

CHAPTER I

NECESSITY OF THE RESEARCH WORK

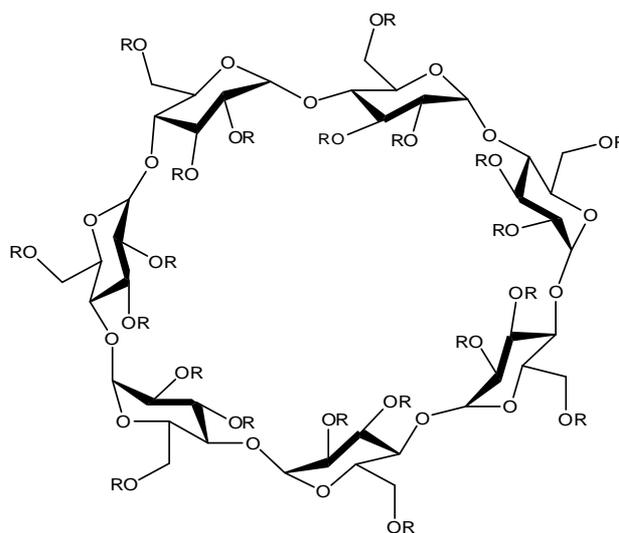
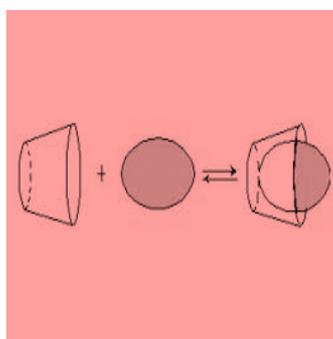
1.1. OBJECT, SCOPE AND APPLICATION OF THE RESEARCH WORK

In general, ionic liquids (ILs) are salts with melting point below 373K (100°C). They consist of organic cation along with an organic or inorganic anion. Some of ionic liquids are stable at higher temperatures up to 500K (227°C). Because of their unique physicochemical properties, such as miscibility of organic and inorganic materials, low vapour pressures, high thermal stability, ability of good solvent characteristics for organic and inorganic materials. They have normally high solvency power for polar and non polar compounds. Moreover, they have also selective catalytic efficiency, chemical and thermal rigidity; non-flammability and high ionic mobility made them significant interest in wide range of industrial applications. Also, Ionic liquids are considered as a 'designer solvents' and green substitute of volatile organic solvents [1].

A biologically active molecule is one that has an effect on living organism, tissue or cell. So, all drug & many naturally available molecules are biologically active molecules. Mainly they are organic molecules having carbon, hydrogen and oxygen and to lesser extent of nitrogen, phosphorus and sulphur. Also they include macromolecules such as polysaccharides, proteins, lipids and nucleic acids as well as small molecules such as natural products etc. Biologically active compounds are widely used as a drug, food or nutrients. These active molecules thus have direct effects on health. These will reduce the many hazards disease, like cancer, cardiovascular disease, diabetes etc. Because of these biological activity, diverse and numerous experimental approach are to be considered to understanding of biological significance of bio-active molecules.

The studies on supramolecular chemistry give a broad idea about the formation of 'inclusion complex' between the host and the guest molecules through non-covalent interactions. In molecular inclusion a guest molecule is actually fit inside another host molecule. Thus, most of this interaction has been performed by host-guest interaction. Cyclodextrin, Cyclodextrin derivatives, crown ethers,

porphyrins, zeolites etc. are seems to be the host molecules. The guest molecules have suitable polarity and dimensions. In host-guest chemistry, an inclusion compound is a complex in which one chemical compound ("host") forms a cavity in which molecules of a second "guest" compound are located [2]. Ionic liquids with suitable hydrophobic long chain can also be considered as a guest molecules for inclusion complexes with cyclodextrins.



Discharge of drugs (Guest) as of inclusion complex across biological cells and membranes is dependent on physicochemical properties of both drugs and inclusion complex. But direct study of the physicochemical properties in physiological media such as blood, intracellular fluids is difficult to achieve. One of the efficient approaches is the study of molecular interactions in liquids by thermodynamic methods as thermodynamic parameters are suitable for interpreting intermolecular interactions in solution phase. Also the study of thermodynamic properties of drug in appropriate medium can be correlated to its therapeutic effects [3, 4] which are obtained from physicochemical and spectroscopic measurements.

A 'liquid system' 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 definite limit in a liquid or solid substance (pure, or a mixture itself) called the solvent. In a liquid system the solute is dispersed uniformly throughout the solvent and substances must have similar intermolecular forces to form solutions. The force of attraction of solid and liquid (solute molecules) with various solvent systems are different. When a solute particle is poured into a

solvent, the solute particles dissolves with the surrounding solvent molecules. For the solid or liquid solute, the interactions between the solute-solvent is so strong that the individual solute molecules. The relative force of attraction of the solute for the solvent is a key factor in determining their solubility [5].

By an IUPAC classification, Solvation Consequences is an interaction of a solute with the solvent, which leads to stabilization of the solute species in the solution. Solvation consequences, also is the process of attraction and association of molecules in a solvent with molecules or ions of a solute. The solvation consequences are closely akin to ionic solvation can be studied from different angles using almost all the available thermodynamic and physicochemical techniques. The solvation consequences also studied from different type of interaction as ion-solvent, electrostatic, ion-dipole, dipole-dipole, van der Waal, hydrophobic interactions, etc. and that can be investigated using the experimental measurable properties such as, surface tension, conductance, density, pH, light scattering (some specific cases), viscosity, refractive index, spectroscopy and various derived parameters factors associated with solvation.

Physicochemical properties are of growing interest of solvent-solvent [6, 7] and solute-solvent [8, 9] systems. The physicochemical properties play a crucial role in interpreting the intermolecular interactions among mixtures and efforts in recent years have been directed at an understanding of such properties at microscopic and macroscopic levels. To understand the mechanism of such interactions thermodynamic, volumetric and transport studies on binary and ternary solvent systems are extremely helpful. The excess thermodynamic properties of the various assorted compounds represent the difference between actual property and the property of the system if the system is ideal. Thus these properties provide important information about the nature and strength of intermolecular forces operating among mixtures. Also physicochemical properties involving excess thermodynamic functions have relevance in carrying out engineering and industrial applications.

The studied surface, thermophysical, thermodynamic, transport, optical and spectroscopic properties are of great significance in characterizing the properties and structural aspects of solutions. The nature of intermolecular interactions can be

exposed from the analysis of the derived properties through the thermophysical and spectroscopic investigations.

Volumetric properties like apparent molar volume are of also immense importance in measured the properties and feature of solutions. The facts therefore encourage us to extent the density study of binary or ternary solvent systems with environmentally friendly solvent water with some bio-molecules. 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. Besides, the derivative parameters derived from experimental density and viscosity measurements and subsequent interpretation of the nature and strength of intermolecular interaction occurring in the diverse systems help in testing and improvement of various theories of solution systems. Thus the properties afford important information about the nature and strength of intermolecular forces functioning among mixtures also [10].

Valuable information relating to the nature and strength of forces of electrolytes/non-electrolytes effective in solutions can be obtained from viscosity measurements. In current times the use of computer simulation of molecular dynamics has led to major progress in the direction of a successful molecular theory of transport properties in liquids and an appropriate understanding of molecular motions and interaction patterns in non-electrolytic solvent mixtures involving both hydrogen bonding and non-hydrogen bonding solvents has been recognized [11,12].

The refractive index is also an essential optical property of liquids and liquid systems. Knowledge of refractive index of various liquid systems provides vital information concerning the molecular interactions occurring in the solutions which is essential for many thermophysical parameters [13, 14]. The refractive index results also help to determine the various volumetric properties [15].

UV-vis, FTIR and FTNMR techniques are used to measure qualitatively and quantitatively the ion-solvent, ion-ion and molecular interactions in different ion-association and host-guest complex systems [16].

1.2. SELECTION OF SOLVENTS, SOLUTES, SURFACTANTS AND BIOLOGICALLY ACTIVE MOLECULES

Distilled water, solution of ionic liquid, ionic liquid based surfactants, solution of cyclodextrin and its derivative along with water, considered as a universal solvent, have been selected as main solvent in this research work because these solvents are industrially and biologically very important as well as environmentally friendly for the study.

Ionic liquids, ionic liquid based surfactants, surface active ionic liquids e.g. 1-butyl-4-methylpyridinium lauryl(dodecyl) sulfate, 1-butyl-3-methylimidazolium lauryl(dodecyl) sulfate, 1-butyl-1-methylpyrrolidinium lauryl(dodecyl)sulfate etc., bio-logically active molecules e.g. trigonelline hydrochloride, citric acid monohydrate, L-cysteine, uric acid were considered as solutes. The study of these solutes is of great interest because of their wide use as surface active agents, solvents solubilising agents, anti-diabetic agent, food supplements' in pharmaceutical, cosmetics and medicinal industries.

1.3. METHODS OF STUDY

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 chemist, 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 various methods, namely conductometry, surface tension, viscometry, density, refractometry, UV-visible, fluorescence, pH, light scattering, high resolution microscope, FTIR and FT-NMR spectroscopic techniques to explore the problem of surface science, solvation consequences and inclusion phenomena.

The surface tension measurements were performed by platinum ring (Du Noüy ring) detachment method using a Tensiometer (K9, KRÜSS; Germany). The accuracy of the measurement was within $\pm 0.1 \text{ mN}\cdot\text{m}^{-1}$. Temperature of the system has been

maintained by circulating auto-thermostated water bath through a double-wall glass vessel containing the solution.

The refractive index is an optical property of the binary and ternary solution which used to measure the compactness of the studied liquid systems.

FTIR spectroscopy is used to confirm the interaction and inclusion occurring in the liquid systems. The total internal energy of a molecule in a first approximation is 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 electromagnetic 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. IR spectroscopy is therefore a very potent method which provides fingerprint information about the chemical composition.

UV-visible spectroscopy termed as absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible region. This means it uses light in the visible and near-UV and near-infrared [NIR] regions. Interacting molecules undergo electronic transitions in this region. Molecules containing π -electrons or non-bonding 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 interacting functional groups within a molecule or complexed molecules.

Spectrofluorometry is a type of important electromagnetic spectroscopy that analyzes fluorescence from a sample. It involves using a beam of light (controlled by slit), usually ultraviolet light, that excites the electrons in molecules of certain compounds and causes them to emit light; typically, but not necessarily, visible light. In surface science fluorescence help to study critical surface parameter, aggregation property, micro viscosity and many more. Fluorescence also helpful in solution as well as in supramolecular chemistry to obtained various important parameters.

Nuclear Magnetic Resonance (NMR) spectroscopy is also applied to study the inclusion mechanism of the molecules. Proton NMR spectroscopy and 2D-NMR is used to confirm the insertion path of inclusion in liquid environments.

In DLS the size distribution of molecules or particles is the property of significance. Here, the distribution explains how much material there is nearby of the different size "slices." In DLS, the local distribution is the concentration distribution which indicates how much light is scattered from the various size "slices" or "bins." Traditionally, this overall polydispersity has also been converted into an overall polydispersity index PDI which is the square of the light scattering polydispersity. For a perfectly uniform sample, the PDI would be (0.0). DLS is very important for obtaining particle size, hydrodynamic diameter, Zeta potential etc. especially in the case of colloidal particle, even in host guest inclusion chemistry and solution chemistry.

A **scanning electron microscope (SEM)** is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The electron beam is scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nm. Specimens can be observed in high vacuum in conventional SEM, or in low vacuum or wet conditions in variable pressure or environmental SEM, and at a wide range of cryogenic or elevated temperatures with specialized instruments. The most common SEM mode is detection of secondary electrons emitted by atoms excited by the electron beam. The number of secondary electrons that can be detected depends, among other things, on specimen topography. By scanning the sample and collecting the secondary electrons that are emitted using a special detector, an image displaying the topography of the surface is created. In surface chemistry this is very important tool to get idea about surface morphology, type of aggregation form etc. In supramolecular chemistry it can give very good idea about change in surface morphology upon inclusion complex formation and resulting change in compositional stoichiometry (EDS mode).

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image. The specimen is most often an ultrathin section less than 100 nm thick or a suspension on a grid. An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen. The image is then magnified and focused onto an imaging device, such as a fluorescent screen, a layer of photographic film, or a sensor such as a charge-coupled device.

Transmission electron microscopes are capable of imaging at a significantly higher resolution than light microscopes. This enables the instrument to capture fine detail-even as small as a single column of atoms, which is thousands of times smaller than a resolvable object seen in a light microscope. TEM is a major analytical method in the physical, chemical and biological sciences. TEMs find application in cancer research, virology, & materials science as well as pollution, nanotechnology and semiconductor research. The first TEM was demonstrated by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolution greater than that of light in 1933 and the first commercial TEM in 1939. In 1986, Ruska was awarded the Nobel Prize in physics for the development of transmission electron microscopy.

In colloids chemistry this is a very important tool to get idea about surface morphology, type of aggregation form etc. In host guest chemistry it can give good idea about change in surface morphology upon inclusion complex.

1.4. DERIVED PARAMETERS AND THEIR CONSEQUENCE

Apparent molar volume (ϕ_V^0) is obtained from experimental density results. The sign and magnitude of apparent molar volume (ϕ_V^0) gives information about the nature and magnitude of ion-solvent interaction while the experimental slope (S_V^*) signifies about ion-ion interactions.

Viscosity *A*-coefficients and *B*-coefficients also provide the valuable information about the ion-solvent interaction, estimated from experimental viscosity data.

The critical micelle concentration (CMC) is a narrow concentration range where the physical properties of the solution of an amphiphile show an abrupt change due to the cooperative formation of micelles in the bulk solution. The CMC value can be obtained by the breakpoint of conductance curve and the dependence of physical properties was observed from there.

Surface excess is the difference between the amount of a component actually present in the system, and that which would be present in a reference system if the bulk concentration in the adjoining phases were maintained up to the arbitrary chosen but precisely determined in position dividing surface. The surface excess concentration Γ is the area-related concentration of a surfactant at the surface or interface. It has the unit mol/m².

The minimum area per surfactant molecule (A_{\min}) or "mean molecular area" at the air-liquid interface. It may be calculated from the relationship viz.

$$A_{\min} = 10^{18} / N_A \Gamma_{\max}$$

Here Γ_{\max} = the surface excess concentration