been specified. The discussion includes ion-solvent/solute-solvent, ion-ion/solute-solute and solvent-solvent interactions in binary, ternary mixed solvent systems and of electrolytes in pure and non-aqueous solvent systems at various temperatures in terms of various derived parameters, estimated from the experimentally observed properties viz., density, viscosity, refractive index and conductance, surface tension, pH, FTIR, UV, NMR, fluorescence, HRMS, SEM, HRTEM. Ionic association and its reliance 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. Crucial assessment of diverse methods on relative merits and demerits on the basis of various assumption have been employed from time to time acquiring the single ion values (viscosity *B*-coefficient and limiting equivalent conductance) and their implications have been discussed. The molecular interactions are interpreted based on various derived parameters in the systems. Moreover the approximate quantum mechanical calculation and cell viability is also done in the present study.

CHAPTER-III

The chapter comprises experimental section which principally involves basic information's, structure, source, purification and uses of imperative compounds i.e., electrolytes/non-electrolytes or solutes, and solvents have been used throughout the entire research work. It also restrains details of the instruments, procedure, working principle and equations that are employed to understand physicochemical, transport, optical and spectroscopic, and approximate quantum mechanical calculations. Cell viability data is also being provided in this chapter.

CHAPTER-IV

Geometry- optimized extended conformation obtained for amino acids (Tyrosine, Tryptophan) prevailing in Aqueous Vitamin C Solutions is studied in this part. The solute – solvent interactions are maximum in Tyrosine is observed. C-13 NMR spectral data and Ab-initio are more reliable and supportive to study the Solute - Solvent interactions. Ascorbic acid acts as a co-enzyme. This leads to the essential benefits of Tyrosine in presence of

Ascorbic acid in various catabolism reactions in human body. The ion-solvent interaction dominates above the ion-ion interactions in studied solution.

CHAPTER-V

Fundamental properties, opportunities, challenge, and latest progress of anode and cathode material research is discussed in this chapter. The guest ions can be inserted into and be removed from host network reversibly. In a Li-ion battery, Li^+ is guest ion and the host network compounds are aqueous ascorbic acid solution which can dissociate in solution and organize to form 2-furanone molecules. As new supplies and strategies are found, Li-ion batteries will no doubt have an ever better impact on our lives in the years to come. Studies of transportation properties of diverse electrolytes in solvent media are of importance to obtain information on the behavior of ions in solution. Molecular interactions can be studied in the solution phase by studying it's thermodynamic, transport properties. These properties provide vital information about the nature and strength of intermolecular forces operating among the components. The ion–ion interactions for LiCl, LiBr and LiI decreases with the increase in temperature, which may be due to more solvation of ions. The temperature effect on B coefficient for LiCl, LiBr and LiI shows a positive sign of dB/dT, viewing thereby that LiCl, LiBr and LiI behaves a structure-breaker in (0.001, 0.003, 0.005) m aqueous ascorbic acid solution. This allows usage for a green battery with high capacity and high voltage. It also paves the way for cheaper consumer electronics.

CHAPTER-VI

The concerned chapter comprises study of two host molecules i.e., beta cyclodextrin, 18 crown 6 along with ionic liquid. It may be expected that, as innovative applications like those in chromatography, electron microscopy, and biochemistry, become more widely appreciated; by the use of the studied Ionic liquid will become properly recognized. The ability to control and enhance proton-catalyzed chemical reactions should be another feature of studied protic ionic liquid chemistry; it is a very effective solvent media for optimum output in several applications with minimum possible environment pollution. Physicochemical investigation of both inclusion and encapsulation complexes for β- CD and 18-Crown-6 with pyrrolidinium based ionic liquid are overviewed in the present work. In the first case ionic liquid combines with α- and β- CD which has interesting variations in thermo chromic behavior of the dye molecules and would be desirable in the near future. On the other hand 18-Crown-6 including hydrophobic ionic liquid has a vital role in electrochemistry. Such type of inclusion complexes are used in recycling

process. This proposed electrochemical process for remediation of extraction solvent preserves the ionic liquid.

CHAPTER-VII

This chapter deals with few ionic oxalates along with Vitamin C in our body. Few of the chemicals which were taken to observe its experimental effects are Lithium Oxalate, Sodium Oxalate, Potassium Oxalate, Ammonium Oxalates and aqueous Vitamin C. Vitamin-C which should be inserted, on the other hand Oxalates are already present in the body. Excess of Oxalates cause negative effects in the body by causing health hazards. Importance lies behind the fact that if the co-solute ascorbic acid along with water is made to interact with oxalates the water along with Oxalates is removed from the body. While Vitamin-C in other way is used by the body for the growth and repair of tissues. It helps the body make collagen, an important protein used to make skin, cartilage, tendons, ligaments, and blood vessels. Vitamin C is needed for healing wounds, and for repairing and maintaining bones and teeth. In my present work the interaction of Sodium Oxalate is best with Vitamin-C.

CHAPTER-VIII

The chapter deals precise measurements on geometry, spectroscopic, conductometric, ab initio methods. Solvation nature of Lithium iodide (LiI) for both polar and nonpolar organic solvents *viz.*, acetonitrile and benzonitrile has been illustrated. Results of vibrational spectroscopic data were compared with experimental values, electrical conductance (Λ) of solutions were also taken. The effect of cations on the infrared spectrum of AcN is well known. Similarly, we have focused on the effect of anion on infrared spectrum of PhcN. Here the effect of anion on the spectral properties of PhcN based on quantum chemical calculations is in agreement with the experimental observations.

Aromatic nitriles have extensive applications in the production of dyes, pesticides and pharmaceuticals. They are used as intermediates in the synthesis of a variety of pharmacologically active compounds which are used as sedatives, muscle relaxants, neuroleptics, etc. Benzonitriles are of immense interest in the ground of organic chemistry for the synthesis of pharmaceuticals, natural products, herbicides, and agrochemicals. In the current work substituted benzonitriles are being studied in order to find its novelty in many reactions in industries at high temperatures.

Lithium-ion battery performance is strongly influenced by ionic conductivity of the electrolyte, which depends on the speed at which Li+ ions drift across cell and relates to their solvation structure. The selection of solvent can greatly impact both solvation and diffusivity of Li+ ions. Schematically the action of these batteries occurs together with an exchange of ions between solution and electrodes. The FTIR spectroscopic analysis of benzonitrile and acetonitrile was carried out to assess the impact of at atomic and molecular level like bond strength, stability, rigidity of structure, etc. As latest supplies and strategies originate, Li-ion batteries will no doubt have an ever superior impact on our lives in the years to come.

CHAPTER-IX

This chapter consist of qualitative and quantitative analysis of molecular interaction established in L-*Tert*-leucine and aqueous solution of α- and β- cyclodextrin have been probed by thermophysical properties. So this {β + [Tle]} is more suitable for the pharmaceutically active compounds, chiral auxillaries & muscular protein**.** The present work adds a dimension in the field of contemporary science of controlled delivery of Tertiary-Leucine which is a derivatized amino acid by means of suitable host molecule as selected here as α- and β-Cyclodextrin. Biological activity relates to the non- toxic nature of the inclusion complexes.

CHAPTER X

This work portrays the importance of Vitamin B complexes and their novelty in the body in regard of In- Vitro Analysis.

CHAPTER XI

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