ABSTRACT

The branch of physical chemistry involving the change in properties in the course of dissolution of one substance in another is termed as 'Solution Chemistry'. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. Solution Chemistry broadly deals with two types of approaches to estimate the extent of solvation by physico-chemical processes in liquid media. Those approaches include the studies of density, viscosity, refractive index and conductance, etc., of electrolytes 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.

Studies on interactions of molecules in solutions are very useful to acquire information on the geometrical effects and intermolecular interactions taking place in the liquid media. Moreover, knowledge of the thermodynamic properties is essential for the proper design of industrial processes. Accurate knowledge of thermodynamic properties of solution mixtures has great relevance in theoretical and applied areas of research.

The exact structure of the solvent molecule is not known with certainity. The addition of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The introduction of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The interactions between solute and solute, solute and solvent, and solvent and solvent molecules and the resulting ion-solvation become predominant. The assessment of ion pairing in these systems is important because of its effect on the ionic conductivity and hence the mobility of the ions in solution. The extent of ion-solvation is dependent upon the interactions taking place between solute-solute, solute-solvent, solvent-solvent species. This explains the spurt in research in solution chemistry to elucidate the exact nature of these interactions through experimental investigations involving

densitometry, viscometry, interferrometry, refractometry and other suitable methods and to interpret the experimental data collected.

The behaviour of electrolytes in solution depends mainly on ion-ion and ion-solvent interactions. The former interaction, in general, is stronger than the latter. Ion-ion interaction in dilute electrolytic solutions is now theoretically well understood, but the ion-solvent interaction or ion-solvation still remains a complex process

Studies on transport properties of electrolytes, along with thermodynamic and compressibility studies, give very valuable information about ion-ion and ion-solvent interactions in solutions. The influence of these ion-solvent interactions is 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.

As a result of extensive studies in aqueous, non-aqueous and mixed solvents, it has become increasingly clear that the majority of the solutes are significantly modified by all solvents. Conversely, the nature of strongly structured solvents, like water, is substantially modified by the presence of solutes.

Barium nitrate, Barium chloride, Lithium perchlorate, Sodium perchlorate and Potassium perchlorate, Potassium acetate, Nicotinic acid, Glycine, L-Alanine, L-Valine,1-methyl-3-octylimidazoliumtetrafluoroborate,Tetrabutylphosphonium tetrafluoroborate, Potassium chloride, Potassium bromide and potassium iodide are used as solutes. On the other hand, Formamide, N,N-Dimethyl formamide, n-Propanol, n-Butanol, n-Pentanol, 1,3-dioxolane, Nitromethane, Dimethyl sulfoxide are considered as solvents.

The study of these solutes and solvents, in general, are of interest because of their wide range of applications in many industries ranging from pharmaceutical to cosmetic products.

In this research work additional emphasis has been given to Biomolecules being the organic molecules produced by a living organism. Amino acid is the

monomeric unit of the Polypeptide (protein) belonging to the class of Biomolecules. Amino acids combine into peptide chains to form the building blocks of linear array of proteins. Because of the key role in biochemistry, amino acids are commonly used in nutrition supplements, fertilizers, food technology and also in the manufacture of biodegradable plastic and drugs in industry.

In order to evaluate the potential health benefits of Biomolecules information about regarding the knowledge of their absorption, metabolism and biological effects, is necessary. Pharmacological activity is often considered to describe beneficial effects of biomolecules. This translates towards recommending a diet rich in a variety of vegetables, fruits, whole grains, legumes, oils, and nuts. Many vital functions are regulated by pulsed or transient release of bioactive substances at a specific time and site in the body under physiological conditions. In drug delivery research, they have been notably used as therapeutic agents to a patient in a palatine or staggered release profile over the last two decades.

Glycine is used as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, and toiletries. Glycine serves as intermediate in the synthesis of a number of products. Glycine is also used for the treatment of schizophrenia, stroke, benign prostatic hyperplasia (BPH), and some rare inherited metabolic disorders. It is also used to protect kidneys from the harmful side effects of certain drugs used after organ transplantation as well as the liver from harmful effects of alcohol. Other uses include cancer prevention and memory enhancement.

Alanine is used for low blood sugar (hypoglycemia), diarrhea related dehydration, liver disease, enlarged prostate benign prostatic hypertrophy, (BPH) fatigue, stress, and certain inherited disorders including glycogen storage disease and urea cycle disorders. Alanine is used as a source of energy for muscle tissue, the brain, and central nervous system, in strengthening the immune system by producing antibodies. It has been used as a source for the production of glucose in order to stabilize blood sugar levels over lengthy periods.

Valine is used to treat amyotrophic lateral sclerosis (ALS, Lou Gehrig's disease), brain conditions due to liver disease (chronic hepatic encephalopathy,

latent hepatic encephalopathy), a movement disorder called tardive dyskinesia, a genetic disease called McArdle's disease, a disease called spino-cerebellar degeneration, and poor appetite in elderly kidney failure patients and cancer patients.

Nicotinic acid is the vitamin B_3, plays a very important role to maintain the normal function of the digestive systems and cholesterol levels in the human body. Nicotinic acid and nicotinamide combinedly act as precursor of the coenzymes nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP). The combination of nicotinic acid and nicotinamide is clinically referred to as niacin. Insufficient niacin in the diet can cause nausea, skin and mouth lesions, anemia, headaches, and tiredness. Chronic niacin deficiency leads to a disease called pellagra.

In summary many biomolecules appear to have beneficial health effects. Much scientific research needs to be conducted before we can set in in motion to make science-based nutritional recommendations.

On the other hand, some naturally-occurring simple compounds are needed by the body for its vital activities. Each compound, with its own specific task, even in the small and often minute quantities necessary, is indispensable for important life functions.

Potassium levels can be low as a result of a disease or from taking certain medicines, or after a prolonged illness with diarrhea or vomiting. Potassium chloride is used to prevent or to treat low blood levels of potassium (hypokalemia). Potassium bromide finds uses in human and veterinary medicine as an anti-seizure medication. Potassium iodide is also used along with antithyroid medicines to prepare the thyroid gland for surgical removal, to treat certain overactive thyroid conditions (hyperthyroidism), and to protect the thyroid in a radiation exposure emergency. Potassium Acetate being a simple compound is widely used as an additive to dialysis fluids, in the manufacture of fire extinguishers and in the petroleum industry. Besides it is used as a food additive as well as a preservative and acidity regulator. Barium nitrate is a strong oxidizer which burns and

explodes with organics. It is used in explosives, fireworks, matches, and fertilizers.

Alkali metal perchlorates are extensively used to block iodine uptake for the patients with subclinical hyperthyroidism. They are also used in the manufacture of chemical sources of energy.

Ionic liquids have potential uses as 'designer solvents' and 'green' replacements for volatile organic solvents used in reactions involving inorganic and bio-catalysis. They are also utilized as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells).

Summary of the Works Done

CHAPTER I

This chapter entails the object and utility of the research work. This mainly comprises of the choice of the main solvents and solutes used and their applications in various fields, methods of investigation and summary of the work done associated with the thesis.

CHAPTER-II

This chapter deals with the general introduction (Review of the Earlier Work) of the thesis and the background of the present work. After presenting a brief review of notable works in the field of solute-solute, solute-solvent and solvent-solvent interactions, the discussion centers on the conductance, density, viscosity, refractive index and adiabatic compressibility of different electrolytes in various liquid systems at different temperatures. The solution properties of the various electrolytes in different solvents are then elaborated and discussed, stressing the importance of the work associated with the thesis.

CHAPTER-III

This chapter states and explains the experimental section consisting of the sources, structure, purification and application of the solutes and solvents

under investigation along with the studied electrolytes and various experimental methods employed for measurement of the transport ,thermodynamic, optical and acoustic properties.

CHAPTER-IV

This chapter involves the study of solvation consequences of α-Amino Acids in aqueous ionic liquid solution probed by physico-chemical approach. The apparent molar volume (ϕ_V), viscosity *B*-coefficient, molar refraction (R) 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 Tetrabutylphosphonium Tetrafluoroborate (Bu_4PBF_4) solutions at 298.15 K from the values of density (ρ), viscosity (η), refractive index (n_D) and speed of sound (u) respectively. The limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) are obtained from the Masson equation and have been interpreted in terms of solute-solvent and solute-solute interactions respectively. Jones-Dole equation were employed to analyse the viscosity data and the interpretation of the derived parameters *A* and *B* have also been carried out in terms of solute-solute and solute-solvent interactions in the solutions respectively. Molar refractions (R) have been determined with the help of Lorentz-Lorenz equation. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) of three amino acids at infinite dilution were evaluated and discussed.

CHAPTER-V

This chapter deals with the physico-chemical study of solution behaviour of alkali metal perchlorates prevailing in N, N- Dimethyl Formamide with the manifestation of ion solvation consequences. Physico-chemical analysis on densities (ρ), viscosities (η) and speed of sound (u) and electrolytic conductivities (Λ) of Lithum Perchlorate, Sodium Perchlorate and Potassium Perchlorate in pure N,N-Dimethyl Formamide have been performed at 298.15K. Limiting molar conductance (Λ_0), Association constant (K_A) and co-sphere diameter (R) for ion-pair formation have been obtained from Fuoss conductance

equation. Masson equation is used to determine the limiting apparent molar volume (ϕ_V^0) and experimental slope (S_V^*) to study the ion-solvent and ion-ion interactions respectively. The derived parameters *A* and *B* obtained from Jones-Dole equation represent ion-ion and ion-solvent interactions respectively. The *u*-values have been used to determine adiabatic compressibility (β_S) and limiting apparent molar adiabatic compressibility (ϕ_K^0).

CHAPTER-VI

This chapter describes physico-chemical study of some Bio-active solutes in aqueous Potassium Acetate Solution. The apparent molar volume (ϕ_V), viscosity *B*-coefficient, molar refraction (R) and adiabatic compressibility (ϕ_K) of Glycine, L-Alanine, and L-Valine have been determined in 0.01, 0.03, 0.05 mol·dm^{-3} aqueous Potassium Acetate solutions at 298.15 K from the measurement of density (ρ), viscosity (η), refractive index (n_D) and speed of sound (u) respectively. Masson equation was employed for the limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) to interpret the solute-solvent and solute-solute interactions respectively. The calculations of Molar refractions (R) have been done using the Lorentz-Lorenz equation. 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. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) of these amino acids at infinite dilution were examined from the u values.

CHAPTER-VII

This chapter includes probing solute-solvent interactions of some bio-active solutes in aqueous Barium Nitrate solution on the basis of physico-chemical contrivances. Apparent molar volume (ϕ_V), molar refraction (R), viscosity *B*-coefficient and adiabatic compressibility (ϕ_K) of some Bio-active solutes such as Glycine, L-Alanine, and L-Valine have been measured in 0.01,

0.03, 0.05 mol·dm^{-3} aqueous Barium Nitrate solutions at 298.15 K. Masson equation was employed for the experimental slopes (S_V^*) and limiting apparent molar volumes (ϕ_V^0) to interpret the solute-solvent and solute-solute interactions respectively. Molar refractions (R) have been calculated using the Lorentz-Lorenz equation. Jones-Dole equation was used to derive parameters *A* and *B* to interpret the interactions. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) at infinite dilution were examined from the sound speed values.

CHAPTER-VIII

This chapter represents an exploration of solution behaviour of potassium halides in mixtures of nicotinic acid and water at 298.15, 308.15 and 318.15 K by physico-chemical approach. Apparent molar volume (ϕ_V) and viscosity B-coefficients were estimated for potassium chloride, potassium bromide and potassium iodide in aqueous mixture of nicotinic acid from measured solution density (ρ) and viscosity (η) at 298.15, 308.15 and 318.15 K at various electrolyte concentrations. The experimental density data were evaluated by Masson equation and the derived data were interpreted in terms of ion–solvent and ion–ion interactions. The viscosity data has been investigated using Jones–Dole equation and the derived parameters, B and A, have also been interpreted in terms of ion–solvent and ion–ion interactions respectively. The structure-making or breaking capacity of the electrolyte under investigation has been discussed in terms of sign $\left(\partial\phi_V^0/\partial T\right)_P$.

CHAPTER-IX

This chapter corresponds to a study on interactions of some Metal Perchlorates prevailing in Formamide by physico-chemical approach. The physico-chemical properties, electrolytic conductivities (Λ), densities (ρ), viscosities (η) and speed of sound (u) of Lithum Perchlorate, Sodium Perchlorate and Potassium Perchlorate have been evaluated in pure Formamide at 298.15 K. Association constants (K_A), Limiting molar conductances (Λ_0), and

co-sphere diameter (R) for ion-pair formation have been obtained from Fuoss conductance equation. Viscosity B-coefficient, apparent molar volume (ϕ_V) and apparent molar adiabatic compressibility (ϕ_K) have been calculated from the measurement of viscosity (η), density (ρ) and speed of sound (u) respectively. Masson Equation has been employed to inspect the ion-solvent and ion-ion interactions from the values of limiting apparent molar volume (ϕ_V^0) and experimental slope (S_V^*) respectively. Ion-ion and ion-solvent interactions have been interpreted with the help of the derived parameters A and B obtained from Jones-Dole equations respectively. The limiting apparent molar adiabatic compressibility (ϕ_K^0) and adiabatic compressibility (β_S) have been assessed using the u values.

CHAPTER-X

This chapter includes the concluding remarks on the works associated with the thesis.