CHAPTER–I

FUNDAMENTAL OF THE RESEARCH WORK

1.1. Object and Utility of The Research Work

Life set in around 4 million years ago. Small cells or so called microorganisms could strap up the energy from inorganic source or sunlight to construct small biomolecules. They gave the impression to obey the laws of Physics and Chemistry yet constitute the diverse living biota. They actually comprised the dynamic and vibrant living world. Thus it becomes very intriguing to be acquainted with these seemingly lifeless molecules, their structure in order to make out how they formed and contribute to the functioning of the living world.

A biomolecule is an organic molecule produced by a living organism, primarily consisting of carbon, hydrogen and oxygen and to lesser extent phosphorus and sulfur. Therefore all living organisms are essentially made up carbon, hydrogen and oxygen. Other elements sometimes are incorporated but are much less common. All these biomolecules work together in an interrelated fashion to form an organism. They include large macromolecules such as proteins, polysaccharides, lipids and nucleic acids, as well as small molecules such as primary metabolites, secondary metabolites and natural products.

Amino acid is the monomeric unit of the Polypeptide (protein). They are molecules that contain an amine group, a carboxylic acid group and a side-chain varying between different amino acids. Since the carboxylic acid group has a proton available for binding with the electrons of another atom, and the amino group has electrons available for binding with a proton from another atom, the amino acid behaves as an acid and a base simultaneously. Carbon, hydrogen, oxygen, and nitrogen are the key elements of an amino acid. In biochemistry the term usually refers to *alpha-amino acids* being important in metabolism. 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.

Glycine is used as a buffering agent in antacids, analgesics, antiperspirants, cosmetics, and toiletries. Glycine becomes intermediate in the synthesis of a number of products. Glycine is 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 numerous 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 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).

Physico-chemical investigation of density and viscosity of liquids, measurements of refractive index and adiabatic compressibility offer insight into the molecular arrangement in liquids to make out the thermodynamic properties in liquid media. Physico-chemical processes help us to be aware of many practical problems regarding mass transport, energy transport, heat transport and fluid flow. Acoustic properties have been the subject of widespread research activity to study the intermolecular interactions in ion-solvent systems. The non-aqueous systems have been of enormous importance to the technologist owing to the occurrence of chemical processes occur in these systems.

Study on interactions by physico-chemical processes play a crucial role to interpret the intermolecular interactions among mixed components at microscopic and macroscopic levels. Such interactions thermodynamic, transport, acoustic and optical studies on binary and ternary solvent systems are highly useful.

The refractive index is a thermodynamic property for a pure fluid depends upon temperature and pressure. The refractive index, n_D, is defined as the ratio of velocity of light in the vacuum to the velocity of light in the medium and, therefore, for a fluid it is greater than unity. For liquids, it is greater than 1 but for gases, the refractive index is very close to unity. The refractive index or refractivity (n_D) can be easily measured by the sodium D line of a simple refractometer at a temperature of interest. The refractive index is used to estimate the physico-chemical properties of solvent/solution mixtures. Properties such as heat capacity, critical constants and transport properties are related to the refractive index.

Rheology is the branch of Science [1] that studies material flow and deformation, and is implicated in the mixing and flow of medicinal formulations and cosmetics and is increasingly applied to the analysis of the viscous behaviour of many pharmaceutical products, [2-6] and to set up their stability and even bio-availability.

The molecular and rheological behaviour of a formulation [7] can effect aspects such as patient acceptability, since it has been well established that density and viscosity both influence the rate of absorption of such products in the body [8, 9]. The study of viscous synergy and antagonism is important in connection with the rheological perspective, since many products are formulated with more than one component in order to yield the desired physical structure and properties [10]. Synergy and antagonism provide the mutual decrement or enhancement of the biological, pharmaceutical activity of different components of a given mixture.

The inspection of the viscous behaviour of pharmaceuticals, foodstuffs, cosmetics or industrial products, etc., is essential for confirming that their viscosity is appropriate for the contemplated use of the products. The system [11, 12] is said to lack interaction if the total viscosity of the system is equal to the sum of the viscosities of each component considered separately.

In solution chemistry, the assessment of ion-solvent interactions can be known thermodynamically and also from the measurement of viscosity B – coefficient, partial molar volumes, and limiting ionic conductivity studies. Suitable values of ion-solvent interactions help the chemists to choose solvents that will enhance (i) the solubility of minerals in leaching operations (ii) the rates of chemical reactions, or (iii) reverse the direction of equilibrium reactions.

The implications of the investigation of reaction in non-aqueous and mixed liquid media have been summarized by Popovych, [13] Bates, [14] Meck, [15] Franks, [16] Parker, [17] Criss and Salomon, [18] Marcus [19] and others [20-22]. The studies on interactive properties of aqueous solutions have provided sufficient information on the thermodynamic aspects of different electrolytes and non-electrolytes, the effects of variation in ionic structure, ionic mobility and common ions along with a host of other properties [23].

On the other hand, different sequence of solubility, difference in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have opened vistas for physical chemists and interest in the organic solvents transcends the traditional boundaries of organic, inorganic, physical, analytical and electrochemistry [24].

Studies of transport properties of electrolytes with thermodynamic and acoustic studies, give very valuable information about molecular interactions in solutions [25, 26]. The changes in ionic solvation have important applications in diverse areas such as studies of reaction mechanisms, organic and inorganic synthesis, non-aqueous battery technology and extraction [27].

Fundamental research on non-aqueous electrolyte solutions has catalysed their wide technical applications in many fields. High-energy primary and secondary batteries, wet double-layer capacitors and super capacitors, electro-deposition and electroplating are some devices and processes for which the use of non-aqueous electrolyte solutions had brought the biggest successes [28-30].

Knowledge of ion-solvent interactions in non-aqueous solutions is extremely important in several practical problems concerning energy transport, heat transport, mass transport and fluid flow. Conversely, the nature of strongly structured solvents like water is substantially modified by the presence of solutes [31].

Exploration of a series of investigations have been performed on the conductometric, volumetric, viscometric, refractometric and interferometric behaviour to investigate the chemical nature and the structure of solutes and solvents and their specific and mutual interactions in the liquid media.

1.2. Scope and Importance of Physico-Chemical Parameters:

The study on interactions by physico-chemical processes involves the departure from ideal behaviour of some physical properties such as viscosity, density, volume, speeds of sound, refractive index etc [32, 33] in liquid media. Density of liquid mixtures and volumetric properties like excess molar volume are indispensable for practical as well as theoretical aspects. The positive values of excess molar volume (V^E) imply the dominance of dispersion forces [34, 35] while the negative values hint specific interactions [35, 36] between the mixing components in the mixture. The negative (V^E) values may arise due to the difference in the dielectric constants of the components of the liquid mixtures. The negative (V^E) values point towards explicit interactions such as intermolecular hydrogen bonding between the mixing components and also the interstitial accommodation of the mixing components owing to the difference in molar volumes.

Viscosity data has become a valuable tool to obtain information regarding the nature and strength of interactions operating within and between the unlike molecules. Recently the enhancement of computer simulation of molecular dynamics has led to noteworthy improvement towards a successful molecular theory of transport properties in fluids and a proper consideration of molecular motions and interaction patterns in non electrolyte solvent mixtures involving both hydrogen bonding and non hydrogen bonding solvents [36, 37].

Deviations in molar refractivity and refractive index also provide important information about molecular interactions prevailing in solution. Positive and negative values of either ΔR or Δn_D have enormous implication to make out the molecular interactions in liquid media.

Physico-chemical processes like dissociation or association can be employed to explore structure and interactions of molecules from the values of adiabatic compressibility with the help of acoustic measurements. It can also be used for the test of a variety of solvent theories and statistical models being quite sensitive to changes in ionic concentrations as well as useful in illuminating the solute-solvent interactions.

The study on interactions of bio-molecules plays a pivotal role in the elucidation of thermodynamic properties of physico-chemical processes taking place in living cells. The noteworthy illustrations of interaction between drug and bio-macromolecules are namely the process of protein binding, drug transport, anaesthesia etc. Physico-chemical properties of drugs control the transport in biological cells and membranes. One of the well-premeditated attempts is the study of molecular interactions in fluids by thermodynamic methods as because the thermodynamic parameters are convenient for the elucidation of intermolecular interactions in liquid media. Moreover, the study of thermodynamic properties of drug in a suitable medium can be synchronized to its therapeutic effects [38, 39].

These facts therefore encouraged to embark on the study of different binary or ternary systems. Besides, the excess properties derived from experimental density, viscosity, refractive index and speeds of sound data alongside the interpretation of the nature and strength of intermolecular interactions facilitate the testing and development of several conjectures and surmises in liquid media.

1.3. Solutes and Solvents Used

During the course of research work the study was made on Barium nitrate, Barium chloride, Lithium perchlorate, Sodium perchlorate and Potassium perchlorate, Potassium acetate, Nicotinic acid, Glycine, L-Alanine, L-Valine, 1-methyl-3-octylimidazolium tetrafluoroborate, Tetrabutyl phosphonium tetrafluoroborate, Potassium chloride, Potassium bromide and Potassium iodide as solutes and Formamide, N,N-Dimethyl formamide, n-Propanol, n-Butanol, n-Pentanol, 1,3-dioxolane, Nitromethane, Dimethyl sulfoxide as solvents.

1.4. Methods of Investigations

The interactions and equilibria of ions in aqueous and non-aqueous media in different concentration ranges are of enormous importance to the theoretician and technologist as most of the chemical processes occur in these systems. The structures and existence of free ions, solvated ions, and ion pairs depend on concentration regions.

The occurrence of ion-solvent, ion-ion, antagonism, synergy, solvent-solvent interactions is intriguing. It is desirable to attack this problem using different experimental techniques. We have, therefore, employed five important methods, namely, conductometry, densitometry, viscometry, refractometry and ultrasonic interferometry and to probe the problem of solvation phenomena. Various techniques [40] have been employed to study the solvation structure, ion-solvent interactions and dynamics of ions by physico-chemical processes in aqueous and non-aqueous liquid media.

The transport properties are investigated using the conductance data, specially the conductance at infinite dilution. Conductance data obtained as a function of concentration are used to explore the ion-association with the help of appropriate equations.

Thermodynamic properties, like apparent molar volumes, partial molar expansibility, etc. obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution. The compressibility, a second derivative of Gibbs energy, is also a susceptible indicator of molecular interactions and provides useful information in such cases where partial molar volume data alone cannot provide an unambiguous interpretation of these interactions.

The change in solvent viscosity by the addition of electrolyte solutions is accredited to interionic and non-solvent effects. The viscosity *B*-coefficients gives an agreeable interpretation of ion-solvent interactions such as the effects of solvation and structure-breaking or structure-making capacity of the solutes [41].

To investigate thermodynamic properties refractive index, molar refractivity and deviation in both have been computed. Various acoustical parameters have been derived in carrying out the investigation.

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