

CHAPTER I

NECESSITY OF THE RESEARCH WORK

OBJECT, SCOPE AND APPLICATION

Research, from the beginning of the era, is the tool for searching and developing new systems and procedures which are already present to be equipped with the environment. This research work is to call attention to the importance of solvent systems and the (studies) on different interactions dominant in solid and liquid phases. The importance of solution in natural procedures is well known. In a word chemistry is meaningless without solution. This was summarised by the alchemists, "Corpora non agunt nisi soluta," or in the equally concise, "Menstrua non agunt nisi fluida." These interpretations are a bit too wide in that period what was known about solutions.

Interaction in chemistry is the key factor for various systems to exist. The word interaction signifies both the attractive or repulsive forces (among) molecules or non-bonded atoms. Molecular interactions are significant in diverse areas of protein folding, designing drug and drug delivery systems, material science, sensors, nanotechnology, separation science and most important origin of life. These types of interactions are recognized as non-covalent interactions [1] [2-4]

The molecule is formed by the association of a set of atoms which are bound strongly enough to overcome various effects when it interacts with the environment in which it is exposed. But the interactions are not specifically the bonds or they are not as strong as covalent bonds. A number of processes such as melting of ice, boiling of water, unfolding of proteins and RNA, disassembling of membrane, vaporization the covalent bonds are not broken or remains unchanged. Such processes do not get completed by means of chemical reactions rather these processes involve changes in molecular interactions. A pair of non-bonded atoms when interact, the enthalpy of that interaction is 1-10 kCal/mol, which is significantly less than a covalent bond. It should be noted that though non covalent interactions are feeble individually, the energies molecular sense are significantly high. One tool is the boiling point of a particular compound which can give qualitative indications about the strength of the interactions in the molecule.

Molecules with high boiling points are considered to have strong molecular interactions. For example water boils at 100°C but nitrogen is in gaseous form in normal temperature. However, this difference is mainly due to the interactions playing the key role in both the systems. The interacting forces among molecules in water are greater than those in nitrogen.

Molecular interactions can be better understood by studying various excess thermodynamic properties. 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 significant 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. Information of these excess thermodynamic functions can also be used for the development of empirical correlations and improvement of new theoretical models.

(REF) Various types of molecular interactions are (i) Van der waals interactions (ii) Short range repulsion (iii) Electrostatic interactions (iv) Hydrogen bonding interactions (v) Dipolar Interactions. Dipolar interactions are of various types such as (a) Dipole-dipole interactions or Keesom Interactions (b) Dipole-induced dipole interactions or Debye Interactions (c) Charge – Dipole (Ion-Dipole) Interactions (d) Fluctuating dipoles interaction, which are Dispersive interactions and London Forces ²²⁻²⁵.

Both the physical and chemical properties of a solution (liquid) are the consequences of strengths of their intermolecular interactions and the forces among molecules arise from the same source varying charges on neighbouring molecules that tend to electrostatic forces of attractions and governed by coulombs law. Assimilation of partial charges in molecules results in dipole-dipole forces, hydrogen bonding, dipole-induced dipole forces etc. and these are collectively named as intermolecular forces. In a solution the intermolecular forces regulate their thermodynamic properties and the comprehension of the solvation thermodynamics is necessary for the characterization and interpretation of any process completed in the liquid phase. All these thermodynamic properties are quantities which are either an aspect of the total system

or are functions of position which is uninterrupted and do not differ fast over nano distances, except in the situations where, there are unexpected changes at borders between different phases of the system. Hence, the thermodynamic studies along with the transport properties of a solution would result a clear concept about the nature of the interactions prevailing within the ingredients of a solution.

In solution chemistry the method for proper understanding of various phenomena concerning the molecular interactions forms the basis of elucidating quantitatively the effect of the solvent and the degree of interactions of ions in solvents. Estimates of ion-solvent interactions can be done thermodynamically as well as from the account of partial molar volumes, limiting ionic conductivity and viscosity *B*-coefficient studies. Approximations of single-ion values make us able to refine our models of ion solvent interactions. Significant values of ion-solvent interactions would support the chemists to select solvents that will improve (i) the solubility of minerals in leaching operations (ii) the rates of chemical reactions, or (iii) reverse the route of equilibrium reactions. Now days the significance and uses of chemistry of electrolytes in mixed solvents are well accepted.

The applications and inferences of the studies of reaction in aqueous and mixed solvent systems have been summarized by Franks[5], Meck[6], Bates[7], Marcus[8, 9], Criss⁹, and others [10].

Though a wide collection of data on different electrolytic and non-electrolytic solutions in water are available, the structure of water and various types of interactions that water goes through with electrolytes are so far properly understood. However, the studies on physicochemical properties of solutions have provided adequate materials on the thermodynamic properties of various electrolytes and non-electrolytes, the effects of the difference in ionic constructions, mobility of ions and common ions along with a host of other properties [6]. The properties of electrolytes or solutes in non-aqueous and solvent mixtures with a view to inspect solute-solute and solute-solvent interactions under diverse conditions the physicochemical properties have provided plenty of information. However, various structures of solubility, differences in solvation power and the probabilities of electrochemical reactions unknown in aqueous chemistry have opened landscapes for physical chemists and interest in these organic solvents exceeds the traditional borders of organic, inorganic, analytical, physical and

electrochemistry [11]. The research on non-aqueous electrolyte solutions has revealed their extensive uses in diverse fields. The Electrolyte solutions in non-aqueous solvents are actually conflicting with other conducting ion, especially at ambient and at significant low temperatures, due to their high flexibility basing upon the selection of abundant solvents, additives and electrolytes with extensively varying characteristics. The high-energy flowing primary and secondary batteries, wet the double-layer capacitors as well as super capacitors, electro deposition and electroplating are some devices and procedures for which the use of non-aqueous electrolyte solutions had carried the major success [12]

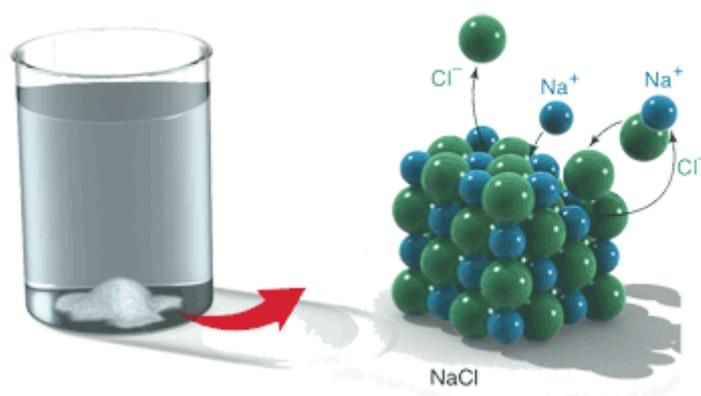


Fig.1. Solvation of a salt

The supramolecular chemistry deals with a wide concept about the development of inclusion complex between the host and the guest molecules. Thus, most of the interactions performed during the formation of inclusion complex are termed as host-guest interaction. There are a number of host molecules being used in the recent era, but cyclodextrin seems to be the most favourable to form inclusion complexes with a plenty of guest molecules having suitable polarity and dimensions. In host-guest chemistry, an inclusion complex is the one in which one molecule (the "host") previously having or forming a cavity incorporate within itself the molecule ("guest") having suitable chemical properties and dimensions. [13] [12]

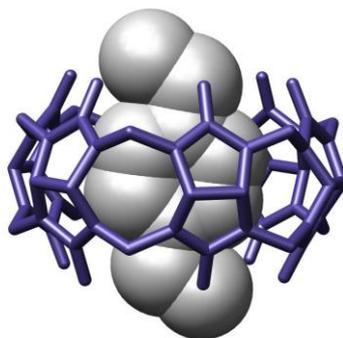


Fig.2. Inclusion complex

The stability of the inclusion complex lies primarily on the hydrophobic non-covalent interactions. Molecules with hydrophobic nature or only the hydrophobic moiety of a polar molecule are encapsulated inside the hydrophobic cavity of CD releasing the water molecules from the cavity, which is preferred due to repulsions between the apolar guest and the water polar molecule as well as the unsuitability of water molecule inside the cavity. This procedure leads to the total or partial incorporation of the guest molecule, increasing solubility of the guest in the aqueous and polar solvents. However, on dilution of the inclusion complex in a greater volume, the phenomenon gets reverted and the guest species becomes free in solution. This special characteristic of the inclusion complexes exposes the vast field of application.

Objectives of the research work

The main object of this research work is to study interactions in various chemical systems and collect thorough information about the nature and the strength of various interactions.

The study of various kinds of chemical systems in solution and in solid phase helped to understand various types of interactions that play the key role during the formation of inclusion complexes.

The study of host-guest chemistry helps to elaborate the engagement of the inclusion complexes in the field of science.

The understanding of the transport properties of various salts, the interactions of biologically active molecules, ionic liquids, drug molecules in green solvents and industrially important solvents along with the study of thermodynamic properties help to characterize molecular interactions in solutions.

1.3. METHODS OF INVESTIGATION

To get a better understanding into the phenomena of various interactions in solvation and inclusion complexation different experimental methodologies in solution and in solid phase have been employed. Therefore, various important methods that have been used are densitometric, viscometric, conductometric, refractometric techniques to probe the solvation and inclusion phenomena.

The use of various spectroscopic studies can elaborately define the various interactions in a broad sense. The specific characteristic properties of various molecules are seen in different spectroscopic studies in aqueous and mixed solvents. Depending on the fact spectroscopic studies like UV-Vis, NMR, FT-IR spectroscopic and Mass spectrometric study have been employed to elucidate various interactions.

Thermodynamic properties, such as partial molar volumes from density measurements, are usually the suitable parameters for understanding solute-solvent or ion-solvent and solute-solute or ion-ion interactions in solution. The sign and magnitude of limiting apparent molar volume (ϕ_v^0) also delivers evidence about the nature and extent of ion-solvent interaction while the experimental slope (S_v^*) offers the evidences of ion-ion interactions [14] Viscosity B-coefficient obtained from the viscosity values indicates the extent of ion-solvent interaction in a solution.

In most of the cases the transport properties are interpreted by means of the data obtained from conductance study, especially at infinite dilution. The conductance data collected as a function of concentration can be used to study the ion-association or molecular association solving appropriate equations.

Scope and applications

In supramolecular chemistry or specifically the host-guest chemistry the development of the inclusion complexes by means of non-covalent interactions offer the root of unique methodologies in medicine and also support to comprehend the interactions taking place in living systems. The formation of the inclusion complex with cyclodextrin improves bio availability from solid and semi-solid formulations, increases stability and shelf-life; reduces side effects, masks unpleasant odour and taste. The characterisation of Physical and structural properties is of specific significance for these host-guest complexes, which are the base of most cyclodextrin applications in fields of

medicine, catalysis, food chemistry, separation science, sensor technology etc. Pharmacological use of cyclodextrin for drug shield or aiming now requires physical characterisations of the administered complexes. To collect understanding of reactivity and selectivity in case of organic reactions so far and also to understand the binding manners of this unique host system, the present work has been carried out by physicochemical characterisation of cyclodextrin inclusion complexes by use of various analytical methodologies [15-17][18] [19]. To find the nature, constructions and interactions in the host-guest inclusion complexes of consecutive surface active imidazolium and pyridinium based ionic liquids with alpha and beta cyclodextrin the effect of size, shape and structural effects have been studied qualitatively and quantitatively using various physicochemical methodologies such as Surface tension, density, viscosity, conductance and NMR, UV-Vis, IR, Mass spectroscopic techniques.

The transport of drug molecules crossing biological cells and membranes depends mainly on the physical and chemical properties of drug molecules. But direct study of the physicochemical behaviour in physiological media like intracellular fluids, blood, is (highly challenging. One of the well-organized methods is the study of the dealing interactions in fluids using thermodynamic methods as thermodynamic parameters are suitable for understanding intermolecular interactions in fluid phase. Moreover, the understanding the thermodynamic properties of drug molecules in appropriate medium can be interrelated to its therapeutic effects[20, 21].

The stabilisation and the controlled release of the drugs now days, are of great concern in pharmacology. To guard drug molecules from environmental effects and to reduce the side effects for their controlled release it is vital to investigate whether they can be entrapped into the cyclodextrin molecule. Thus to fulfil such aim, the inclusion complex formation of drug molecules such as pentoxifylline and Pralidoxim with alpha and beta cyclodextrin have been studied(to achieve such goal) in detail based on physicochemical measurements including some spectroscopic techniques and the factors affecting the inclusion process are described.

Lithium and its compounds have several industrial applications, including heat-resistant glass and ceramics, high strength-to-weight alloys used in aircraft lithium batteries, and lithium-ion batteries. Lithium salt is used in lithium-ion batteries because of its high electrochemical potential. Lithium batteries are not to be confused with

lithium-ion batteries, which are high energy-density rechargeable batteries. Other rechargeable batteries include the lithium-ion polymer batteries, lithium-iron phosphate batteries, and the nanowire batteries.

Study of the biologically active molecules in various solvents experience their changed properties due to various interactions in solution. Study of such interactions in solution systems is useful in medicinal chemistry.