CHAPTER I

NECESSITY OF THE RESEARCH WORK

1.1. OBJECTIVE, SCOPE AND APPLICATION OF THE RESEARCH WORK

Solution thermodynamics 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. This deviation from ideality is expressed in terms of many thermodynamic parameters, by excess properties in case of liquid-liquid mixtures and apparent molar properties in case of solid-liquid mixtures.

Physicochemical studies are of great importance, providing a wide range of forces and products by modifying the inner properties of raw materials. Despite the great benefits obtained from these practices, a complete understanding of the properties of raw materials is essential to the success of process design.

The last decade has witnessed an upsurge in the research activities related to green chemistry. Most of the efforts in this direction have been focused on replacing the abundantly used volatile organic solvents (VOC) by suitable alternate solvent systems for easy chemical transformations with minimum chemical waste and environmental pollution. Several alternate methodologies based on water reaction medium, ionic liquids, supercritical fluids, microwave, sonochemical treatment etc., have been developed. Ionic Liquids (ILs) are a new class of materials, which has attracted a lot attention in scientific and industrial research recently. Due to their combination of chemical and physical properties they significantly differ from common molecular liquids. ILs is often defined as salts with low melting point, usually below 373K [1].

Ionic liquids have gained worldwide attention as green solvents in the last decade. In general, an ionic liquid is a wholly composed of ions. There are several reasons that ionic liquids are considered as “green solvents”. The most important reason is that ionic liquid possess negligible vapour pressure and hence do not evaporate to environment. Ionic liquids can be recycled to offer comparable performance in chemical transformations. The chemical and physical properties of ionic liquids can to some extent, be modified by proper selection of the type of anion and cation that compose the ionic liquids as well as any substituent groups.

Substance that is produced by or extracted from a biological source such as micro-organism, organs and tissues of either plant or animal origin, cell or fluids of human or animal origin called biologically active. Biologically active compounds are being intensively studied to evaluate their effects on health. These will reduce the risk of many diseases, including cancer, cardiovascular disease. Because of the number of bioactive compounds and the diversity of likely biological effects, diverse and numerous experimental approaches must be taken to increase our understanding of the biology of bioactive compounds.

Many bioactive compounds have been discovered. These compounds vary widely in chemical structure and function. Most of them are chiral, like, naturally occurring amino acids (the building blocks of proteins) and sugars. In biological systems, most of these compounds are same chirality, the configurations of most amino acids are L. Amino acid serves as a buffering agent in antacids, antiperspirants, analgesics, cosmetics and toiletries. It is used as a source of energy for muscle tissue, the brain and central nervous system, in strengthening the immune system by producing antibodies. Uric acid is another important bioactive compound, the crystallization of uric acid, often related to relatively high levels in the blood of human body is the cause of gout. Uric acid is a strong reducing agent and potent antioxidant [2]. Citric acid, that is, 2-hydroxypropane-1,2,3-tricarboxylic acid, is a tribasic, environmentally acceptable, and versatile chemical. It is a natural preservative/conservative and is also used to add an acidic or sour taste to foods and drinks [3]. In biochemistry, the conjugate base of citric acid, citrate, is important as an intermediate in the citric acid cycle, which occurs in the metabolism of all aerobic organisms.

In supramolecular chemistry, host-guest chemistry describes complexes that are composed of two or more molecules or ions that are held together in unique structural relationships by forces other than those of full covalent bonds. Host-guest chemistry encompasses the thought of molecular recognition and interactions through noncovalent bonding. Common host molecules are cyclodextrins, calixarenes, pillararenes, porphyrins crown ethers, zeolites, cryptophanes etc. Host-guest chemistry is observed in inclusion compounds, intercalaton compounds, clathrates and molecular tweezers. 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. There are various applications of Host-guest chemistry such as host-guest systems have been used to remove hazardous substances from the environment. It has been used to remove carcinogenic aromatic amines, and their N-nitroso derivatives from water. These waste substances are used in many industrial processes and found in variety of products such as pesticides, drugs and cosmetics [4]. It improves the drug delivery methods in medical science.

The term 'solution' is mostly used for the special case of a mixture between dissimilar components, i.e. when a small amount of substance, called solute (solid, liquid or gas), dissolves to a certain limit in a liquid or solid substance (pure, or a mixture itself) called the solvent.

A solution may be considered, prima facie, as a large assembly of molecules held together by non-covalent interactions. An investigation of such interactions in physical systems of increasing complexity should start with dimers, continue through larger clusters, and end with solutions. In general, solutions are more complex than assemblies of weakly interacting molecules, and, in particular, the study of reactivity in the presence of a solvent cannot be reduced to that of non-covalent interactions.

The properties, both physical and chemical, of a solution (liquid) is a result of the strength of their intermolecular forces and the forces between molecules arises from the same source: differing charges on adjacent molecules that lead to electrostatic attractions and governed by coulombs law. Partial charges acquired by molecules results in dipole-dipole forces, dipole-induced dipole forces, hydrogen bonding, etc and are collectively termed as intermolecular forces. Intermolecular forces in a solution control their thermodynamic properties and the understanding of the solvation thermodynamics is essential to the characterization and interpretation of any process carried out in the liquid phase. These thermodynamic properties are quantities which are either an attribute of an entire system or are functions of position which is continuous and does not vary rapidly over microscopic distances, except in cases where there are abrupt changes at boundaries between phases of the system. Therefore, the studies on the thermodynamic along with the transport properties of a solution would give a clear idea about the nature of the forces existing within the constituents of a solution.

Hence, the main objective of the present research work is to investigate and to understand the interactions prevailing in solutions by studying their thermodynamic and transport properties.

The study of molecular interaction in fluids by thermodynamic methods has attracted attention, as thermodynamic parameters are convenient for interpreting intermolecular interaction patterns in non-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents. The different sequence of solubility, difference in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have open vistas for chemists and interest in the organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry [5].

The facts, therefore, encourage us to extent the study of binary or ternary solvent systems with some industrially important solvents: polar, weakly polar and non polar solvents as well as with some solutes/electrolytes.

The thermodynamic and transport properties are of great importance in characterizing the properties and structural aspects of solutions. The sign and magnitude of partial molar volume (ϕ_V^0), a thermodynamic quantity, provides information about the nature and magnitude of ion-solvent interaction while the experimental slope (S_V^*) provides information about ion-ion interactions [6]. Furthermore, the excess properties derived from experimental density, viscosity and speeds of sound data and subsequent interpretation of the nature and strength of intermolecular interaction help in testing and development of various theories of solution. The excess thermodynamic properties of the mixtures correspond to the difference between actual property and the property if the system behaves ideally. Thus the properties provide important information about the nature and strength of intermolecular forces operating among mixed components. Valuable information about the nature and strength of forces operating in solutions can be obtained from viscosity data. Recently the use of computer simulation of molecular dynamics has led to significant improvement towards a successful molecular theory of transport properties in fluids and a proper understanding of molecular motions and interaction patterns in non-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents has been established [7,8].

The refractive index is an important physical property of liquids and liquid mixtures, which affects the solution of different problems in chemical engineering in order to develop industrial processes. Knowledge of refractive index of multi component mixtures provides information regarding the interactions in these mixtures [9-11] which is essential for many physicochemical calculations, including the correlation of refractive index with density [12-14].

The study of physicochemical behaviours like dissociation or association from acoustic measurements and from the calculation of isentropic compressibility has gained much importance. Excess isentropic compressibility, intermolecular free length etc. impart valuable information about the structure and molecular interactions in pure and mixed solvents. The acoustic measurements can also be used for the test of various solvent theories and statistical models and are quite sensitive to changes in ionic concentrations as well as useful in elucidating the solute-solvent interactions. Physico-chemical properties involving excess thermodynamic functions have relevance in carrying out engineering applications in the industrial separation processes. The importance and use of the chemistry of electrolytes in non-aqueous and mixed solvents are well-recognised. However, the studies on properties of aqueous solutions have provided sufficient information on the thermodynamic properties 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 [15].

The importance and uses of the chemistry of electrolytes in non- aqueous and mixed solvents have been summarized by Meck [16], Popovych [17],Franks [18], Bates [19,20], Parker [21,22], Criss and Salomon [23], Mercus [24] and others [25-27]. The solute-solute and solute–solvent interactions have been subject of wide interest and have been explicitly presented in Faraday Trans. of the Chemical Society [28]. Fundamental research on non-aqueous electrolyte solution has catalysed their wide technical application in many fields. Non-aqueous electrolyte solutions are actually competing with other ionic conductors, especially at ambient and at low temperatures, due to their high flexibility based on the choice of numerous solvents, additives and electrolytes with widely varying properties. 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 electrolytes solutions have brought the biggest success [29-31]. Other fields where the non-aqueous electrolyte solutions are used broadly include electrochromic displays and smart windows, photoelectrochemical cells, electro machining, etching, polishing and electrosynthesis. In spite of the wide technical applications, our understanding of these systems at a quantitative level is still not clear. The main reason for this is the absence of detailed information about the nature and strength of molecular interactions and their influence on the structural and dynamic properties of non-aqueous electrolyte solution.

Drug transport across biological cells and membranes is dependent on physicochemical properties of drugs. But direct study of the physicochemical properties in physiological media such as blood, intracellular fluids is difficult to accomplish. One of the well-organized approaches is the study of molecular interactions in fluids by thermodynamic methods as thermodynamic parameters are convenient for interpreting intermolecular interactions in solution phase. Also the study of thermodynamic properties of drug in a suitable medium can be correlated to its therapeutic effects [32,33].

1.2. CHOICE OF SOLVENTS AND SOLUTES USED

Industrially important solvents have been used for the research work. 1-Hexanol, 1-Heptanol, 1-Octanol, solution of ionic liquids, solution of uric acid, solution of cyclodextrin, solution of crown ether along with water considered as universal solvents have been choosen as a 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 contants .

Ionic liquids(1-methyl-3-octylimidazolium chloride, 1-ethyl-3-methylimidazolium tosylate and benzyltrimethyl ammonium chloride), Amino acids (glycine, L-alanine, L-isoleucine, L-serine, L-proline and L-histidine), Citric acid were considered as solutes.

The study of these solvents and solutes is of great importance because of their wide use as solvents, solutes and solubilizing agents in many industries ranging from pharmaceutical to cosmetics.

1.3. 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 solution. 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, densitometry, viscometry, conductometry, refractometry, UV-Visible and NMR spectroscopic technique to probe the problem of solvation phenomena.

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution.

The change in viscosity by the addition of electrolyte solutions is attributed to inter-ionic and ion-solvent effects. The viscosity B-coefficients are also separated into ionic components by the 'reference electrolyte' method and from the temperature dependence of ionic values, a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, structure-breaking or structure-making, polarization, etc. may be given .

The transport properties in most cases are studied using the conductance data, especially the conductance at infinite dilution. Conductance data obtained as a function of concentration can be used to study the ion-association with the help of appropriate equations.

The optical property, refractive index is an useful tool to understand the interaction occurring in the solution systems.

The surface tension experiments were done by platinum ring detachment mehod using a Tensiometer (K9, KRŰSS; Germany) at the experimental temperature. The accuracy of the measurement was within ±0.1mN.m^{-1}. Temperature of the system has been maintained by circulating auto-thermostated water through a double-wall glass vessel containing solution.

The pH values of the experimental solutions were measured by a Mettler Toledo Seven Multi pH meter. The measurement of pH of the solution state is very useful to understand the molecular form of solute and solvent and the type of interactions occurring in solution.

Nuclear Magnetic Resonance (NMR) spectroscopy is used to study the structure of molecules, the kinetics or dynamics of molecules and the composition of mixtures of biological or synthetic solutions or composites.

UV-visible spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in Ultraviolet-visible region. This means it uses light in the visible and ultraviolet region. In this region of electromagnetic spectrum, molecules undergo electronic transitions. Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher antibonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb. The wavelength of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups (specially conjugation) within a molecule.

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