

CHAPTER -II

General Introduction (Review of the Earlier Works)

11.1. IONIC LIQUIDS

Ionic liquids (ILs) are very important salt that exist in liquid state/phase. In some contexts, the term has been categorized to ionic species existing in liquid state. The melting point of ionic liquid is below some arbitrary temperature, 100°C (212°F). In general, Ionic Liquids (ILs) are liquid state salts that involve organic-organic or organic-inorganic cation or anions respectively (Figure II. 1).

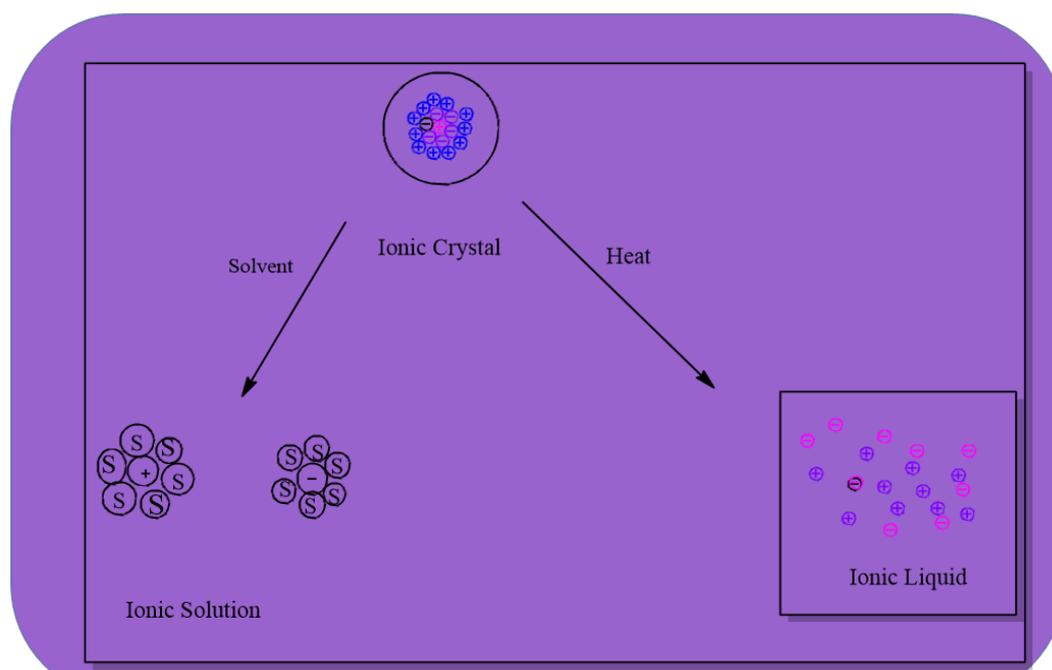


Figure II.1: Difference between an ionic solution and an ionic liquid.

Decreasing of melting temperature ^(II.1) of ionic liquid by increasing size of the ions and making them asymmetric. This is easily elucidated as follows: owing to electrostatic forces happens in ionic liquid system they tends to attract to each other. If the size of the ions are very small and symmetric, as for example, in sodium chloride, the ions will become very near to each other and interact among strongly. Furthermore, due to their nature of symmetry, the crystals formation is favourable. If the size of the ions

is increased, the distance between them will increase and as consequence, the electrostatic attractive force will decrease. The above-mentioned process is used to control the melting point of ionic liquid. Due to their versatile nature, it is possible to synthesize thousands of ionic liquid by only varying a functional group, and the variation of the functional groups will determine the final macroscopic features of that ionic liquid. In the last years, it has been found that ionic liquids have different applications at different field of science, e.g. as catalysers, electroplating solvents and electrolytes.^(II.2) For the specific case of electrolytes, the interest in ionic liquid has greatly increased and already some possible applications are found in fuel cells,^(II.3) in solar cells,^(II.4) and lithium-ion batteries.^(II.5) Inspire of it has already mentioned qualities of the ionic liquids, they are relatively new as elect roles, and as such, there are some draw backs of the ionic liquid such as compatibility, toxicity, with the actual materials used, production cost, and all the problems that come with the introduction of a new technology.

In the last periods, many research groups at different place around the world, focused on a new class of compounds of ionic liquids (IL). The last ten years it was observed that the count of publications with the topic “*ionic liquids*” grew gradually. However, it seem to be what are ionic liquids and why are they so interesting? The following section gives a short overview over this broad field. A much more comprehensive overview about the possible properties and applications of ionic liquids can be observed in the recent book “*Ionic Liquids in Syntheses*”, edited by Peter Wasserscheid and Tom Welton.^(II.6) The generally conventional definition of ionic liquids is that they are “*ionic materials that are liquid below 373 K*”.^(II.7) However, the ideas about the definition of “*ionic material*” are more spread. Many organic solvents that have been proposed over the last two decades. Water frequently used as the ultimate green solvent can be consider in this respect. Ideally solvent-free conditions or the use of water as the ultimate green solvent can be considered. However, most of the organic compounds do not dissolve in water frequently, and especially a solids cannot be processed without a solvent. Therefore suitable alternatives have been sought and found in the classes of (I) ionic liquids; ionic liquids have gained a lot of attention as emerging environmentally benign solvents.^(II.7) Ionic liquids used as a replacement solvents instead of conventional organic solvents in several applications due to their unique features. The melting point of Ionic liquids is below 373 K. ILS consist of an

organic cation that combined with an organic or inorganic anion^(II.6) In generally Ionic liquids display, a very interesting set of properties, used for different applications in chemical industry. Stability of some ionic liquid are up to 500K.^(II.8) the melting points of these organic salts are commonly found below 150 °C^(II.9) and rarely as low as -96 °C.^(II.10) At room temperature due to their ionic nature, they have no measurable vapour pressure.^(II.6) they typically have high solvency power for polar and non-polar compounds. Billions or more than billions of ionic liquids can be considered and synthesized by selecting different ion pair combinations, which allow them to possess specific properties. Besides, the ability to adjust the solvent properties of the ionic liquids is one of their outstanding properties. It's makes them unique solvents for various reactions and separations.^(II.11) Moreover ionic liquids are practically highly thermally and non-flammable, and (electro)chemically stable and ILS present a large liquid range.^(II.6) The key challenges of ionic liquids in the field is that it has the large scale application due to their high costs, their high toxicity (many ionic liquids contain halogens) the unknown long term stability and their relatively high viscosity compared to most common molecular solvents. The latter decreases the rate of mass transfer decrease during the reaction and the separation processes. Though, the viscosity of ionic liquids can drop ominously by addition of co-solvents such as carbon dioxide (CO₂)^(II.6) The whole comparison between ionic liquids and organic solvents is represented in Table II.1.^(II.12)

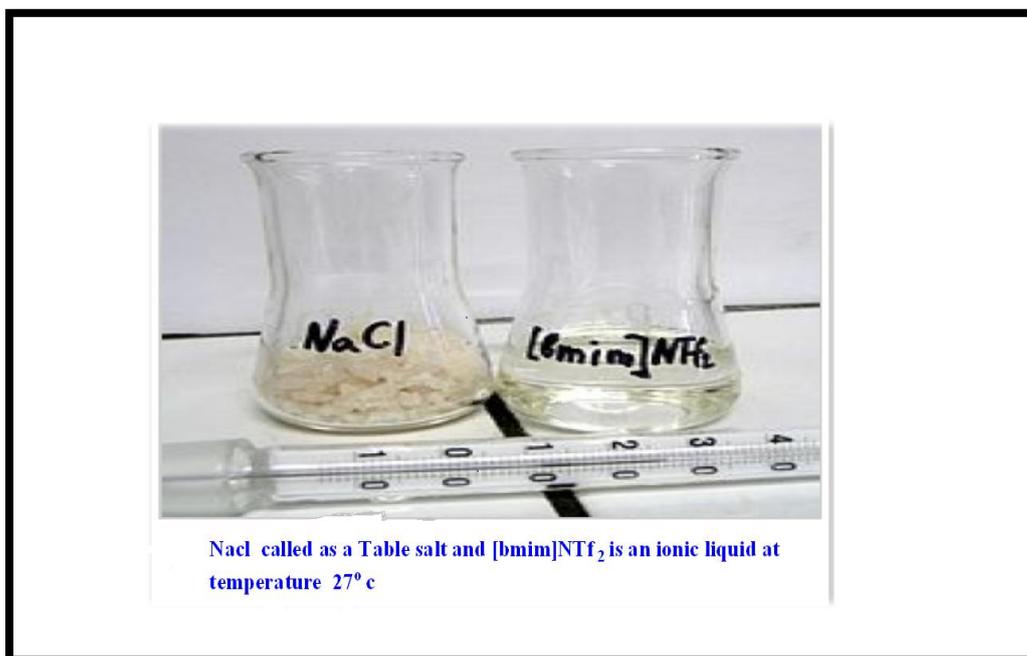
Table II.1. Comparison between organic solvents and ionic liquids.^(II.13)

characteristic	Organic solvent	Ionic Liquid
Number of Solvent	> 1000	> 10000
Catalytic Ability	rare	Common and tunable
Applicability	Single function	Multifunction
Solvation	Most of case weakly Solvating	Strongly solvated in solution
Chirality	rare	Common and tunable
Polarity	Conventionally polarity concepts apply	Concept of polarity is Questionable
Vapour Pressure	Obeys the rule of Clausius-Clapeyron equation	It has Negligible Vapour pressure under Normal condition
Flammability	Usually flammable	Usually nonflammable

characteristic	Organic solvent	Ionic Liquid
Recyclability	Green imperative	Economic imperative
Tunability	Available for limited solvents	Huge range of solvents means "Green solvents"
Cost	Generally cheap	It is Typically two to hundred times more than organic solvent
Density(kg/m ³)	600 to 1700	800 to 3300
Viscosity(pa.s)	0.0002-0.1	0.022-40
Refractive index	1.3 to 1.6	1.5 to 2.2

II.1.2 Room Temperature Ionic Liquids (RTILs)

At room temperature ILs which are liquid is called room temperature ionic liquid (RTIL). From the older and some current literature, ionic liquids are sometimes called liquid organic salts, fused salts, molten salts, ionic melts, NAILs (non-aqueous ionic liquids), OILs (organic ionic liquids) room-temperature molten salts, and ionic fluids. (II.14) sodium chloride (NaCl, *mp* 801°C), normal salts, when heating to high temperature produces also a liquid, that involves entirely of ions, but this is term as a molten salt and do not called them as an ionic liquid.



Commonly, ILs contain of a large bulky and asymmetric organic cations based on 1-alkyl-3-methylimidazolium (abbreviated [C_nmim]⁺), where *n* is the number of

carbon atoms in a linear alkyl chain) tetraalkylammonium (Bu_4N^+) or tetraalkylphosphonium (Bu_4P^+) cations. N-alkylpyridinium (accordingly abbreviated $[\text{C}_n\text{py}]^+$), and many others; and inorganic anions such as tetra fluoroborate $[\text{BF}_4]^-$, hexafluorophosphate $[\text{PF}_6]^-$, alkylsulfates $[\text{RSO}_4]^-$, alkyl sulfonates $[\text{RSO}_3]^-$, halides as chloride $[\text{Cl}]^-$, bromide $[\text{Br}]^-$ or iodide $[\text{I}]^-$, nitrate $[\text{NO}_3]^-$, sulphate $[\text{SO}_4]^-$, aluminium chloride $[\text{AlCl}_4]^-$, triflate ($[\text{CF}_3\text{SO}_3]^- = [\text{TfO}]^-$), bis(trifluoromethylsulfonyl)imide ($[(\text{CF}_3\text{SO}_2)_2\text{N}]^- = [\text{Tf}_2\text{N}]^-$), etc.^(II.15, II.16) Lately when the amino acids are act as anionic part of the ionic liquids and then ionic liquids are called amino acid based ionic liquids (AAILs).^(II.17) Some commonly used ionic liquid systems are presented in Figure II. 2. in the following.

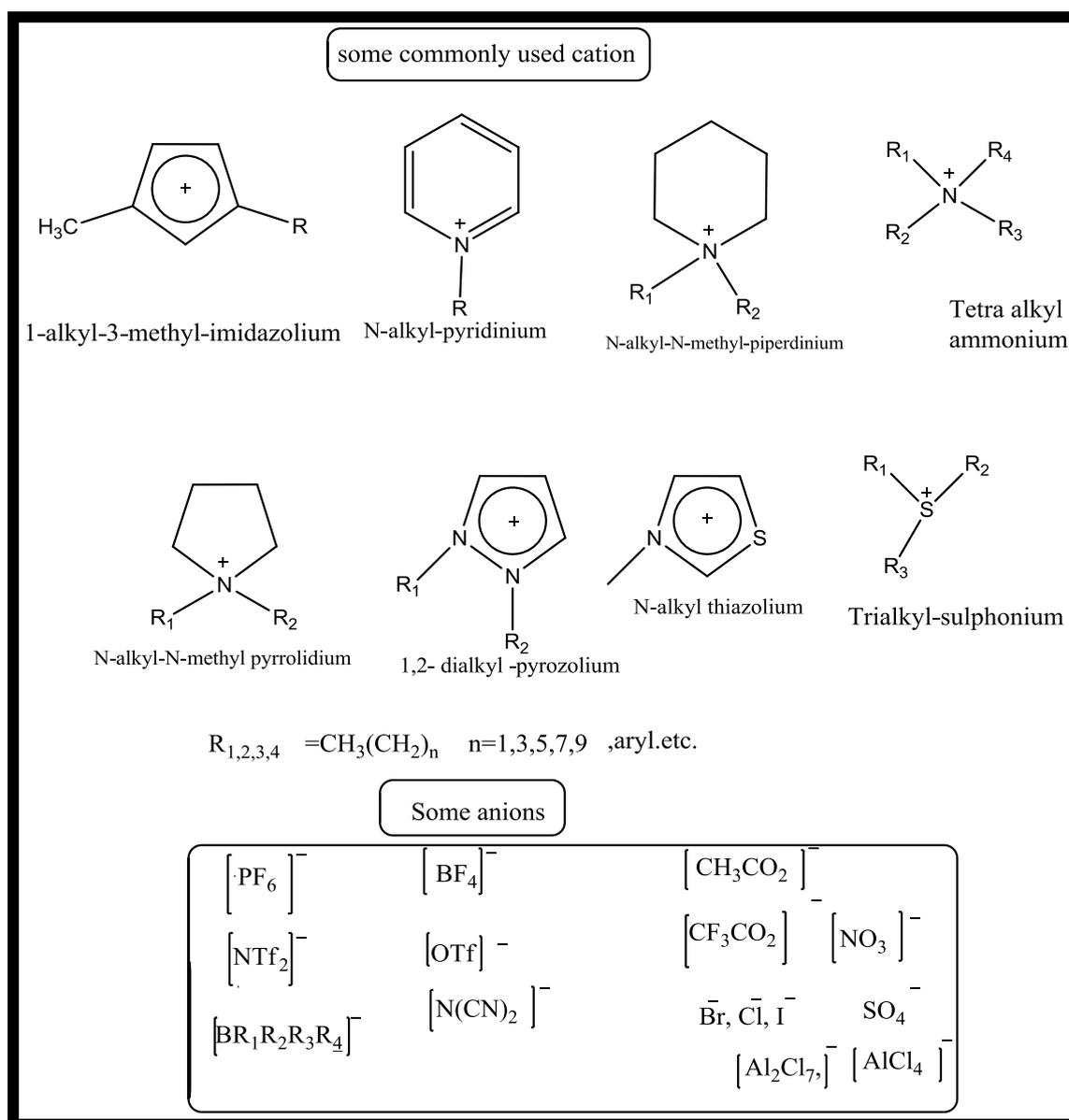


Figure II. 2: Some commonly used ionic liquid systems given in the above chart.

Ionic liquids are eco-friendly used as green solvents due to their no volatility compared to conventional solvents, which are often volatile and it has much contribute both to air pollution and the greenhouse effect. Due to suitable for reuse oils consumption of solvent is very less. However, the normally used ILs are toxic in nature and are hard to biodegradable, which are naturally not intrinsically green. In detail, ILs can be designed to be environmentally benign, which is the direction to research and industry should steer towards.

II.1.3. Properties of Ionic Liquids:

The melting points of ionic liquid is very low due to asymmetry nature of cation is believed to be responsible for the fact., while the nature of the anion part of the ionic liquid is considered to be responsible for many of the physical properties of ionic liquids such as their miscibility with conventional solvents and hygroscopicity. ^(II.18) “*Green Solvents*” are commonly referred to ILS due to their immeasurably low vapour pressure. A crucial feature of ionic liquids is that their various physical properties such as melting point, density, viscosity, and hydrophobicity can be tailored to design different ionic liquids with a specific end use in mind by selection of different cation, anion, and substituents respectively. For this reason, the ionic liquids are also described as “*Designer Solvent*”. ^(II.19) There are number of advantages of ionic liquid as a solvents over molecular Ionic liquids such as high thermal stability negligible vapour pressure, , non-flammability, wide temperature range, hydrophobicity, Lewis acidity gas solubility and hydrogen-bonding capability, therefore, these fluids have been proposed as an attractive alternative to volatile organic compounds (VOCs) for “*green processing*”. To prevent the emission of VOCs, a major source of environmental pollution the ionic liquids used as the replacement of conventional solvents. ^(II.20)

Properties of ionic liquid has listed in the table form:

property	value
Freezing point	< 373.15K
thermal stability	Very high
liquid range	298.15K-473.15K
dielectric constant	< 30(F/m)
viscosity	< 100cp
polarity	47-49
specific conductance	<10 (mS/cm)
molar conductance	<10(Scm ² /mol)

11.1.4 Generations of ILS

Three categories of Ionic Liquids are first-generation; Second-generation; and Third-generation ionic liquids. ^(II.21)

For the first-generation ionic liquids consist of bulky cations such as one, 3-dialkylimidazolium (or *N*, *N'*-dialkylimidazolium) or 1-alkylpyridinium (or *N*-alkylpyridinium), and anions commonly based on halo aluminate (III); these have been studied widely. Ionic liquid has their merit as a tuneable Lewis acidity. Ionic liquids has their great drawback due to extremely sensitivity towards water, which forms hydroxoaluminate(III) species with the aluminium(III) chloride and therefore it decomposes to ionic liquid easily. The sensitivity of ionic liquids towards water necessitates their handling in a dry-box.

The ionic liquids of the second category gradually absorb water from the atmosphere. ^(II.22), are usually air-stable and water-stable and can be used on the bench-top. However, it must be carefully noticed that water-stable does not imply that there is no interaction with water at all.

Recently, a third generation of “task-specific” ionic liquids have developed. ^(II.23) These novel ionic liquids have very interesting feature for chemical functionalities which have been designed for particular applications. From the physical properties of ionic liquid very little is known and the future will show if they can bring about an ecological or economic benefit; but that future does look positive.

II.1.5. History and New Developments

Ionic liquids have their extensive use solvents in chemical processes for synthesis, separation processes and catalysis has recently become noteworthy. By Paul Walden in 1914 ^(II.24) Synthesized the first low melting salt (ionic liquid), ethyl ammonium nitrate ($[\text{EtNH}_3]^+ [\text{NO}_3]^-$), having melting point of 12°C. Aluminium chloride-based molten salts were utilized during 1940s, for electroplating at temperatures of hundreds of degrees Celsius. In 1951, low melting salts with chloroaluminate ions for low-temperature electroplating of aluminium were developed. ^(II.25) During the 1970s and 1980s, these liquids were studied mostly for electrochemical applications in the field of nuclear warheads batteries. ^(II.26) In the early 1970s, Wilkes tried to develop better batteries for nuclear warheads and space probes which is very essential for molten salts to operate. These salts were so hot enough to damage the nearby

materials. For this, reason chemists investigated for salts, which remain liquid at lower temperatures, and finally they identified one, which is liquid at room temperature. For the improvements of ionic liquid, Wilkes and his colleagues use as battery electrolytes and then a small community of researchers began to make ILs and test their properties. (II.27, II.28) In the mid 1980s, low melting point ionic liquids for organic synthesis were suggested. (II.29, II.30) Ionic liquids became one of the most promising chemicals as solvents in the late 1990s. These ILs were very active towards various organic compounds. Due to their instability nature towards air and water new ionic liquids such as organoaluminum, have limited range of applications+. Besides, these ILs were not inert towards various organic compounds. In 1992, synthesis and applications of water and air stable ILs as for example, 1-*n*-butyl-3-methylimidazolium tetra fluoroborate ([bmim] [BF₄]) and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim] [PF₆]), the number of air and water stable ILs have started to increase quickly.

It is very Interest in ionic liquids that it has now been grown dramatically in the scientific community (both in academia as well as industry) in the last decade. (II.15) with over 8000 papers have been published. This growth of publication can be observed in Figure II.3. (II.15) (number of publications per year) and Figure II.4. (II.15) (number of patents per year), it is clear from the given figure that the number of publications and patents are increasing exponentially. In the laboratory, there are about one million (10^6) simple ionic liquids that can be easily synthesised by combination of different cations and anions and this total are just for simple primary systems (Figure II.5). There are one billion (10^{12}) possible binary combinations of these, and one trillion (10^{18}) ternary possible IL systems that can be prepared from the combination of anions, cations, and substituents respectively If there are one million possible simple systems of ionic liquid present. Now days only about 300 ionic liquids are commercialized so one can imagine this in depth, how many chances in this field are still undiscovered and why this field of chemistry is so trying or tempting.

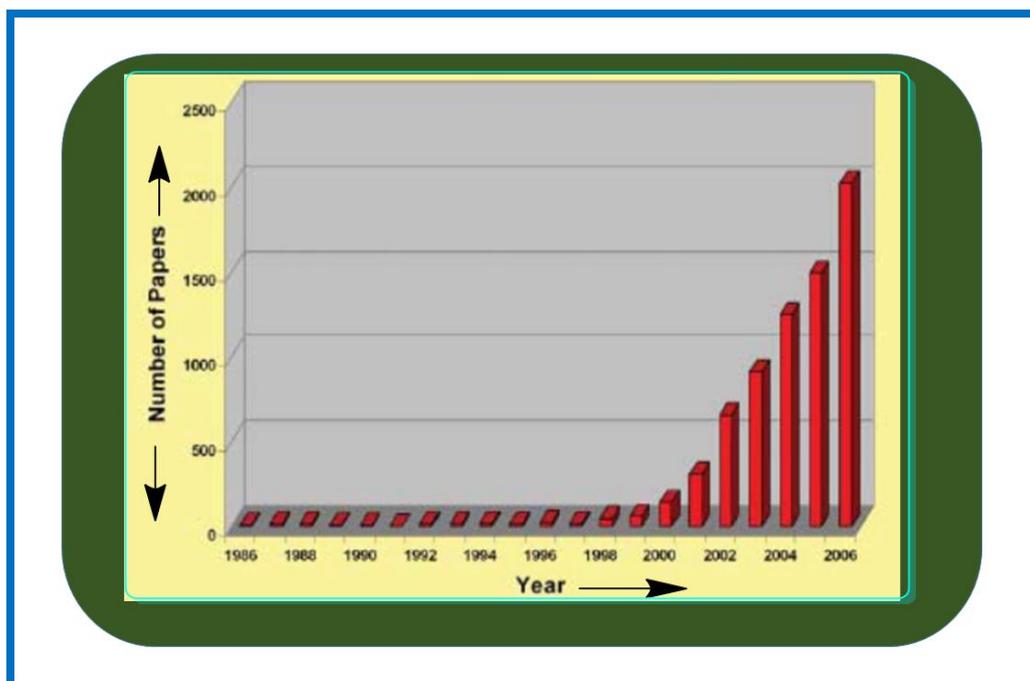


Figure II. Three: Growth rate of ionic liquid publications from 1986 to 2006.

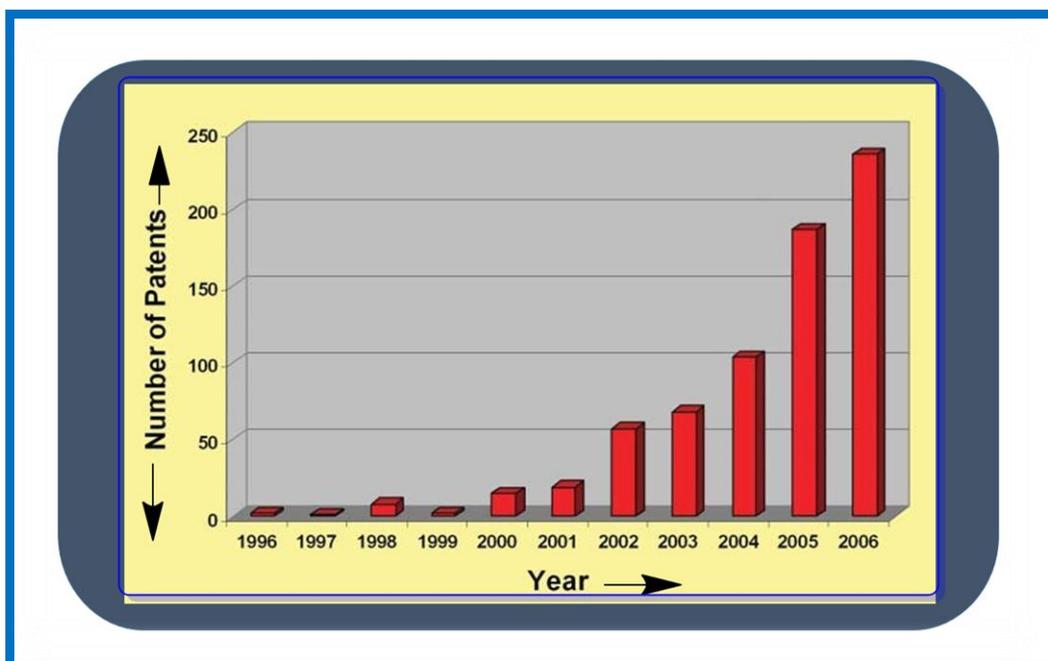


Figure II. Four: Annual growth of ionic liquid patents from 1996 to 2006.

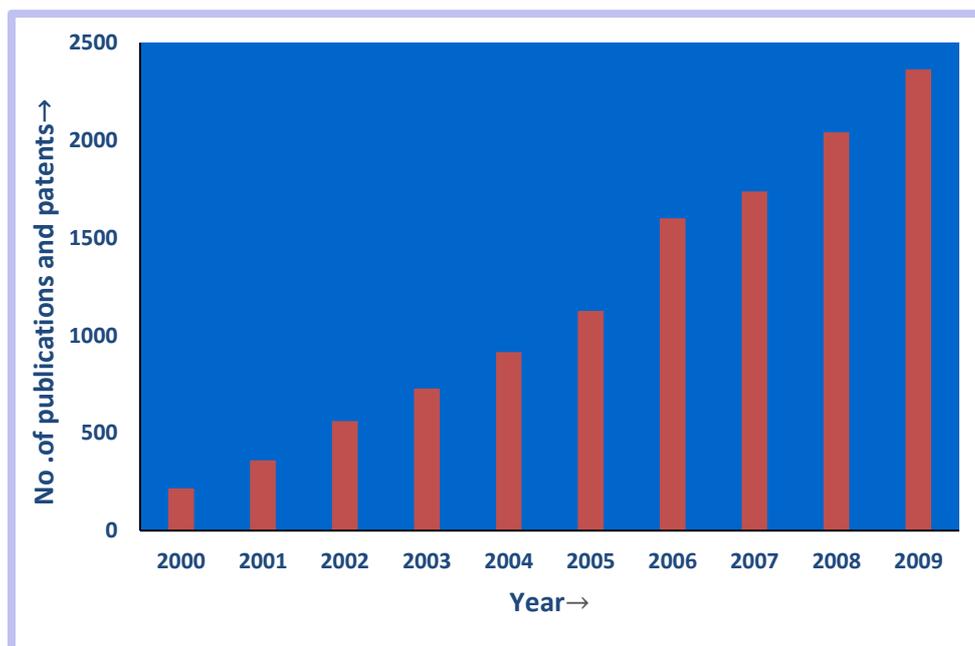


Figure II. Five: Annual growth of ionic liquid paper and patents, up to 2009

It was observed from the plot Until 1998, the number of entries of publications and papers with the terms “*ionic liquid*” or “*ionic liquids*” in the Chemical Abstracts was below or around twenty per year. After this number is increasing 45 per year to 1255 from 1999 to 2005 and 1717 in 2006 with their different applications in various field of science.¹⁴⁷ The total number of entries is over 8000 (in 2007) which indication in different areas, huge potential of ionic liquids applications as shown in Figure II.6.

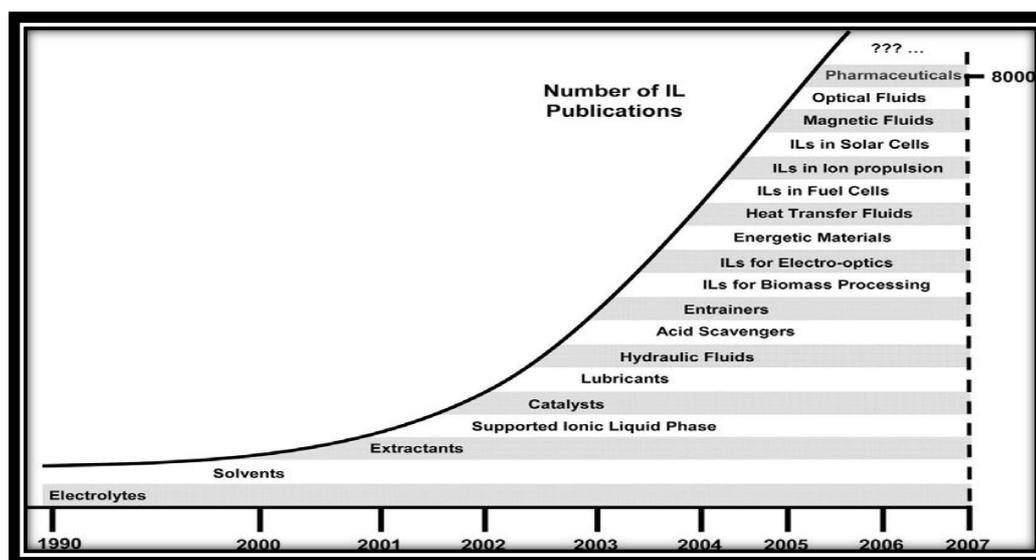


Figure II.6: Growth in the number of IL publications per year and representative areas of interest. (Data achieved from Sci Finder Scholar using the search terms “*ionic liquid*” OR “*ionic liquids*” and then refined by publication year. The data for entire publications

includes the number of patents, and the area of the particular field does not represent the number of publications in the subfield).

In the 2000s as the IL field grew there are three distinct forces led to ILs becoming the hunting of overgeneralizations that still plague the field today, including a plethora or abundance of new researchers in many different disciplines with little or no background in the IL field (or often not even chemistry). The rise in societal significance of green chemistry and sustainability, and the interesting new science and applications assured by the study of ILs. As shown in [Figure II. 7](#) the inherent concepts of ILs as solvents and green chemistry scolded a dramatic increase in publications in this field (which is not yet slowing down) and primarily an increase in the citations to Fuller et al.^(11.31)

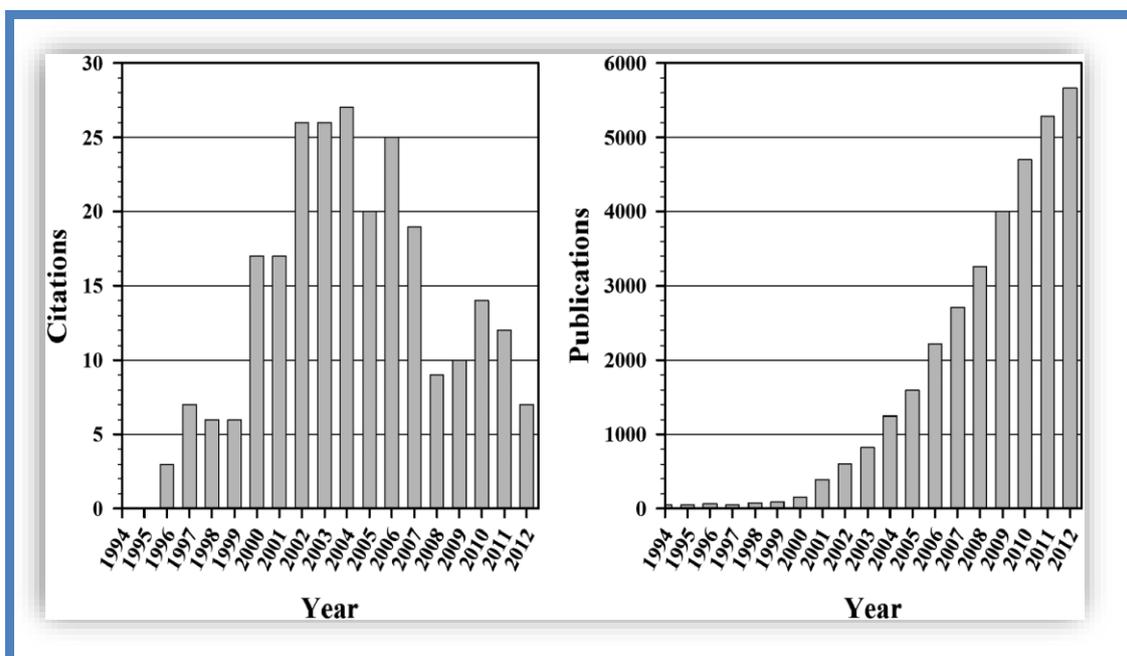


Figure II. Seven: The inherent ideas of ILs as solvents and green chemistry scolded a dramatic increase in publications in this field.

II. 1. 6. Potential Applications of Ionic Liquids

Ionic liquid is very important as a solvent, in recent years; it has been used for an extensive variety of applications at lab scale, such as desulfurization of diesel oil, the recovery of bio-fuels, and supercritical fluid extractions etc. In addition, Ionic liquids have potential as lubricants, in solar cells, for heat storage, lubricants, in nuclear fuel processing, as sol-gel templates and in the dissolution of cellulose in membrane

technology. The various application in different application of ionic liquids are given in Figure II.8a, II.8b.

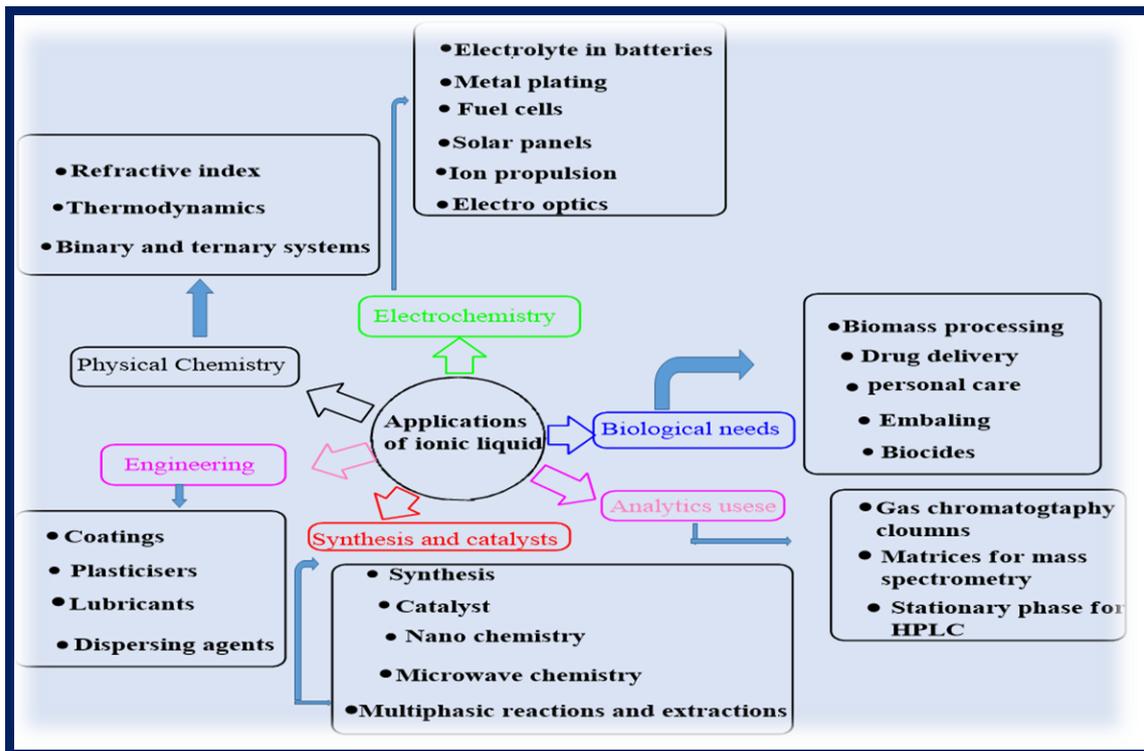


Figure II. 8a: The diverse application of ionic liquids in different field.

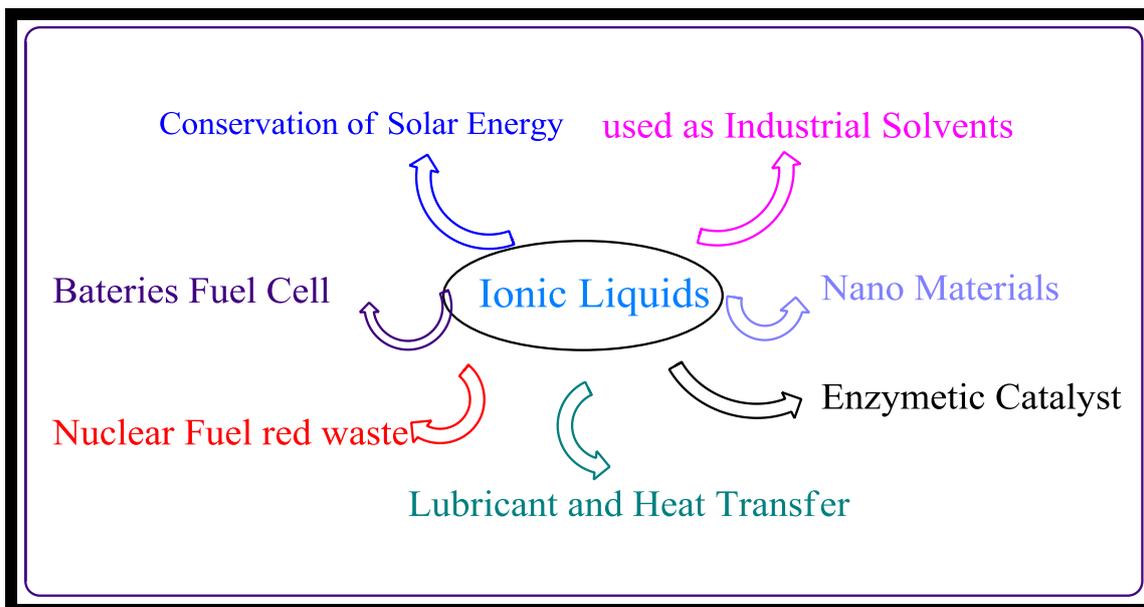


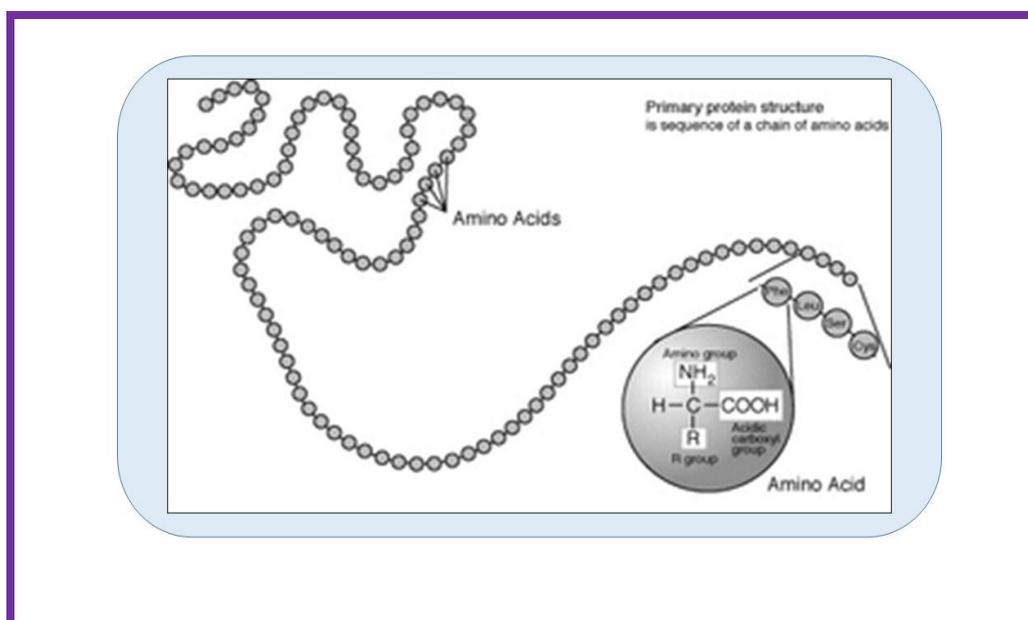
Figure: II.8(b) Selection of applications where ionic liquids have been used

11.2. AMINO ACIDS

A very brief description of amino acids are given in **Chapter: I**. Here utility of amino acids are given as below:

II.2.1 Occurrence and Functions in Biochemistry:

A polypeptide is the unbranched chain of amino acids. Amino acids are very important to make the structural units that make up proteins. Amino acids combine to form short polymer chains which called peptides or longer chains called either polypeptides or proteins. These Polymers are linear within the chain with each amino acid attached to two neighbouring amino acids. The amino acids are added is study through the genetic code from mRNA template, which is a RNA copy of one of the organism's genes.



II. 2.2. Human Nutrition

When the amino acids taken up into the human body from the diet, proteins and other biomolecules are synthesized by using about twenty-two standard amino acids, which are oxidized to urea and carbon dioxide as a source of energy in human body.

Essential	Nonessential	
Histidine	Alanine	Proline*
Isoleucine	Arginine*	Selenocysteine*
Leucine	Asparagine	Serine*

Essential	Nonessential	
Lysine	Aspartic acid	Taurine*
Methionine	Cysteine*	Tyrosine*
Phenylalanine	Glutamic acid	
Threonine	Glutamine*	
Tryptophan	Glycine	
Valine	Ornithine*	

* Essential only in certain cases. (II.32, II.33)

II.2.3. Uses in Technology

In industrial purpose, Amino acids are used for a variety of applications. but their key use is as additives to animal feed, such as soybeans, either have low levels or lack some of the essential amino acids: The food industry is also used as a major user of amino acids, in particular, glutamic acid is used as a flavor enhancer and aspartame (aspartyl-phenylalanine-1-methyl ester) as a low-calorie artificial sweetener. The effect of chelating ability of amino acids has been used in fertilizers for agriculture, to assist the delivery of minerals to plants in order to maintain the correct mineral deficiencies, such as iron chlorosis. The remaining part of production of amino acids are utilized in the synthesis of drugs and cosmetics purpose.

II.2.4. Thermophysical Properties of Amino Acids

Based on different genetic code of amino acids are directly encoded. Based on their properties, amino acid can be divided into several groups. Important factors are hydrophilicity or hydrophobicity, charge, size, and functional groups. the structure of protein and protein-protein interactions are very important properties of amino acids .The water-soluble proteins tend to have their hydrophobic residues (Leu, glu ,asp, Ile, Val, Phe, and Trp) submerged in the middle of the protein, whereas hydrophilic side-chains are manifested to the aqueous solvent. Some modifications of amino acid can readily produce hydrophobic lipoproteins, or hydrophilic glycoproteins. These types of modification permit the reversible targeting of a protein to a membrane. For example, the accumulation and Elimination of the fatty acid palmitic acid to cysteine residues in some signaling proteins result the proteins to attach and then detach from cell membranes.

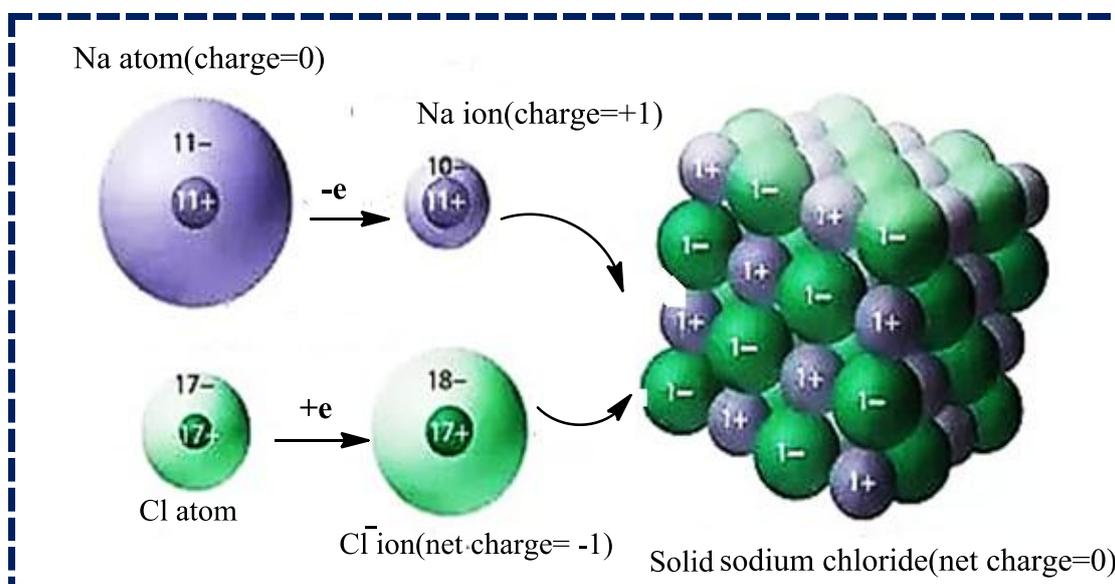
11.3. SOLUTION CHEMISTRY

Solution chemistry is the branch of physical chemistry that studies the change in properties that arise when one substance dissolves in another one. In 'Solution Chemistry' the extent of solvation broadly three types of approaches have been made to estimate. In 'Solution Chemistry'. The first is the solvation approach involving the investigation of viscosity, conductance, of electrolytes and the derivation of various factors associated with ionic solvation, (II.34) the second is the thermodynamic approach by measuring the enthalpies, entropies and free energies of solvation of ions from which factors associated with solvation can be elucidated, (II.35) and the third is to measurements of spectroscopic where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature. (II.36)

Ideality of solution mixture do not obey containing different solute or solvent mixed with another solute or solvent. This deviation from ideal behaviour of solution is expressed in terms of thermodynamic parameters, in case of liquid-liquid mixture by excess properties and apparent molar properties in case of solid-liquid mixtures. The above thermodynamic properties of solvent mixtures that corresponds to the difference between the actual property and the property of the system if it behaves an ideally and this is very useful in the study of molecular interactions and arrangements. In reality, they reflect the interaction that take place between solute-solute, solute-solvent and solvent-solvent species respectively. When the solute molecules or ion added with solvent that modified the structure of solvent as well as solute also modified. The extent of interaction taking place between solute- solute, solute-solvent, solvent-solvent species mainly depends on ion-solvation properties of the mixtures. The assesment or measurement of ion-pairing in these systems is very much important because of its effect on the ionic mobility and hence on the ionic conductivity of the ions in solution. The above phenomenon is associated with the path of paves for research in solution chemistry to clarify the nature of interactions through different experimental studies involving densitometry, viscometry, refractometry and other suitable methods involves and to interpret or explanation the experimental data collected. The whole of the phenomena of solution chemistry could understood in reality only when solute-solute, solute-solvent and solvent-solvent interactions are elucidated and thus the present research work is closely related to the studies of solute-solute, solute –solvent and solvent-solvent interactions in some industrially important liquid systems.

II. 4. VARIOUS DRIVING FORCES OF INTERACTION

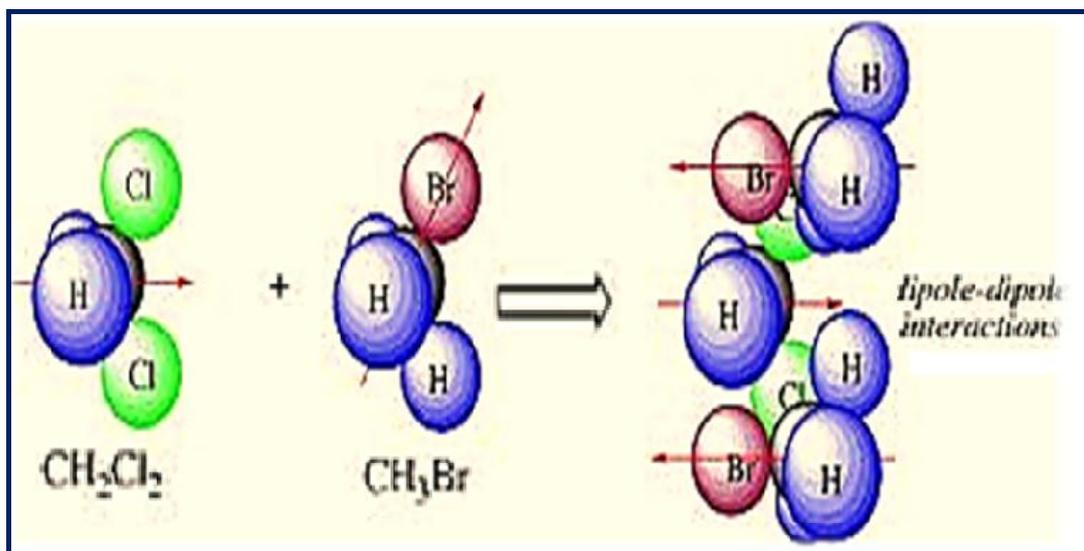
Attraction or repulsion between neighboring particles (atoms, molecules or ions) this term as Intermolecular forces of interactions. In a molecule, the forces of binding nature of atoms are due to chemical bonding. Bond energy is the energy that is required to break the particular bond. For example, it was calculated the average bond-energy for O-H bonds in water is 463kJ/mol. The forces that holding molecules together are generally called intermolecular forces. Typical bond-energy is greater than the energy required to break the apart molecules. Intermolecular forces among the molecules take place very important roles in determining the properties of a substances. [Intermolecular forces](#) are mainly important in terms how molecules can interact with each other and form biological organisms or even life. This connection introduces the interactions consisting between molecules.



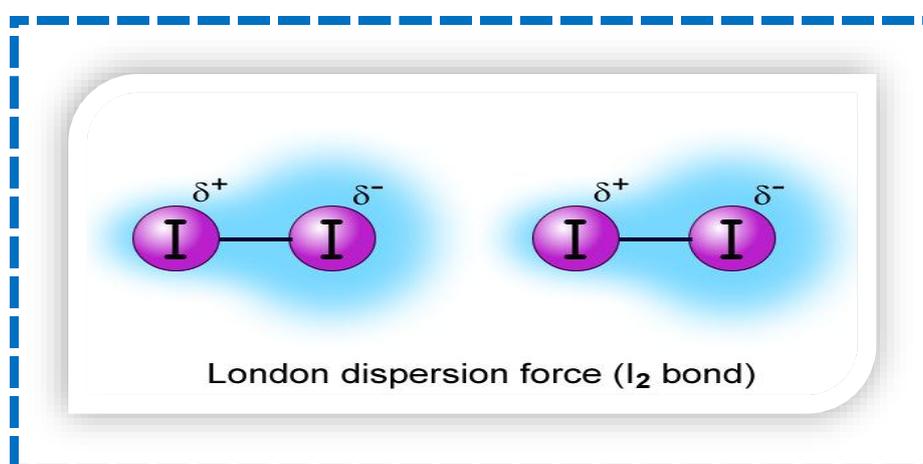
In over-all, there are several types of intermolecular forces can be categorized. The distinguished types are describes in the following.

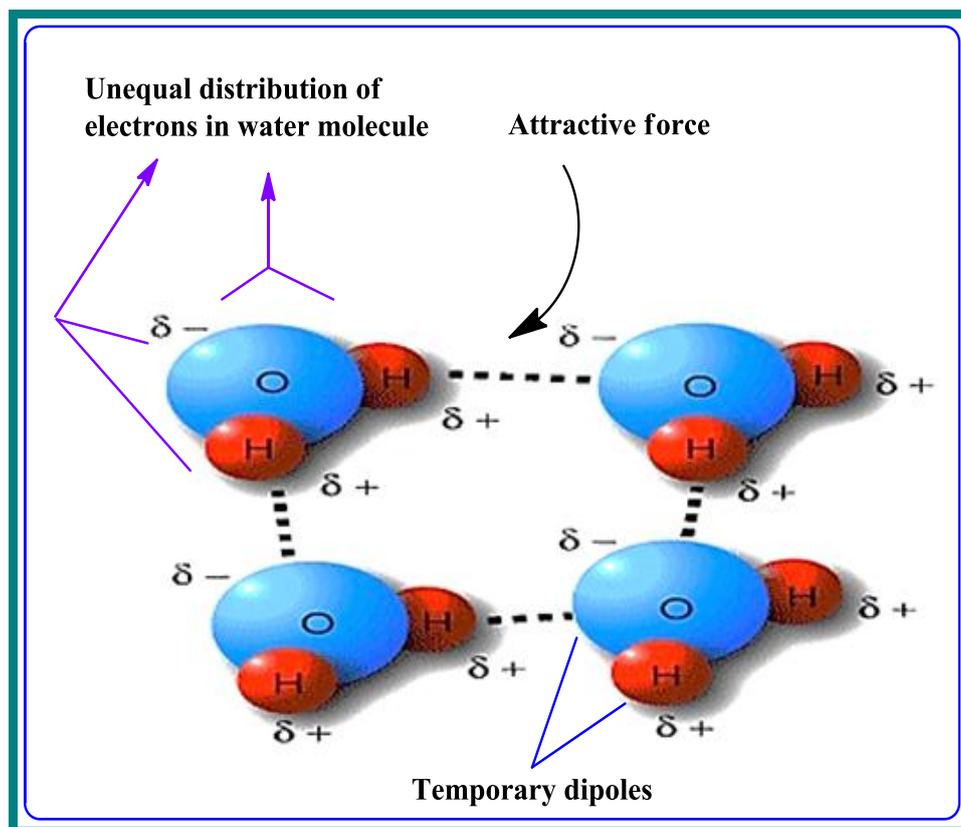
(a) **Strong ionic interaction:** strong ionic interaction is associated with the properties of solids. Higher the lattice energy of solid higher the ionic nature of solid. Here given some ionic solids and their lattice energy respectively, LiF, 1036; LiI, 737; KF, 821; MgF₂, 2957 kJ/mol. It has been observed from the lattice energy value of ionic solids that the strong ionic interaction is associated with the MgF₂ ionic solid.

(b) **Intermediate dipole-dipole forces:** If the substance of molecules have permanent dipole moment, have higher melting point or boiling point than those of similar molecular mass, having no dipole moment.

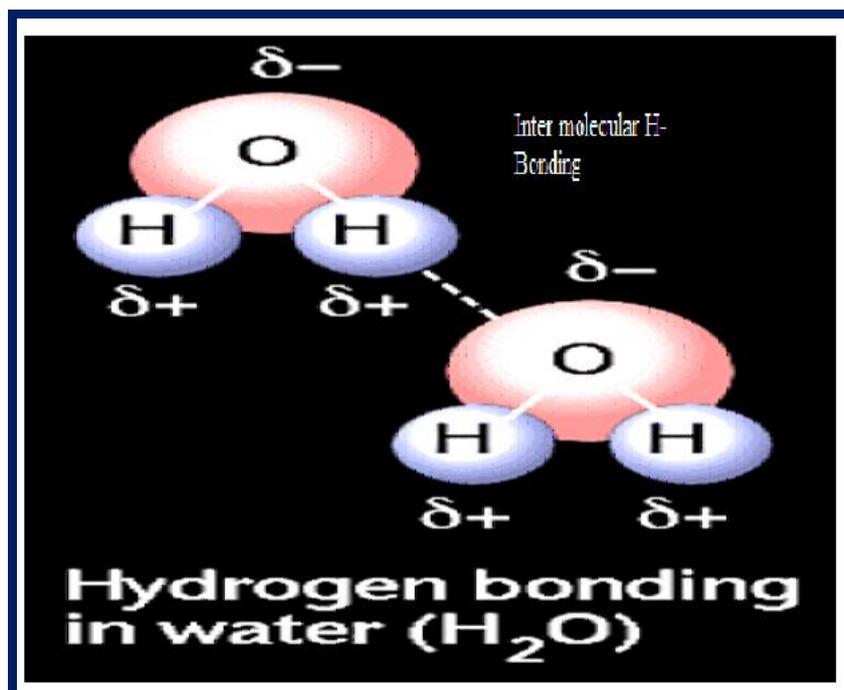


(c) **Weak London dispersion forces or van der Waal's force:** These forces always operate in any substance. The force arisen from induced dipole- dipole interaction and the interaction is obtained due to induce that is weaker than the dipole-dipole interaction. In common, the stronger the van der Waals force of interaction the heavier will be the molecule. As for example, the boiling points of inert gases increase as their atomic masses increases due to stronger Landon dispersion interactions. Weak vander waaal's or Landon dispersion force of interactions is shown by two molecule I_2 and H_2O .

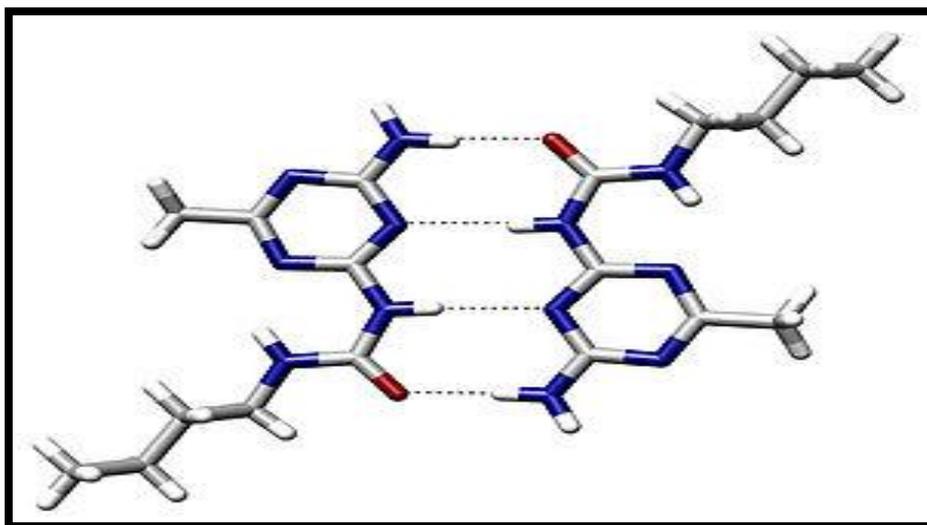




(d)Hydrogen bonding: Hydrogen bonding is considered as the attractive interaction of a [hydrogen](#) atom with an [electronegative](#) atom, such as [nitrogen](#), [oxygen](#) or [fluorine](#) (thus the name "hydrogen bonding," it is not necessary to form covalent bond with hydrogen). The hydrogen must be covalently bonded to another electronegative atom to form a bond. These bonds may be between different molecules (intermolecular) or within different parts of a same molecule (intramolecular). The hydrogen bond energy 5-30KJ/mole is stronger than of a [van der Waals interaction](#), but this bond is weaker than [covalent](#) or [ionic bonds](#). This type of bond generally or often occurs in both inorganic molecules such as water and [organic molecules](#) such as DNA. There are certain substances such as H_2O , HF , NH_3 form hydrogen bonds. The formation of hydrogen bond, which causes some properties (m.p, b.p, solubility) of substance.



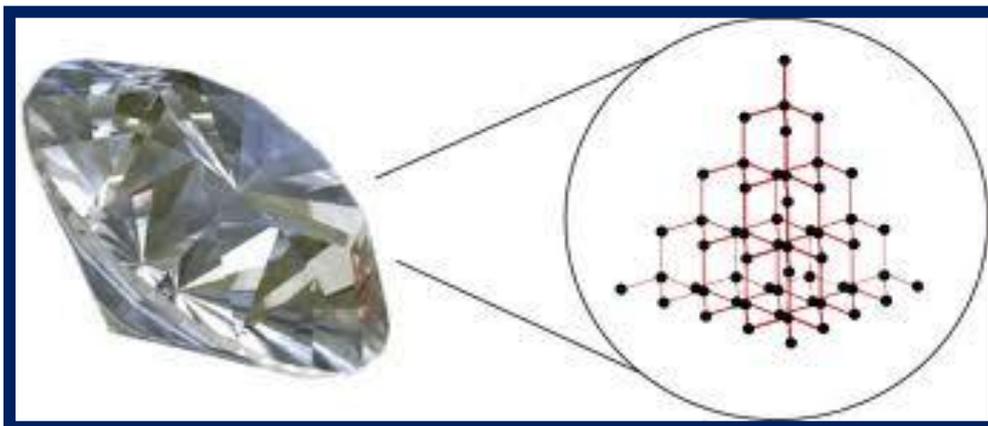
There are another compounds containing OH and NH_2 groups form hydrogen bonds. Molecules of many organic compounds like alcohols, acids, and amino acids amines contain these groups, and thus formation of [hydrogen bonding](#) plays an important role in biological science.



The above cited example is the Intermolecular hydrogen bonding in a [self-assembled](#) dimer complex.

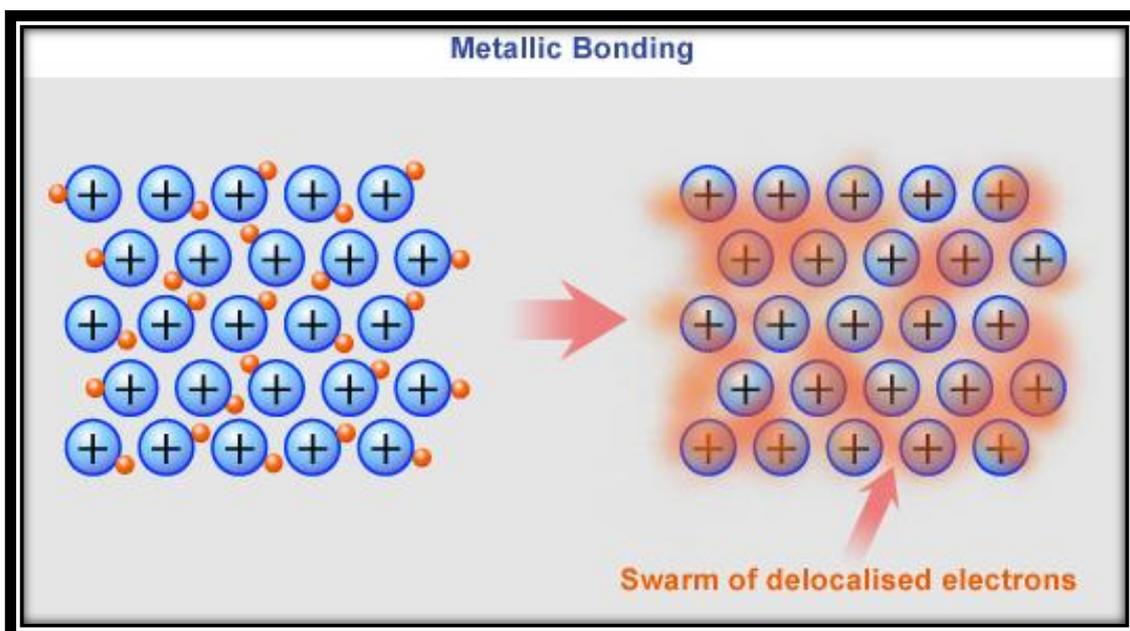
(e)**Covalent bonding:** Covalent is mainly intramolecular force rather than intermolecular force. It is mentioned here, because there are some solids are formed due to formation of covalent bonding. For example, in diamond, silicon, quartz etc., covalent bonding links the whole atoms in the entire crystal structure together. These solids are

very hard, brittle, and have very high melting points. Atoms of molecules in covalent bonding holds atoms tighter than ionic attraction.



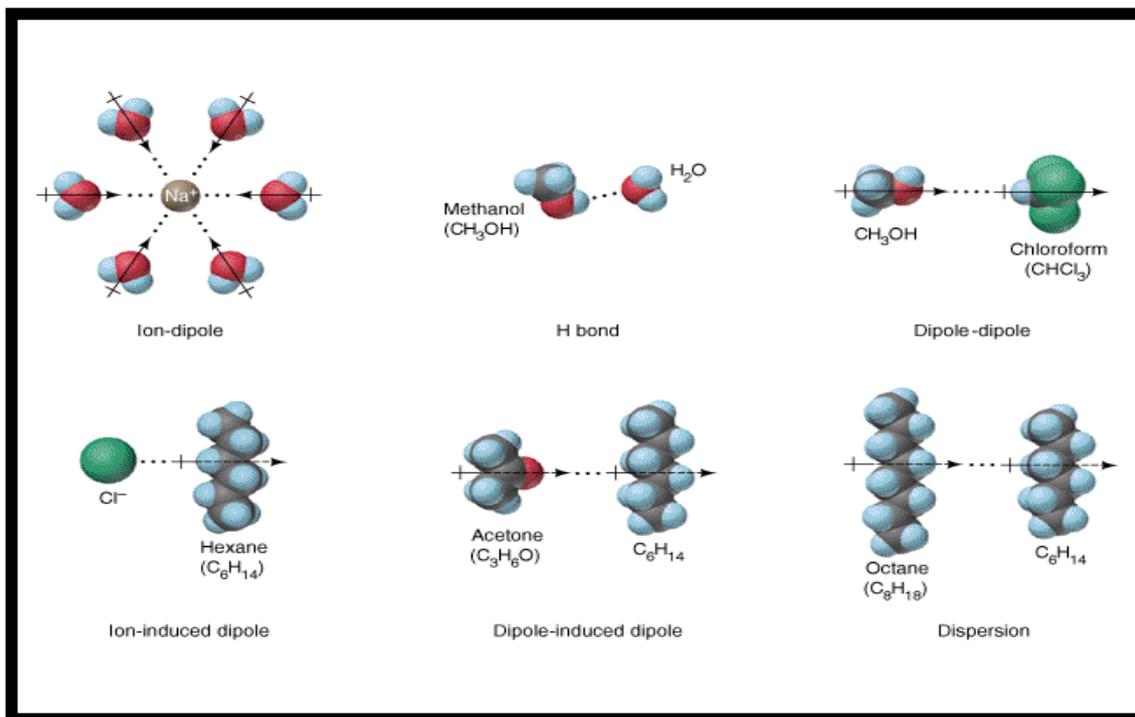
Covalent Bonding in Diamond

(f) **Metallic bonding:** Forces consist between atoms in metallic solids belong to another category. Valence electrons in metals are widespread. The valence electron are not restricted to certain atoms or bonds. Rather than they run freely in the entire solid crystal that providing good conductivity for heat and as well as electric energy. These behaviors of electrons in the solid crystal give exceptional properties such as ductility and mechanical strength to metals.

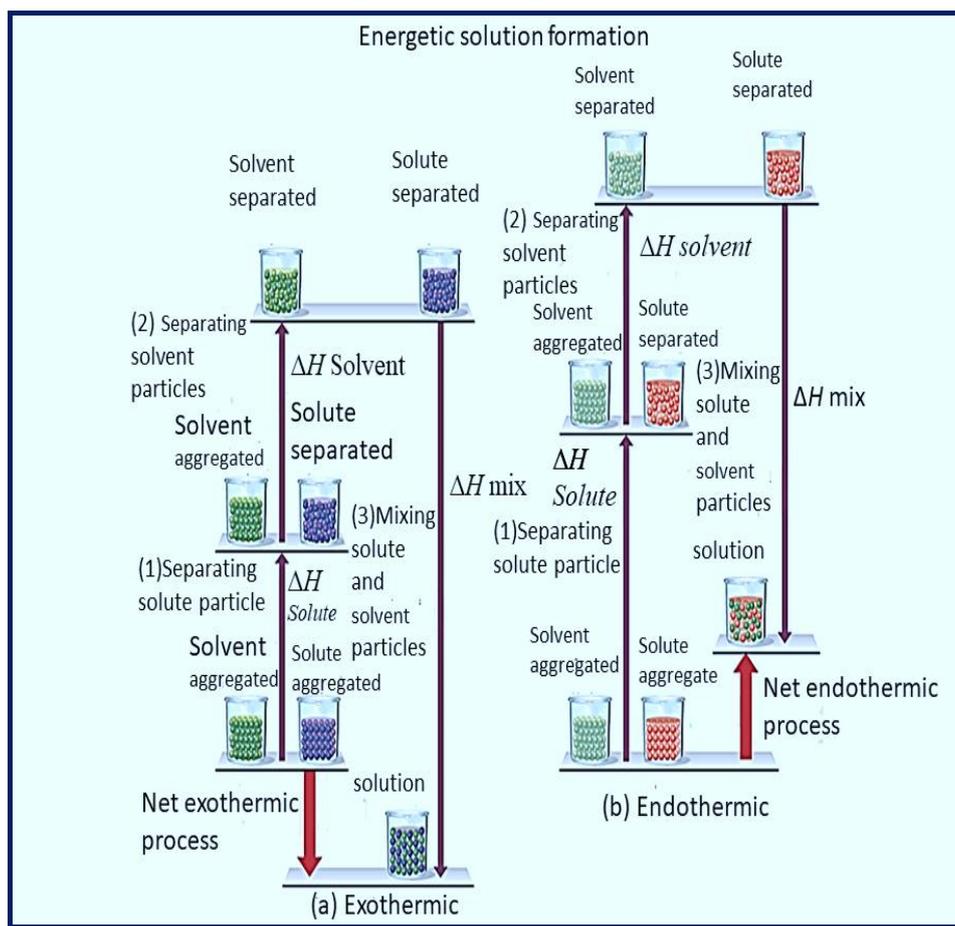


All kinds of of interactions can be present simultaneously for many substances. Usually, intermolecular forces of substance are discussed together with "[The States of](#)

Matter". Intermolecular forces also play vital or important roles in solutions. A brief summary of the interactions is illustrated in the following diagram:



In solution chemistry, the majority of reactions are of chemical or biological in nature. It was supposed earlier that the solvent molecules only provides an inert medium for chemical reactions. The important of ion-solvent interactions was understood after intensive studies in aqueous, non-aqueous and mixed solvents. (II.37, II.38) The solubility of a substance depends on Intermolecular forces. For “Like” intermolecular forces for solute molecule and solvent molecule will make the solute soluble in the solvent frequently. In this regard, the value of ΔH_{soln} is sometimes negative and sometimes positive.



Furthermore, solubility is affected by the following factor

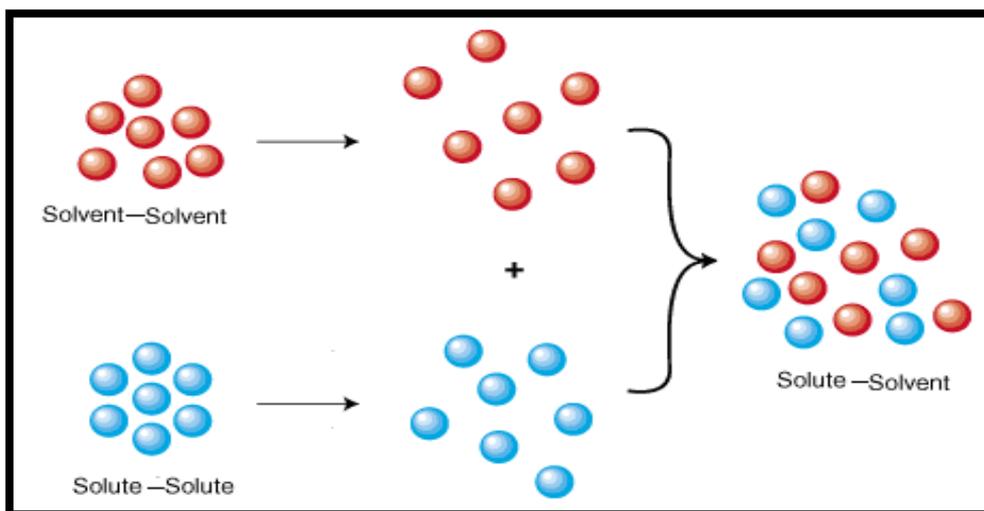
- (i) Due to ion–dipole force the energy of attraction affects the solubility.
- (ii) Lattice energy (the ions holding together in the lattice).
- (iii) Depends on Charge of ions: larger charge means higher lattice energy.
- (iv) Size of the ion: larger the size of ions mean smaller lattice energy.

II. 5. INTERACTIONS IN SOLUTION SYSTEMS

There are three types of interactions that exist in the solution systems are:

- (a) Solvent–solvent interactions:** In this interaction, less energy is required to break weak bonds between solvent molecules. The solvent molecules isolated from each other .
- (b) Solute–solute interactions:** more energy is required to break intermolecular bonds between the solute molecules. In this process solute molecules separate from each other.

- (c) **Solute–solvent interactions:** Since such type of interaction, value of ΔH is negative since bonds are formed easily between them. Solvent and solute molecules mixed together.



The macroscopic properties are usually quite well known for liquid systems, the studied of microscopic structure is often much less used. The characterized of liquid phase by local order and long-range disorder, and to study processes in liquid systems, it is therefore very important or valuable to use methods that prod the local surrounding of the constituent particles. This is also true for solvation processes: a local probe is very important or significant to obtain insight into the physical and chemical processes going on.

11.6. INVESTIGATION ON DIFFERENT KIND OF INTERACTIONS

The ions of the salt dissociate from each other and associate with the dipole of the water molecules at the time when salt is dissolved in water, the ions of the salt dissociate from each other. This result in a solution called an ‘electrolyte’.

This means that the forces of interaction (attraction or repulsion) depending on whether like or unlike charges are closer together. Motion of dipoles takes place in a liquid system, themselves to form attractive interactions with their neighbours, but their thermal motion makes some instantaneous configurations unfavourable.

Therefore, if a crystal salt is put in water, the polar water molecules are attracted to ions on the crystal surfaces. The water molecules gradually surround in crystal and isolate the surface ions very effectively. The ions become hydrated. They gradually move

away from the crystal very easily into the solution. 'Dissociation' is the process of separation of ions from each other. The surrounding of solute molecules by solvent molecules is called 'solvation'. When the ions are dissociated, each ionic species in the solution acts as though it were present alone. Thus, a solution of sodium chloride performs as a solution of sodium ions and chloride ions.

The determination of thermodynamic, transport, acoustic and optical properties of different electrolytes in various solvents would thus provide an important step in this direction. Naturally, in the development of theories, dealing with electrolyte solutions, much attention has been devoted to 'ion-solvent interactions' which are the controlling forces in infinitely dilute solutions where ion-ion interactions are absent. It is very much important to separate these functions into ionic contributions to determine the contributions due to cations and anions in the solute-solvent interactions. Thus ion-solvent interactions play a crucial role to understand the thermophysical, thermodynamic and physicochemical properties of solutions.

The ion-solvent interactions can also be studied from the thermophysical, and thermodynamic point of view, where the changes of free energy, enthalpy and entropy, etc. associated with a particular reaction. Qualitatively and as well as quantitatively estimated various thermophysical parameters, from which concluded regarding the factors associated with the ion-solvent interactions occurred in the studied solutions.

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

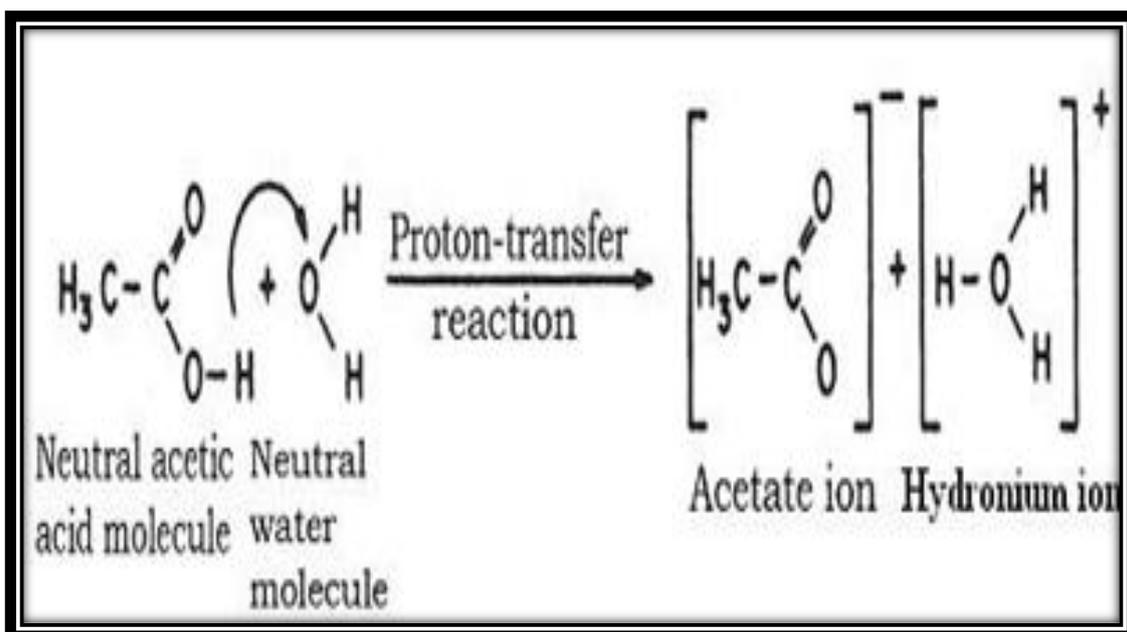
We shall mainly dwell upon the different outlook of these thermophysical, thermodynamic, transports and optical properties as the present research work is warmly allied to the studies of ion-ion, ion-solvent and solvent-solvent interactions.

II.6.1. Ion-Solvent Interaction

Ion-solvation is a fact of primary attention in many framework of chemistry because solvated ions are omnipresent on Earth. Hydrated ions occur in aqueous solution in many chemical and biological systems.^(II.39) Solvated ions appear in high concentrations in living organisms, where their presence or absence can fundamentally alter the functions of life. Ions solvation in organic solvents, mixtures with water and

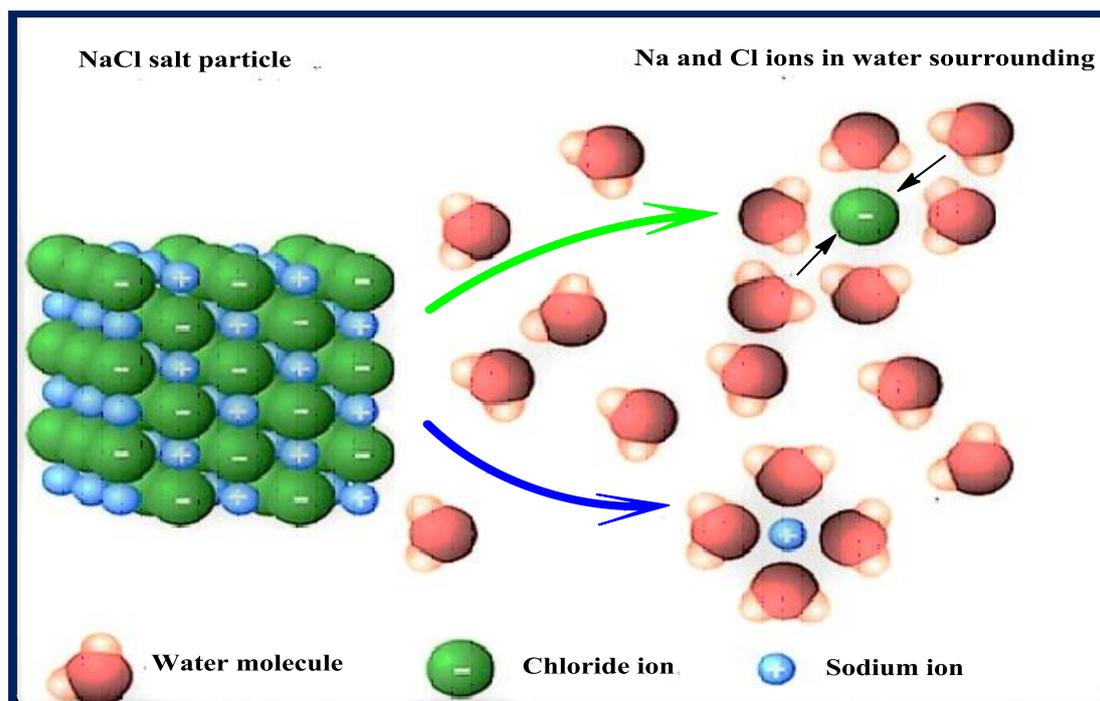
other organic solvents are very common. ^(II.40) The exchange of solvent molecules around ions in solutions is fundamental clue to the understanding of the reactivity of ions in solution. ^(II.41) Solvated ions also play a key role in electrochemical applications, where for instance the conductivity of electrolytes depends on ion-solvent interactions. ^(II.42)

The mobile ions formation in solution is a basic aspect to electrochemistry. There are two distinct ways that mobile ions are formed in solution to create ionically conducting phases. As for example, first one is an illustrated for aqueous acetic acid below.



Producing ionic solutions by the chemical method.

The second one involves dissociation of a solid lattice of ions such as the lattice of sodium chloride. In case ion formation, the solvent molecules colliding with the walls of the crystal gives the ions in the crystal lattice is energetically a better deal than they have within the lattice. It attracts them out and into the solution. Thus, there is an appreciable energy of interactions between the ions and the solvent molecules. These types of interactions are collectively termed as ion-solvent interactions.



The spherically symmetrical electric field of the ion may pull apart solvent dipoles out of the solvent lattice and orient them with appropriate charged end toward the central ion. Thus, viewing the ion as a point charge and the solvent molecules as electric dipoles, ion-dipole forces become the principal source of ion-solvent interactions. It was believed earlier that the solvent molecule only provides an inert medium for chemical reactions. The consequences of ion-solvent interactions was understood after extensive studies in aqueous, non-aqueous and mixed solvents. ^(II.43-II.52)

Most of the chemical processes of individual and also biological importance occur in solution. The role of solvent is so great that million fold rate changes take place in some reactions simply by changing the reaction medium. 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. With the exceptions of heterogeneous catalytic reactions, most reactions in technical importance occur in solutions. In addition, molecules not only have to travel through a solvent to their reaction partner before reacting, but also need to present a sufficiently unsolved rate for collision. The solvent governs the movement and energy of the reacting species to such an extent that a reaction undergoes a several-million fold change in rate when the solvent is changed. 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. Still our knowledge of molecular interactions in water is extremely limited.

Moreover, the uniqueness of water as a solvent has been questioned^(II.53, II.54) and it has been realized that the studies of other solvent media like non-aqueous and mixed solvents would be of appreciable help in understanding different molecular interactions and a host of complicated phenomena. The organic solvents have been classified on the basis of dielectric constants, organic group types, acid base properties, or association through hydrogen bonding⁽³⁹⁾ donor-acceptor properties^(II.55, II.56) hard and soft acid-base principles^(II.57) etc. As a consequence, the different solvents show a wide change in properties, ultimately influencing their thermophysical, thermodynamic, transport and acoustic properties qualitatively and quantitatively, in presence of electrolytes and non-electrolytes in these solvents. The determination of different thermodynamics parameters like thermophysical, thermodynamic, transport and acoustic properties for various electrolytes or non-electrolytes in a variety of solvents would thus provide important information in this direction. In future, in the improvement of theories of electrolytic solutions, much attention has been devoted to the controlling forces 'ion-solvent interactions' in infinitely dilute solutions where in ion-ion interactions are almost absent. By separating these functions into ionic contributions, it is possible to determine the contributions of cations and anions in the ion-solvent interactions. 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 interactions of solvent-solvent in solution become predominant, though the isolated picture of any of the forces is still not known completely to the solution chemist.

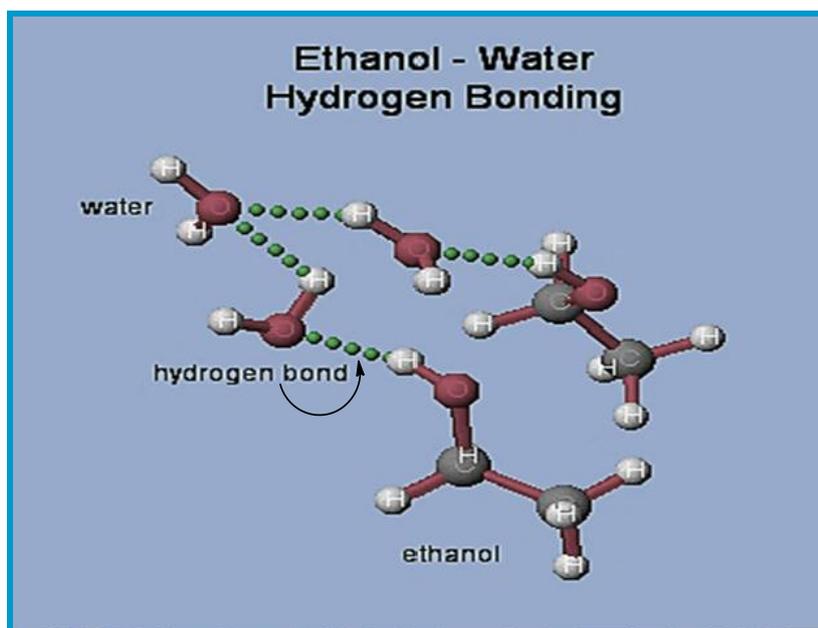
Qualitative analysis of ion-solvent interactions can be studied by FTIR spectrometry.^(II.58, II.59) The spectral solvent shifts or the chemical shifts can determine the qualitative and quantitative nature of ion-solvent interactions. The real understanding of the ion-solvent interaction is a very difficult task. The outlook embraces a wide range of topics but we concentrated only on the measurement of transport properties like viscosity, conductance etc.; thermophysical, thermodynamic properties as apparent or partial molar volumes, apparent molar adiabatic compressibility, and spectral properties as FTIR spectroscopy ,uv- visible spectroscopy etc .

II. 6.2. Ion-Ion Interaction

Ion-solvent interactions are only a part of the history of an ion related to its environment. The mutual interactions between these ions represent the essential part 'ion-ion interactions'. The degree of ion-ion interactions that affects the properties of solution and depends on the nature of electrolyte under investigation. Interactions of Ion-ion in general, are stronger than ion-solvent interactions. Theoretically ion-ion interaction occurring in dilute electrolytic solutions is now well understood, but ion-solvent interactions or ion-solvation remains a complex process. While proton transfer reactions are particularly sensitive to the nature of the solvent, it has become cleared that the solvents significantly modify the majority of the solutes. Conversely, the nature of the strongly structured solvents, such as water, is substantially modified by the presence of solutes. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute/ion-ion, solute-solvent/ ion-solvent and solvent-solvent interactions are elucidated. Thus, the present thesis is affectionately related to the studies of solute-solute/ion-ion, solute-solvent/ ion-solvent and solvent-solvent interactions in some liquid systems.

II. 6. 3. Solvent-Solvent Interactions (Theory of Mixed Solvents)

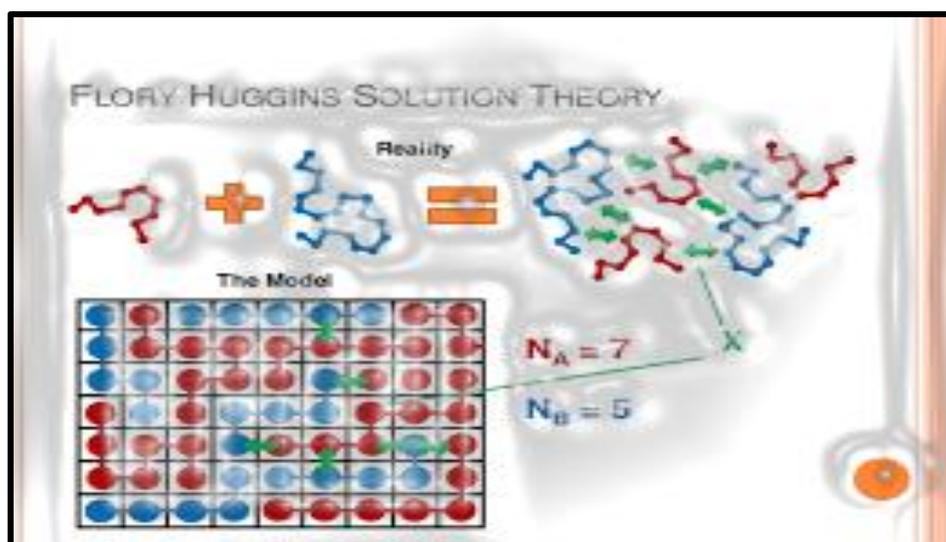
As the mixed and non-aqueous solvents are increasingly used in chromatography, solvent extraction, in the elucidation of reaction mechanism, in preparing high density batteries, etc. a number of molecular theories, based on either the radial distribution function or the choice of suitable physical model, have been developed for mixed solvents. L. Jones and Devonshire^(II.60) both were first to evaluate the thermodynamic functions for a single fluid in terms of interchange energy parameters. They used "Free volume" or "Cell model". Prigogine and Garikian^(II.61) extended the above methodology to solvent mixtures. Prigogine and Bellemans^(II.62) developed a two fluid version of the cell model. They found that while excess molar volume (V^E) was negative for mixtures with molecules of almost same size, it was large positive for mixtures with molecules having small difference in their molecular sizes. Treszczanowicz *et. al.*^(II.63) suggested that V^E is the result of several contributions from several opposing effects. These may be divided arbitrarily into three types, viz., physical chemical and structural. This is the example of two solvent namely ethanol and water where solvent –solvent interactions can be explain by the hydrogen bonding between two solvent.



Physical contributions contribute a positive term to V^E . The chemical or specific intermolecular interactions result in a volume decrease and contribute negative values to V^E . The mostly structural contributions are negative and arise from several effects, especially from interstitial accommodation and changes in the free volume. The actual volume change would therefore depend on the relative strength of these effects. However, it is generally assumed that when V^E is negative, viscosity deviation ($\Delta\eta$) may be positive and vice-versa. This supposition is not a real one, as evident from some studies. ^(II.64, II.65) Rastogi *et al.* ^(II.66) therefore suggested that the observed excess property is a combination of an interaction and non-interaction part. The non-interaction part of the molecules in the form of size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter. Pitzer ^(II.67), L. Huggins ^(II.68) introduced a new approach in his theory of conformal solutions. Using a simple perturbation approach, he showed that the properties of mixtures could be obtained from the knowledge of intermolecular forces and thermophysical and thermodynamic properties of the pure components.

Rowlinson *et al.* ^(II.69- II.71) reformulated the average rules for Vander Waal's mixtures and their calculated values were in much better agreement with the experimental values even when one fluid theory was applied. The more recent independent effort is the perturbation theory of Baker and Henderson. ^(II.72) a more successful approach is due to Flory who made the use of certain features of cell theory ^(II.73, II.75) and developed a statistical theory for predicting the excess properties of binary

mixtures by using the equation of state and the properties of pure components along with some adjustable parameters. This theory is applicable to mixtures containing components with molecules of different shapes and sizes. Patterson and Dilamas^(II.76) united both Prigogine and Flory theories to a unified one for rationalizing various contributions of free volume, internal pressure, etc. to the excess thermodynamic properties. Heintz^(II.77-II.79) and coworkers recommended a theoretical model which is based on a statistical mechanical derivation and accounts for self-association and cross association in hydrogen bonded solvent mixtures is termed as Extended Real Associated Solution model (ERAS). The combination of the effect of association with non-associative intermolecular interaction occurring in solvent mixtures based on equation of state developed originally by Flory. Subsequently the ERAS model has been successfully applied by many workers^(II.80- II.82) to describe the excess thermodynamic properties of alkanol-amine mixtures. A new symmetrical reformation on the Extended Real Association (ERAS) model has been described in the literature.^(II.83) The symmetrical-ERAS (S-ERAS) model that makes it possible to discuss the excess molar enthalpies and excess molar volumes of binary mixtures containing very similar compounds described by extremely small mixing functions.^(II.84) Gepert *et al.*^(II.85) applied this model for studying some binary systems containing alcohols.



11.7. Volumetric Measurements

The concept of volumetric information includes 'Density' as a function of composition on the bases of weight, volume and mole fraction and excess volumes of mixing. Thermodynamic assets of solutions are not useful for estimating the feasibility

of reactions in solution, but also offer one of the better methods of investigation of theoretical aspects of solution structure. This is particularly true for the heat capacity standard partial molal entropy and volume of the solutes, values of which are sensitive to the rearrangement of solvent molecules around a solute molecule. The above mentioned physical parameters are very need for interpreting the solute-solvent as well as solute – solute interactions.

Various ideas regarding molecular processes in solutions such as, hydrophobic hydration^(II.86) electrostriction^(II.87), micellization^(II.88) and co-sphere overlap during solute-solute interactions^(II.89) have to a large extent been resulting and explained from the partial molar volume data of many compounds.

11.7.1 APPARENT AND PARTIAL MOLAR VOLUME

The molar volume of a pure substance can be determined by using the data of density. The multi-component systems in a complex such as solutions, it is very easier to define a system in terms of the intrinsic or molal properties rather than the extensive properties. Any extensive property such as partial molal volume of a system can be calculated as the sum of the respective if all the components have a known concentration. Although the preservative definition of partial molal properties is suitable, direct measurement of these solution properties are difficult, due to interactions with other species contribute to partial molal properties. When dealing with solutions it is more common to measure the apparent molal quantities, ϕ_Y , which can be defined as the change in property, Y , due to a known amount of solute in a known amount of solvent, assuming the contribution by the solvent is the same as that of the pure species. In other words, all changes in the state properties can be attributed to the presence of the solute, even if these changes contribute to a change in partial molal property of the solvent. The apparent molal property of any solute, $\phi_{2,Y}$ can be defined as

$$\phi_{2,Y} = \frac{Y - n_1 \bar{\phi}_Y^0}{n_2} \quad (\text{II. 1a})$$

Where, n_1 and n_2 characterize the mole of the solvent and solute respectively, in the system. $\bar{\phi}_Y^0$, represents the partial molal property of the pure solvent. Then the solvent is expected to contribute a definite, constant quantity for all concentration of solute

molecules at particular temperature and pressure, the partial derivative of the extensive property with respect to the number of moles of solute molecules can be well defined in terms of the apparent molal quantity:

$$\left(\frac{\partial Y}{\partial n_2}\right)_{n_1, T, P} = \left(\frac{\partial \phi_{2,Y}}{\partial n_2}\right)_{n_1} + \phi_{2,Y} \quad (\text{II. 1b})$$

Eqs (II.1a) and (II.1b) displays the partial molal property can be calculated if the apparent molal property and its derivative with respect to moles of solute is known. In other words, if any fitting of the above equations for the apparent molal property with respect to any concentration scale, which is in good, agreement with experimental data is known, the apparent molal property can also be found out at infinite dilution of the experimental solutions. Theoretically, as the concentration approaches to zero, also the apparent molal property approaches to the partial molal property of the solute at infinite dilution, because by definition the solvent is already expected to be in its pure form. If the apparent molal property is supposed to reflect the apparent molal property of the solute molecules only and not for the the solute-solvent complex, then at infinite dilution the apparent molal property, $\phi_{2,Y}^{\infty}$ would be equal to the standard state molal property of the solute, as defined by Henry's law. Ignoring the earlier equality, equation of state developed for standard state partial molal variables have been used effectively to describe partial molal quantities at infinite dilution.

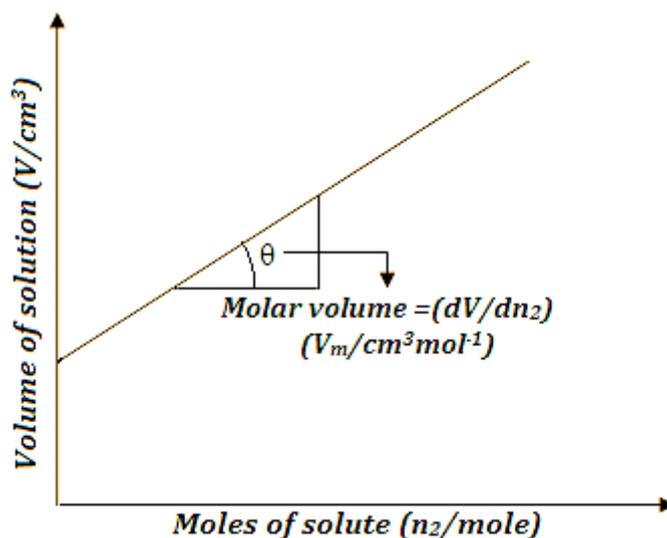


Figure II.9a: molal volume explanation diagram

The easiest process to explain this is in terms of the molal volume, V_m that is given in the Figure II.9a, with adding the solute molecules, and the volume simultaneously increases. A dissolved solute molecule has its individual property, referred to as partial molal property. Figure II.9b shows an extremely large tank containing one $\text{mol}\cdot\text{L}^{-1}$ solution of a solute with a certain volume, shown at position (a). If 1 mole of solute is added to the solution in the container, the volume will increase to (b); however, the concentration of the other species of the solution will not change by any noticeable amount.

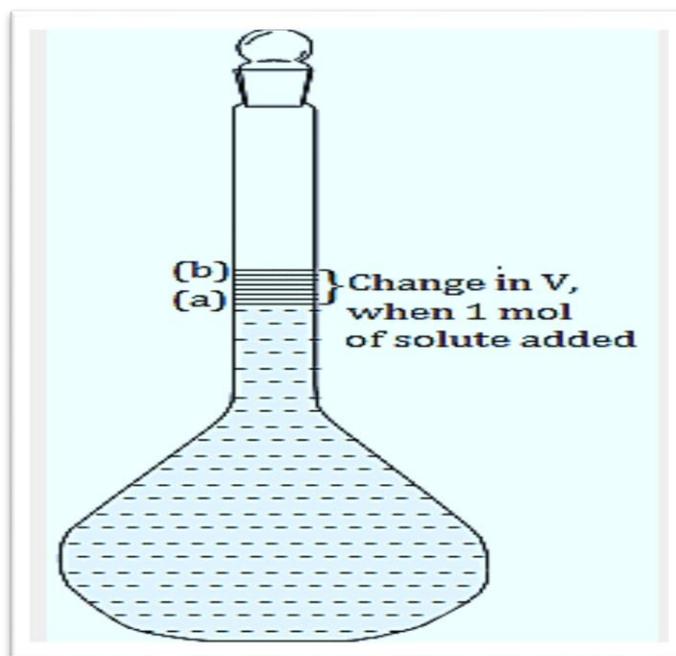


Figure II.9b: A diagram to support in the explanation of a partial molal volume

Therefore, for a two-component system, where one component is the solvent and another component is solute, the total volume of the system can be represented as the sum of the partial molal volumes of the solvent, \bar{V}_1 and the solute, \bar{V}_2 :

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad (\text{II. 1c})$$

Dividing equation (11.1c) by $n_1 + n_2$, the molal volume of the solution is obtained as:

$$V_m = x_1 \bar{V}_1 + x_2 \bar{V}_2 \quad (\text{II. 1d})$$

Where, x_1 and x_2 denote the mole fraction of the solvent molecule and the solute molecule, respectively. The property of partial molal of a solute is defined as the change in the total property of the system with respect to the change in the number of moles of solute added, with all other variables (T , P , and the amount of the solvent) are detained constant. An alternative, broadly used property of the solute is the apparent molal property. The apparent molal volume of the solute in solution is the volume that should be attributed to the solute molecules, if it is expected that in pure state of solvent contribute the exact volume.

Under this supposition, Harned and Owen defined the apparent molal volume of the solute, $\phi_{2,V}$ is the difference between the total volume (and the total molal volume) and the partial molal volume of the pure solvent (\bar{V}_1^0) divided by the number of moles (or the mole fraction) of the solute present:

$$\phi_{2,V} = \frac{V - n_1 \bar{V}_1^0}{n_2} \quad (\text{II. 1e})$$

$$\phi_{2,V} = \frac{V_m - x_1 \bar{V}_1^0}{x_2} \quad (\text{II. 1f})$$

In investigation, at constant temperature and pressure, \bar{V}_1^0 is generally considered constant over the range of solute concentration. Hence, $\phi_{2,V}$ can be easily obtained or calculated by using Eq. (II. 1e) or (II. 1f) when the total volume or molal volume of solution mixture is known. In order to find out the apparent molal volume of a solute Eq. (II. 1e) can be modified by using density of the solution containing the solute and the density of the pure solvent, ρ and ρ_0 , respectively. Supposing there is 1 kilogram (kg) of solvent:

$$n_1 = \frac{1}{M_1}, \quad \text{therefore,} \quad V = \frac{\bar{V}_1^0}{M_1} + m_2 \cdot \phi_{2,V} \quad (\text{II. 1g})$$

Where, M_1 denotes the molal mass of the solvent.

Since $\rho_1 = \frac{\bar{V}_1^0}{M_1}$, Eq. (II. 1g) becomes:

$$V = \frac{1}{\rho_1} + m_2 \cdot \phi_{2,v} \quad (\text{II. 1h})$$

Where, m_2 is the molality of the solute, which is equivalent to n_1 (if 1kg of solvent is present). The total mass of the solution will be collected of the mass of the solvent (1kg) and the mass of the solute ($m_2 \cdot M_2$). Since (v) volume is the ratio of mass to density, the equation becomes:

$$\frac{1 + m_2 \cdot M_2}{\rho_1} = \frac{1}{\rho_1} + m_2 \cdot \phi_{2,v} \quad (\text{II. 1i})$$

An equation for apparent molal volume for 1 kg of the solute is obtained by rearranging this Eq. (II. 1h) and solving for $\phi_{2,v}$.

$$\phi_{2,v} = \frac{\rho_2 - \rho_1}{m_2 \rho_1 \rho_2} + \frac{M_2}{\rho_2} \quad (\text{II. 1j})$$

However, the volume contributed to a solvent by the addition of one mole of an ion is difficult to determine. This is so because, upon access into the solvent, the ions change the volume of the solution due to a breakup of the solvent structure near the ions and the compression of the solvent under the effect of the ion's electric field i.e., Electrostriction. The effective volume of an ion in solution and the partial molar volume obtained from a directly attainable quantity apparent molar volume (Φ_v). The following relation is used to calculate the apparent molar volumes of solute molecules: ^(II.90)

$$V_\phi = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \quad (\text{II.2})$$

Where, ρ_0 and ρ are the densities of solvent and solution respectively M is the molecular weight of the solute and c is the molarity of the solution.

The partial molar volumes, $B_{K^+} = B_{Cl^-} \bar{V}_2$ can be obtained from the following equation ^(II.91)

$$\bar{V}_2 = V_\phi + \frac{(1000 - cV_\phi)}{2000 + c^{3/2} \left(\frac{\partial V_\phi}{\partial \sqrt{c}} \right)} c^{1/2} \left(\frac{\partial V_\phi}{\partial \sqrt{c}} \right) \quad (\text{II.3})$$

The expression of the concentration dependence of the apparent molar volume and the extrapolation of the apparent molar volume of electrolyte to infinite dilution have

been made by four main equations over a period of years. Namely the Masson equation, (II.92) the Redlich-Meyer equation, (II.93) the Owen-Brinkley equation, (II.94) and the Pitzer equation. (II.95) The apparent molar volume of electrolyte, V_ϕ vary with the square root of the molar concentration by the following linear equation:

$$V_\phi = V_\phi^0 + S_v^* \sqrt{c} \quad (\text{II.4})$$

Where, V_ϕ^0 is the limiting apparent molar volume (equal to the partial molar volume at infinite dilution), and S_v^* is the experimental slope. The majority of V_ϕ data in

Water (II.96) and nearly all V_ϕ data in non-aqueous (II.97-II.101) solvents have been extrapolated

To infinite dilution with equation (II.4).

The temperature dependence of V_ϕ^0 for various investigated electrolytes in various solvents expressed by the general equation as follows:

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \quad (\text{II.5})$$

The limiting apparent molar expansibilities (ϕ_E^0) of the electrolyte in solutions can be calculated from the

$$\phi_E^0 = \left(\frac{\partial V_\phi^0}{\partial T} \right)_p = a_1 + 2a_2 T \quad (\text{II.6})$$

The limiting apparent molar expansibilities (ϕ_E^0) of the solute molecule in solutions change in magnitude with the variation of temperature. During the past few years, different workers emphasized that (S_v^*) is not the sole criterion for determining the structure-making or structure-breaking nature of any solute. Hepler 73 developed a technique of examining the sign of ($\partial^2 V_\phi / \partial T^2$) for various solutes in terms of long range structure-making and breaking capacity of the solutes in solution using the general thermodynamic expression:

$$\left(\frac{\partial C_p}{\partial P} \right)_T = \left(\frac{\partial^2 V_\phi^0}{\partial T^2} \right)_p \quad (\text{II.7})$$

Depends based on the above expression, it has been assumed that structure-making solutes should have positive value, where as the structure breaking of solute molecules should have negative value.

However, Redlich and Meyer (II.102) have shown that equation (11.7) cannot be more than a limiting law and for a given solvent and temperature the slope, (S_v^*) should depend only upon the valence type. They suggested an equation for representing as follows:

$$V_\phi = V_\phi^0 + S_v \sqrt{c} + b_v c \quad (\text{II.8})$$

$$\text{Where,} \quad S_v = Kw^{1/2} \quad (\text{II.9})$$

S_v^* is the theoretical slope, based on molar concentration, including the valence factor:

$$w = 0.5 \sum_i^j Y_i Z_i^2 \quad (\text{II.10})$$

$$\text{And,} \quad K = N^2 e^2 \left(\frac{8\pi}{1000 \epsilon^3 RT} \right)^{1/2} \left[\left(\frac{\partial \ln \epsilon}{\partial p} \right)_T - \frac{\beta}{3} \right] \quad (\text{II.11})$$

Where (β) is the compressibility of the solvent? However, the deviation of dielectric constant with pressure was not known accurately sufficient, even in water, to calculate exact values of the theoretical limiting slope.

Thus for polyvalent electrolytes, the more complete Owen-Brinkley equation (II.103) can be used to help in the extrapolation to infinite dilution and satisfactorily represent the concentration dependency of The Owen-Brinkley equation resulting by including the ion-size parameter is given by:

$$V_\phi = V_\phi^0 + S_v \tau (Ka) \sqrt{c} + 0.5 w_v \theta (Ka) c + 0.5 K_v c \quad (\text{II.12})$$

Where the symbols have their usual significance. However, equation (11.12) has not been widely employed for the treatment of results for non-aqueous solutions

Lately, Pogue and Atkinson ^(II.104) to fit the apparent molal volume data have used the Pitzer formalism. The Pitzer give an equation for the determination of apparent molar volume of a single salt $M \gamma_X$ is:

$$\phi_V = \phi_V^0 + V |Z_M Z_X| A_V |2b \ln \left(I + bI^{\frac{1}{2}} \right) + 2\gamma_M \gamma_X RT \left[mB_{MX}^2 + m^2 (\gamma_M \gamma_X)^{\frac{1}{2}} C_{MX}^V \right] \quad (\text{II. 13})$$

Where the symbols have their usual significance.

11.7.2. Limiting Ionic Partial Molar Volumes

The individual partial ionic volumes is very significant tools which provide the information appropriate to the general question of the structure near the ion, i.e., its solvation. The calculation of the ionic limiting partial molar volumes is very difficult task in organic solvents. At present, however, in organic solvents most of the existing ionic limiting partial molar volumes were obtained by the application of procedures originally developed for aqueous solutions to non-aqueous electrolyte solutions. In the last few years, Conway *et al* ^(II.105) suggested a method that has been used more frequently. To determination of the limiting partial molar volumes, the authors used the procedure of the anions for a series of homologous tetra-alkyl ammonium chlorides, bromides and iodides respectively in aqueous solution. They plotted the limiting partial molar volume $\phi_{V_{R_4NX}}^0$, with a halide ion as a common function for a series of these salts of the formula weight of the cation, $M_{R_4N^+}$ and obtained straight-lines for each series. Thus, they suggested the following equation:

$$\phi_{V_{R_4NX}}^0 = bM_{R_4N^+} + \phi_{V_{X^-}}^0 \quad (\text{II. 14})$$

The limiting partial molar volumes of the halide ions $\phi_{V_{X^-}}^0$ obtained from the extrapolation to zero on the cationic formula weight. Uosaki *et al.* ^(II.106) Krumgalz ^(II.107) used both this technique for the separation of some literature values and of their own $\phi_{V_{R_4NX}}^0$ values into ionic contributions in organic electrolyte solutions in a wide range of temperature

II.7.3. Excess Molar Volumes

V^E , the excess molar volumes are calculated from the molar masses M_i and the densities of pure liquids and the mixtures according to the following equation; ^(II.108, III.109)

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

where ρ_i and ρ are the density of the i^{th} component and density of the solution mixture respectively. V^E is the subsequent of contributions from several contrasting effects. These contributions may be divided randomly into three types, namely, chemical, physical and structural. Contribute a positive term to V^E . Decrease in volume from the chemical or specific intermolecular interactions, thereby contributing negative V^E values. These type of phenomena are getting from the results of difference in energies of interaction among molecules being in solutions and in packing effects. The ordered structure of pure component is disruption during the formation of the mixture leads to a positive effect detected on excess volume and in case of order formation in the mixture leads to negative contribution.

Viscosity is the fundamental and significant property of liquids that provide a lot of information on the structures and molecular interactions in liquid systems. Viscosity and volume are not same types of properties of one liquid, and there is a definite relationship between them. So, Viscosity and volume measuring and studying them together, relatively more convincing and comprehensive information expected to be gained. The 'Viscosity' as a function of composition based on weight, volume and mole fraction and comparison of experimental viscosity values with those calculated with several set of equations and excess Gibbs free energy of viscous flow.

One of the most important transport properties is the Viscosity, which is used for the determination of Solute-solvent and solute-solute interactions and studies extensively (II.110-111). Viscosity is not a thermodynamic property but viscosity of an electrolyte solution along with the thermodynamic property, partial molar volume, gives much information and insight concerning the solute-solvent interactions, structures of electrolytic solutions and solvation properties.

11.8. Viscosity of Pure Liquids and Liquid Mixtures

Since the movement of molecules in liquids is actually controlled by the influence of the adjacent molecules, at ordinary pressures the transport of momentum in liquids takes place, in sharp contrast with gases, not by the actual movement of molecules but by the strong influence of intermolecular force fields. This is the very importance aspect of the mechanism of momentum transfer, which forms the basis of the techniques for predicting the variations in the viscosity of liquids and liquid mixtures.

Early Theoretical Considerations on Liquid Viscosity

In early stages Frenkel^(II.113) and Andrade^(II.112) has been reviewed for the theoretical development of liquid viscosity, considering the forces of collision to be the only important factor and supposing that at the melting point, the frequency of vibration is equal to that in the solid state and that one-third of the molecules are vibrating along each of the three directions normal to one another. According to Frenkel^(II.113) considered the shape of molecules of a liquid to be spheres and the molecules are moving with an average velocity with respect to the neighboring medium and using Stokes' law and Einstein's relation for self-diffusion-coefficient, attained at a complicated expression for viscosity of liquid with only limited applicability Andrade^(II.112) developed equations that is checked well against data on mono atomic metals at their melting point. Furth^(II.114) and Zmed give the idea of transfer of momentum that take place by the irregular Brownian movement of the holes^(II.115) that were connected or linked to clusters in a gas and thus, in similarity with the gas theory of viscosity and with guess of the equipartition law of energy, showed that for liquids:

$$\eta = 0.915 \frac{R_g T}{V} \left(\frac{M}{\sigma} \right) e^{\frac{A}{R_g T}} \quad (\text{II. 16})$$

Where η , V and M denotes the viscosity, volume and mass respectively is the temperature in kelvin scale, σ is the surface tension, R_g is the universal gas constant and A signify as the work function at the melting point. Andrade^(II.113) and Ewell & Eyring,^(II.116) Auluck, De & Kothari^(II.117) compared his theory with experiment as well as with the theories and they further modified the theory and successfully clarified the variations of the viscosity with pressure. Eisenschitz gives a critical review of these simple theories and their abilities to explain the momentum transport in liquid systems.^(II.118)

11.8.1. Viscosity of Electrolytic Solutions

The relationships of viscosity of electrolytic solutions are extremely complicated. Because solute-solute (ion-ion) and solute-solvent (ion-solvent) interactions are occurring in the solution and separation of the related forces is a difficult task. However, from very careful analysis, vivid and valid conclusions can be drawn regarding the structure and the nature of the solvation in solution of the particular system. As viscosity is a measure of measurement of viscosity, is depends on the friction between adjacent, relatively moving parallel planes of the liquid, if the interaction among the planes of liquids increase or decrease, which also give the result of viscosity increase or decrease respectively. If placed a large spheres in the liquid system the planes will be keyed together in increasing the viscosity. Likewise, increase in the average degree of hydrogen bonding between the planes that will increase the friction between the planes, as well as viscosity. An ion associate with a large rigid co-sphere for a structure-promoting ion

will perform as a rigid sphere placed in the liquid and increase the inter-planar friction. Similarly, an ion increasing the degree of correlation or the degree of hydrogen bonding among the adjacent solvent molecules will increase the viscosity. Conversely, the viscosity would decrease for the ions destroying correlation. In 1905 Grüneisen^(II.119) First performed the systematic measurement of viscosities over a extensive range of concentrations of a number of electrolytic solutions. He noted non-linearity and negative curvature in the viscosity concentration curves regardless of low or high concentrations. An empirical equation (II.16), quantitatively correlating the relative viscosities of the electrolytes with molar concentrations (c) suggested in 1929 by Jones and Dole^(II.120):

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc \quad (\text{II. 17})$$

Rearrange the above equation as follows:

$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} \quad (\text{II. 18})$$

Where A and B are constants which detonates the specific to ion-ion and ion-solvent interactions. The equation is not applicable to only aqueous systems but also equally non-aqueous solvent systems where there is absence of ionic association and that has been used extensively. The term of the equation AVC , originally ascribed to Grüneisen effect, arose from the long-range columbic forces between the ions. The significance of the term had since then been realized due to the development Debye-Hückel theory^(II.121) of inter-ionic attractions in 1923. The flakenhagen coefficient A , depends on the ion-ion interactions, can be calculated from the theory of interionic attraction [III.167-III.169], and is given by the Falkenhagen Vernon^(II.122) equation

$$A_{Theo} = \frac{0.2577 A_o}{\eta_o (\epsilon T)^{0.5} \lambda_+^o \lambda_-^o} \left[1 - 0.6863 \left(\frac{\lambda_+^o \lambda_-^o}{A_o} \right)^2 \right] \quad (\text{II.19})$$

where the symbols in the above equation have their usual meaning. The coefficient A has been obtained by fitting η_r to equation (II. 18) in very careful work on aqueous solutions,^(II.123) and this was compared with the values calculated from equation (II. 19), the agreement was excellent with the result. However, the correctness attained with partially aqueous solutions was poorer.^(II.124) it is suggested that A -coefficient should be calculated from conductivity measurements. Crudden *et al.*^(II.125) suggested that if association of the ions occurs to an ion pair formation, the viscosity of the solution should be altered and that investigated by the following equation:

$$\frac{\eta_r - 1 - A\sqrt{\alpha c}}{\alpha c} = B_i + B_p \left(\frac{1 - \alpha}{\alpha} \right) \quad (\text{II. 20})$$

Where A , B_i and B_p are the characteristic constants and α is the degree of dissociation of ion-pair formation. Therefore, a plot of $\frac{\eta_r - 1 - A\sqrt{\alpha c}}{\alpha c}$ vs $\left(\frac{1 - \alpha}{\alpha} \right)$ it give the intercept value B_i when extrapolated to $\left(\frac{1 - \alpha}{\alpha} \right) = \text{zero}$ in the equation. However, both aqueous and non-aqueous of electrolytic solutions the [equation \(II. 20\)](#) is valid up to 0.1 (M) [\(II.126, II.127\)](#) within experimental errors. At higher concentration of the solutions the extended Jones-Dole [equation \(II. 21\)](#), involving an additional coefficient D , originally used by Kaminsky, [\(II.128\)](#) has been used by several workers [\(II.129, II.130\)](#) and is given below:

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc + Dc^2 \quad (\text{II. 21})$$

The coefficient D in the above equation cannot be calculated properly and the significance of the constant (D) is also not constantly meaningful and consequently, the most of the workers are used to the [equation \(II. 20\)](#).

The value of A -coefficient should be obtained from the plots of $\frac{(\eta/\eta_o - 1)}{\sqrt{c}}$ against \sqrt{c} for the electrolytes. But occasionally, the negative or considerably scatter values come out and also deviation from linearity arise. [\(II.131, II.132, II.133\)](#) Thus, for determining the A -coefficient, Falkenhagen-Vernon [equation \(II. 19\)](#) is used instead the value obtained least square method. A -coefficient should be zero for non-electrolytes. According to Jones and Dole, the A -coefficient possibly represents the stiffening outcome on the solution of the electric forces between the ions that is solute-solute interaction involving with the solutions, which tend to keep or maintain space-lattice structure. [\(II.120\)](#) The value of viscosity B -coefficient may be either positive or negative and it is really the ion-solvent interaction parameter. Using the least square method the B -coefficients are obtained as slopes of the straight lines and intercepts equal to the A -coefficient.

The following factors influencing the Viscosity B -coefficients are reported as [\(II.134, II.135\)](#)

- a) The result of destruction of the three-dimensional structure of solvent molecules (i.e., structure breaking effect or depolymeriation effect), as a result decreases η values.

- b) The result of ionic solvation in solutions and the action of the arena of the ion in generating long-range order in solvent molecules, increase η or B -value.
- d) Reduced B -values are create when the primary solution of ions is sterically hindered in high molal volume solvents or if either ion of a binary electrolyte cannot be specifically solvated.
- e) High B -values for similar solvents, which yield the very high molal volume and very low dielectric constant.

11.8.2. Principle of Corresponding States and Liquid Viscosity

The principle of the corresponding states has been applied to liquids in the similar way as well as gases. ^(II.136) The elementary assumption existence that the intermolecular potential between two molecules is a universal function of the reduced intermolecular separation. This hypothesis is a good approximation for the spherically symmetric mono atomic non-polar molecules. In common, more parameters are introduced in the corresponding state correlations on somewhat empirical grounds in the hope that such modification in some method or way that compensates the shortcomings of the above stated assumption. In this link the studies by Rogers and Brickwedde, ^(II.137) Boon and Thomaes ^(II.138-II.139) Boon, and Hollman and Hijmans ^(II.140) Legros and Thomaes, ^(II.141) are worth mentioning.

11.8.3. The Reaction Rate Theory for Viscous Flow

Regarding the viscous flow of a chemical reaction in which a molecule moving in a plane infrequently acquires the activation energy, which is necessary to sleep over the potential barrier to the succeeding equilibrium position in the same plane. The viscosity of the liquid according to Eyring ^(II.142) is given by:

$$\eta = \frac{\lambda_1 h F_n}{\kappa \lambda^2 \lambda_2 \lambda_3 F_a^*} \exp \frac{\Delta E_{act}}{kT} \quad (\text{II. 22})$$

Where λ confines, the average distance between the equilibrium positions in the direction of motion, λ_1 is denotes the perpendicular distance between two adjacent layers of molecules in relative motion, λ_2 is the distance between nearby molecules in the same direction and λ_3 is measure the distance from molecule to molecule in the plane normal to the direction of motion. The term (κ), transmission coefficient is the measure of the chance that a molecule having once crossed the potential barrier will react and not recross in the opposite direction. For normal molecules F_n is denotes the partition function, F_a^* denotes that of the activated molecule with a degree of freedom corresponding to flow, energy of activation for the flow process is denoted by ΔE_{act} is the energy of activation, h is Planck's constant and Boltzmann constant is k . For a

molecule to passage into a hole, Ewell and Eyring argued it is not necessary that the latter be of the same size as the molecule. So they assume that for viscous flow ΔE_{act} is a function of ΔE_{vap} , because ΔE_{vap} is the energy essential to make a hole in the liquid of the size of a molecule. Applying the idea and criteria, certain relations ^(II.116, II.143) finally gets

$$\eta = \frac{N_A h (2\pi mkT)^{\frac{1}{2}}}{Vh} \frac{bRTV^{\frac{1}{3}}}{N_A^{\frac{1}{3}} \Delta E_{vap}} \exp \frac{\Delta E_{vap}}{nRT} \quad (\text{II. 23})$$

Where n and b are two constant. It was observed that the theory could reproduce the trend in temperature dependence of η but the observed values are less compare with computed values by a factor of two or three for most liquids. Kincaid, Eyring and Stearn ^(II.144) have shortened all the working relations.

II.8.4. the Significant Structural Theory and Liquid Viscosity

The "holes in solid" model theory ^(II.144-II.149) improved by Eyring and coworkers ^(II.145-II.148) to picture the liquid state by identifying three very important structures. In short-term, a molecule has solid like properties for the short time it vibrates about an equilibrium position and then it assumes rapidly the gas like behavior on jumping into the nearby vacancy. The above idea of significant structures leads to the following relation for the viscosity of liquid; ^(II.150, II.151)

$$\eta = \frac{V_s}{V} \eta_s + \frac{V - V_s}{V} \eta_g \quad (\text{II. 24})$$

Where the term V_s is the molar volume of the solid at the melting point and V is the molar volume of the liquid at the temperature of interest. η_s and η_g are the viscosity contributions from the solid-like and gas-like degrees of freedom, respectively. Carlson, Eyring and Ree ^(II.151) Eyring and Ree ^(II.152) have discussed for the the expressions of η_s and η_g and in detail the evaluation of η_s from the reaction rate theory of Eyring ^(II.152) assuming that a solid molecule can jump into all adjacent empty sites. The expression for η_s takes the following equation. ^(III.152)

$$\eta = \frac{N_A h}{Z_K} \left(\frac{V}{V_s} \right) \frac{6}{2^{\frac{1}{2}}} \left(\frac{1}{V - V_s} \right) \frac{1}{(1 - e)^{\frac{\theta}{T}}} \exp \left(\frac{aE_s V_s}{(V - V_s) RT} \right) \quad (\text{II. 25})$$

Where Avogadro's number is N_A , Z is the number of nearest neighbors, the term of the equation θ is the Einstein characteristic temperature, E_s is the energy of sublimation and a' is the proportionality constant. The following relation obtains the term η_g from the kinetic theory of gases ^(II.153):

$$\eta_g = \frac{2}{3d^2} \left(\frac{MkT}{\pi^3} \right)^{\frac{1}{2}} \quad (\text{II. 26})$$

Where d and M represent the molecular diameter and molecular mass respectively.

11.8.5. Viscosities at Higher Concentration

The viscosity at high concentration (1M saturation) can be obtained by the empirical formula suggested by Andrade: (II.154)

$$\eta = A \exp^{b/T} \quad (\text{II.27})$$

The several substitute formulations have been suggested for representing the results of viscosity measurements in the high concentration range (II.155-II.159) and the equation proposed by Angell (II.160, II.161) based on an extension of the free volume theory of transport phenomena in liquids and fused salts to ionic solutions is particularly remarkable.

$$\text{The equation is as: } \frac{1}{\eta} = A \exp \left[\frac{-K_1}{N_0 - N} \right] \quad (\text{II.28})$$

Where, N denotes the concentration of the salt in eqv.Litre⁻¹, A and K_1 are constants imaginary to be independent of the salt composition and N_0 is the proposed concentration at which the system becomes glass. The equation was changed by Majumder ET al. (II.162-II.164) presenting the limiting condition, that is; which is the viscosity of the pure solvent. Thus, we have:

$$\ln \frac{\eta}{\eta_0} = \ln \eta_{Rel} = \frac{K_1 N}{N_0 (N_0 - N)} \quad (\text{II.29})$$

The above equation predicts a straight line passing through the origin for the plot of $\ln \eta_{Rel}$ vs. $N / (N_0 - N)$ if N_0 is made for a suitable choice. Using the literature data as well their own experimental data Majumder et al. tested the equation (11.29). The best choice can get for N_0 and K_1 was selected by trial and error methods. The set of K_1 and N_0 generating minimum deviations between η_{Rel}^{Exp} and η_{Rel}^{theo} was accepted. $N \ll N_0$ for very dilute solutions and we have:

$$\eta_{Rel} = \exp \left(\frac{K_1 N}{N_0^2} \right) \cong 1 + \frac{K_1 N}{N_0^2} \quad (\text{II.30})$$

Equation (11.29) is nothing but similar to the Jones-Dole equation with the ion-solvent interaction term characterized as $B = \frac{K_1}{N_0^2}$. The arrangement between B-values determined in

this technique and using Jones-Dole equation has been set up to be good for several electrolytes.

Further, the equation (11.29) written in the form:

$$\frac{N}{\ln \eta_{Rel}} = \frac{N_0^2}{K_1} - \frac{N_0 N}{K_1} \quad (\text{II.31})$$

It closely resembles the Vand's equation^(II.165) for fluidity.

$$\frac{2.5c}{2.303 \log \eta_{Rel}} = \frac{1}{V} - Qc \quad (\text{II.32})$$

Where, c represent the molar concentration of the solute and V is the effective rigid molar volume of the salt and the interaction constant symbolizes as Q .

11.8.5 Division of B -Coefficients into Ionic Values

The viscosity B -coefficient undergoes splitting into the contributions of individual ions can not be done in the same mode as the division of limiting equivalent conductance's, as there is no quantity analogous or corresponding to the transport numbers. Therefore, the separation of the experimental B -coefficient has been an arbitrary process^(II.166-168).

In order to classify the separate contributions of both cations as well as anions to the completely solute-solvent interactions, the viscosity B -coefficients that can be determined by Jones-Dole's equation has to be resolved into ionic components. For this purpose Gurney^(11.167), Cox and Wolfenden^(II.168), Sacco *ET al*^(II.169), Tuan and Fuoss^(II.170), and several authors used different approximations and norms or approximations for different kinds of systems. As for example, Sacco *et al*^(II.169) suggested the widely used 'reference electrolyte' method. Thus, for Ph_4PBPh_4 in water, we take,

$$B_{\text{BPh}_4^-} = B_{\text{PPh}_4^+} = B_{\text{BPh}_4\text{PPh}_4} / 2 \quad (\text{II.33})$$

(Since Ph_4PBPh_4 is barely soluble in water). These values obtained from the above formula are in good agreement with those obtained by other methods.

$$B_{\text{BPh}_4\text{PPh}_4} = B_{\text{NaBPh}_4} + B_{\text{PPh}_4\text{Br}} - B_{\text{NaBr}} \quad (\text{II.34})$$

However, the process have been strongly criticized by Krumgalz (II.171). According to him, any technique of resolution emerged on the equality of equivalent conductance for certain ions bears from the drawback that it is very difficult to select any two ions for which *cataionpart = anaion part* in all solvents and at suitable temperatures. At infinite dilution, even if the mobility's of some ions are equal but it is not essential to equality of concentrations. Furthermore, equality of *B*-coefficients of these ions are not necessary with the equality of ionic dimensions, as they are likely to be solvent and dependent on Ionic- structure.

Recently, Krumgalz (II.172) has suggested a method for the resolution of *B*-coefficient. The method is depends on the fact that in organic solvents the large tetra alkyl ammonium ions are not solvated properly. For large R_4N^+ cation, the *B*-values of the ionic species in organic solvents are proportional to their ionic dimensions. (Where $R \geq Bu$)

$$B_{R_4NX} = a + br^3 R_4N^+ \quad (II.35)$$

Where, *an* equal to B_x^+ and *b* is a constant quantity independent of temperature and nature of solvent. When extrapolation of the plot of BR_4NX ($R > Pr$ or Bu) against

To zero cations, dimension that give the result of B_x^+ directly from which other ionic *B*-values can be calculated in the proper solvent. The following equations help to calculate the Ionic *B*-values as:

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \quad (II.36)$$

$$\frac{B_{R_4N^+}}{B_{R'_4N^+}} = \frac{r^3_{R_4N^+}}{r^3_{R'_4N^+}} \quad (II.37)$$

Using accurate conductance data (II.173). The radii of the tetraalkylammonium ions have been calculated from the above equation.

Gill and Sharma (II.173) on similar reason used Bu_4NBPh_4 used as a reference electrolyte and proposed the equations

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \left(\frac{5.35}{5.00} \right)^3 \quad (II.38)$$

$$B_{\text{Bu}_4\text{N}^+\text{BPh}_4^-} = B_{\text{Bu}_4\text{N}^+} B_{\text{Ph}_4\text{B}^-} \quad (\text{II.39})$$

Since the ionic radii of both cationic part Bu_4N^+ (5.00 Å) and anionic part Ph_4B^- (5.35 Å) have been observed to remain same in different non-aqueous and mixed non-aqueous solvents.

Recently, to modify the reference electrolyte Lawrence and Sacco ^(II.174-176) used Bu_4NBBu_4 as reference electrolytes because cations part and anions part of the electrolyte are symmetrically shaped and have practically equal van der Waals volumes. Thus, we have,

$$B(\text{Bu}_4\text{N}^+)/B(\text{Bu}_4\text{B}^-) = V_w(\text{Bu}_4\text{N}^+)/V_w(\text{Bu}_4\text{B}^-) \quad (\text{II.40})$$

Or

$$B(\text{Bu}_4\text{N}^+) = B(\text{Bu}_4\text{NBBu}_4) / 1 + V_w(\text{Bu}_4\text{B}^-) / V_w(\text{Bu}_4\text{N}^+) \quad (\text{II.41})$$

The results and the conclusions obtained from the theory of Thomson *et al* ^(II.177) agreed well with the above reported values.

It is noticeable that most of these procedures are based on certain approximations and exceptional results may arise unless appropriate mathematical theories are developed to calculate B -values.

11.8.6. Thermodynamics of Viscous Flow

According to Eyring's ^(II.178) approaches assuming viscous flow as a rate process the viscosity (η) can be represented as

$$\eta = A e^{\frac{E_{\text{vis}}}{RT}} = \left(\frac{hN_A}{V} \right) e^{\frac{\Delta G^*}{RT}} = \left(\frac{hN_A}{V} \right) e^{\left(\frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \right)} \quad (\text{II.42})$$

Where E_{vis} is the experimental entropy of activation, which can be obtained from a plot of $\ln \eta$ against $1/T$. ΔG^* , ΔH^* and ΔS^* are signify as free energy, enthalpy and entropy of activation, respectively?

Nightingale and Benck ^(II.179) both of them share out in the problem in a different procedure or way for measuring the thermodynamics feature of viscous flow of salts in aqueous solution by the assistance of the Jones-Dole equation (neglecting both the A , c term). Thus, we have:

$$R \left[\frac{d \ln \eta}{d \left(\frac{1}{T} \right)} \right] = r \left[\frac{d \ln \eta_o}{d \left(\frac{1}{T} \right)} \right] + \frac{R}{1+Bc} \frac{d(1+Bc)}{d \left(\frac{1}{T} \right)} \quad (\text{II. 43})$$

$$\Delta E_{\eta(\text{Soln})}^{\neq} = \Delta E_{\eta(\text{Soln})}^{\neq} + \Delta E_V^{\neq} \quad (\text{II. 44})$$

Where ΔE_V^{\neq} can be understood as the increase or decrease of the activation energies due to the presence of ions, for viscous flow of the pure solvents i.e., the actual effect of the ions upon the viscous flow of the solvent molecules.

Data of viscosity can also be studied in the light of transition state theory of the relative viscosity of electrolytic solutions proposed by Feakins *et al* (II.180). According to his opinion, B -coefficient is given as,

$$B = \frac{(\phi_{v,2}^0 - \phi_{v,1}^0)}{1000} + \phi_{v,2}^0 \frac{(\Delta \mu_2^{0\neq} - \Delta \mu_1^{0\neq})}{1000RT} \quad (\text{II.45})$$

$\phi_{v,1}^0$ and $\phi_{v,2}^0$ denotes the partial molar volumes of the solvent and solute respectively and $\Delta \mu_2^{0\neq}$ is the contribution per mole of solute to the free energy of activation for viscous flow of solution. $\Delta \mu_1^{0\neq}$ Signify the free energy of activation for viscous flow per mole of the solvent, which is given by:

$$\Delta \mu_1^{0\neq} = \Delta G_1^{0\neq} = RT \ln(\eta_0 \phi_{v,1}^0 / h N_A) \quad (\text{II. 46})$$

Further, if B is known at various temperatures, we can calculate the entropy and enthalpy of activation of viscous flow respectively from the following equations as given below:

$$\frac{d(\Delta \mu_2^{0\neq})}{dT} = -\Delta S_2^{0\neq} \quad (\text{II. 47})$$

$$\Delta H_2^{0\neq} = \Delta \mu_2^{0\neq} + T \Delta S_2^{0\neq} \quad (\text{II. 48})$$

11.8.7. Effects of Shape and Size

Stokes and Mills have dealt in the characteristic of shape and size comprehensively. The ions remain in solution can be regarded as a rigid spheres suspended in range. Einstein (II.181) leads to the following equation for the treatment of hydrodynamic phenomenon involving in the solution.

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi \quad (\text{II. 49})$$

Where ϕ is symbolize the volume fraction occupied by the particles. (I) Sinha ^(II.182) proposed for the modification of the equation based on departures from spherical shape and (ii) according to Vand based on dependence of the flow patterns around the adjacent particles at higher concentrations. However, regarding the different aspects of the problem, spherical shapes for electrolytes having hydrated ions of large effective size have been assumed. (Especially polyvalent monatomic cations). Thus, we have from [equation \(II. 49\)](#):

$$2.5\phi = A\sqrt{c} + Bc \quad (\text{II. 50})$$

Since the term $A\sqrt{c}$ can be neglected in comparison with Bc and $\phi = c\phi_{v,1}^0$ where $\phi_{v,1}^0$ denotes the partial molar volume of the ion, we get the following equation

$$2.5\phi_{v,1}^0 = B \quad (\text{II. 51})$$

In case of an ideal situation, the viscosity B -coefficient is a linear function of partial molar volume of the solute molecules $\phi_{v,1}^0$ with slope to 2.5. Thus, B_{\pm} can be associated to:

$$B_{\pm} = 2.5\phi_{\pm}^0 = \frac{2.5 \times 4 (\pi R_{\pm}^3 N)}{3 \times 1000} \quad (\text{II. 52})$$

Supposing that the ions behave as rigid spheres with effective radii, R_{\pm} moving in a continuum. Using the above [equation \(II. 52\)](#) R_{\pm} , can be calculated that should be close to crystallographic radii or corrected Stake's radii if the ions are hardly solvated and perform as spherical entities. However, in common, the radii obtained from the crystallographic, which is less than the radii (R_{\pm}), obtained from the above equation that indicating appreciable solvation.

By comparing, the Jones-Dole equation with the Einstein's equation the number n_b of solvent molecules bound to the ion in the primary solvation shell can be easily calculated:

$$B_{\pm} = \frac{2.5}{1000(\phi_i + n_b\phi_s)} \quad (\text{II. 53})$$

Where ϕ_i and ϕ_s is the molar volume of the base ion, the molar volume of the solvent respectively. To study the nature of solvation and solvation number [equation a number of workers has used \(II. 53\)](#) properly.

II. 8. 8. Viscosity of Non-Electrolytic Solutions

The three equations of Vand,^(II.183) Thomas,^(II.184) and Moulik^(II.185-II.187) proposed chiefly to account for the determination of viscosity of the concentrated solutions of bigger spherical particles have been also established to correlate with the mixture of viscosities of the normal nonelectrolytes.

$$\text{Vand equation: } \ln \eta_r = \frac{\alpha}{1-Q} = \frac{2.5V_h c}{1-QV_h c} \quad (\text{II. 54})$$

$$\text{Thomas equation: } \eta_r = 1 + 2.5V_h + 10.05cV_h^2 c \quad (\text{II. 55})$$

$$\text{Moulik equation: } \eta^2 = I + Mc^2 \quad (\text{II. 56})$$

where η_r is clarify as the relative viscosity, a is constant quantity depending on the axial ratios of the particles associated in solution, the interaction constant is Q , V_h is express as the molar volume of the solute including rigidly held solvent molecules due to hydration, c is the molar concentration of the solute molecules; I and M both are constants. The viscosity equation proposed by Eyring and coworkers for pure liquids based on pure noteworthy liquid structures theory, can be extended to predict the viscosity of mixed liquids also. The final expression for the liquid mixtures takes the following form:

$$\eta_m = \frac{6N_A h}{\sqrt{2}r_m(V_m - V_{Sm})} \left[\sum_i^n \left\{ 1 - \exp\left(\frac{-\theta_i}{T}\right) \right\}^{-x_i} \right] \exp\left[\frac{a_m E_{Sm} V_{Sm}}{RT(V_m - V_{Sm})} \right] + \frac{V_m - V_{Sm}}{V_m} \left[\sum_i^n \frac{2}{3d_i^2} \left(\frac{m_i kT}{\pi^3} \right)^{\frac{1}{2}} x_i \right] \quad (\text{II. 57})$$

Where n is two for binary and three for ternary liquid mixtures. r_m , E_{Sm} , V_m , V_{Sm} and a_m the mixture parameters were calculated from the corresponding pure component parameters by using the following relations:

$$r_m = \sum_i^n x_i^2 r_i + \sum_{i \neq j} 2x_i x_j x_{ij} \quad (\text{II. 58})$$

$$E_{Sm} = \sum_i^n x_i^2 E_{Si} + \sum_{i \neq j} 2x_i x_j E_{Sij} \quad (\text{II. 59})$$

$$V_m = \sum_i^n x_i V_i \quad V_{Sm} = \sum_i^n x_i V_{Si} \quad a_m = \sum_i^n x_i a_i \quad (\text{II. 60})$$

$$r_{ij} = (r_i r_j)^{\frac{1}{2}} \quad \text{And } E_{Sij} = (E_{Si} E_{Sj})^{\frac{1}{2}} \quad (\text{II. 61})$$

$$\theta = \frac{h}{\kappa 2\pi} \left(\frac{b}{m} \right)^{\frac{1}{2}} \quad (\text{II.62})$$

$$b = 2Z\varepsilon \left[22.106 \left(\frac{N_A \sigma^2}{V_s} \right)^4 - 10.559 \left(\frac{N_A \sigma^3}{V_s} \right)^2 \right] \frac{1}{\sqrt{2}\sigma^2} \left(\frac{N_A \sigma^3}{V_s} \right)^{\frac{2}{3}} \quad (\text{II. 63})$$

Where σ , ε_r are Lennard-Jones potential parameters respectively and the other symbols have their usual significance.

For the purposes, interpolation and limited extrapolation, the viscosities of ternary mixture can be interrelated to a high degree of accuracy in terms of binary contribution by the following equations. [\(II.188-II.194\)](#)

$$\begin{aligned} \eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] \\ & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_3 - x_1) + C_{31}(x_3 - x_1)^2] \end{aligned} \quad (\text{II. 64a})$$

The modification of correlation of ternary system is given in the following form:

$$\begin{aligned} \eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] \\ & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_3 - x_1) + C_{31}(x_3 - x_1)^2] \\ & + A_{123}(x_1 x_2 x_3) \end{aligned} \quad (\text{II. 64b})$$

$$\begin{aligned} \eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] \\ & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_3 - x_1) + C_{31}(x_3 - x_1)^2] \\ & + x_1 x_2 x_3 [A_{123} + B_{123} x_1^2 (x_2 - x_3)^2 + C_{123} x_1^3 (x_2 - x_3)^3] \end{aligned} \quad (\text{II. 64c})$$

Where character of A_{12} , B_{12} , C_{12} , A_{23} , B_{23} , C_{23} , A_{31} , B_{31} and C_{31} , are the constants for binary mixtures; A_{123} , B_{123} and C_{123} are constants for the ternaries mixture; and the other symbols have their common importance.

11.9. REFRACTIVE INDEX

Optical data (refractive index, n_D) provide interesting information related to molecular interactions and structure of the solutions, as well as complementary data on practical procedures, such as concentration measurement or estimation of the extent of salvation of electrolytes/non-electrolytes in liquid systems. (II.195)

The light bending property is a result of variation of the velocity with which light is transmitted. Refractive index (n_D) of liquid, changes not only with the wavelength of light used but also with the temperature. Influence of Molar refractions are characterized by the organization of atoms in the molecule or by factors like unsaturation, ring closure etc. linear optical properties of liquids and liquid mixtures have been widely studied to obtain information on their physical, chemical, and molecular properties. Fialkov ET. al. (II.196, II.197) stated that the refractive index is an additive property of pure components when composition is expressed in terms of volume fraction. Several researchers have estimated the refractivity of liquid systems using the well-known mixing rules viz. Arago-Biot, Newton, Heller, Gladstone-Dale, Eyring-John, Eykman, Lorentz-Lorenz, Weiner and Oster relations. (II.198-II.201) these empirical approaches for calculating the excess properties attempt to explain the non-ideality in terms of specific and non-specific intermolecular interactions. Refractive index or refractivity is very important property of intrinsic attention in the fields of pharmaceutical research such as in optoelectronic, formulation of eye preparations and photonic applications.

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

Whenever the speed of light changes when it crosses a boundary from one medium into another, and changes the actual direction of travel of applying light. i.e., it is refracted. The relationship between the speed of light in the selected two mediums (V_A and V_B), the angles of incidence ($\sin \theta_A$) and refraction ($\sin \theta_B$) and the n_A and n_B are the refractive indexes of the two mediums is shown below:

$$\frac{V_A}{V_B} = \frac{\sin \theta_A}{\sin \theta_B} = \frac{n_B}{n_A} \quad (\text{II. 65})$$

Thus, it is not very essential to measure the speed of light in a sample in order to determine its refractive index. In its place, by measuring the angle of refraction, and knowing the index of refraction of the layer of the concerned medium that is in contact with the sample, it is also possible to determine the refractive index of the sample quite accurately.

The refractive index of mixing can be correlated by the application of a composition-dependent polynomial equation. Molar refractivity, was obtained from the Lorentz-Lorenz relation (II.202, II.203) by using, n_D experimental data according to the following expression

$$R_M = \frac{(n_D^2 - 1)}{(n_D^2 + 2)} \left(\frac{M}{\rho} \right) \quad (\text{II. 66})$$

Where M refers to the mean molecular weight of the mixture and ρ is the mixture density. n_D Can be expressed as the following:

$$n_D = \sqrt{\frac{(2A+1)}{(1-A)}} \quad (\text{II. 67})$$

Where A is given by:

$$A = \left[\left\{ \frac{(n_1^2 - 1)}{(n_1^2 + 2)} (1/\rho_1) \right\} - \left\{ \frac{(n_1^2 - 1)}{(n_1^2 + 2)} (w_2/\rho_1) \right\} + \left\{ \frac{(n_2^2 - 1)}{(n_2^2 + 2)} (w_2/\rho_2) \right\} \rho \right] \quad (\text{II. 68})$$

Where n_1 and n_2 are the refractive indices of pure component, w_j refers the weight fraction, ρ is the mixture of density, and ρ_1 and ρ_2 are the pure component of densities.

The deviation of molar refractivity is calculated by the following expression is as follow:

$$\Delta R = R - \phi_1 R_1 - \phi_2 R_2 \quad (\text{II. 69})$$

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

The deviations of refractive index were used for the correlation of the binary solvent mixtures:

$$\Delta n_D = n_D - x_1 n_{D1} - x_2 n_{D2} \quad (\text{II. 70})$$

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

The computed deviations of refractive indices of the binary mixtures are fitted using the following Redlich-Kister expression. (II.204)

$$\Delta n_{Dew} = w_e w_w \sum_{P=0}^S B_p (w_e w_w)^P \quad (\text{II. 71})$$

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

In case of salt-solvent solution, the binary systems were fitted to polynomials of the form:

$$n_{Ds,sol} = n_{Dsol} + \sum_{i=1}^N A_i m^i \quad (\text{II. 72})$$

For the ternary systems of the salt + solvent-1 + solvent-2 solutions a polynomial expansion (II.205) has been employed, similar to that obtained for the salt + solvent solutions was used to represent ternary refractive indices:

$$n_D = n_{Dw} + \sum_{i=1}^P C_i m^i \quad (\text{II. 73})$$

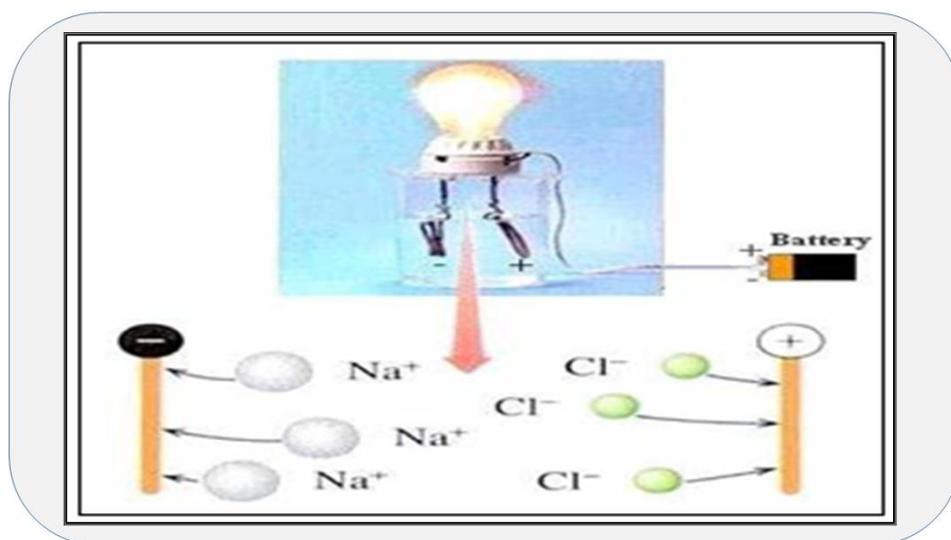
Where n_D is the refractive index of the ternary solution, C_i are the parameters, and P is the number of terms in the polynomial.

There is no common or general rule that states how to calculate the deviation of refractivity function. The ideal behavior may be expressed in terms of mole fraction: in this case, smaller deviations occur but values are more scattered because of the higher compassion of the expression to rounding errors in the mole fraction. For the sake of inclusiveness, deviation function of both calculations of refractivity and also molar

refraction was fitted to a Redlich and Kister-type expression ^(II.204) and the adaptable parameters and the relevant standard deviation δ can be calculated for the expression in terms of volume fractions and in terms of mole fractions, correspondingly.

11.10. CONDUCTANCE:

Conductance is the most important and also an accurate and direct method available to determine the extent of the dissociation constants of electrolytes in aqueous, mixed and non-aqueous solvents is the “*conducti metric method.*” Conductance data in combination with viscosity measurements, gives much more information pertaining the ion-ion and ion-solvent interaction.



Dissolved Ions Conduct Electricity

The measurements of conductance studies were followed vigorously throughout the last five decades, both theoretically and as well as experimentally and a number of vital theoretical equations have been evolved. We shall be located in briefly on some of these prospects in relation to the studies in aqueous, non-aqueous, pure and mixed solvents respectively. The successful application of the Debye-Hückel theory of interionic attraction was made by Onsager, ^(II.206) to derive the Kohlrausch's equation representing the molar conductance of an electrolyte.

$$\Lambda = \Lambda_0 - S\sqrt{c} \quad (\text{II. 74})$$

Where,

$$S = \alpha\Lambda_0 + \beta \quad (\text{II. 75})$$

$$\alpha = \frac{(z^2)k}{3(2 + \sqrt{2})\epsilon_r kT \sqrt{c}} = \frac{82.406 \times 10^4 z^3}{(\epsilon_r T)^{\frac{3}{2}}} \quad (\text{II. 76a})$$

$$\beta = \frac{z^2 e F k}{3\pi\eta\sqrt{c}} = \frac{82.487 z^3}{\eta\sqrt{\epsilon_r T}} \quad (\text{II. 76b})$$

The equation took no account for the short-range of interactions and of shape or size of the ions in solution. The ions were considered as rigid charged spheres in an electrostatic and as well as hydrodynamic continuum, i.e., the solvent. (II.207) In the subsequent years, Pitts (1953) (II.208) and Fuoss and Onsager (1957) (II.209) independently calculate the solution of the problem of electrolytic conductance bookkeeping for both interactions long-range and short-range respectively. However, the A_o values obtained for the conductance at infinite dilution using Fuoss-Onsager theory differed considerably from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation. (II.210, II.211) Fuoss and Hsia (II.212) who again calculated the relaxation field, retaining the terms which had previously been neglected.

The results obtained from the conductance theories can be expressed in a general form:

$$A = \frac{A_o - \alpha A_o \sqrt{c}}{(1 + \kappa\alpha)} \left(\frac{1 + \kappa\alpha}{\sqrt{2}} \right) - \frac{\beta\sqrt{c}}{(1 + \kappa\alpha)} + G(\kappa\alpha) \quad (\text{II. 77})$$

Where $G(\kappa\alpha)$ is a complicated function of the variable. The simplified form:

$$A = A_o - S\sqrt{c} + Ec \ln c + J_1 c + J_2 \sqrt[3]{c} \quad (\text{II. 78})$$

However, it has been found that these equations have certain limitations, in some cases it fails to fit experimental data. Some of these results have been deliberate elaborately by Fernandez-Prini. (II.213, II.214) Fuoss and Accascini made more correction of the equation (II. 89). For considering the change in viscosity of the concerned solutions, they assumed the backbone of Walden's rule. The new equation becomes in the following form.

$$A = A_o - S\sqrt{c} + Ec \ln c + J_1 c + J_2 \sqrt[3]{c} - FAc \quad (\text{II. 79})$$

$$\text{Where, } Fc = \frac{4\pi R^3 N_A}{3} \quad (\text{II. 80})$$

In most cases, however, J_2 is made zero but this leads to a systematic deviation of the experimental data from the theoretical equations. It has been observed that Pitt's equation gives better fit to the experimental data in aqueous solutions. (II.215)

11.10.1. Ionic Association

The behavior of completely dissociated electrolytes successfully can be represents by the equation (II. 89). The nature of dissociation or association of electrolytes can be obtained by the plotting of Λ against \sqrt{c} (limiting Onsager equation). The association between cations and anions result the large electrostatic interactions. The difference in $\Lambda_{o\text{ exp}}$ and $\Lambda_{o\text{ theo}}$ would be more prominent with increasing association among the ions. (II.216)

Conductance measurements is very helpful for the determination of values for the ion-pair association constant, K_A for the process:



$$K_A = \frac{(1-\alpha)}{\alpha^2 c \gamma_{\pm}^2} \quad (\text{II. 82})$$

$$\alpha = 1 - \alpha^2 K_A c \gamma_{\pm}^2 \quad (\text{II. 83})$$

Where, mean activity coefficient denotes γ_{\pm} of the free ions at concentration αC . The value of constant K_A and Λ_o have been determined using Fuoss-Kraus equation (II.217) or Shedlovsky's equation. (II.218)

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda_o} + \frac{K_A}{\Lambda_o^2} \cdot \frac{c \gamma_{\pm}^2 \Lambda}{T(z)} \quad (\text{II. 84})$$

According to (Fuoss-Kraus method $T(z) = F(z)$) and $1/T(z) = S(z)$ signify the (Shedlovsky's method).

$$F(z) = 1 - z(1 - z(1 - \dots))^{\frac{1}{2}} \quad (\text{II. 85a})$$

$$\text{And} \quad \frac{1}{T(z)} = S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \dots \quad (\text{II. 85b})$$

A plot of $T(z)/\Lambda$ vs $c\gamma_{\pm}^2\Lambda/T(z)$ should be a straight line having the value of intercept parameter is $1/\Lambda_0$ and slope of the plot is K_A/Λ_0^2 . Wherever K_A is large, there will be great uncertainty in the determined values of Λ_0 and K_A from equation (II. 84).

The conductance equation for associated electrolytes is given by Fuoss-Hsia (II.219)

$$\Lambda = \Lambda_0 - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{\frac{3}{2}} - K_A\Lambda\gamma_{\pm}^2(\alpha c) \quad (\text{II. 86})$$

Justice modified the above equation. (II.220) The conductance of symmetrical electrolytes in dilute solutions can be represented by the following equations:

$$\Lambda = \alpha(\Lambda_0 - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1R(\alpha c) - J_2R(\alpha c)^{\frac{3}{2}}) \quad (\text{II. 87})$$

$$\frac{(1-\alpha)}{\alpha^2 c \gamma_{\pm}^2} = K_A \quad (\text{II. 88})$$

$$\ln \gamma_{\pm} = \frac{-k\sqrt{q}}{(1+kR\sqrt{\alpha c})} \quad (\text{II. 89})$$

From least square treatment, the parameter of conductance are obtained least after setting, $R = q = \frac{e^2}{2\epsilon kT}$ (Bjerrum's critical distance).

According to equity the method of fixing the J -coefficient by setting, $R = q$ clearly consents a better value of K_A to be found. Since the equation (II. 87) is a series expansion truncated at the $c^{3/2}$ term, it would be better that the resulting errors be immersed as must as possible by J_2 rather than by K_A , whose theoretical interest is greater as it covers the information concerning short-range cation-anion interaction. From the experimental values of the association constant K_A , one can use two methods in order to determine the distance of closest approach, 'a', of two free ions to form an ion-pair. Fuoss; (II.221) proposed the following equation to determination of K_A ,

$$K_A = \frac{4\pi N_A \alpha^3}{3000} \exp\left(\frac{e^2}{\alpha \epsilon kT}\right) \quad (\text{II. 90})$$

In most of the cases, the magnitude of K_A was too small to allow or permit a calculation of a . The distance parameter was lastly considered from the more common equation due to Bjerrum. ^(II.222)

$$K_A = \frac{4\pi N_A \alpha}{1000} \int_{r=a}^{r=q} r^2 \exp\left(\frac{z^2 e^2}{r \epsilon k T}\right) dr \quad (\text{II. 91})$$

In the above equation there is absent of specific short-range interactions except for solvation in which the solvated ion can be approximated by a hard sphere model. Douheret has successfully applied the process. ^(II.223)

11.11. FTIR SPECTROSCOPY

The spectroscopic study has been established by the investigation of FTIR spectroscopy. The study has been taking into account to qualitative interpreting the molecular as well as ionic association of the electrolytes in the solutions. FTIR spectroscopy is one of the most appropriate optical properties, which qualitatively interpreted the nature, mode, manner of the electrolytes and non-electrolytes in the solution system, eventually it also is able to give information about the configurational structure of the solute or solvents present in the solutions.

Both organic and inorganic chemists is used the Infrared (IR) spectroscopy which is one of the most common spectroscopic techniques in science. It is the measurement of absorption of different IR frequencies by a sample placed in the path of an IR beam. The main aim of IR spectroscopic investigation is to determine the chemical functional groups present in the sample. The characteristic frequencies of IR radiation absorb by various functional groups exist in the sample. Infrared spectrometers can accept a wide range of sample types such as gases liquids, and solids using various sampling accessories. Thus, IR spectroscopy is a significant and exoteric tool for structural elucidation and identification of compound.

Approximately 13,000 to 10 cm⁻¹, or wavelengths from 0.78 to 1000 μm are the wave number electromagnetic spectrum range of Infrared radiation. This spectrum region is bounded at high frequencies and at low frequencies by the red end of the visible and microwave region respectively.

Either positions of absorption of IR are generally represented as wavelengths (λ) or wavenumbers (ν). Definition of Wavenumber is the number of waves per unit length.

Thus, wavenumbers are not only directly proportional to frequency and as well as the energy of the IR absorption. The unit of wavenumber is denoted as (cm^{-1} , reciprocal centimetre) is more frequently applied in modern IR instruments that are linear in the cm^{-1} scale. In the contrast, where the wavelengths are inversely proportional to frequencies and their associated energy. At present, the suggested unit of wavelength is m (micrometres), but μ (micron) is often used in some older literature.

Information of IR absorption is generally represented in the form of a spectrum with wavelength or wavenumber as remain in the x-axis and intensity of absorption percentage of transmittance as in the y-axis.

T, Transmittance, is the ratio of radiant power transmitted by the sample (I) with respect to the radiant power incident on the sample (I_0).

$$A = \log_{10}(1/T) = -\log_{10}(T) = -\log_{10}\left(\frac{I}{I_0}\right) \quad (\text{II.92})$$

The spectra of the transmittance provide better disparity between intensities of strong and weak bands as the ranges of transmittance from zero to 100% T whereas the absorbance ranges from infinity to zero. It will appear only if some of IR bands have been contracted or expanded.

Near IR, mid IR, and far IR are three IR region is usually divided into three smaller areas:

	Near IR	Mid IR	Far IR
Wavenumber	13,000–4,000 cm^{-1}	4,000–200 cm^{-1}	200–10 cm^{-1}
Wavelength	0.78–2.5 μm	2.5–50 μm	50–1,000 μm

This chapter emphasizes on the most commonly used mid IR region, between 4000 and 400 cm^{-1} (2.5 to 25 μm).

From the analysis of the above, it is apparent that the problem of molecular interactions is intriguing as well as interesting. We have, therefore, utilized five important methods, viz., and volumetric, viscometric, interferometric, conduct metric and refract metric as the quantitative and FT-IR spectroscopy as the qualitative analysis for the studies of the thermophysical, physicochemical, thermodynamics, transport properties

occurring in different studied liquid systems. Utilizing the theoretical and experimental results, we have employed all the studies for application in different fields.

II.12.UV-Visible-Spectroscopy

Various electronic energy level of molecules can undergoes electronic excitation from lower energy level to higher energy level and as a result a broad peak in UV-Visible spectrum. Bonding and non-bonding electrons in different energy level of molecules absorb different energy in the form of ultraviolet or visible light, which is responsible to excite these electrons from lower energy level to higher or anti bonding orbital. If the energy gap between HOMO and LUMO is not so high then the electron can easily excited to lower energy state to higher energy state. There are four possible types of transitions are $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$ $n \rightarrow \sigma^*$. The order of energy gap among the four is given as $n \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^* < \sigma \rightarrow \sigma^*$.

The following is the equation of Lambert-Beers law, which shows the relation of absorbance of light of a sample in a UV-Visible spectrum.

$$A = \log(I_0/I) = \epsilon cl \text{ for a particular wavelength of light}$$

A= denotes as Absorbance

I_0 = signify the Intensity of incident light

I= Intensity of the light that leaving from sample

ϵ = Molar absorptivity

c= signify molar concentration of solution of the sample

l=denotes as a length of cuvette containing sample

In this thesis of my research work, the data obtained from UV-Visible spectroscopy were fitted with the Benesi –Hildebrand equation for calculation the binding or stability constant to determination the different interactions occurring between the amino acids with ionic liquids.

II.13 Fluorescence Spectroscopy

It is the opposite spectra from UV-Visible spectra. It is called emission spectra. This spectra of emission is originated by the transitions of electron from higher energy state to lower energy state, shows fluorescence. In molecules, there are different electronic energy level as well as different vibrational energy level. In florescence, a

photon excited at first the species from its ground state to the next higher vibrational level of different states in the excited electronic state. After the excitation of the molecules, the molecules undergoes collisions with other molecules and as a result deactivates of the molecules. The excited species lose their vibrational energy simultaneously and reaches lowest vibrational energy of electronic state according to the opinion of Jablonski diagram. At last the molecules drops to one of the different vibrational energy state as a result again photons get emitted process giving the fluorescence.

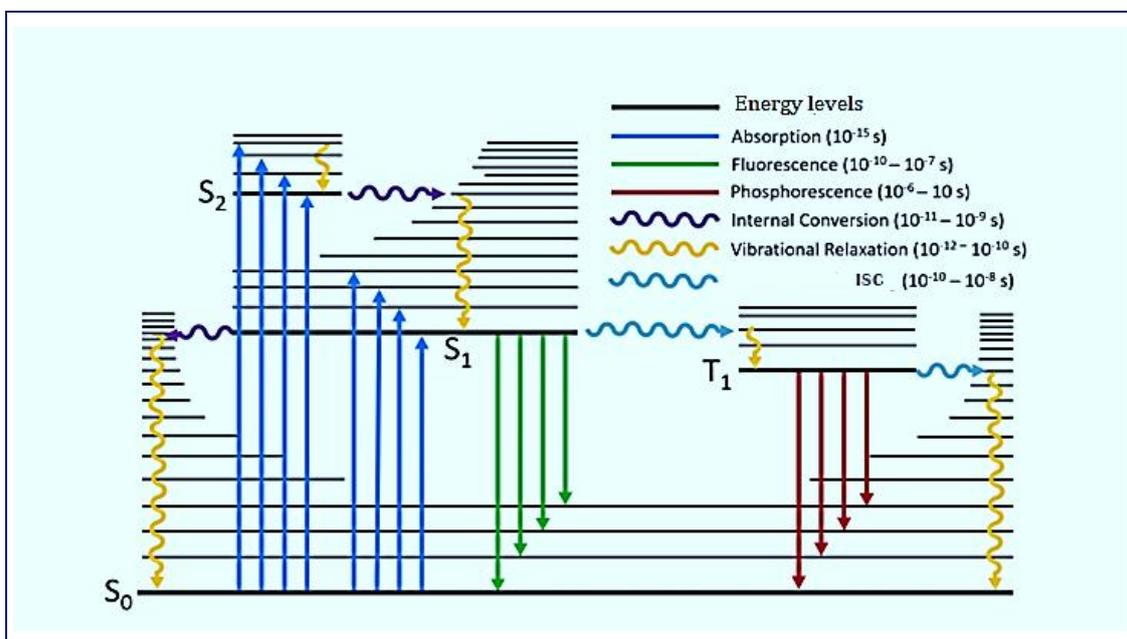


Fig: Jablonski diagram

II.14 Surface Tension Measurements

Molecules at the surface of a liquid exerted by the molecules at the bulk and trends to molecules towards the bulk of the liquid. In this situation the shape of the liquid, assume the least surface area.

In my research work, using ionic liquids in Aquous medium and amino acids in ionic liquid solutions. The surface tension of pure ionic liquid in water is less than pure water because hydrophobic part of the ionic liquid encapsulated in water molecules as a result the surface tension decrease. But with addition of some amino acid into the ionic liquid solutions again increase the surface tension. This is beau case the amino acid interact with ionic liquid as a result water molecules come out from the ionic liquid solution. Higher the interaction between amino acid with the ionic liquid higher is the value of surface tension

II.15.1H NMR Spectroscopy

NMR Spectroscopy is very important and most acceptable technique among all of the spectroscopic techniques to determination of characteristic an organic compound. From these techniques, it gives us the information about the neighboring magnetic environment of atomic nuclei and magnetically different environment of total number of hydrogen atoms.

In a magnetic field, the experimental sample is put and NMR signal is generated by the excitation of the nuclei of the sample into nuclear magnetic resonance with radio waves which is collected with sensitive radio receivers. The resonance frequency of an atom changes with the help of surrounding intramolecular magnetic field. NMR also gives us the nature of electronic structure of a molecule and associate individual functional groups. Since these fields are generally unique for particular compounds therefore in modern organic chemistry, NMR technique is definitive process to detect monomolecular organic molecules. In the same way, biochemists apply this technique also to detect the structure of protein as well as complex molecules. Not only identification, but also NMR spectroscopy procedure gives the detailed information about the structure of molecules, state of reaction, dynamics and chemical environment of the molecules. Proton NMR and ¹³-carbon NMR Spectroscopy is the most common types of NMR, but it is only acceptable when the nuclei of atoms of molecule processing spin.

Long timescale of NMR Spectroscopy that does not indicates the fast phenomenon, so it produce an average spectrum. NMR spectrum does not show the spectra of samples having a large extent of impurities of the samples. Therefore, for higher sensitivity of the instrument higher strength of external field may be required to detect the spectrum of the samples.

Integrals and integrations

We can analysis the peak intensity as well as the number of protons of different types with the help of software very easily. With the help of intregation we can measure the intensity of the signal obtained from NMR Spectroscopy and also the total number of atoms presents. The number of protons is directly proptional with the intensity of the NMR signal obtained from the simplest NMR technique. The integral of signals obtained

from ^{13}C -NMR spectra also depends on the dipolar coupling constants and also the relaxations rate of the concentrate nucleus of atoms.

Chemical shift

Nature of proton in NMR spectroscopy can be determined from the chemical shift value. With the help of chemical shift values of protons the magnetic environment and also the signal in different positions obtained in ^1H NMR spectrum. The position of signals in spectrum depends on the strength of the external magnetic field. TMS (tetramethylsilane) is usually used as a reference for calculating the chemical shift value determination in NMR Spectrum of corresponding protons of a molecule. A local magnetic field is generated by the electron density around the nucleus which is opposed the external magnetic field. As a result of shielding of proton in ^1H NMR spectrum take place. If electronegative atom consisting around the nucleus which withdraw itself around its neighboring atoms as a result the electron density of neighboring atom decrease, hence the proton experience downfield shift.

In my research work in this thesis, interacting protons of amino acids with the ionic liquids result in shifting of chemical shift values from the chemical shift value of pure amino acid and pure ionic liquid.