CHAPTER I

NECESSITY OF THE RESEARCH WORK

1.1. OBJECT, SCOPE AND APPLICATION OF THE RESEARCH WORK

Ionic liquids, vitamins and amino acids are considered as the vital compounds. The term 'vital' is mostly used for the special case of important compounds, i.e. Ionic liquids, vitamins and amino acids. To understand the physicochemical properties of these vital compounds in different solvent systems I have measured various experiments. The understanding of the behavior of ILs and their properties is crucial for any practical application. But the available chemical and physical data are unfortunately scarce in comparison to the amount of already commercially available ILs. Moreover, the existing data are often inconsistent. In this work we focused on the reliable determination of thermodynamic properties of ILs using different independent methods.

An ionic liquid (IL) is an electrolyte in the liquid state or phase, whose melting point is below some arbitrary temperature, such as 100^0C. In general, ionic liquids (ILs) are liquid electrolytes that consist of combinations of organic–organic or organic–inorganic cation/anions. Because of their unique physicochemical properties, such as the favorable solubility of organic and inorganic compounds, low vapor pressures, low melting points, high thermal stability, good solvent characteristics for organic, inorganic and polymeric materials, adjustable polarity, selective catalytic effects, chemical and thermal stability, non-flammability and high ionic conductivity, ionic liquids have generated significant interest in wide range of industrial applications [1].

A vitamin is an organic compound requisite by an organism as a vital nutrient in restricted amounts. An organic chemical compound is called a vitamin when it cannot be produced in sufficient quantities. Vitamins are necessary precursors for various coenzymes. These coenzymes are therefore required in almost all metabolic pathways [2]. Nicotinic acid has gained huge attention over the years since it was synthesized in 1867 by Huber [3]. This is because of its versatility in terms of chemical, biochemical

and therapeutic applications [3]. Vitamin C plays an important role for the synthesis of several important peptide hormones neurotransmitters and creatinine. It also enhances the eye's ability and delay the progression of advanced age related muscular degeneration[4]. Importantly ascorbic acid (vitamin C) is also able to regenerate other antioxidants as vitamin E. Vitamin C with Zn is also important for the healing of wounds. It is also needed for the metabolism of bile acids which may have implications for blood cholesterol levels and gallstones.

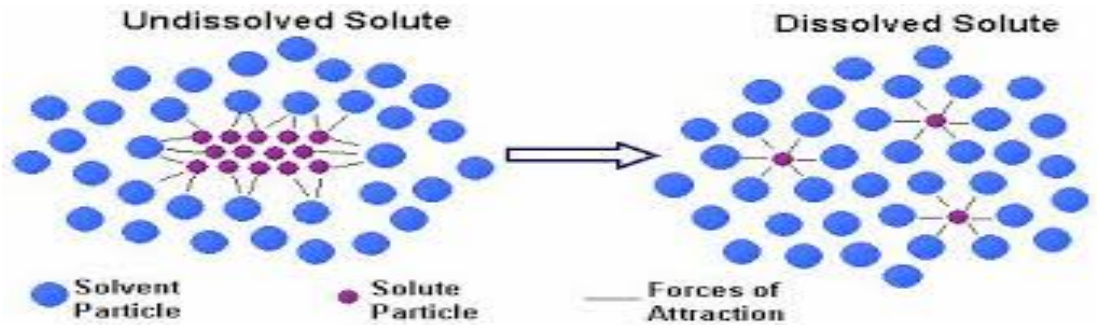
The properties, both physical and chemical, of a solution (liquid) is a result of the strength of their intermolecular forces and the forces between molecules arises from the same source: differing charges on adjacent molecules that lead to electrostatic attractions and governed by coulombs law. Partial 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 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.

A 'solution' is a homogeneous mixture of two or more substances, consisting of ions or molecules, 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. In a solution the solute is dispersed uniformly throughout the solvent and substances must have similar intermolecular forces to form solutions. When a soluble solute is introduced into a solvent, the particles of solute can interact with the particles of solvent. In the case of a solid or liquid solute, the interactions between the solute particles and the solvent particles are so strong that the individual solute particles separate from each other and, surrounded by solvent molecules, enter the solution. The relative force of attraction of the solute for the solvent is a major factor in their solubility.

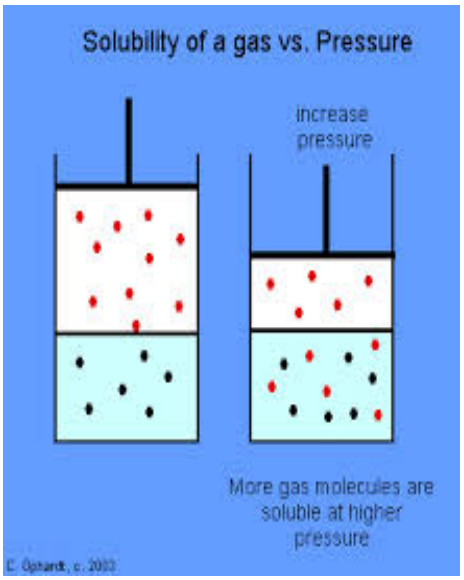


Solution chemistry is an important branch of physical chemistry that studies the change in properties that arise when one substance dissolves in another substance. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. The mixing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

We know matter in three states of aggregation — solid, liquid, and gaseous. Matter in every one of these three states can be dissolved in matter of the same state of aggregation as itself and in both of the other states. Thus, we have solutions of gases in gases, or mixtures of gases which do not act chemically upon one another. The characteristic here is unlimited solubility, the properties of the mixture being the sum of the properties of the constituent gases.

Solutions of gases, liquids, and solids in liquids are the best and longest known types of solutions. Gases dissolve in liquids to only a limited extent, the amount, in

keeping with Henry's law, increasing with the pressure to which the gas is subjected. The solubility of a gas in a liquid is directly proportional to its pressure.



Dissolution of gas in liquid

The presence of intermolecular H-bonding in water and alcohol, after mixing new H-bonding prevails in the mixture due to solvent-solvent interaction. Liquids dissolve in liquids, many of them to an unlimited extent. Liquids which, at ordinary temperatures, have only limited solubility in other liquids, often become infinitely soluble at more elevated temperatures.

Solids dissolve in liquids to a limited extent, the amount for any solid being a function of the temperature. An ionic solid such as sodium chloride dissolves in water because of the electrostatic attraction between the cations (Na^+) and the partially negatively charged oxygen atoms of water molecules, and between the anions (Cl^-) and the partially positively charged hydrogen atoms of water.

Ions are held together in the lattice due to electrostatic force
&
Inter molecular attraction between solvent molecules

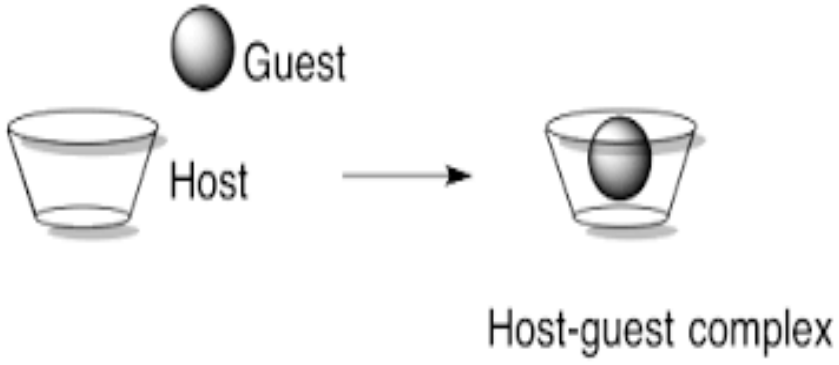
Solubility of solid in liquid

One of the newest and most interesting types of solutions is that of solid in solid. Solid-Solid solutions particularly of metals are sometimes called ALLOYS.

In recent years there has been an increasing interest in the study of physicochemical properties of solvent-solvent [5, 6] and solute-solvent [7, 8] systems. The physicochemical properties play a pivotal role in interpreting the intermolecular interactions among mixed components and efforts in recent years have been directed at an understanding of such properties at microscopic and macroscopic levels. In order to gain insight into the mechanism of such interactions thermodynamic, transport and acoustic studies on binary and ternary solvent systems are highly useful. The excess thermodynamic properties of the mixtures correspond to the difference between actual property and the property if the system behaves ideally. Thus these properties provide important information about the nature and strength of intermolecular forces operating among mixed components. Also physico-chemical properties involving excess thermodynamic functions have relevance in carrying out engineering applications in the process industries and in the design of industrial separation processes.

The studies on supramolecular chemistry give a broad idea about the formation of inclusion complex between the host and the guest molecules. Thus, most of this interaction has been performed by host-guest interaction. 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. In host-guest chemistry, an inclusion compound is a complex in which one chemical compound (the "host") forms a cavity in which molecules of a second "guest" compound are located. Here I have iinvestigated the inclusion behavior of a guest ionic liquid (IL) 1-methyl-3-octylimidazolium tetrafluoroborate into the host cavity of *β*-cylodextrin in aqueous solution.



Drug transport across biological cells and membranes is dependent on physicochemical properties of drugs. But direct study of the physico-chemical 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 [9, 10].

The studied thermophysical, thermodynamic, transport, optical, acoustic and spectroscopic properties are of great importance in characterizing the properties and structural aspects of solutions. The nature of intermolecular interactions can be exposed from the interpretation of the derived properties through the thermophysical study.

Density of solvent mixtures and related volumetric properties like apparent molar volume are of also immense significance in measured the properties and feature of solutions. 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 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.[11] Furthermore, the derivative parameters 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. Thus the properties provide important information about the nature and strength of intermolecular forces operating among mixed components also.

Precious information concerning the nature and strength of forces of electrolyres/non-eletrolytes effective in solutions can be obtained from viscosity data. Recently the use of computer simulation of molecular dynamics has led to major development in the direction of a unbeaten 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.[12,13]

The study of interactions like dissociation or association from ultrasonic speed measurements and from the calculation of isentropic compressibility has achieved a great deal. It can also be used for the test of various solvent theories, statistical models and are fairly responsive for alteration in ionic concentration in addition to useful in illuminating the solute-solvent interactions.

The refractive index is also important optical physical property of liquids and liquid mixtures influence the solution of different problems in chemical engineering in order to develop industrial processes. Knowledge of refractive index of multicomponent systems provides decisive information regarding the molecular interactions occurring in the solutions,[14,15] that is essential for many thermophysical calculations counting the correlation of refractive index with density.[16]

1.2. CHOICE AND IMPORTANCE OF SOLVENTS AND SOLUTES USED

Propanol, butanol, pentanol, Solution of ionic liquid, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulphoxide, solution of nicotinic acid and solution of cyclodextrin 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.

Ionic liquids, Amino acids (glycine, L-alanine, L-valine, phenyl alanine and histidine), 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.

1.3. METHODS OF INVESTIGATION

The existence of free ions, solvated ions, and ion-pairs 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. I have, therefore, employed eight important methods, namely Conductometry, Surface chemistry (surface tension), viscometry, densitometry, Ultrasonic Interferometry, Refractometry, UV-Visible and FTIR spectroscopic technique to probe the problem of solvation phenomena.

1.4. PHYSICO-CHEMICAL PARAMETERS AND THEIR SIGNIFICANCE

Limiting molar conductance (Λ_0) obtained from specific conductance as well as molar conductance gives a central idea about the ion-solvent interaction the solution. More the magnitude of conductance of the solution less is the ion-solvent interaction.

Another parameter obtained from the conductance study i.e. association constant (K_A) gives an idea about the solvation of the ions by the solvent molecules.

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

Apparent molar volume (ϕ_V^0) is estimated from experimental density values. The sign and magnitude of apparent molar volume (ϕ_V^0) 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*-coefficients are another tool gives the useful scheme of ion-solvent interaction, estimated from experimental viscosity values.

From experimental speed of sound values, deviation in isentropic compressibility (β_S), limiting apparent molar isentropic compressibility (ϕ_K^o) 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 optical property as refractive index and spectroscopic property as FTIR spectroscopy is are used as supporting parameters to confirm the interaction occurring in the solution systems. The total internal energy of a molecule in a first approximation can be resolved into the sum of rotational, vibrational and electronic energy levels. Infrared spectroscopy is the study of interactions between matter and electromagnetic fields in the IR region. In this spectral region, the EM waves mainly couple with the molecular vibrations; i.e., a molecule can be excited to a higher vibrational state by absorbing IR radiation. The probability of a particular IR frequency being absorbed depends on the actual interaction between this frequency and the molecule. A frequency will be strongly absorbed if its photon energy coincides with the vibrational energy levels of the molecule. IR spectroscopy is therefore a very powerful technique which provides fingerprint information on the chemical composition of the sample.

Ultraviolet–visible spectroscopy or ultraviolet-visible spectrophotometry (UVVis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the

ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared [NIR]) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the 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 anti-bonding 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 wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule.