

CHAPTER II

GENERAL INTRODUCTION (REVIEW OF THE EARLIER WORKS)

2.1 SOLUTION CHEMISTRY

'Solution Chemistry' is a branch of physical chemistry that include the studies of the change in properties that arise when a substance dissolves in another. In solution chemistry, basically, there are three major approaches for the estimation of the extent of solvation. First one is the solvation approach that involves the studies of viscosity, conductance etc., of electrolytes and the derivation of different factors associated with ionic solvation [1], next is the thermodynamic approach by measuring the enthalpies, free energies, and entropies of solvation of ions from which the factors associated with solvation can be explicated [2], and the last one involves using spectroscopic measurements where the qualitative and quantitative nature of the solvation is interpreted in terms of spectral solvent shifts or the chemical shifts. [3]



Generally, the solutions obtained by mixing different solute or solvent with another solvent or a solvent mixture, do not behave ideally. The deviation from ideality can be expressed in terms of thermodynamic parameters; by apparent molar properties in case of solid-liquid mixtures and by excess properties in case of liquid-liquid mixtures. These thermodynamic properties of solvent mixtures are very significant in the study of molecular interactions and arrangements as they corresponds to the difference between the actual property and the property if the system behaves ideally. More specifically, they reflect the interactions taking place between solute-solute, solute-solvent and solvent-solvent systems. When an ion or

solute is added to a solvent, the solvent structure gets modified, atleast, to some extent and nevertheless, solute molecules are also modified. The amount of ion-solvation is a consequence of the interactions taking place between solute-solute, solute-solvent, solvent-solvent species. The evaluation of ion-pairing in these systems is very important as it affects the ionic mobility and the consequent ionic conductivity of the ions in solution.

The quantitative elucidation of the solvation consequences and evaluation of the nature of various interactions are possible by the determination of precise and accurate thermophysical properties of the components in a solution. Remember, a comprehensive understanding of the phenomenal solution chemistry is possible only when solute-solute, solute-solvent and solvent-solvent interactions are revealed. The present research work has also dealt with the studies of these interactions in some industrially important liquid systems by utilising densitometry, viscometry, refractometry, interferometry, and other suitable methods.

2.2. IONIC LIQUIDS

Ionic Liquids are a unique class of salt-like, purely ionic materials which are liquid at remarkably low temperatures. "These special ionic compounds are liquid below 100 °C." More commonly, these have melting points below room temperature; some of them even have melting points below 0°C. Ionic Liquids are liquid over a wide temperature range (300–400 °C), right from the melting point to their decomposition temperature.

Usually, a salt which melts without decomposing or vaporizing, yields an ionic liquid. By comparing a typical ionic liquid, e.g., 1-ethyl-3-methylimidazolium ethylsulfate (m.p. <-20°C), with a typical inorganic salt, for example, table salt (NaCl, m.p. 801 °C), it becomes obvious why there is a difference. The ionic liquid has a significantly lower symmetry! Furthermore, the charge of the cation as well as the charge of the anion is distributed over a larger volume of the molecule by resonance. As a consequence, the solidification of the ionic liquid will take place at lower temperatures. In some cases, especially if long aliphatic side chains are involved, a glass transition is observed instead of a melting point. The key point about ionic liquids is that they are liquid salts, which

means they consist of a salt that exists in the liquid phase and have to be manufactured, they are not simply salts dissolved in liquid.

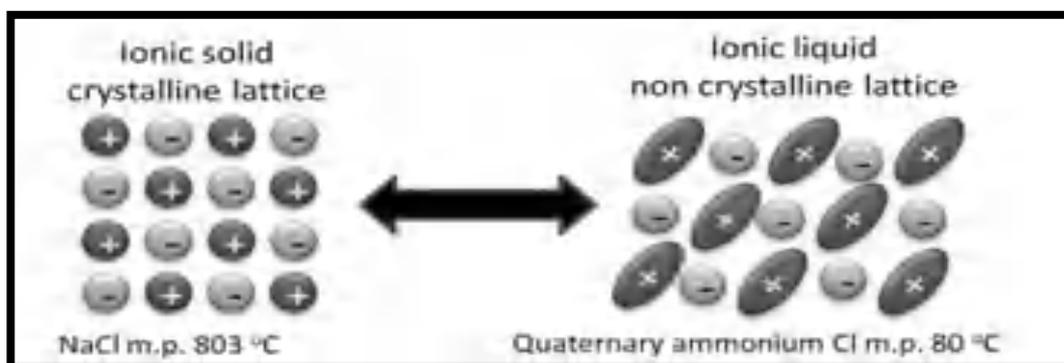


Figure II.1. Ionic Liquids

Ionic liquids have different properties than solid ionic compounds. The strong ionic interaction within these substances results in a negligible vapour pressure, a non-flammable substance, and in a high thermally, mechanically as well as electrochemically stable product. In addition to this very interesting combination of properties, they offer other favourable properties: for example, very appealing solvent properties and immiscibility with water or organic solvents that result in biphasic systems.

However, the choice of the cation has a strong impact on the properties of the ionic liquid and will often define the stability. The chemistry and functionality of the ionic liquid is, in general, controlled by the choice of the anion. Till date, many ionic liquids have been based on the imidazolium cation, while, in a lesser proportion on alkyipyridinium cations, trialkyl amines and other cations. [4]

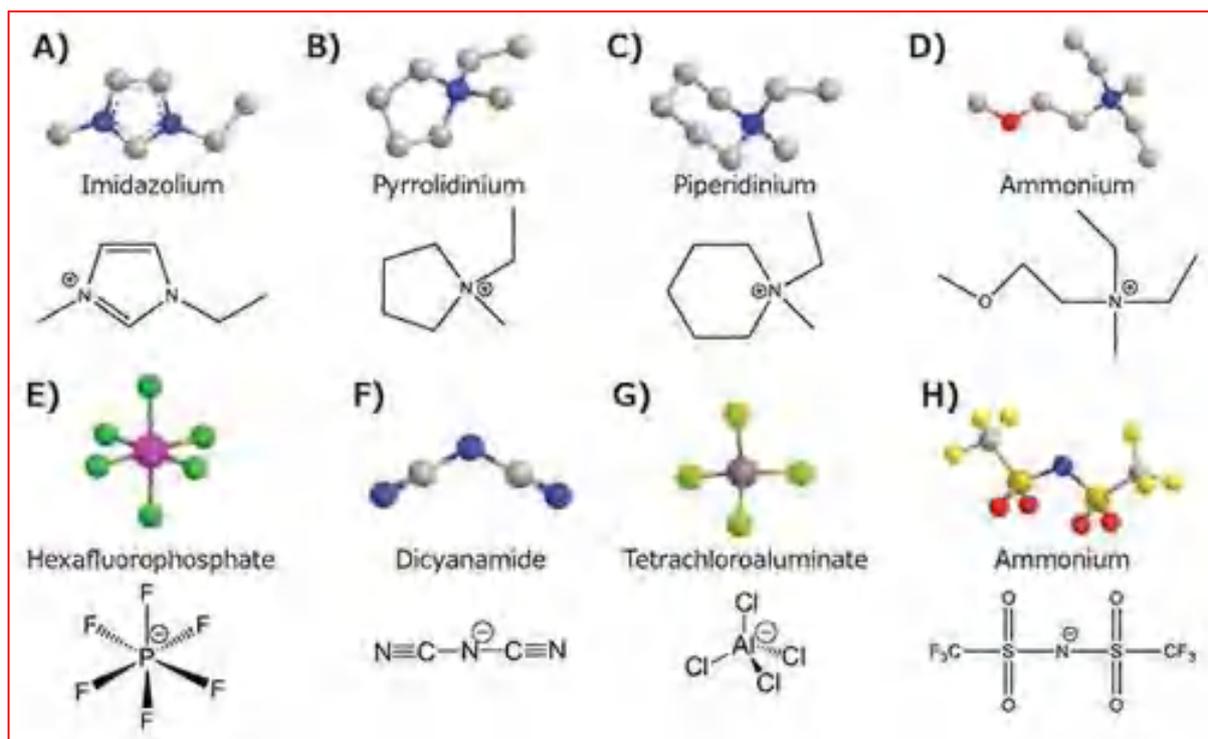


Figure II.2. Common constituent cations and anions in ionic liquid

Ionic liquids are attractive solvents as they are non-volatile, non-flammable, have a high thermal stability and are relatively inexpensive to manufacture. They usually exist as liquids well below room temperature up to a temperature as high as 200°C. Ionic liquids are highly solvating, non-coordinating medium in which a variety of organic and inorganic solutes are able to dissolve. They are outstanding good solvents for a variety of compounds, and their lack of a measurable vapour pressure makes them a desirable substitute for volatile organic solvents and they have been used as 'green' solvents in different industrial practices. [5-7] They have a low viscosity, which means they flow easily. The use of ionic liquids as thermal fluids combines their heat capacity with thermal stability and a negligible vapour pressure. They also tend to have high electrical conductivity, allowing electricity to flow through them well, and thus they have been used as electrically conductive liquids in electrochemistry (batteries and solar cells). [8-10]

In modern technology, the application of the salt is well understood by studying the ionic solvation or ion. [11-12] Their properties also make ionic liquids useful for gas

transport and storage. Instead of using pressurized containers, gases can be dissolved into ionic liquids and easily removed when needed. Ionic liquids can also be useful in recycling, aiding in the separation of similar but different materials from one another. For example, separating polymers from plastics.

Ultimately, the possible combinations of organic cations and anions places chemists in the position to design and fine-tune physical and chemical properties by introducing or combining structural motifs and, thereby, making tailor-made materials and solutions possible. The following chart summarizes their important properties, potential and current applications-

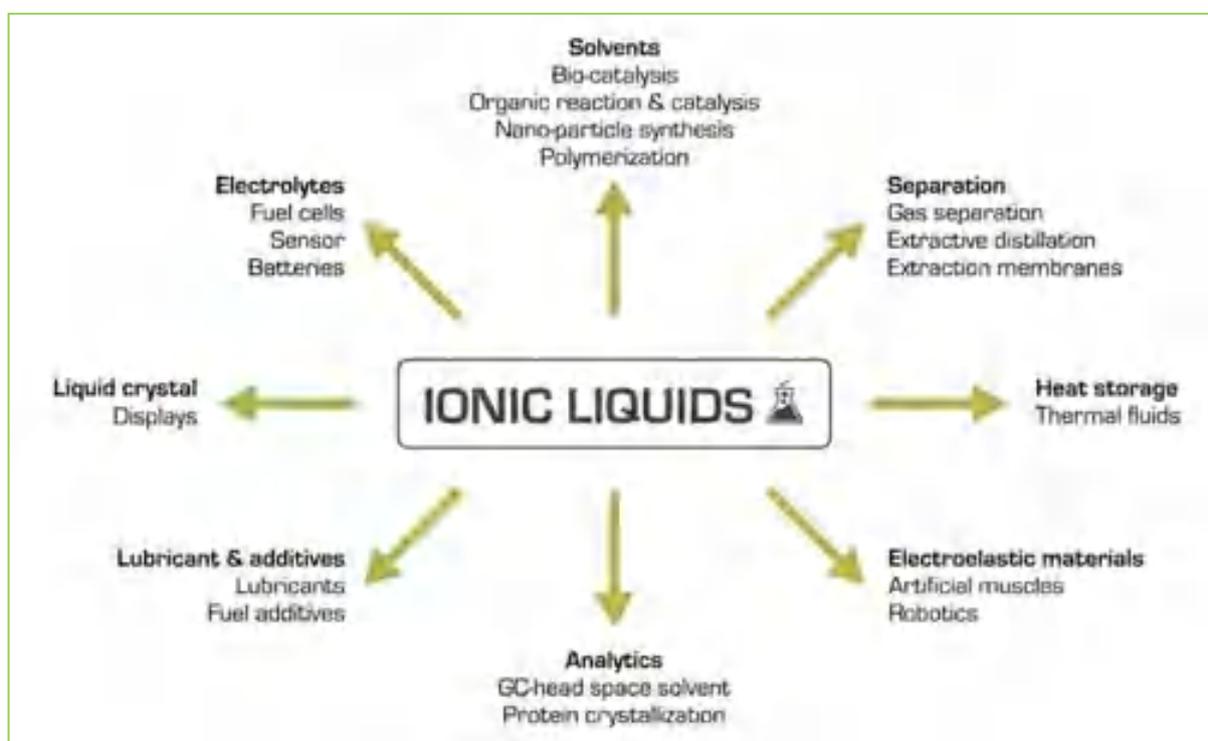


Figure II.3. Present and potential applications of Ionic Liquids

Other interesting applications have also been suggested, derived from the unique combination of physical properties. It is quite feasible to expect that many more applications will be brought forward by potential users and some of them will be realized in the next few years.

2.3. SUPRAMOLECULAR CHEMISTRY

Supramolecular Chemistry concern chemical systems composed of a discrete number of molecules i.e., it is the study of systems containing more than one molecular assembly. Lehn truly defined supramolecular chemistry as “chemistry beyond molecule”. It deals with understanding the structure, function and properties of these assemblies. The basic aim of this domain of chemistry is to design new functional systems of interest by combining multiple chemical entities through various non-covalent interactions. Supramolecular chemistry features phenomena like molecular self-assembly, molecular recognition, host-guest chemistry, mechanically-interlocked molecular architectures, folding of protein etc. The principles, backdrops and existing outgrowths in the field have been achieved exponentially in last few decades. [13-20]

The knowledge of host-guest chemistry exposes the way to construct supramolecular (inclusion) complexes having superior physicochemical properties compare to those of the guest. There are various types of host molecules available now, including ethers, cryptands, carcerands, spherands, cyclodextrins along with many of their derivatives. All of them are able to act as ‘artificial receptors’ and enclose completely, or at least, partially, the guest molecules like ionic liquids, vitamins, amino acids, drugs etc. Such host-guest inclusion complexes comprising of a smaller guest molecule encapsulated within the cavity of host, also represent another class of intermolecular association. The most common non-covalent interactions involved therein are ionic bonds, hydrogen bonds, van der Waals forces, and hydrophobic interactions.

Cyclodextrins (CDs) are doughnut-shaped cyclic oligosaccharides consist of glucopyranose units connected by α -(1,4) linkages. [21]

There are some types of cyclodextrins, commons amongst are having six, seven, and eight D-glucopyranose units and are known as α -, β -, and γ -CDs, respectively. While, the cavity diameter of α -CD is 4.7\AA , that for β -CD is 6.0\AA . The conical structure of CDs have hydrophobic interior and hydrophilic rim with primary and secondary -OH groups. Due to the presence of cavity of hydrophobic nature, CDs show a phenomenal property of accommodating organic molecules into its cavity to form inclusion complexes. The hydroxyl groups are responsible of forming hydrogen bonding with guest molecules

(Szejtli, 1996). The macromolecule remarkably shields the embedded guest molecules from degradation by auto-oxidation, hydrolysis, proteolysis in the solid state. The controlled release of CD has useful application in many industrial purposes e.g., in food, cosmetic, paint industry and elimination of various toxic materials, pollutants, waste products without a chemical change (Connors, 1997).

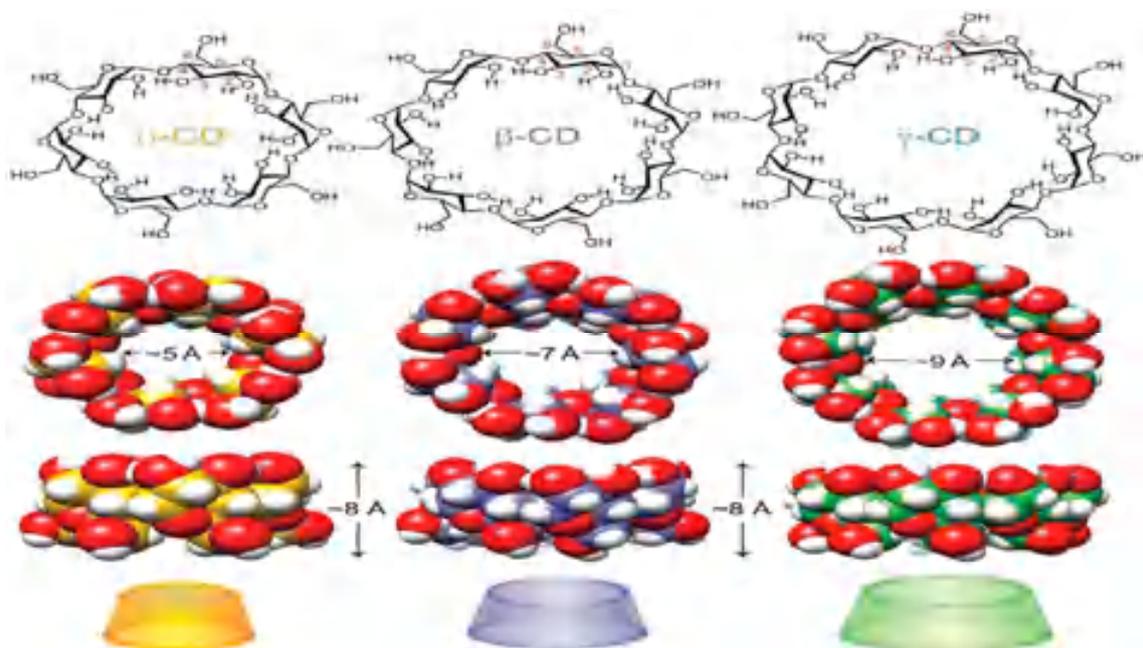


Figure II.4. 2D and 3D Structures of α -, β -, and γ -CDs

It is vital to know the thermodynamics of binding between host and guest. The thermodynamic principles of supramolecular interactions between host and guest molecules explicitly states that there is a lower overall Gibbs free energy because of the interaction between host and guest molecules. A state of equilibrium is achieved between the unbound state (prior to complexation), and the bound state (host-guest complex),

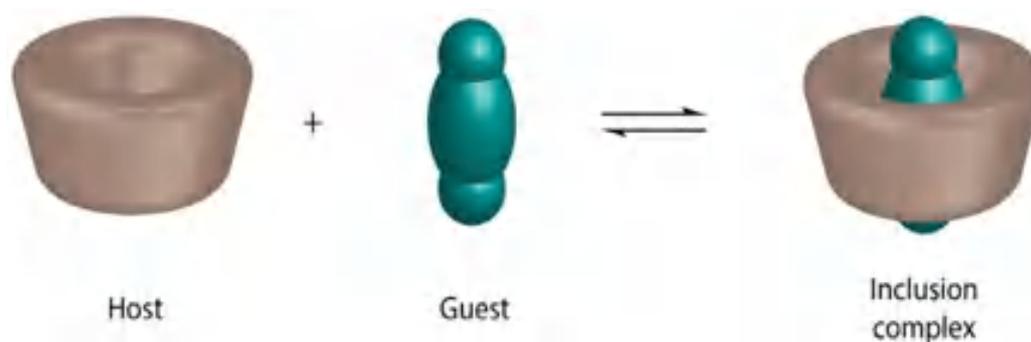


Figure II.5. Formation of Host-Guest Inclusion Complex

Focusing on the energy exchange of various binding interactions, chemists are trying to develop scientific experiments for quantification of the fundamental origins of these non-covalent interactions by exploiting different techniques, for example, NMR spectroscopy, Raman spectroscopy, isothermal titration calorimetry, surface tension, UV-Vis spectroscopy etc. The experimental data are quantified and explained through analysis of binding constants K_a , Gibbs free energy ΔG_o , Enthalpy ΔH_o , and ΔS_o .

Physico-chemical studies reveal the **Stoichiometry** of the inclusion complexes formed. The stoichiometry depends upon the size of the guest molecule as well as the cavity of the host. These factors determine probable stoichiometric ratio of host and guest, such as 1:1, 1:2, 2:1, 2:2 and higher. [22-28]

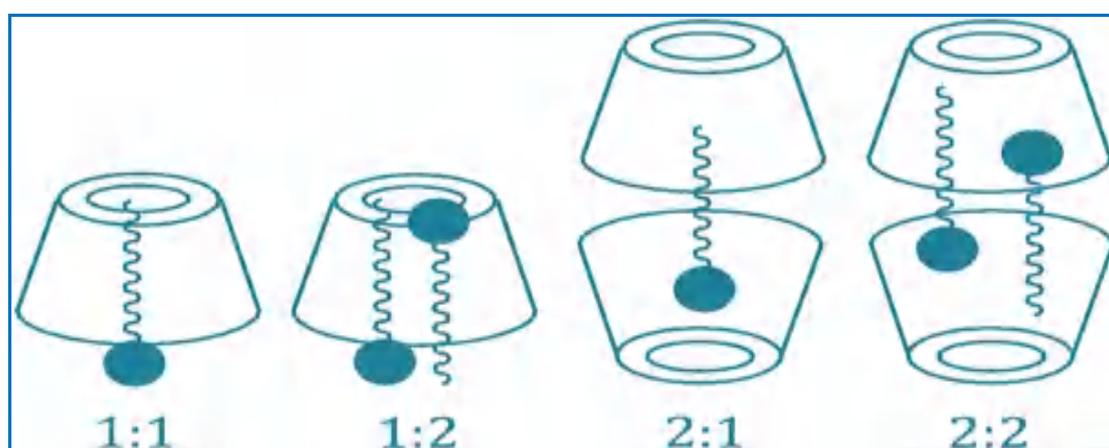


Figure II.6. Host-guest inclusion complexes with various stoichiometric ratios.

The Association Constant gives idea about the extent of encapsulation of the guest into the cavity of the hosts as also the stability of the inclusion complexes thus formed. Association constant or binding constant can be determined utilising various chemical approaches like UV-Vis, Fluorescence spectroscopy, NMR gas and liquid chromatography etc.

Benesi-Hildebrand method (eqn.1) is often used to quantify the association constant for the host-guest inclusion compounds by means of UV-VIS spectroscopic study. [29]

$$\frac{1}{\Delta A} = \frac{1}{\Delta \varepsilon [H] K_a} X \frac{1}{[H]} + \frac{1}{\Delta \varepsilon [G]} \quad (1)$$

Characterization of Inclusion Complex

By elucidating of the structure of the inclusion complexes formed significant information can be obtained about the formation of the inclusion complexes. Various spectroscopic studies like ¹H NMR, 2D ROESY NMR, FTIR, UV-Visible spectroscopy, Mass Spectrometry as well as physicochemical properties such as Conductivity, Surface Tension, Refractive Index, Density and Viscosity etc. are employed to confirm the formation of inclusion complex.

2.4 THEORY OF INVESTIGATIONS

2.4.1. HYDROPHOBIC INTERACTIONS:

Hydrophobic interactions tend to happen between two or more nonpolar molecules if they are in a polar environment, most ordinarily in water. They usually have a long chain of carbons that do not interact with water molecules. Their 'dislike' to water causes the molecules to stick together or fold in a certain way, in order to interact with the polar environments as little as possible. However, the interactions between nonpolar molecules and water molecules do not seem to be as favorable as interactions simply amongst the water molecules. This may be attributed to the inability of nonpolar molecules to be engaged in hydrogen bonding or electrostatic interactions. When nonpolar molecules are brought in contact with the water molecules, initially, they get surrounded by the water molecules, "cages" are formed around the molecules. Nevertheless, there is a tendency among nonpolar molecules to be associated with one another that draw such molecules together, to result a non-polar aggregation.

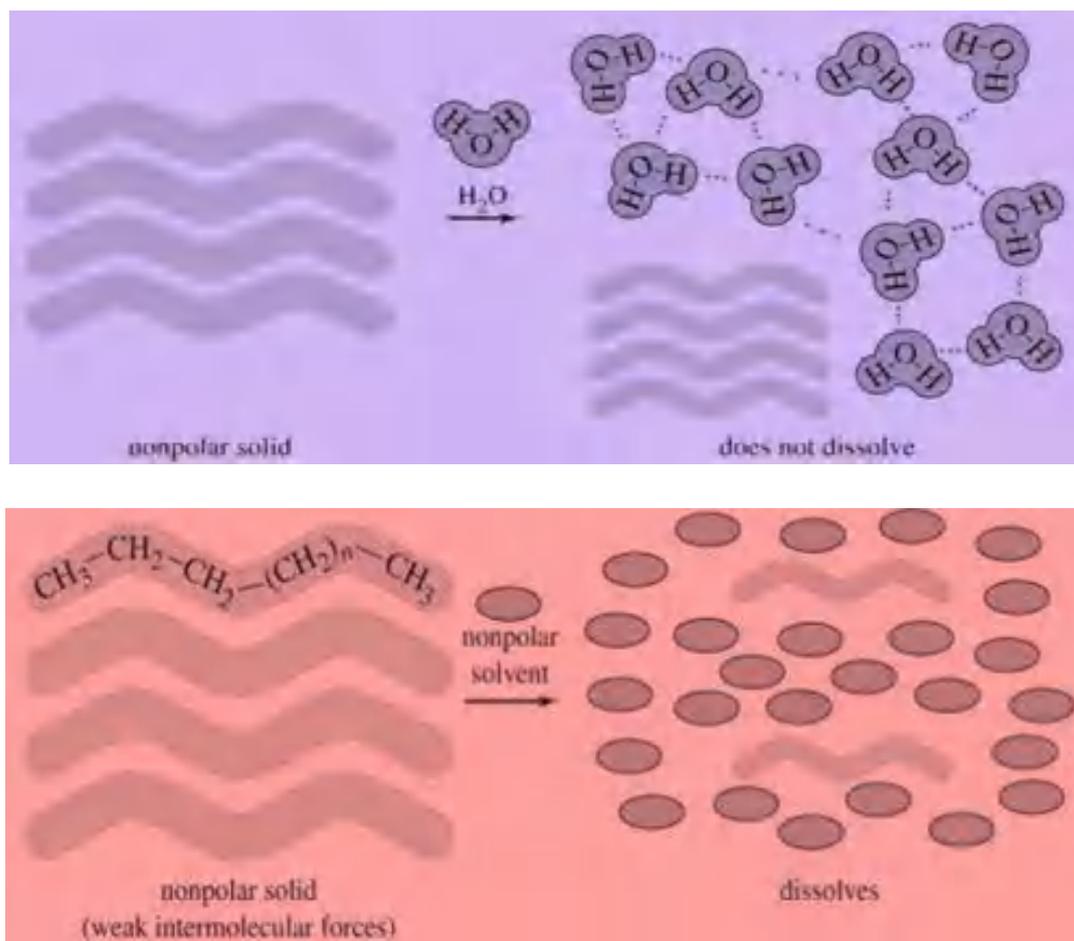


Figure II.7. Non-polar solute in polar and non-polar solvent

The mixing of fat and water may be an ideal example of this specific interaction. We thought fat does not mix with water because of the reason that Van der Waals that are acting upon both water and fat molecules are very weak. However, this is not the case. The behavior of a fat droplet in water has more to do with the enthalpy and entropy of the reaction than its intermolecular forces. According to the second law of thermodynamics, the sum of entropy i.e., the entropy of the system plus its surrounding, should always be increasing. Therefore, for the nonpolar molecules, it is more favourable to associate without the interference of water. The water molecules that initially "caged" the nonpolar molecules, get released from the nonpolar molecule's surfaces, thereby increasing the entropy in the surrounding. The release of water molecules from nonpolar surfaces is highly favourable and causes the phenomenon of hydrophobic effect.

The specific double helical structure of DNA, the folding of the tertiary structure in proteins, has been associated with hydrophobic interactions. This has significant role in keeping a protein stable and biologically active, as it allows the protein to reduce surface area thereby decreasing the adverse interactions with water. Besides from proteins, there are many other biological substances that rely on hydrophobic interactions for its survival and functions, like the phospholipid bilayer membranes in every cell of our body.

2.4.2. VAN DER WAALS FORCES:

Van der Waals forces are the weakest, among the forces that fall into category of 'weak chemical forces', contributing to intermolecular bonding between molecules. With increasing the distance between the interacting molecules, these sort of forces diminishes. Covalent bonds and ionic bonds are significantly stronger than Van der Waals forces, the strength of Van der Waals forces are typically ranges from $0.4\text{kJ}\cdot\text{mol}^{-1}$ to $4\text{kJ}\cdot\text{mol}^{-1}$.

These forces originate from the interactions between atoms or molecules having no charges. Molecules inherently possess energy and their electrons are always in motion, so transient concentrations of electrons in one region or another lead electrically positive regions of a molecule to be attracted to the electrons of another molecule. Similarly, negatively charged regions of one molecule are repulsed by negatively charged regions of another molecule.

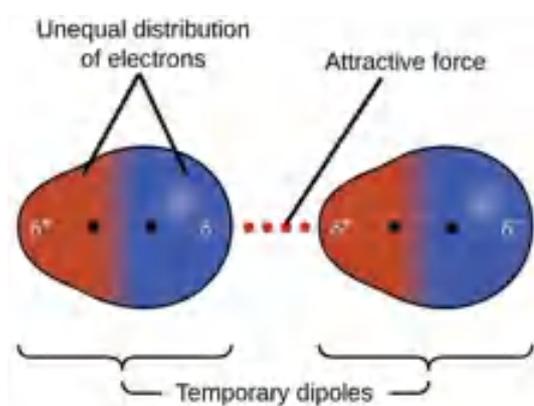


Figure II.8. Van der Waals attractive force

Van der Waals force shows an ultimate part in fields as diverse as supramolecular chemistry, polymer science, structural biology, surface science and nanotechnology. It also explain many properties of organic compounds and the formation of molecular solids, as well as the driving force that causes a solute molecule to undergo solvolysis in polar and non-polar media. The ability of geckos to hang on a glass surface by using only one toe to climb on steep surfaces, for many years has been attributed mainly to the van der Waals forces between these surfaces and the spatulae, or microscopic projections, which cover the hair-like setae found on their footpads. [30-31]

2.4.3 HYDROGEN BONDS:

A hydrogen bond is a distinctive type of dipole-dipole attraction. Hydrogen bonding interactions take place when a hydrogen atom bonded to a strongly electronegative atom situated in the proximity of another electronegative atom having a lone pair of electrons. In a molecule, when a hydrogen atom is linked to a highly electronegative atom (usually fluorine, oxygen, or nitrogen), the electronegative atom attracts the shared pair of electrons more. Consequently, this end of the molecule becomes slightly negatively charged and the other end becomes slightly positively charged. The attraction between the negative end of one molecule and the positive end of the other results in the formation of a weak bond which is called the hydrogen bond.

There are two distinct types of Hydrogen bonds, When hydrogen bonding takes place between different molecules of the same or different compounds, it is called intermolecular hydrogen bonding, but, if the hydrogen bonds are formed within the same molecule, it is then called intramolecular hydrogen bonding. Hydrogen bonds are somewhat weaker than a completely covalent or ionic bond, but, stronger than a Van der Waals interaction. The energy of a hydrogen bond varies between 1 and 40 kcal/mol.

Hydrogen bonds occur both in inorganic molecules, as well as, organic molecules. Following are some molecules which can form hydrogen bonds:

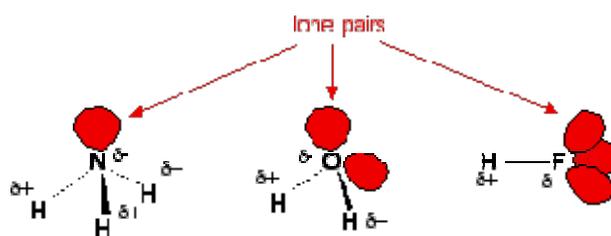


Figure II.9. Some molecules capable of forming H-bonds

Water is an ideal example that forms hydrogen bonding. It is noticeable that every water molecule is potentially capable of forming four hydrogen bonds with adjacent water molecules: two with the hydrogen atoms and two with the oxygen atoms. There are exactly the right numbers of $\delta+$ hydrogens and lone pairs for every one of them to be involved in hydrogen bonding.

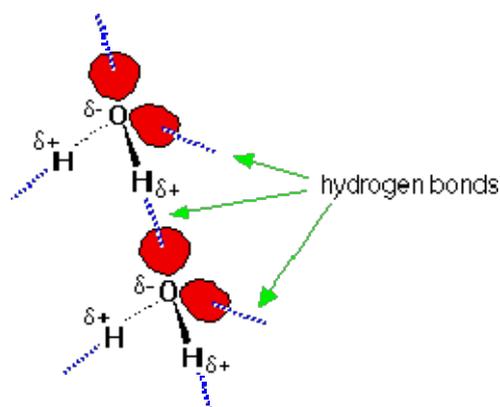


Figure II.10. Intermolecular H-bonds in water

This is the reason why the boiling point of water is higher than that of ammonia or hydrogen fluoride. In ammonia, each nitrogen atom has only one lone pair of electron. Thus, in a group of ammonia molecules, due to the lack of sufficient number of lone pairs to go around to satisfy all the hydrogens, the extent of hydrogen bonding gets restricted. While, in case hydrogen fluoride, the problem is the scarcity of hydrogens. But, in water molecule, the presence of two hydrogen bonds and two lone pairs facilitate the hydrogen bonding interactions in a lattice composed of water molecules. Water can thus be regarded as an ideal hydrogen bonded system.

The secondary, tertiary, and quaternary structures of proteins and nucleic acids, can be, at least partly, attributed to the intramolecular hydrogen bonding. The hydrogen bonding interactions help them to form and maintain specific shapes. Hydrogen bonds between complementary nucleotides (A&T, C&G) hold the two complementary strands of DNA together. Hydrogen bonding in water also contribute to its unique properties like its high surface tension. It is the hydrogen bonding that allows the lower alcohols to be soluble in water. Various compounds in which molecules are associated via hydrogen bonding, have a higher boiling point and hence, less volatility.

2.4.4. ELECTROSTATIC FORCES:

The electrostatic force, or, the Coulomb Force are caused between particles owing to their electric charges. The electrostatic forces may be attractive or repulsive and are named after the French physicist Charles-Augustin de Coulomb. These sort of forces are operative over a distance of about one-tenth the diameter of an atomic nucleus or 10^{-16} m. The forces are repulsive between the like charges and attractive between the opposite charges. To explain, two cations or two positively charged protons repel each other. Two anions or two negatively charged electrons also doing the same. But cations and anions attract each other, so are the protons and electrons.

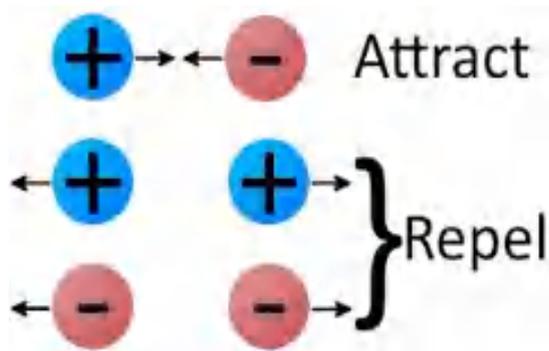


Figure II.11. Attractive and repulsive electrostatic forces

Electrostatic force is regarded as one among the four fundamental forces of nature. We make use of the Coulomb's law to solve the forces created by configurations of charge.

According to Coulomb's law, the electrostatic force existing between two point charges, is directly related to their magnitude and inversely related to the square of the distance between them.

Thus the force F , between the charges q_1 and q_2 staying at a distance r apart, may be given as

$$F = k \frac{q_1 q_2}{r^2} \quad (2)$$

Electrostatic force is extremely important in chemistry and physics because it describes the force between parts of an atom and between atoms, ions, molecules, and parts of molecules. An increase in the distance between the charged particles would reduce the attractive or repulsive forces between them thereby making the formation of an ionic bond less favourable. But the force is increased when the charged particles come closer to each other and the ionic bonding becomes more favourable.

2.4.5. ION-DIPOLAR ATTRACTIONS:

The ion-dipole interaction is nothing other than an electrostatic interaction. The interaction subsists between a charged ion and a molecule having a dipole. These attractive forces commonly arise in solutions, especially when an ionic compound dissolves in polar liquids. When a cation come closer to a polar molecule, it attracts the partially negative end of the molecule. While the anion attracts the positive end of the polar molecule. If the charge on the ion increases or the magnitude of the dipole of the polar molecule increases, ion-dipole attractions become stronger. In many chemical situations, these interactions are known to be very significant.

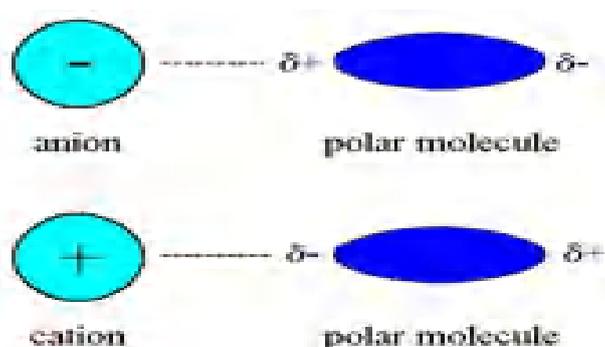


Figure II.12. Ion-Dipolar attraction between the ion and polar molecules

2.4.6. DIPOLE-DIPOLE ATTRACTIONS:

Dipole-Dipole interaction refers to the interaction between two dipolar molecules through space. Molecular dipoles result from the unequal sharing of electrons between the atoms in a molecule. More electronegative atom attracts the bonded electrons towards themselves. The accumulation of electron density around an atom or a discrete region of a molecule may result in a molecular dipole. When this occurs, the partially negative portion of one of the polar molecules is attracted to the partially positive portion of the second polar molecule. This type of interaction between molecules accounts for many physically and biologically significant phenomena such as the elevated boiling point of water.

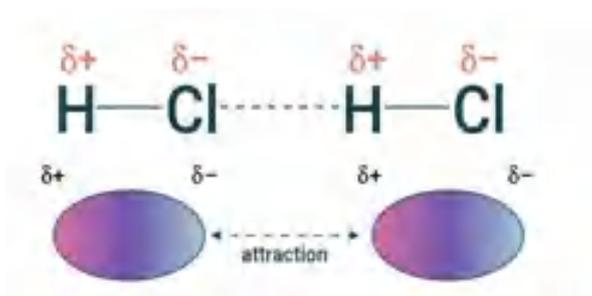


Figure II.13. Dipole–Dipole attraction between HCl molecules

2.4.7. INTERACTIONS IN SOLUTION SYSTEM

In a solution, there are three major types of interactions:

Solvent–Solvent interactions: Energy compulsory for dissociating weak bonds between solvent molecules.

Solute–Solute interactions: Energy mandatory to dissociate intermolecular bonds between the solute molecules.

Solute–Solvent interactions: ΔH is negative, due to the formation of bonds between them.

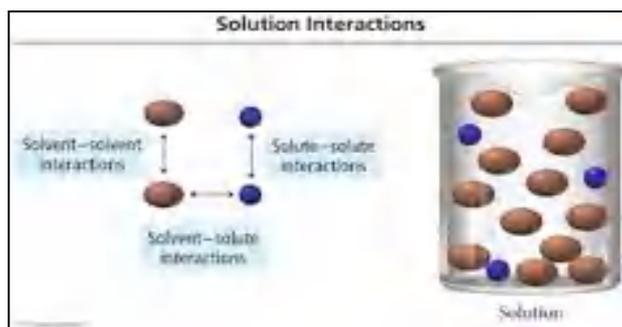


Figure II.14. Diverse types of interaction in solution system

The macroscopic properties for liquid system are usually quite well known, whereas the microscopic properties are often much less studied. The local order and long-range disorder characterises a liquid phase. Therefore, while studying processes in liquids, it is valuable to utilise methods that probe the local surrounding of the constituent particles. It is also true for solvation processes, a local probe is necessary to get insight into the physical and chemical processes going on.

Investigation of different types of interactions

When salts are dissolved in water, the ions constituting the salt gets dissociated from each other and then becomes associated in solution with the dipoles of the water molecules. An electrolyte is one that produces ions in fused state or in a suitable solvent. Thus, an electrolytic solution is obtained when a salt is dissolved in water.

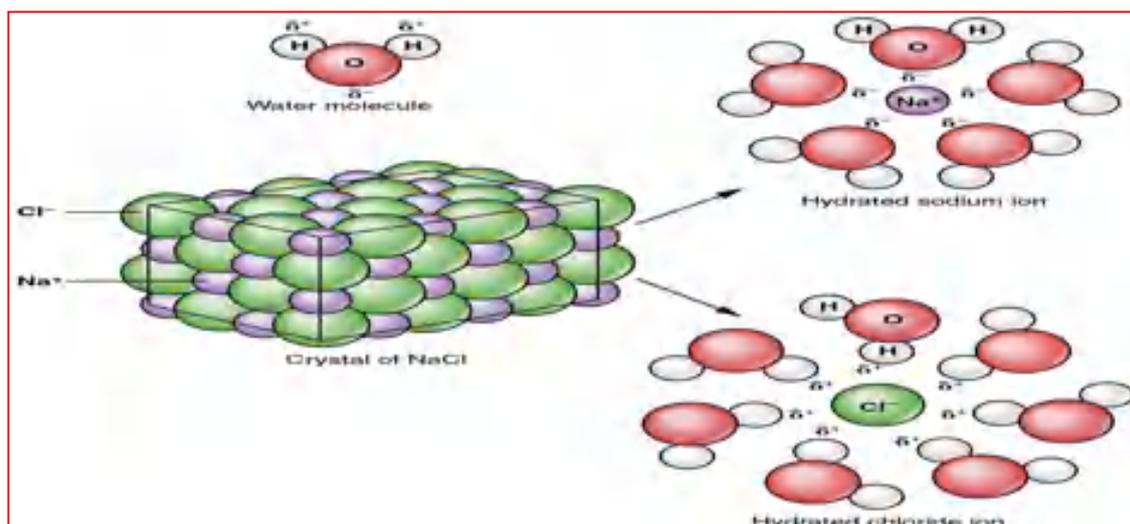


Figure II.15. Example of investigation of different type of interactions

Whether the forces between the ions are attractive or repulsive, is determined by the nature of the charge ions carry. These forces are attractive between dissimilar charges but repulsive between similar charges. Dipoles in a liquid, on average, orient themselves so as to make attractive interactions with their neighbours, though, thermal motion renders them unfavourable by generating some instantaneous configurations.

When a salt crystal is added to water, the ions in the crystal attracts the polar water molecules. As a result water molecules moves to the crystal surfaces and the ions get surrounded by water molecules. The surrounding of solute particles by solvent molecules is called hydration (solvation). The hydrated ions gradually moves away from each other into the solution and gets dissociated. The dissociated ions in the solution acts as though they were present alone. Thus an aqueous solution of sodium chloride behaves as a solution of sodium and chloride ions.

The evaluation of various thermodynamic, transport and optical properties of electrolytes in different solvents provide significant upshots in this direction. The development of theories for such electrolytic solutions mainly focused on ion-solvent interactions. In infinitely dilute solutions, in absence of ion-ion interactions, ion-solvent interactions are the controlling forces. In the solute-solvent interactions, the contributions due to cations and anions can be determined by separating these functions into ionic contributions. Hence, ion-solvent interactions play an essential role to understand the physico-chemical properties of solutions.

The uncertainty about the structure of the solvent molecule mostly causes intricacies in solution chemistry. When a solute is introduced, the solvent structure is modified to an uncertain magnitude alongwith the modification of the solute itself. As a result, the interplay of forces like solute-solute, solute-solvent and solvent-solvent interactions dominate. However, the isolated picture of these forces is still not known absolutely. Various physico-chemical techniques can be applied for studying problems of ion-solvent interactions akin to ionic solvations.

The ion-solvent interactions can also be studied from the thermodynamic point of view where the changes of free energy, enthalpy and entropy etc., associated with a particular reaction can be qualitatively and quantitatively evaluated using various

physico-chemical techniques from which conclusions regarding the factors associated with the ion-solvent interactions can be worked out.

Similarly, the ion-solvent interactions can be studied using solvational approaches involving the studies of different properties such as, density, viscosity, ultrasonic speed, refractive index and conductance of electrolytes and various derived factors associated with ionic solvation.

As this research work is intimately related to the studies of ion-ion, ion-solvent and solvent-solvent interactions, so, we need to focus particularly on the different aspects of these thermodynamic, acoustic, transports, and optical properties.

■ ION-SOLVENT INTERACTIONS

The solvated ions are ubiquitous on Earth. Hence, ion-solvation phenomena are of primary interest in many contexts of chemistry. Aqueous solution in many chemical and biological systems contain hydrated ions. [32] In living organisms, solvated ions are usually appeared in high concentrations. Their presence or absence can essentially alter the functions of life. Ions solvated in organic solvents or mixtures of water and organic solvents are also very common. [33] The exchange of solvent molecules around ions in solutions is fundamental in understanding the reactivity of ions in solution. [34] Solvated ions also have a crucial role in electrochemical applications. [35]

In electrochemistry, the formation of mobile ions in solution is a fundamental aspect. These mobile ions are formed in solution by two distinct ways, to create ionically conducting phases. The first one has been explained for aqueous acetic acid as given below:

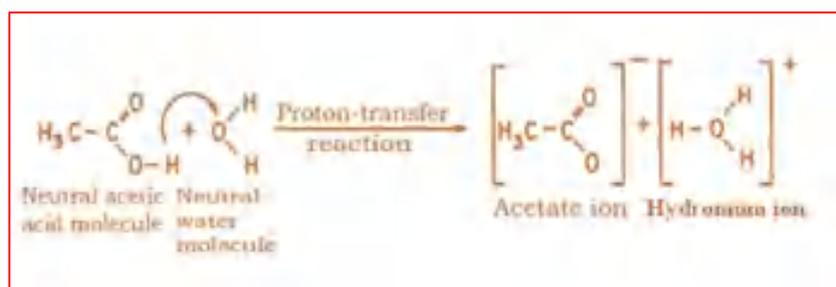


Figure II.16. The chemical method of producing ionic solutions

The second one involves dissociation of a solid ionic lattice, such as, the lattice of sodium chloride. During the ionic dissociation, solvent molecules collide with the crystal surfaces. This energetically provides a better deal to the ions in the crystal lattice, than they have within the lattice. It induces them out and into the solution. Thus there is a significant energy of interaction between the ions and the solvent molecules. These interactions are collectively known as ion- solvent interactions.

Ions as a point charge orient dipoles among the solvent molecules. The spherically symmetrical electric field of the ion drag solvent dipoles out of their lattice and orient them with proper charged end toward the central ion. Thus, ion-dipole forces become the prime source of ion-solvent interactions. The reactions occurring in solutions are mostly chemical or biological in nature. Previously, it was assumed that the solvent only provides an inert medium for chemical reactions. The importance of ion-solvent interactions was realized after extensive studies in aqueous, non-aqueous and mixed solvents. [36-45]

With the exceptions of heterogeneous catalytic reactions most reactions in technical importance occur in solutions. Moreover, molecules not only have to travel through the solvent to their reaction partner before reacting, in addition to, to present a sufficiently unsolvated rate for collision. The role of solvent is so great that million fold rate changes take place in some reactions simply by changing the reaction medium. As water is the most abundant solvent in nature and its major importance to chemistry, biology, agriculture, geology, etc., water has been extensively used in kinetic and equilibrium studies. Our bodies contain 65 to 70 % water, which acts as a lubricant, as an aid to digestion and more specifically as a stabilizing factor to the double helix conformations of DNA. But still our knowledge of molecular interactions in water is extremely limited.

Furthermore, the uniqueness of water as a solvent has been questioned [46,47] and it has been realized that the studies of other solvent media like non aqueous and mixed solvents would be of great help in understanding various molecular interactions. The organic solvents have been categorised on the basis of dielectric constants, organic group types, acid base properties or association via hydrogen bonding[45], donor-acceptor properties [48,49], hard and soft acid-base principles[50] etc. As a consequence, different solvents show a wide disagreement of properties eventually

influencing their thermodynamic, transport and acoustic properties in presence of electrolytes and non-electrolytes in these solvents. The determination of thermodynamic, transport and acoustic properties of different electrolytes or non-electrolytes in different solvents would thus provide essential information in this direction. Hence, much attention has been devoted, while developing theories of electrolytic solutions, to the controlling forces- 'ion-solvent interactions' in infinitely dilute solutions where ion-ion interactions are negligible. By separating these functions into ionic contributions, it is possible to determine the contributions due to cations and anions in the solute-solvent interactions. Thus ion-solvent interactions play a vital role to understand the physico-chemical properties of solutions. One of the causes for the intricacies in solution chemistry is the uncertainty about the structure of the solvent molecules in solution. The introduction of a solute modifies the solvent structure to an uncertain magnitude, the solvent molecule and the interplay of forces like solute-solute, solute-solvent also modify the solute molecule and solvent-solvent interactions dominate, although, the insulated depiction of any of the forces is still not thoroughly known to the solution chemist. Ion-solvent interactions can be studied by spectrometry . [51,52] The spectral solvent shifts or the chemical shifts can estimate the qualitative and quantitative nature of ion-solvent interactions. However, the qualitative or quantitative allotting of the ion-solvent interactions into different possible factors is still a tenacious task to do. So, the precise understanding of the ion-solvent interaction is a bit challenging. The aspect embraces a vast range of topics but we concentrated only on measuring the transport properties like viscosity, conductance etc. and such thermodynamic properties as apparent and partial molar volumes, apparent molal adiabatic compressibility etc.

■ ION-ION INTERACTION

Ion-solvent interactions, however, are not the whole story of an ion related to its environment. In the surrounding of an ion, there are not only solvent molecules but also other ions. The 'ion-ion interactions' are caused by the mutual interactions between these ions. The extent of ion-ion interactions depend on the nature of electrolyte and affects the properties of solution. Generally, the ion-ion interactions are stronger than the interactions between ion and solvent molecules. Though, ion-

solvation still remains a complex process, but theoretically, ion-ion interaction in dilute solutions is a well understood behaviour. While proton transfer reactions are particularly sensitive to the nature of the solvent, it has become clear that the solvents significantly modify the majority of the solutes. On the contrary, the presence of solutes substantially modified the nature of the intensely structured solvents like water. However, the complete understanding of the phenomena of solution chemistry would become possible only after the proper illustration of solute-solute, solute-solvent and solvent-solvent interactions. This is why the present thesis is intimately concerned with the studies of solute-solute, solute-solvent and solvent-solvent interactions in varied solvent media.

■ SOLVENT-SOLVENT INTERACTION (THEORY OF MIXED SOLVENTS)

The overwhelming use of mixed and non-aqueous solvents, for example, in solvent extraction, in chromatography, in elucidating the reaction mechanism, in preparing high density batteries etc., leads to the formulation of a number of molecular theories, based either on the radial distribution function or the choice of appropriate physical model. Theories of perturbation type have been extended from their successful applicability in pure solvents to mixed solvents. Devonshire and L. Jones were first to calculate the thermodynamic functions for a single fluid in terms of interchange energy parameters by using "Free volume" or "Cell model". [53] The above approach was further extended to solvent mixtures by Prigogine and Garikian mainly assuming random mixing of solvents provided the molecules have similar sizes. [54] Prigogine and Bellemans established a two fluid version of the cell model. [55] They observe a large positive excess molar volume (V^E) for mixtures with molecules having small difference in their molecular sizes, but, it was negative for mixtures with molecules of almost same size. According to Treszczanowicz *et al.*, several opposing effects contribute toward V^E , which can arbitrarily be divided into three types, viz., physical, chemical and structural. [56]

Physical contributions provide a positive term to V^E . The chemical or specific intermolecular interactions contribute negative values to V^E thereby resulting in a decrease in the volume. The structural contributions may arise from several effects,

mainly from interstitial accommodation and changes in the free volume. The relative strength of these effects determine the actual volume change. Nevertheless, the general assumption is that that when V^E is positive, viscosity deviation ($\Delta\eta$) may be negative and vice-versa. However, this not applicable everywhere, as evident from some studies. [57,58] In fact, in many systems, no simple correlation was observed between the strength of interaction and the observed properties. Thus, Rastogi *et al.*, suggested that the observed excess property is indeed a combination of an interaction and non-interaction part. [59] The non-interaction part in the form of size effect can be comparable to the interaction part and may be satisfactory to reverse the trend set by the latter. L. Huggins presented a new approach in his theory of conformal solutions [60] based on the principle of corresponding states as suggested by Pitzer. [61] He applied a simple perturbation approach to show that the knowledge of intermolecular forces and thermodynamic properties of the pure components could provide the properties of mixtures.

Rowlinson *et al.* have recently reformulated the average rules for Van der Waal's mixtures. [62-64] A much better agreement in their calculated values with the experimental values were observed even when one fluid theory was applied. Flory provided a more successful approach by making use of certain features of cell theory [65-67] and developed a statistical theory to predict the excess properties of binary mixtures by applying the equation of state and the properties of pure components together with some adjustable parameters. This theory has been applied to mixtures containing components with molecules of dissimilar shapes and sizes. Patterson and Dilamas, on the other hand, combined both Prigogine and Flory theories to an amalgamated one to rationalize various contributions of free volume, internal pressure, etc. to the excess thermodynamic properties. [68]

Heintz and co-workers recently proposed a theoretical model based on a statistical mechanical derivation to account for self-association and cross association in hydrogen bonded solvent mixtures. [69-71] This has been termed as Extended Real Associated Solution model (ERAS). Later on, many researchers successfully applied the ERAS model to evaluate the excess thermodynamic properties of alkanol-amine mixtures. [72-74] A new symmetrical reformation on the Extended Real Association (ERAS) model has recently been defined in the literature. [75] The Symmetrical-ERAS (S-ERAS) model

describes excess molar volumes and excess molar enthalpies of binary mixtures comprising of very similar compounds defined by exceedingly small mixing functions. The S-ERAS Model is however, a simple continuation of the earlier ERAS model, developed to widen its applicability to the thermodynamic properties of systems, which the ERAS model could not describe satisfactorily. [75,76]

2.4.8. ¹H NMR SPECTROSCOPY

Nuclear magnetic resonance (NMR) spectroscopy is one of the most essential analytical tools for the chemists. The application of NMR spectroscopic studies has made the modern chemical researches, especially in organic laboratories to gain a new height of excellence. This analytical technique is indeed an integral part of organic chemistry, right from the structure elucidation and verification to monitoring of reactions. It is the only one of all the spectroscopic methods, which deals with a complete analysis as well as illustration of the entire spectrum. In addition to provide structural informations, it can also be used to determine the content and purity of a sample. It is equally significant in other areas of chemistry giving rare insight into such aspects as structure of catalysts, the state and reactions associated with electrolytes in batteries. Proton NMR (or ¹H NMR) is the most extensively used NMR technique out of all. The behaviour of a proton in a molecule depend on their surrounding chemical environment and this allow elucidating the molecular structure. Though, a large amount of sample is needed than for mass spectroscopic measurement, NMR is still non-destructive. Nowadays, modern instruments are available delivering a good data from samples weighing even less than a milligram.

NMR spectroscopy is indeed the study of molecules by recording the interaction of radiofrequency(Rf) electromagnetic radiations with the nuclei of molecules placed in a strong magnetic field. It is the influence of the magnetic field that causes an energy transfer from the base to a higher energy level (usually, a single energy gap). The energy transfer occurs a wavelength corresponding to the radio frequencies. The returning of the spin to its base level is associated with an emission of energy at the same frequency. The signal matching this transfer can be measured in many ways and processed to result the NMR spectrum for the nucleus concerned.

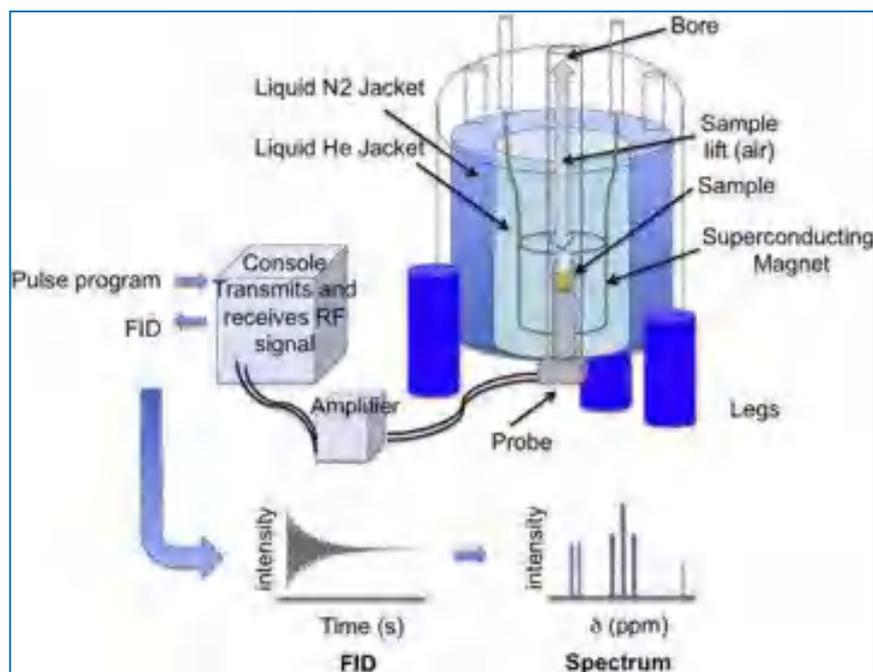


Figure II.17. Simplified diagram of a Nuclear Magnetic Resonance spectrometer

Chemical shift. The specific resonant frequency for this energy transition is dependent on the effective magnetic field at the nucleus. Again this field is affected by electron shielding which is in turn dependent on the chemical environment. Thus the chemical environment of a nucleus is quite perceptible from its resonant frequency. It is found that if the nucleus is more electronegative, the resonant frequency is also higher. Factors like ring currents (anisotropy), bond strain etc. also affect the frequency shift. Tetramethylsilane (TMS) is customarily used as the proton reference frequency. The applied magnetic field shifts the resonant frequency of each nucleus.

So, chemical shift can be characterized as the difference between the resonant frequency of the spinning protons and the signal of the reference molecule. The significant shifting of the interacting protons of both the host and guest molecules infers diamagnetic or paramagnetic shielding of host and guest protons.

2.4.9. 2D ROESY

2D-ROESY spectroscopy is useful for determining signals arising from protons that are close to each other in space even if they are not bonded, will show a correlation through space via spin-spin relaxation thereby registering an off diagonal cross peak. Hence, it

gives crucial information about the spatial vicinity between molecules through space. It can also detect chemical and conformational exchange. The spectrum contains a diagonal and cross peaks. The diagonal consists of the 1D spectrum. The cross peaks signals are due to the protons that are close in space.

Thus, the 'host-guest' interaction can be well visualised utilising 2D ROESY spectroscopy. 2D ROESY spectra of the inclusion complexes with α and β -CD shows significant correlation of aromatic protons of various guest molecules with the H₃ and H₅ protons cyclodextrins. This establishes the encapsulation of guest into the cyclodextrin cavities.

2.4.10. FTIR SPECTROSCOPY

Fourier-transform infrared spectroscopy (FTIR) is a widely used technique to get an infrared absorption or emission spectrum of a solid, liquid or a gas. FTIR spectrometer can concurrently collect high-spectral-resolution data over a wide spectral range. A typical FTIR spectrometer comprises of several key components – a light source, usually an infrared radiator, a sample compartment, an interferometer such as a Michelson containing both fixed and moving mirror, and a photonic or thermal detector.

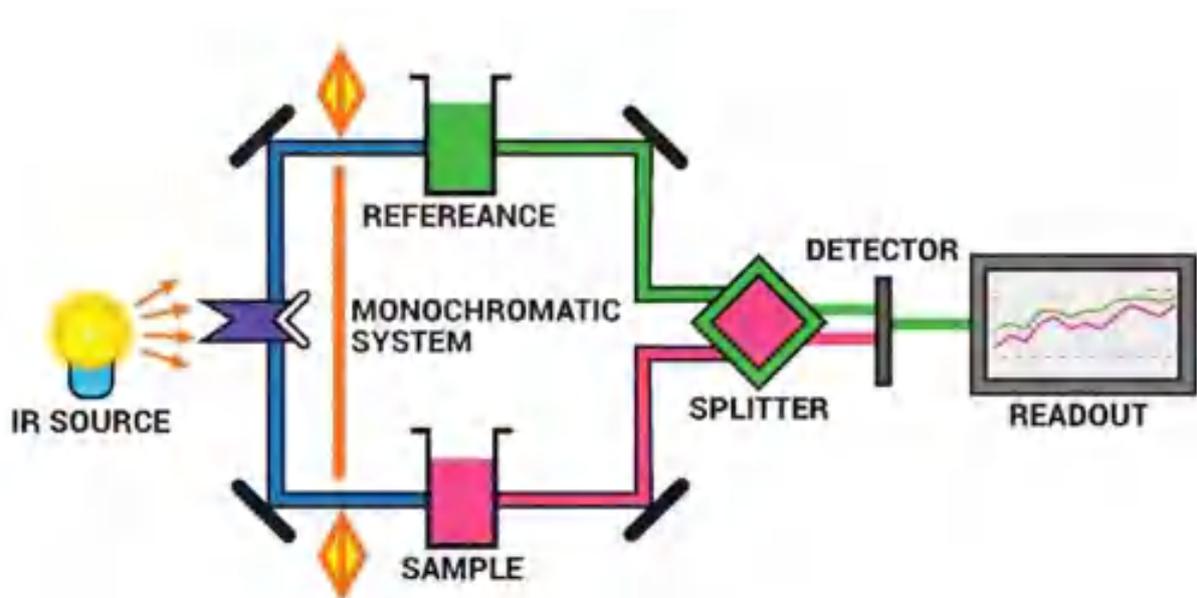


Figure II.18. The basic configuration of the FTIR spectrometer

The absorption of infrared light occurs at particular frequencies regarding the vibrational bond energies of the functional groups present in the molecule. This results into a characteristic band pattern, which is the vibrational spectrum of the molecule. Based on the position and intensity of these spectral bands, a fingerprint of molecular structure is provided, making FTIR spectroscopy a vastly adaptable and convenient technique. The more accessibility of using FTIR spectroscopy over the traditional dispersive infrared approach can be attributed to a number of reasons, for example, the entire FTIR spectrum can be collected within a fraction of a second and by co-adding spectra, signal to noise can be improved.

FTIR spectroscopy has wide use and applicability for the analysis of molecules which are important in the chemical, pharmaceutical, and polymer industries. Also it is useful in academic laboratories for a better understanding of reaction kinetics, mechanism as well as the catalytic cycles.

In this way, the solid inclusion complexes are characterised by FT-IR spectroscopic study. Any deviation of the bands in the spectra of solid complex from those of pure components can be informative to justify the formation of the inclusion complex. [77-80]

2.4.11. UV-VISIBLE SPECTROSCOPY

UV-Vis spectroscopy is undoubtedly one of the most common analytical techniques used in the laboratory. Here, the absorption of ultraviolet or visible light by chemical compounds yield distinct spectra. Molecules possessing bonding and non-bonding electrons (n-electrons) absorb energy from the ultraviolet or visible region so as to excite those electrons to high energy anti-bonding molecular orbitals. The lower is the energy gap between the HOMO and LUMO, more easily the electrons get excited, longer is the wavelength of light it can absorb. The probable transitions are $\pi-\pi^*$, $n-\pi^*$, $\sigma-\sigma^*$, and $n-\sigma^*$, which can be ordered as: $\sigma-\sigma^* > n-\sigma^* > \pi-\pi^* > n-\pi^*$

UV-Vis spectrophotometers mostly uses a deuterium lamp for the UV range that can produce light from 170–375 nm, along with a tungsten filament lamp for the visible range that produce light from 350–2,500 nm. Following Beer's Law, absorbance equals

the molar attenuation coefficient times the path length and concentration. The compound's ability to absorb light of a particular wavelength is related to the molar attenuation coefficient. The distance traveled by light through the sample, is referred to as the path length and usually, it is 1cm for standard cuvettes. The concentration of the sample can be calculated by using Beer's law for known absorptivity, if the absorptivity is known, a calibration curve can be used as well.

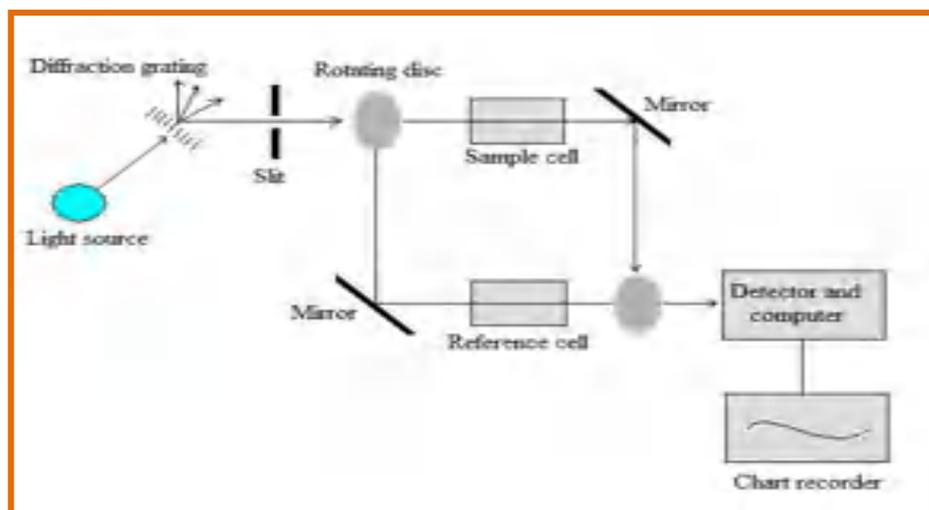


Figure II.19. Schematic diagram of a UV-VIS spectrometer

In the field of analytical chemistry, UV-Visible spectroscopy is extensively used for the quantitative analysis of a specific analyte. For example, the UV-Visible spectroscopy has been used for the quantitative analysis of conjugated organic compounds and transition metal ions. In some conditions, this type of spectroscopy can also be used to examine solid and gaseous analytes.

We have fitted UV-Visible spectroscopic data to the Benesi-Hildebrand equation in order to calculate the binding constants of various inclusion complexes. Stoichiometries of those inclusion complexes were also obtained from the UV-Visible spectroscopy.

2.4.12. FLUORESCENCE SPECTROSCOPY

Fluorescence spectroscopy or spectrofluorometry is another kind of electromagnetic spectroscopy to analyze fluorescence from a sample. It is consistently used to study structural changes in conjugated systems, aromatic molecules, and planar, rigid molecules owing to changes in temperature, ionic strength, pH, solvent or ligands. A

single fluorophore is sufficient to generate thousands of detectable photons which can be repeatedly excited and detected. This is what makes fluorescence spectroscopy to be an extremely sensitive technique.

Fluorescence occurs when energy is absorbed by a molecule at a wavelength where it has a transition dipole moment. As a result, the molecule at the ground state promote photons to an excited singlet state. Then, they decay to the lowest vibrational energy level of this excited singlet state in accordance with the Jablonski diagram(Figure 20). Further, this energy is relaxed back by emitting photons, to the ground state of the molecule. The vibrational energy levels of the ground state have different energies and, therefore, the energies of the emitted photons will have different energies. This will result in the determination of the structure of different vibrational levels.

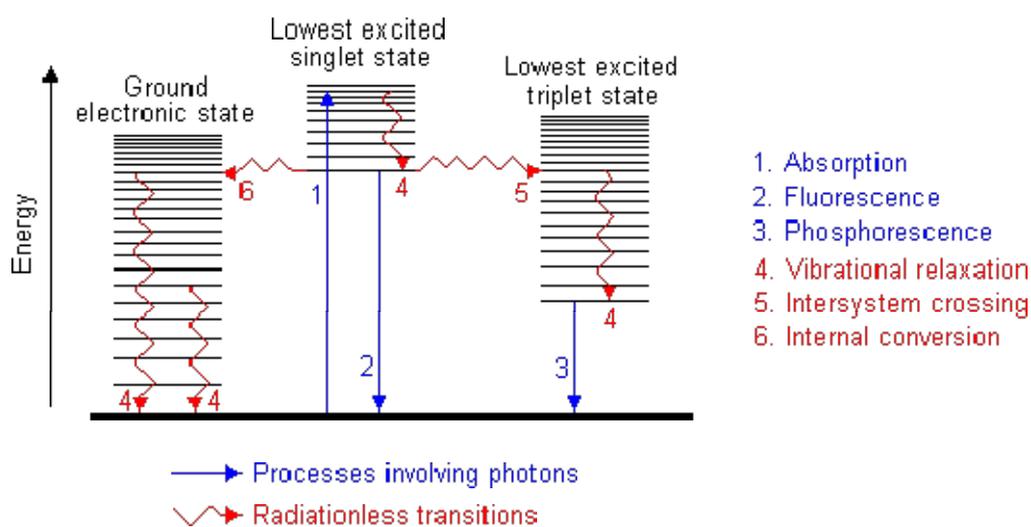


Figure II.20. Jablonski energy diagram illustrating various transitions between energy states of a molecule.

The association constants as obtained from the UV-Visible spectroscopic study, were further verified utilising Fluorescence Spectroscopic measurement.

2.4.13. MASS SPECTROMETRY

Mass spectrometry is an influential analytical tool used to quantify known materials, for the identification of anonymous compounds within a sample, and off course, for the elucidation of structure and chemical behaviour of different molecules. The thorough process includes the transformation of the sample into gaseous ions, with or without fragmentation, which can then be characterized by their mass to charge ratios (m/z) and relative abundances.

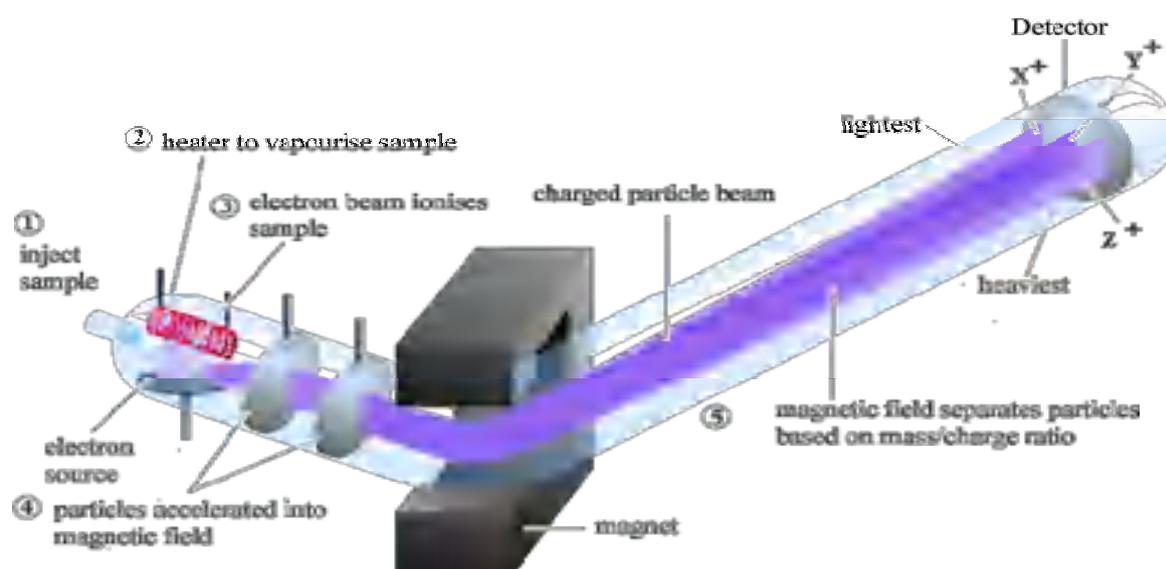


Figure II.21. Diagrammatic representation of working principle of HRMS

In a mass spectrometric analysis, the gas phase ions of the compound are produced first, usually by electron ionization. The molecules thus formed then undergo fragmentation. The primary product of ions, resulting from the molecular ion, yet again, undergoes fragmentation, and so on. Based on their mass-to-charge ratio, the ions get separated in the spectrometer, and are identified in proportion to their abundance. Consequently, a mass spectrum of the molecule is produced displaying the result in the form of a plot of ion abundance versus mass-to-charge ratio. Informations relating to the nature and the structure of the precursor molecule are obtained from the ions. The molecular ion appears at the highest value of m/z (followed by ions with heavier isotopes) in the spectrum of a pure compound. This gives the molecular mass of the compound.

2.4.14. SCANNING ELECTRON MICROSCOPY (SEM)

A focused beam of high energy electrons is used in a Scanning Electron Microscope (SEM) to produce various signals at the surface of solid specimens. The signals derived from the electron-sample interactions provide information about the sample, such as, the chemical composition, external morphology(texture), crystalline structure and orientation of materials constituting the sample. Generally, data are collected over a selected surface area of the sample to generate a 2-dimensional image displaying spatial variations in these properties. Moreover, a selected point location on the sample can also be analysed by the SEM measurement. This is an useful approach for a qualitative determination of chemical compositions (using EDS), crystal structure, and crystal orientations (using EBSD).

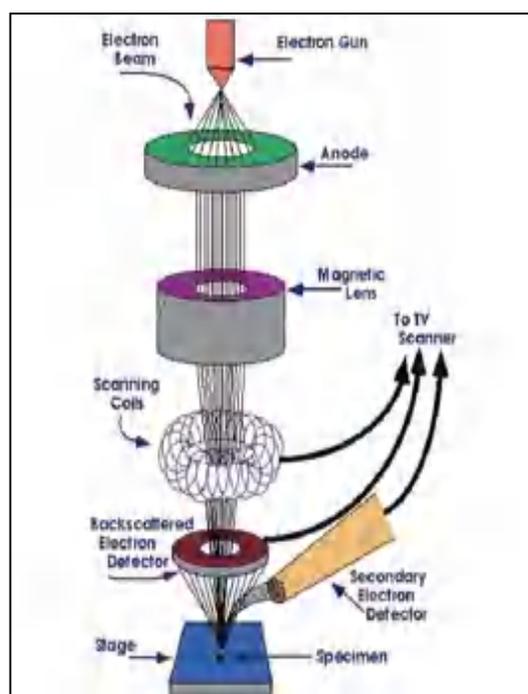


Figure II.22. Schematic representation of the basic SEM components

The kinetic energy carried by the accelerated electrons is dissipated as a variety of signals formed due to electron-sample interactions when the incident electrons are decelerated. These signals consist of back scattered electrons (BSE), secondary electrons (that produce SEM images) which are commonly used for imaging samples.

Secondary electrons determine morphology and topography on samples, while, back scattered electrons are valuable for elucidating contrasts in composition in multiphase.

2.4.15. DENSITY MEASUREMENTS

The study of physicochemical properties of liquid mixtures have enticed considerable attention from the points of view of both theoretical and engineering applications. In all material states, whether solid, liquid, or gaseous, density plays an important role. Throughout industry, measurement of density has significant relevance to gain insight into materials, for example, to determine their purity, composition of components, and their concentration. The evaluation of quantitative data on the density of liquid mixtures are the basis in many engineering applications. Density measurements also provide valuable information about the nature and molecular interactions between liquid mixture components in a liquid mixture.

The volumetric information includes 'Density' as a function of weight, volume and mole fraction and excess volumes of mixing. Thermodynamic approaches are highly recognized for studying the molecular interactions occurring in solutions. The solute-solvent and solute-solute interactions in the fluids can be conveniently interpreted by studying their thermodynamic properties. In this aspect, the volumetric informations are of enormous significance. The change in the molar volume of the solute molecules depend on the nature of the solvent. Thus, calculation of apparent molar volume of a solution can be used to evaluate interactions taking place between the components. Again, by using partial molar volume data, many processes in solutions, for example, electrostriction [81], micellization [82], hydrophobic hydration [83], and co-sphere overlap during solute-solvent interactions [84] can be interpreted.

■ APPARENT AND PARTIAL MOLAR VOLUMES

The molar volume of a pure substance can be determined by using density data. However, the determination of the volume contributed to a solvent by the addition of one mole of an ion is not an easy task to do. This happens because, when the ions enter into the solvent, the volume of the solution changes owing to a breakup of the solvent structure near the ions and the solvent is compressed under the influence of the ion's electric field that is electrostriction. The compression of ions and molecules is likely to

be significant whenever there are electric fields of the order of 10^9 - 10^{10} V m⁻¹. The effective volume of an ion in solution, the partial molar volume, can be determined from apparent molar volume (ϕ_V), which is a directly obtainable quantity. By using the following equation, the apparent molar volumes (ϕ_V), of the solutes can be obtained [85],

$$\phi_V = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \quad (3)$$

Where, M is the molar mass of the solute, ρ_0 and ρ are the densities of the solvent and the solution respectively and c is the molarity of the solution. The partial molar volumes, ϕ_{2V} , can be determined from the equation given below [86],

$$\phi_{2V} = \phi_V + \frac{(1000 - c\phi_V)}{2000 + c^{3/2} \left(\frac{\partial \phi_V}{\partial \sqrt{c}} \right)} c^{1/2} \left(\frac{\partial \phi_V}{\partial \sqrt{c}} \right) \quad (4)$$

The apparent molar volume of electrolyte at infinite dilution and its dependence on the concentration have long been made by four major equations, namely, the Masson equation[87], the Redlich-Meyer equation[88], the Owen-Brinkley equation [89], and the Pitzer equation[90]. According to Masson, the apparent molar volume ϕ_V changes with the square root of the molar concentration,

$$\phi_V = \phi_V^0 + S_V^* \sqrt{c} \quad (5)$$

Here, ϕ_V^0 is the apparent molar volume at infinite dilution and S_V^* is the the experimental slope. By using the equation (3), the majority of ϕ_V data in water [91] and almost all ϕ_V data in non-aqueous solvents have been extrapolated. [9-96]

The equation given below shows how ϕ_V^0 of various investigated electrolytes in various solvents depend on temperature,

$$\phi_V^0 = a_0 + a_1T + a_2T^2 \quad (6)$$

Where, T is the temperature in Kelvin, while, a_0, a_1, a_2 are the coefficients of a particular electrolyte.

The limiting apparent molar expansibilities (ϕ_E^0) can be determined by the equation given as under,

$$\phi_E^0 = \left(\delta \phi_V^0 / \delta T \right)_P = a_1 + 2a_2 T \quad (7)$$

The magnitude of limiting apparent molar expansibilities (ϕ_E^0) change with the change of temperature. It is now well established that S_V^* is not the sole criterion for determining the structure-making or breaking tendency of any solute. Hepler developed a technique to examine the sign of $\left(\delta \phi_E^0 / \delta T \right)_P$ for the solute, in terms of long-range structure-making and structure-breaking capacity of the electrolytes in the mixed solvent systems.[97] The following is the general thermodynamic expression used for the purpose,

$$\left(\delta \phi_E^0 / \delta T \right)_P = \left(\delta^2 \phi_V^0 / \delta T^2 \right)_P = 2a_2 \quad (8)$$

The electrolyte acts as a structure maker if the value of $\left(\delta \phi_E^0 / \delta T \right)_P$ is positive or small and, but, when the value of $\left(\delta \phi_E^0 / \delta T \right)_P$ is negative, it is a structure breaker. Redlich and Meyer have suggested that the equation (5) cannot be more than a limiting law, where, for a particular solvent and temperature, the slope S_V^* should depend only upon the valence type.[88] They suggested the following equation,

$$\phi_v = \phi_v^0 + S_v \sqrt{c} + b_v c \quad (9)$$

$$\text{Where, } S_v = Kw^{3/2} \quad (10)$$

The theoretical slope S_V , is based on molar concentration and includes the valence factor where ,

$$w = 0.5 \sum_i^j Y_i Z_i^2 \quad (11)$$

And,

$$K = N^2 e^2 \left(\frac{8\pi}{1000 \epsilon^3 RT} \right)^{1/2} \left[\left(\frac{\partial \ln \epsilon}{\partial p} \right)_T - \frac{\beta}{3} \right] \quad (12)$$

K signifies the compressibility of the solvent, the other terms have their usual significance.

The concentration dependence of numerous 1:1 and 2:1 electrolytes in dilute solutions, can be adequately shown by the Redlich-Meyer's extrapolation equation. [88] Nevertheless, studies on some 2:1, 3:1 and 4:1 electrolytes have shown significant deviation from this equation. [88-99] A more complete Owen-Brinkley equation [89], which includes the ion-size parameter, $a(\text{cm})$, can therefore be used to aid in the extrapolation to infinite dilution and to adequately represent the dependency of ϕ_V upon concentration,

$$\phi_V = \phi_V^0 + S_V \tau(\kappa a) \sqrt{c} + 0.5 w_V \theta(\kappa a) c + 0.5 K_V c \quad (13)$$

Where, the symbols have their usual significance. But, this equation has limited use for non-aqueous solutions.

Pogue and Atkinson [100] have recently used the Pitzer formalism to fit the apparent molal volume data. The apparent molar volume for a single salt $M \gamma_M M \gamma_X$, the Pitzer equation is,

$$\phi_V = \phi_V^0 + V |Z_M Z_X| A_V |2b \ln \left(I + bI^2 \right) + 2\gamma_M \gamma_X RT \left[m B_{MX}^2 + m^2 (\gamma_M \gamma_X)^{1/2} C_{MX}^V \right] \quad (14)$$

Here, all the symbols having their usual significance.

■ EXCESS MOLAR VOLUMES

The excess molar volumes, V^E can be determined from the molar masses M_i and the densities of pure liquids and the mixtures by using the following equation [101,102],

$$V^E = \sum_{i=1}^n x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (15)$$

where ρ_i and ρ are the density of the i^{th} component and density of the solution mixture respectively. V^E is the resultant of contributions from various opposing effects. According to their nature, they may broadly be divided into three types, namely, physical, chemical, and structural. Physical contributions involve non-specific interactions between the real species present in the mixture and are contributing a positive term to V^E . The chemical or specific intermolecular interactions are contributing negative V^E values so as to result in a volume decrease. While, the structural contributions are mostly negative and arises from a number of effects, mainly from interstitial accommodation and changes of free volume. [103] These phenomena are the results of difference in interaction energies between molecules being in solutions and packing effects. While forming the mixture, the disruption of the ordered structure of pure component leads to a positive effect on excess volume. Conversely, order formation in the mixture is associated with a negative contribution.

2.4.16. REFRACTIVE INDEX MEASUREMENTS

Refractive index measurements provide valuable informations about the structure and molecular interactions of the electrolytic solutions. In addition, refractometric study can also be helpful in assessing complementary data on practical procedures, for example, measurement of concentration or the estimation of other properties. [104]

For a substance, the Index of Refraction (n_D), is the ratio of the speed of light in vacuum to that in some other medium. Thus, it can be expressed as,

$$\text{Refractive Index } (n_D) \text{ of substance} = \frac{\text{Speed of light in vacuum}}{\text{Speed of light in substance}}$$

When light crosses a boundary from one medium to another, its speed changes with a concurrent alteration in its path of travel and this causes refraction.

Suppose, the refractive indexes of the two mediums (say A and B) are n_A and n_B respectively. These are related with the light's speed in the two mediums (V_A and V_B) and the angles of incidence ($\sin \theta_A$) and refraction ($\sin \theta_B$) as given below,

$$\frac{V_A}{V_B} = \frac{\sin \theta_A}{\sin \theta_B} = \frac{n_B}{n_A} \quad (16)$$

So, it may be concluded that the determination of the index of refractions can be also possible without measuring the speed of light in a sample. Rather, knowing the index of refraction of the layer in touch with the sample, refractive index of the sample can be determined quite accurately, by measuring the angle of refraction.

The refractive index of mixing can be correlated by using a composition dependent polynomial equation. The molar refractivity can be obtained from the Lorentz- Lorenz relation [105] by using n_D experimental data according to the following expression,

$$R_M = \frac{(n_D^2 - 1)}{(n_D^2 + 2)} \left(\frac{M}{\rho} \right) \quad (17)$$

Here, M and ρ stands respectively for the mean molecular mass and is the density of the mixture. The expression for n_D can be given as,

$$n_D = [(2A + 1) / (1 - A)]^{0.5} \quad (18)$$

Where, A is given by:

$$A = \left[\left\{ \frac{(n_1^2 - 1)}{(n_1^2 + 2)} (1 / \rho_1) \right\} - \left\{ \frac{(n_1^2 - 1)}{(n_1^2 + 2)} (w_2 / \rho_1) \right\} + \left\{ \frac{(n_2^2 - 1)}{(n_2^2 + 2)} (w_2 / \rho_2) \right\} \rho \right] \quad (19)$$

Here, n values represent the refractive indices of pure components, ρ the mixture density, whereas, ρ_1 and ρ_2 are the densities of pure components, and, w_j denotes the weight fraction.

Following expression gives molar refractivity deviation,

$$\Delta R = R - \phi_1 R_1 - \phi_2 R_2 \quad (20)$$

Where, R , R_1 , and R_2 stands for molar refractivity of the mixture and the pure components respectively, and ϕ_1 and ϕ_2 are the volume fractions.

The deviations of refractive index were determined for the correlation of the binary solvent mixtures,

$$\Delta n_D = n_D - x_1 n_{D1} - x_2 n_{D2} \quad (21)$$

Where, Δn_D is the deviation of refractive index for the binary system, while, n_D , n_{D1} and n_{D2} are the refractive index of the binary mixture, component 1, and component 2, respectively, and, x is the mole fraction.

The calculated deviations of refractive indices of the binary mixtures are fitted using the Redlich-Kister expression given as under [106],

$$\Delta n_{Dew} = w_e w_w \sum_{P=0}^S B_p (w_e w_w)^P \quad (22)$$

Where, B_p are the adjustable parameters obtained by a least squares fitting method, S is the number of terms in the polynomial and w is the mass fraction.

For a salt-solvent solution, the binary systems were fitted to polynomials of the form:

$$n_{Ds,sol} = n_{Dsol} + \sum_{i=1}^N A_i m^i \quad (23)$$

where $n_{Ds,sol}$ is the refractive index of the salt + solvent system, n_{Dsol} is the refractive index of the solvent, m is the molality of the solution, N is the number of terms in the polynomial and A_i are the fitting parameters.

For the ternary systems of the salt + solvent-1 + solvent-2 solutions, a similar polynomial expression [107] was used to represent ternary refractive indices:

$$n_D = n_{Dw} + \sum_{i=1}^P C_i m^i \quad (24)$$

n_D is the refractive index of the ternary solution, P is the number of terms in the polynomial, and, C_i are the parameters.

There is no common rule that can be stated so as to compute a refractivity divergence. Hence, on account of completeness, both the calculations of refractivity deviation function, molar refractivity deviation was fitted to a Redlich and Kister-type expression. The adjustable parameters and the relevant standard deviations are measured in terms of volume fractions and mole fractions, respectively.

So far as the whole discussion is concerned, it may be argued that the problem of molecular interactions is intriguing as but interesting. Thus, utilisation of different investigational techniques is enviable to expose the scenario. [108-111]

2.4.17. VISCOSITY MEASUREMENT

The viscometric analysis of an electrolytic solution truly has multifarious aspects. As the ion-ion and ion-solvent interactions are taking place in solution, it is very tedious to distinguish the related forces. However, careful analysis enables valuable and valid conclusions to be made regarding the structure and the nature of the solvation of a particular system. Viscosity is a measure of the frictional forces acting between the adjacent, relatively moving parallel planes in a liquid. An increase or decrease in the interactions between such planes is associated with a consequent increase or lowering of the viscosity. Thus, monitoring of viscosities of a solution, is associated with a simultaneous dealing with diverse interactions taking place between solute and solvents in solution.

■ Viscosity A- and B- coefficients

If in a liquid, a large sphere is placed, the planes will be set together in increasing the viscosity. The viscous force also increases with increasing the degree of hydrogen bonding between the planes, because hydrogen bonding introduces more frictions between the planes.

Similarly, increase in the average degree of hydrogen bonding between the planes will increase the friction between the planes, thereby viscosity. For a structure-promoting ion, an ion having a large rigid co-sphere acts as a rigid sphere placed in the liquid thereby increasing the inter-planar friction. Similarly, an ion increasing the degree of

hydrogen bonding or the degree of correlation among the adjacent solvent molecules will increase the viscosity.

On the contrary, ions destroying correlation would lower the viscosity. Viscosity was measured systematically for the very first time by Grüneisen, in 1905. Viscosities of various electrolytic solutions were measured over a wide range of concentrations. He noted non-linearity and negative curvature in the viscosity concentration curves irrespective of low or high concentrations. In 1929, Jones and Dole suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations(c),

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc \quad (25)$$

The above equation can be rearranged as-

$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} \quad (26)$$

Here, the constants A and B are related to ion-ion and ion-solvent interactions. The equation has been used extensively as it is equally applicable to aqueous and non-aqueous solvent systems provided that there is no ionic association. The term $B\sqrt{c}$, also known as Grüneisen effect, describes the coulombic forces between the ions when they are at a long distance. The significance of the term had since then been realized due to the development Debye-Hückel theory of inter-ionic attractions in 1923. The A - coefficient depends on the ion-ion interactions, can be calculated from interionic attraction theory and is given by the Falkenhagen Vernon equation-

$$A_{Theo} = \frac{0.2577 A_o}{\eta_o (\epsilon T)^{0.5} \lambda_+^o \lambda_-^o} \left[1 - 0.6863 \left(\frac{\lambda_+^o \lambda_-^o}{A_o} \right)^2 \right] \quad (27)$$

Where, the symbols have their usual significance.

The plots of $(\eta/\eta_o - 1)/\sqrt{c}$ against \sqrt{c} for the electrolytes should give the value of A- and B-coefficient. But, sometimes, the values come out to be negative or considerably scatter and also deviation from linearity occur. Thus, instead of determining A- coefficient from

the plots or by the least square method, the A-coefficient are generally calculated using Falkenhagen-Vernon equation. A-coefficient should be zero for non-electrolytes. According to Jones and Dole, the A-coefficient probably represents the stiffening effect on the solution of the electric forces between the ions, which tend to maintain a space-lattice structure.

The viscosity B-coefficient may be either positive or negative, that represents the ion-solvent interaction parameter. The B-coefficients are obtained as slopes of the straight lines using the least square method and intercepts equal to the A values.

■ The factors influencing viscosity B - coefficients

- (1) The effect of ionic solvation and the action of the field of the ion in producing long-range order in solvent molecules, increases η or B - value.
- (2) The destruction of the three-dimensional structure of solvent molecules (i.e., structure breaking effect decreases η values.
- (3) Low dielectric constant and high molal volume yields high B-values for similar solvents.
- (4) If either ion of a binary electrolyte cannot be specifically solvated, or, the primary solution of ions is sterically hindered in high molal volume solvents, then reduced B-values are obtained.

■ Temperature dependence of viscosity B-coefficient

Regularity in the behaviour of B and dB/dT in both aqueous and non-aqueous solvents led Kaminsky to make some useful generalizations, (i) within a group of the periodic table the B-ion values decrease as the crystal ionic radii increase, (ii) within a group of periodic system, the temperature co-efficient of B_{ion} values increase as the ionic radius. The results has been summarized as below-

(i) A and $dA/dT > 0$

(ii) $B_{ion} < 0$ and $dB_{ion}/dT > 0$, characteristic of the structure breaking ions.

(iii) $B_{\text{ion}} > 0$ and $\frac{dB_{\text{ion}}}{dT} < 0$, characteristic of the structure making ions.

First derivative of viscosity B-coefficient over temperature is an upgradation of viscosity B-coefficient in predicting the nature of solute-solvent interaction as structure maker or structure breaker. The energy of activation required for the viscous flow of a liquid can be determined by measuring dB/dT . The measurement of dB/dT is indicative towards the structure making or breaking capability than sign or magnitude of the B-coefficient. The negative or small positive value of dB/dT signifies structure-making (kosmotropic) whereas the larger positive value identifies it as structure-breaking (chaotropic).

2.4.18. CONDUCTIVITY MEASUREMENT

The ionic content of a solution can be determined by measuring its conductivity (or specific conductance). Conductivity is a measure of ability to conduct electricity of an electrolytic solution. Conductivity measurement is very significant in different industrial and environmental applications because the electrolytic behaviour of the solution can be obtained in a fast, inexpensive and reliable way. For example, the performance of a water purification system can be monitored in a typical way by measuring the product conductivity.

In supramolecular chemistry, the extent of Host-Guest interaction as well as the stoichiometry of the inclusion complexes formed thereby, can be obtained by conductimetric study. With regard to this particular thesis, the aqueous solution of guest which were all indeed organic molecules, showed considerable conductivity. On increasing the concentration of hosts (CDs) gradually, a simultaneous decrease in conductivity (κ) of the aqueous guest solutions was observed. This is probably due to the molecular encapsulation of conducting species into the hydrophobic cavity of the CDs. At a certain concentration, a single break point was observed. After the break point, conductivity remained almost unchanged. Single break point in the conductivity curve indicates the 1:1 stoichiometries of the inclusion complexes.

2.4.19. IONIC ASSOCIATION

The dissociation or association of electrolytes in a solution can be assigned from the plot of Λ vs \sqrt{c} (limiting Onsager equation). If positive deviation occurs (attributed to the short range hard core repulsive forces between the ions), that is, if $\Lambda_{o\text{exp}}$ is greater than $\Lambda_{o\text{theo}}$, the electrolyte can be supposed to be completely dissociated. But, a negative deviation (i.e., $\Lambda_{o\text{exp}} < \Lambda_{o\text{theo}}$), or, positive deviation from the Onsager limiting tangent ($\alpha\Lambda_o + \beta$) signifies the association among electrolytes. Here, the greater electrostatic interactions cause association between the cations and anions. Furthermore, the difference in $\Lambda_{o\text{exp}}$ and $\Lambda_{o\text{theo}}$ would be significant with increasing association.[112]

Conductance measurements also help to determine the values of the ion-pair association constant, K_A for the process,



$$K_A = \frac{(1-\alpha)}{\alpha^2 c \gamma_{\pm}^2} \quad (29)$$

$$\alpha = 1 - \alpha^2 K_A c \gamma_{\pm}^2 \quad (30)$$

Here γ_{\pm} is the mean activity coefficient for the free ions at concentration αc

The Fuoss-Kraus equation [113], or, Shedlovsky's equation [114] can be applied for the determination of K_A and Λ_o for strongly associated electrolytes,

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda_o} + \frac{K_A}{\Lambda_o^2} \cdot \frac{c \gamma_{\pm}^2 \Lambda}{T(z)} \quad (31)$$

where $T(z) = F(z)$ (Fuoss-Kraus method) and $1/T(z) = S(z)$ (Shedlovsky's method).

$$F(z) = 1 - z(1 - z(1 - \dots)^{\frac{1}{2}})^{\frac{1}{2}} \quad (32)$$

And,

$$\frac{1}{T(z)} = S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \dots \quad (33)$$

A plot of $T(z)/\Lambda$ against $c\gamma_{\pm}^2\Lambda/T(z)$ is a straight line having intercept $1/\Lambda_0$, and the slope K_A/Λ_0^2 . However, there will be considerable uncertainty in the values of Λ_0 and K_A , determined from equation (31).

The Fuoss-Hsia [115] conductance equation for electrolytes associated in solution is given as,

$$\Lambda = \Lambda_0 - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{\frac{3}{2}} - K_A\Lambda\gamma_{\pm}^2(\alpha c) \quad (34)$$

Justice modified the equation. [116] The conductance of a symmetrical electrolytes in dilute solutions can be given by the equations,

$$\Lambda = \alpha(\Lambda_0 - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1R(\alpha c) - J_2R(\alpha c)^{\frac{3}{2}} \quad (35)$$

$$\frac{(1-\alpha)}{\alpha^2 c \gamma_{\pm}^2} = K_A \quad (36)$$

$$\ln \gamma_{\pm} = \frac{-k\sqrt{q}}{(1+kR\sqrt{\alpha c})} \quad (37)$$

The conductance parameters are obtained from a least square treatment after setting,

$$R = q = \frac{e^2}{2\epsilon kT} \text{ (Bjerrum's critical distance).}$$

The Justice method fixes the J -coefficient by setting, $R = q$ to permit a better value of K_A to be obtained. Since the equation (35) is a series expansion truncated at the $c^{3/2}$ term, it would be preferable that the resulting errors be absorbed as much as possible by J_2 rather than by K_A , whose theoretical interest is greater as it contains the information concerning short-range cation-anion interaction. It is possible to determine the distance of closest approach, α , between two free ions forming an ion-pair using the experimental values of the association constant K_A . Fuoss has proposed the following equation,

$$K_A = \frac{4\pi N_A \alpha^3}{3000} \exp\left(\frac{e^2}{\alpha \epsilon kT}\right) \quad (38)$$

Calculation of α , in some cases, becomes tedious when the magnitude of K_A is too small. Rather, a more general equation due to Bjerrum is applied for determining the distance parameter ,

$$K_A = \frac{4\pi N_A \alpha}{1000} \int_{r=a}^{r=g} r^2 \exp\left(\frac{z^2 e^2}{r \epsilon k T}\right) dr \quad (39)$$

The equations ignore specific short-range interactions, excepting solvation in which the solvated ion have been approximated by a hard sphere model. The method has been successfully utilized by Douheret. [117-119]

2.4.20. LIMITING EQUIVALENT CONDUCTANCE

The limiting equivalent conductance of an electrolyte can be easily determined from the theoretical equations and experimental observations. At infinite dilutions, as the ions are infinitely apart, their motion is influenced merely by the interactions with the surrounding solvent molecules. Under these conditions, the validity of Kohlrausch's law of independent migration of ions is almost axiomatic. Thus,

$$\Lambda_0 = \lambda_o^+ + \lambda_o^- \quad (40)$$

The limiting equivalent conductance can be divided into ionic components using experimentally determined transport number of ions,

$$\lambda_o^+ = t_+ \Lambda_0 \quad \text{and} \quad \lambda_o^- = t_- \Lambda_0 \quad (41)$$

The separate contributions of solute-solvent interactions due to cations and anions can be obtained from the accurate λ_0 values. However, determination of accurate transference numbers are confined only to few solvents.

Various attempts have been made for developing indirect methods to determine the limiting ionic equivalent conductance, in ionic solvents but experimental transference numbers needed for that are yet not available.

2.4.21. SOLVATION

In a solution, different types of interactions can exist between the ions. The orientation of the solvent molecules towards the ion are presumably because of these interactions. Ions in the solution gets solvated and the number of solvent molecules involving in the

solvation of a particular ion is called its solvation number. The region of solvation can be classified as primary and secondary solvation regions. We are here, concerning with the primary solvation region. The primary solvation number is defined as the number of solvent molecules which surrender their individual translational freedom and remain strongly bound, with the ion, as it moves around, or the number of solvent molecules getting aligned in the force field of the ion.

the effective radius of the solvated ions can be calculated from Stokes' law, provided that the limiting conductance of the ion i of charge Z_i is known. The volume of the solvation shell can be given by the equation given below,

$$V_s = \left(\frac{4\pi}{3}\right)(r_s^3 - r_c^3) \quad (42)$$

Where, r_c is the crystallographic radius of the ion. The solvation number (n_s) would then be determined as,

$$n_s = \frac{V_s}{V_0} \quad (43)$$

Assuming Stoke's relation to hold well, the ionic solvated volume can be determined, the considering the packing effects [120], from

$$V_s^o = 4.35r_s^3 \quad (44)$$

Where, V_s^o is expressed in mol/lit. and r_s in angstroms. But, this method can't be applied to medium sized ions, although, a number of empirical and theoretical corrections have been proposed so as to apply it to most of the ions. [121-124]

2.4.22. SURFACE TENSION MEASUREMENT

So far as the host-guest chemistry is concerned, the study of surface tension (γ) provides strong testimony about the inclusion phenomenon and also the stoichiometry of the inclusion complexes formed. Molecules, within a liquid, attract each other equally in every directions. However, at the surface, as there is no force attracting the molecules outwards, they are pulled towards the interior of the liquid. This attractive

force in a liquid that pulls surface molecules into the rest of the liquids minimizing the surface area is called the Surface tension of that liquid.

In the structure of the guests , there is a polar group, and a non polar hydrophobic moiety. We have used pure water (or aqueous ethanol) as solvent for the surface tension studies. For, CDs while dissolved in this solvent, a very small change in the surface tension values were observed for a wide range of concentration. Therefore, the change of the surface tension must be on account of the varying concentration of the guest molecule. Indeed, the values of surface tension of the guest solutions were determined with the gradually increasing concentrations of both the CDs at 298.15 K. The γ -values were found to be increasing with increasing the concentration of CDs, most probably owing to the insertion of the guest molecule into the CD cavity producing inclusion complexes. The remarkable observation was, at a definite concentration of CD, a sudden break point obtained. Moreover, after the break point, the curve remains almost flattened. This is an indication of the respective stoichiometry of the inclusion complexes formed. The break points around the concentration of 5 mM of the CDs imply the 1:1 stoichiometry of different inclusion complexes.