

## CHAPTER II

### GENERAL INTRODUCTION (REVIEW OF THE PREVIOUS WORKS)

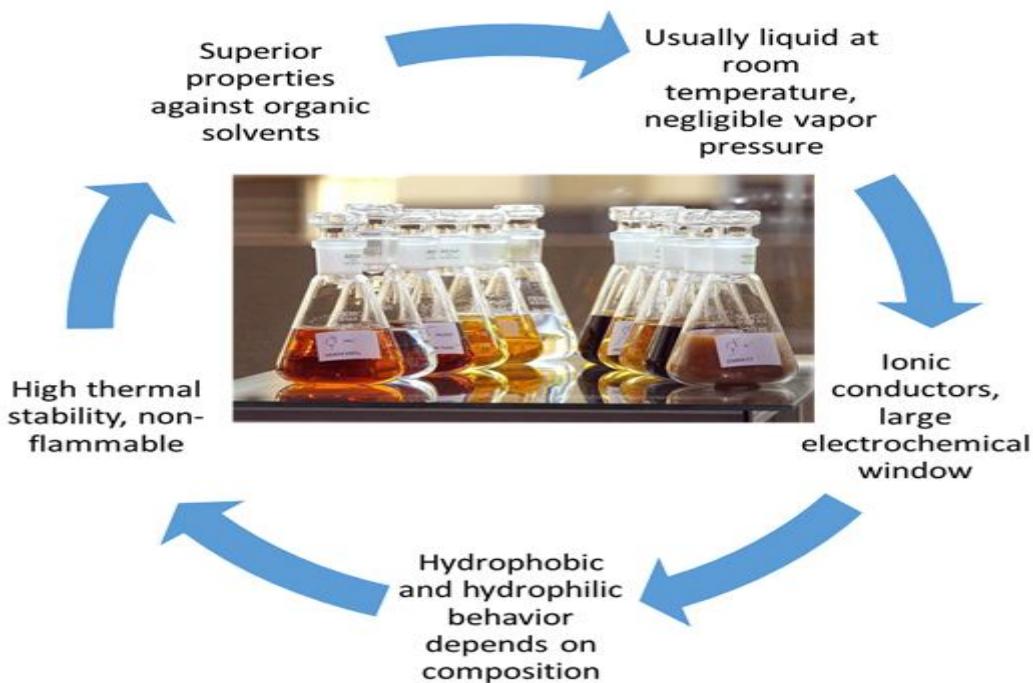
#### 2.1. IONIC LIQUIDS

In the last few decades a new class of materials came into the focus of researcher around the world: ionic liquids (IL). There physical and chemical characteristics are growing interests to contemporary scientists. A more comprehensive outline about the possible applications and properties of ionic liquids can be found in the recent book "*Ionic Liquids in Syntheses*", edited by Peter Wasserscheid and Tom Welton [1]. The commonly accepted definition of ionic liquids is that they are "*ionic materials that are liquid below 373 K*" [2]. Ionic liquids are salts with melting points below 373 K. They consist of an organic cation combined with an organic or inorganic anion [3]. However, the opinions about the definition of "*ionic material*" are more spread. Many alternatives to organic solvents have been proposed over the last two decades. However, many organic compounds do not dissolve in water, and particularly solids cannot be assorbed without a solvent. Thus appropriate alternatives of water have been required and it was found that ionic liquids have gained a lot of attention as emerging green replacements of water, i.e., ideal solvent[4]. The melting points of these organic salts are frequently found below 150 °C (423K) and occasionally as low as – 96 °C (177K). They normally have high solvency power, low vapour pressure and high ionic conductivity for polar and non-polar compounds. Furthermore, the ability to tune the solvent properties of the ionic liquids is one of their outstanding features, which makes them unique solvents for various reactions and separations [5, 6].

Room temperature ionic liquid (RTIL) are ILs which are liquid at room temperature. In the older (and some current) review, ionic liquids are occasionally called liquid organic salts, it may be fused salts or molten salts or ionic melts. RTIL have also termed as non-aqueous ionic liquids, room-temperature molten salts, organic ionic liquids and ionic fluids [7]. In existing times Ionic liquids (IL) have appeared as room temperature ionic liquids (RTILs) and atmosphere responsive solvents for the development of the industrialized chemical compounds. Ionic

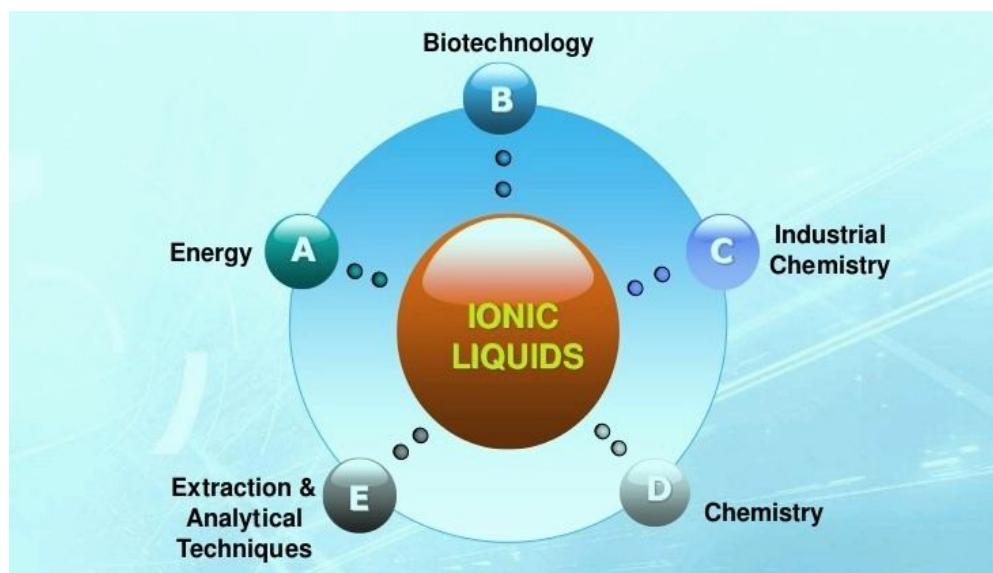
## General Introduction (Review of the Earlier Work)

liquids now have been increasingly used for various commercial and prospective purposes such as organic synthetic chemistry, catalytic process, electrochemical industries and solvent extraction techniques. Usually, organic or inorganic part of the IL is cation and inorganic part is anion [8].



Commonly ILs consist of a large bulky and asymmetric organic cations based on 1-alkyl-3-methylimidazolium (abbreviated  $[C_n\text{mim}]^+$ , where  $n$  = number of carbon atoms in a linear alkyl chain),  $N$ -alkylpyridinium (accordingly abbreviated  $[C_n\text{py}]^+$ ) or 1-butyl-1-methylpyrrolidinium (accordingly abbreviated  $[C_n\text{Pyrr}]^+$ ), or many others; and inorganic anions such as hexafluorophosphate  $[\text{PF}_6]^-$ , tetrafluoroborate  $[\text{BF}_4]^-$ , some alkylsulfates  $[\text{RSO}_4]^-$ , halides as chloride  $[\text{Cl}]^-$ , bromide  $[\text{Br}]^-$  or iodide  $[\text{I}]^-$ , nitrate  $[\text{NO}_3]^-$ , sulfate  $[\text{SO}_4]^-$ , 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.

Ionic liquids have wide uses, such as the recovery of bio-fuels, desulfurization of diesel oil and supercritical fluid extractions etc. Ionic liquids also have potential applications in lubricants, in solar cells, heat transfer and storage, in nuclear fuel processing, in membrane technology and for the dissolution of cellulose.



Because of these versatile applications and properties, scientific community have immense demand of ionic liquids (both in academia and industry). Almost 8000 papers have been published in the last decade. There are about one million ( $10^6$ ) simple ionic liquids that can be easily prepared in the laboratory by combination of different cations and anions and this total are just for simple primary systems. If there are one million possible simple IL systems, then 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 other substituent. At present only about 300 ionic liquids are commercialized. This number in the case of ionic liquid based surfactants is even much more less. The all-round and extremely useful properties of ILs have been documented in the current millennium; this led to an explosive growth in the number of basic research on ILs. Soon afterward, it was recognized that these properties should also apply to compounds that carry long hydrocarbon chains, that is, compounds with surface activity. [9, 10]

## 2.2. SOME BIOLOGICALLY ACTIVE MOLECULES

Biologically active molecules have at least one practical effect on living organism, tissue or cell of the living organism. For this reason all the drug molecules are biologically active molecules including some vitamin, amino acid, alkaloid and other organic acid molecules. Basically they are organic molecules having carbon, hydrogen and oxygen and to lesser extent of nitrogen, phosphorus and sulphur. They include macromolecules such as polysaccharides, proteins, lipids, alkaloids and

nucleic acids as well as small molecules such as natural products etc. Biologically active compounds are widely used as a drug, food or nutrients. These active molecules thus have direct effects on health. These will reduce many hazardous diseases, like cancer, cardiovascular disease, diabetes etc. Because of these biological activity, diverse and numerous experimental approach are to be considered to understanding of biological significance of bio-active molecules. Thus bio-active molecules are therefore required in almost all metabolic and therapeutic purposes.

Cyclodextrins ( $\alpha$  and  $\beta$ ) are cyclic polysaccharides, both of them contain glucose unit, widely applied in production of medicine and food, cosmetics, paint, and textile industries. In the production of medicine, it can strengthen the stability of medicine without being oxidized and resolving. And the effect on living of medicine, lower the toxic and side-effect of medicine and cover the strange and bad smell. In the production of food, it can mainly cover strange and bad smell of food, improve the stability of perfume and condiment and keep food dry or wet at will. Cyclodextrins ( $\alpha$  and  $\beta$ ) are most commonly used as a complexing agent in hormones, some vitamins and many other compounds normally used in tissue and cell biology [11,12].

India with the highest number of people suffering from diabetic disorders has been considered as the diabetic capital of the world by the "International Journal of Diabetes in Developing Countries." There is an alarming rise in diabetes patients in India; approximately 3.4 million deaths occur due to complication related to high blood sugar. Trigonelline is a pyridine alkaloid known to be mostly found in leguminosae members and is reported to be metabolically active as a hypcholesterolemic agent along with potential hypoglycemic effect [11-14][13-17]. Fenugreek has been successfully implemented as antidiabetic remedy for both types I and II diabetes [15] [18]. Moreover, fenugreek has been reported to be enriched with wide spectrum of pharmacological and folkloric consequence [16] [19].

## 2.3. INCLUSION COMPLEXES

Inclusion Complexes are those in which a guest molecule or part of the molecule is inserted into the molecular host. The molecular approach taking place for these host-guest complexes is non-covalent in nature. Cyclodextrin, crown ethers, porphyrins, calixarenes etc. are seems to be the host molecules. The host

molecules have suitable polarity and cavity size. In host-guest chemistry, an inclusion complex is a complex in which one chemical species ("host") forms a cavity in which molecules of a second "guest" molecule or entity are situated in the host cavity and thus form inclusion complex through various favourable weak interactions. Ionic liquids, surfactants, ionic liquid surfactants, alkaloids, amino acid and amino acid derivatives are considered as guest molecules for inclusion complexes with cyclodextrins, calixarenes, crowns etc. and their derivatives.

The solubility and dissolution properties of drugs play an important role in the process of formulation progress. Problem of solubility of some bio-molecules is a major challenge for formulation chemist. Solid dispersion, solvent deposition, micronization are some vital approaches routinely employed to improve the solubility of feebly water soluble drugs. Each direction suffers with some boundaries and advantages. Among all, complexation technique has been employed more precisely to improve the aqueous miscibility, dissolution rate, and bioavailability of feebly water soluble drugs. Various physicochemical, microscopic and reliable spectroscopic techniques have been investigated to explain and understand the nature of interactions and of inclusion complexes.

Drug molecules are difficult to deliver due to bioavailability problems. Formulation of such tricky molecules are being tried to improve their solubility and bio-availability by physical modification. For such physical modifications, various excipients such as cyclodextrins, carbohydrates, and dendrimers are utilized. Most of the drugs are poorly water soluble drugs. There are numerous approaches available and reported in literature to enhance the solubility of poorly water soluble drug. The techniques are selected on the basis of definite aspects such as properties of drug under contemplation, nature of excipients to be selected and nature of intended dosage form. Among these approaches salting nature, solubility, particle size reduction, solid dispersion, and solvent deposition technique are most frequently used. Inclusion complex with cyclodextrins and other host molecules are the most attractive technique to enhance aqueous solubility of poorly soluble drugs. CyDs, act as the useful solubilizer enabling both solid and liquid oral and parenteral dosage forms. Solid binary system of drug and CyDs are capable to modify the physicochemical properties of drugs. The CyDs, due to their high aqueous solubility,

they became capable to enhance the dissolution rate and bio-availability of the poorly soluble drugs. The permeation of insoluble drugs through various biological membranes can also be enhanced by preparing drug-CyD inclusion compounds [19, 20] [22, 23].

## 2.4. SOLUTION CHEMISTRY

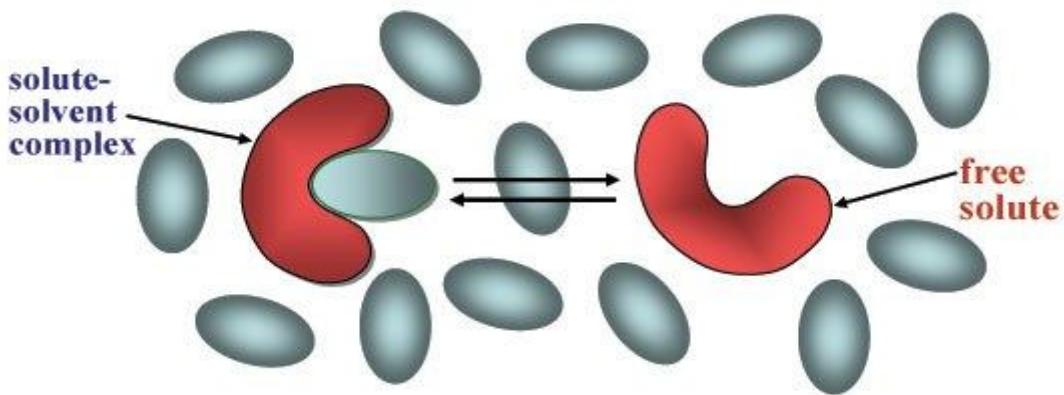
Solution chemistry investigates the miscibility of substances and it deals with the change in properties and chemical nature of both solute and solvent. There are three types of approach have been made to estimate the degree of solvation. The first is the solvation approaches connecting the studies of viscosity, density, conductance, etc., of electrolytes and the derivation of various factors related with ionic solvation [21], the second is the thermodynamic input by measuring the free energies, enthalpies and entropies of solvation of ions from which factors related with solvation can be exposed [22] and the third is to use spectroscopic measurements where the spectral shifts or the chemical shifts find out their qualitative and quantitative nature[23].

Therefore, understanding of the solvation phenomena will become authenticity only when solute-solute, solute-solvent and solvent-solvent interactions are operated in the solution or liquid systems and hence the present research work is quite thoroughly related to the studies of solute-solute, and solvent-solvent interactions in some industrially and biologically important liquid systems.

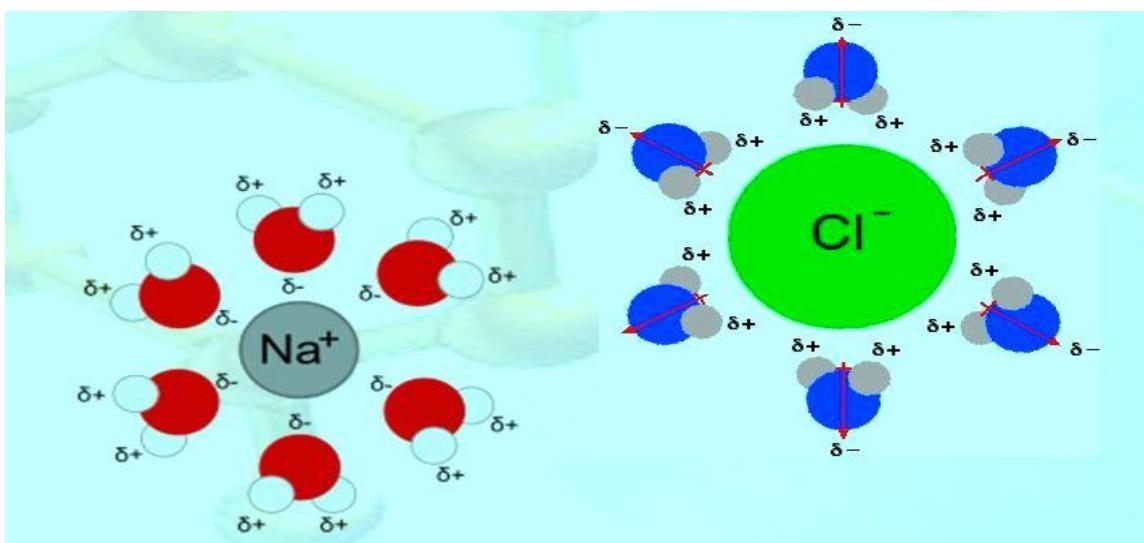
## 2.5. INTERACTIONS IN LIQUID PHASE

**There three types of interactions in the liquid systems:**

- a. **Solvent – solvent interactions:** energy necessary to break weak bonds between solvent molecules.
- b. **Solute – solute interactions:** energy necessary to break intermolecular bonds between the solute molecules.
- c. **Solute – solvent interactions:** comprises  $\Delta H$  negative because of bonds are formed between them.



The liquid phase is described by local order and long-range disorder, and to study processes in liquid systems, it is therefore valuable to use methods that probe the local surrounding of the constituent particles. The same is also true for solvation processes: a local probe is important to obtain insight into the physical and chemical processes occurring in solvent media.



**Schematic presentation of possible processes for solvation of a molecule.**

### 2.5.1. VARIOUS KINDS OF INTERACTIONS

The forces of interactions can be attractive or repulsive depending on charges of the solute and solvent molecules. On average, dipoles in a liquid orient themselves to form attractive interactions with their neighbors, but thermal motion makes the process unfeasible.

Polar solvent molecules are attracted by the ions of the solute molecules. For sake of simplicity, if the water molecules are on the crystal surfaces of ionic crystals then water molecules gradually surround and isolate the surface ions of the soluble crystals. They gradually move away from the crystal into solution, is called dissociation. The surrounding of solute particles by solvent particles 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 NaCl acts as a solution of  $\text{Na}^+$  &  $\text{Cl}^-$ .

The determination of thermodynamic, transport and volumetric properties of different electrolytes in aqueous medium would thus give an essential step in this direction. So, the development of theories, involving with electrolyte solutions, much interest has been devoted to ion-solvent interactions which are the determining forces in infinitely dilute solutions where ion-ion interactions are absent. Also, the contributions due to cations and anions of the solute can determine by the ionic-contribution estimation in the solute-solvent systems. Thus, ion-solvent interactions explain a very key role to know the physicochemical behaviour of the solute particles in diverse liquid systems.

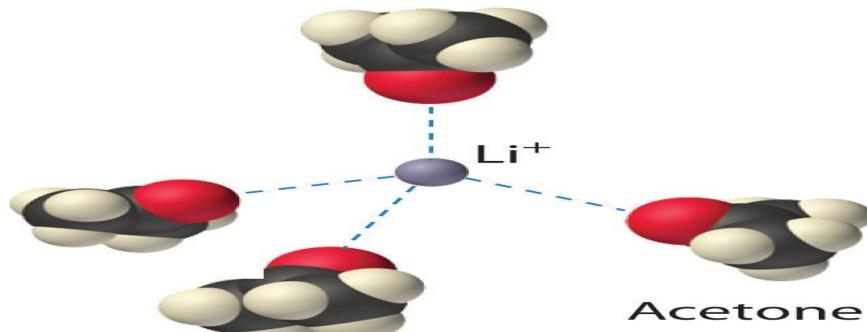
The ion-solvent interactions can also be investigated from the evaluation of thermodynamic parameters, e.g., changes of free energy, enthalpy and entropy, etc. associated with a particular reaction.

### **2.5.2. ION-SOLVENT INTERACTION**

Every living organism has solvated ions with their optimum existence. The exchange of solvent molecules around ions in solutions is basic to the understanding of the reactivity of ions in solution [24]. Solvated ions also play a key function in electrochemical industries, where for instance the conductivity of electrolytes depends on ion-solvent relations [25].

**Step 1: Holes opens in the solvent****Step 2: Molecules of the solid breaks away from the bulk****Step 3: The freed solid molecule is integrated into the hole in the solvent****The possible chemical method of producing ionic solutions**

In the ionic states, the solvent have collision with the walls of the crystal gives the ions in the crystal lattice and the process is energetically favourable. Thus there is a substantial energy of interaction between the ions and the solvent molecules, termed as ion-solvent interactions.

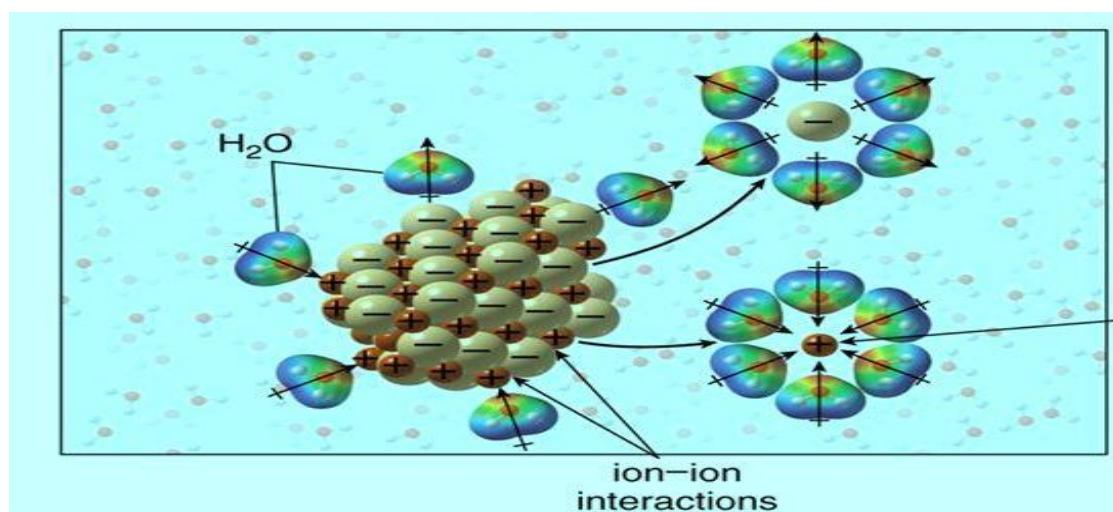


Water is the universal solvent in nature and its major consequence to applied science. Water has been broadly used in kinetic and equilibrium studies. But still our knowledge of molecular interactions in water is very limited. Moreover, the uniqueness of water as a solvent has been a subject of debate [26].

Ion-solvent interactions can also be investigated by spectrometry [30]. The spectral shifts of solvent or the chemical shifts can determine the qualitative and quantitative nature of ion-solvent associations.

### 2.5.3. ION-ION INTERACTION

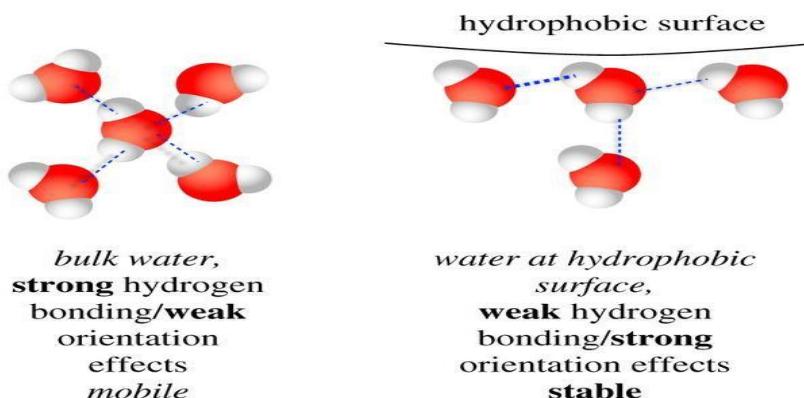
The surrounding of an ion sees not only solvent molecules but also other ions. The mutual interactions between these ions comprise the fundamental part - 'ion-ion interactions'. The extent of an ion-ion interaction affects the properties of solution and depends on the nature of electrolyte under investigation. These interactions are usually stronger than ion-solvent interactions. Ion-ion interaction in dilute solutions is now theoretically well implicit. While proton transfer reactions are predominantly sensitive to the nature of the solvent, it has become cleared that the solvents appreciably modify the majority of the solutes. On the contrary, the nature of the strongly structured solvents, such as water, is significantly modified by the presence of solutes.



### 2.5.4. SOLVENT-SOLVENT INTERACTION (THEORY OF MIXED SOLVENTS)

Non-aqueous and mixed solvents are gradually more used in chromatography, solvent extraction, in the verification reaction mechanism, in batteries, etc. Theories of perturbation type have been extended from their successful applicability in pure solvents to mixed solvents. Prigogine and Bellemans [33] 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 equal size, it was large positive for mixtures with molecules having little difference in their molecular sizes. Treszczanowicz *et al.* [34] 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.



Physical contributions add a positive term to  $V^E$ . The chemical intermolecular interactions result in a volume decrease and add negative values to  $V^E$ . The structural contributions are mostly 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 variation ( $\Delta\eta$ ) may be positive and vice-versa. This postulation is not a concrete one, as evident from some studies [35, 36]. It is observed in many systems that there is no simple correlation between the strength of interaction and the observed properties. Rastogi *et al.* [37] therefore suggested that the observed excess property is a combination of an interaction and non-interaction part. Then ion-interaction part 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. Based on the principle of corresponding states as suggested by Pitzer [38], L. Huggins [39] introduced a new move towards in his theory of conformal solutions. Using a easy perturbation approach, he showed that the properties of mixtures could be obtained from the knowledge of intermolecular forces and thermodynamic properties of the pure components. Recently, Rowlinson *et al.* [40-42] 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. A successful approach is due to Flory who made the use of certain features of cell theory [44-46] and developed a statistical theory for predicting the excess properties of binary

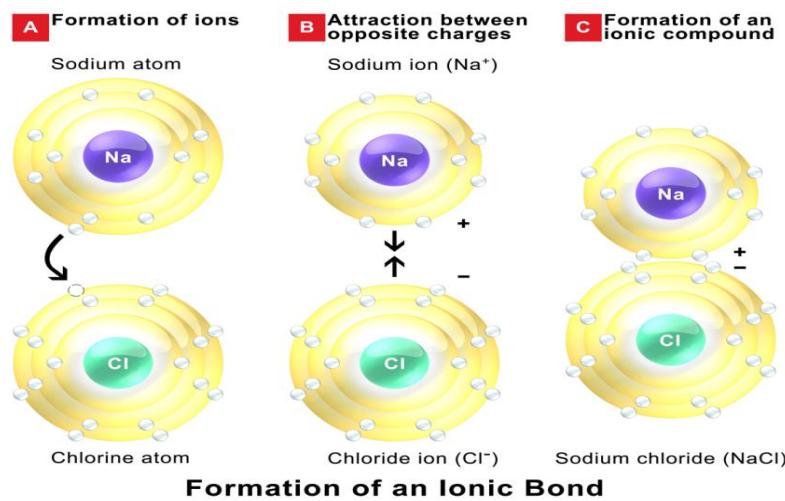
mixtures by using the equation of state and the properties of pure components along with some variable parameters. This theory is applicable to mixtures containing components with molecules of different shapes and sizes. Patterson and Dilamas [47] combined both Prigogine and Flory theories to a unified one for rationalizing various contributions of free volume, internal pressure, etc. to the excess properties. Recently, Heintz [46-51] and co-workers suggested a theoretical model 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). It combines the effect of association with non-associative intermolecular interaction occurring in solvent mixtures based on equation of state developed originally by Flory *et.al.* Subsequently the ERAS model has been successfully applied by many workers [52] to describe the excess thermodynamic properties of alkanol-amine mixtures. Recently, a new symmetrical reformation on the Extended Real Association (ERAS) model has been described in the literature [53]. The symmetrical-ERAS (S-ERAS) model makes it possible to describe excess molar enthalpies and volumes of binary mixtures containing very similar compounds described by extremely small mixing functions. The symmetrical Extended Real Associated Solution Model (S-ERAS) is, in fact, a simple continuation of the ERAS model. It was developed in order to widen its applicability to the thermodynamic properties of systems that could not be satisfactorily described by the equations of the ERAS model [54, 55].

#### **2.5.5. BINDING FORCES OF ATOMS IN A MOLECULE**

Molecular interactions between two or more molecules are known as intermolecular interactions and the interactions between the atoms within a molecule are called intramolecular interactions. Intermolecular interactions presence all types of molecules or ions in all states of matter. The energy required to break a chemical bond is called the bond-energy, e.g. the average bond-energy for O-H bonds in H<sub>2</sub>O is 463kJ/mol. The forces holding molecules together are generally called intermolecular forces. The energy required to break molecules apart is much smaller than a characteristic bond-energy, but intermolecular forces play vital roles in determining the properties of a substances. Intermolecular forces are mainly important in terms how molecules interact & form biological organisms or even life.

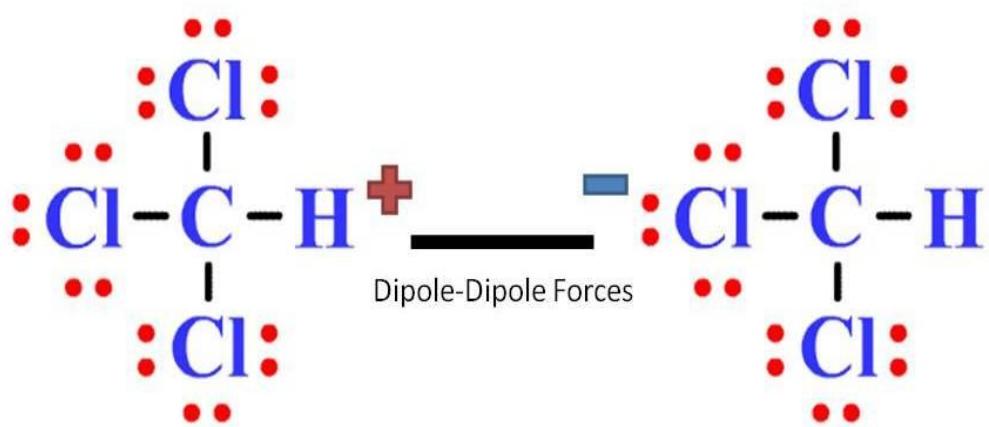
An assortment of intermolecular forces of interactions are-

- a. **Strong ionic attraction:** It relates to properties of ionic solids. The more ionic compound has the higher lattice energy. The following trends can be explained by ionic attraction: LiF, 1036; LiI, 737; KF, 821; MgF<sub>2</sub>, 2957 kJ/mol.

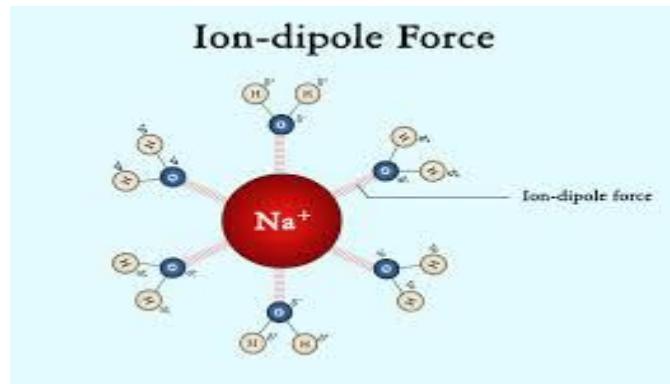


- b. **Dipole-dipole forces:**

Molecules have permanent dipoles can interact with other polar molecules through dipole-dipole interactions and this type of interactions are electrostatic in nature. Higher dipole moment material show greater melting and boiling point than lower dipole moment material.

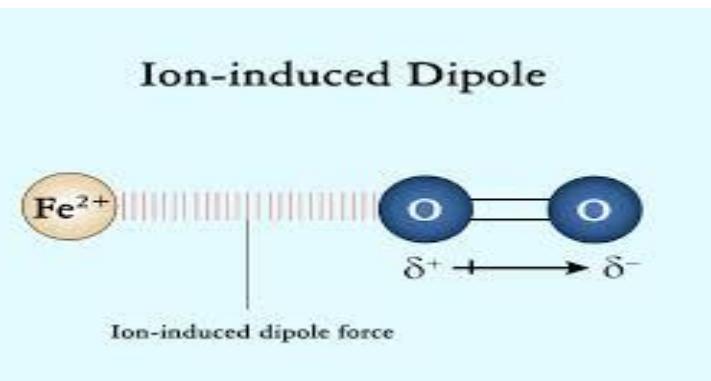


- c. **Ion-dipole forces:** This is the attractive interaction between ion and a dipolar molecule.

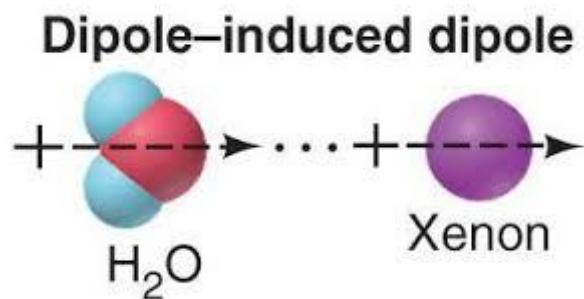


**d. Weak London dispersion forces or Van der Waal's force:**

This type of attractive interactions arises as a result of temporary dipoles induced atoms or molecules. Dispersion forces also identified as London forces or induced dipoles. It is two types; one is ion-induced dipole and other one is dipole – induced dipole.

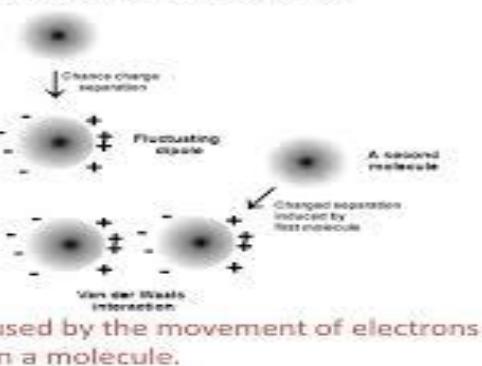


A permanent dipole molecule can induce a near about molecule and create a dipole in the second molecule that is located nearby in space. The strength of the interaction depends on the dipole moment of the first molecule and the polarizability of the second.



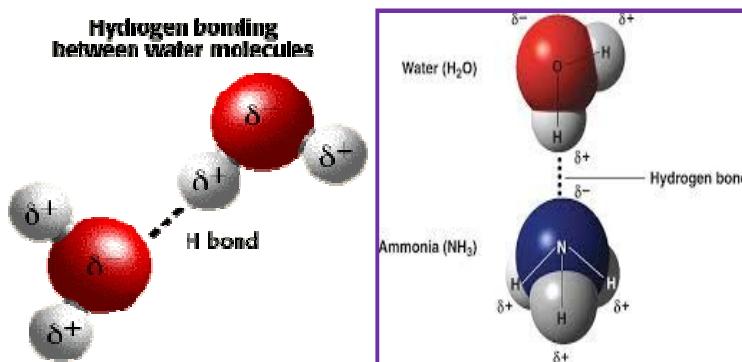
## London Dispersion Forces

The electron clouds get off-balance and attract each other slightly.

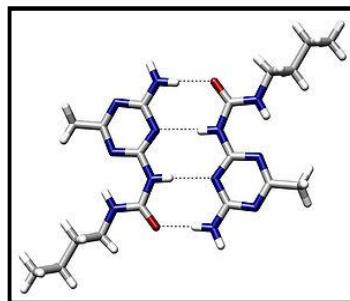


Temporary dipoles caused by the movement of electrons in a molecule.

e. **Hydrogen bond:** Hydrogen (H) bond is the attractive force of interaction between polar molecules in which hydrogen is bound to highly electronegative atom, such as nitrogen, oxygen or fluorine. The H atom so covalently bonded to other electronegative atoms of the other molecule or itself to create the new type of bond. This type of bond can occur intermolecularly or intramolecularly.

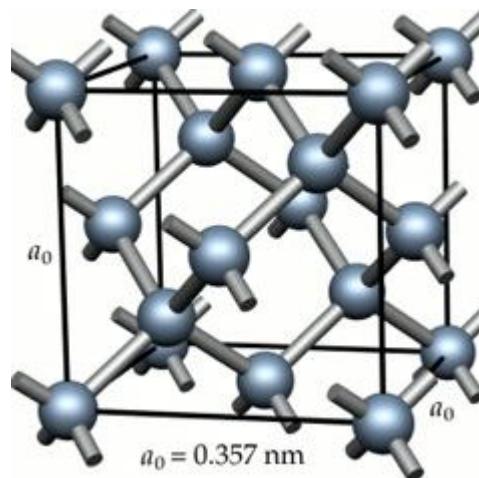


The H bond (5 to 30  $\text{kJ mole}^{-1}$ ) is stronger than a van der Waals interaction, but weaker than covalent or ionic bonds. Certain substances such as  $\text{H}_2\text{O}$ ,  $\text{HF}$ ,  $\text{NH}_3$  form H bonds, and the formation of which affects properties (m.p, b.p, solubility) of substance.



### Intermolecular hydrogen bonding in a self-assembled dimer complex

f. **Covalent bonding:** Covalent bond is a chemical bond that involves the sharing of electrons pairs between two atoms. Covalent is actually intramolecular force rather than intermolecular force. Covalent bonds are strong, and their enthalpies are on the order of  $100 \text{ kcal mole}^{-1}$  and weaker than ionic bond. It is declared here, because some solids are formed by the covalent interactions, e.g. in diamond molecule, silica and quartz etc., atoms in the whole crystal are correlated together by covalent bonding. So, the solids are hard, brittle, and have high melting & boiling points.



### Covalent Bonding in Diamond

Intermolecular interactions are important in decisive the solubility of a substance. "Like dissolve like" i.e., polar molecules dissolve in polar solvent and vice versa.

## 2.6. DENSITY

The physicochemical properties of liquid systems have alarmed much attention from both theoretical and engineering application. The volumetric properties include "Density" as a function of weight, volume, mole fraction and excess volumes of mixing. One of the recognized approaches to the study of molecular interactions in liquids is the utilization of thermodynamic methods. These properties are generally some thermodynamic parameters, such as enthalpy, entropy and Gibbs energy represents the macroscopic state of the system. The appearance of these macroscopic properties in terms of molecular phenomena is typically difficult. Various concepts regarding molecular processes in solutions like electrostriction, hydrophobic hydrations, micellization and co-sphere overlap during solute-solvent interactions [57-59] have been derived and interpreted from the partial molar volume data.

### 2.6.1. APPARENT AND PARTIAL MOLAR VOLUMES

In dilute solutions the molar volume data are useful understand the solute-solvent interaction, is obtained from the density measurements. The volume contributed to a solvent by the addition of one mole of an ion is difficult to know because, upon admission 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 influence of the ion's electric field, i.e., electrostriction. It's a general phenomenon & whenever there are electric fields of the order of  $10^9\text{-}10^{10}\text{ V m}^{-1}$ , the compression of ions and molecules is likely to be important. The effective volume of an ion in solution, the partial molar volume, can be determined from an easily obtainable quantity-apparent molar volume ( $\phi_v$ ). The apparent molar volumes, ( $\phi_v$ ), of the solutes can be calculated by using the following relation [52].

$$\phi_v = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \quad (1)$$

Where, M is the molar mass of the solute,

c is the molarities of the solution,

$\rho_0$  and  $\rho$  are correspond to the densities of the solvent and the solution,

The partial molar volumes,  $\phi_{2v}$ , can be obtained from the equation [60]:

$$\phi_{2v} = \phi_v + \frac{(1000 - c\phi_v)}{2000 + c^{\frac{3}{2}} \left( \frac{\partial \phi_v}{\partial \sqrt{c}} \right)} c^{\frac{1}{2}} \left( \frac{\partial \phi_v}{\partial \sqrt{c}} \right) \quad (2)$$

The extrapolation of the apparent molar volume of electrolyte to infinite dilution solution obtained by four most important equations over a decade's viz. the Masson [61], the Redlich-Meyer [62], the Owen-Brinkley [63], and the Pitzer equation. Masson found that the apparent molar volume of electrolyte,  $\phi_v$ , differ with the square root of the molar concentration by the use of linear equation:

$$\phi_v = \phi_v^0 + S_v^* \sqrt{c} \quad (3)$$

Where,  $\phi_v^0$  is the apparent molar volume or the partial molar volume at infinite dilution and  $S_v^*$  the experimental slope. The majority of  $\phi_v$  data in H<sub>2</sub>O & nearly all  $\phi_v$  data in non-aqueous [52-63] solvents have been extrapolated to infinite dilution through the use of equation (3).

The temperature dependence of  $\phi_v^0$  of different investigated electrolytes in various solvents can be articulated as follows:

$$\phi_v^0 = a_0 + a_1 T + a_2 T^2 \quad (4)$$

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

The limiting apparent molar expansibilities ( $\phi_E^0$ ) can be designed by the following equation:

$$\phi_E^0 = (\delta \phi_v^0 / \delta T)_P = a_1 + 2a_2 T \quad (5)$$

The limiting apparent molar expansibilities ( $\phi_E^0$ ) change in magnitude with the variation of temperature. Different workers emphasized that  $S_v^*$  is not the only norm for determining the structure-making or breaking tendency of any solute. So, Helper [65] developed a method of examining the sign of  $(\delta \phi_E^0 / \delta T)_P$  for the solute in terms

of long-range structure-making and breaking capacity of the electrolytes in the mixed solvent systems. The general thermodynamic expression used for structure oriented purpose is as follows:

$$\left(\delta\phi_E^0/\delta T\right)_P = \left(\delta^2 \phi_V^0/\delta T^2\right)_P = 2a_2 \quad (6)$$

If the sign of  $(\delta\phi_E^0/\delta T)_P$  is positive or small negative the electrolyte is a structure maker and vice versa. Redlich and Meyer [63] have shown that an equation (3) cannot become a limiting law where for a given solvent and temperature, the slope  $S_v^*$  should depend only upon the valence type. They recommended the equation:

$$\phi_v = \phi_v^0 + S_v \sqrt{c} + b_v c \quad (7)$$

$$\text{where } S_v = K w^{3/2} \quad (8)$$

$S_v$  is the theoretical slope, based on molar concentration, with the valence factor where

$$w = 0.5 \sum_i^j Y_i Z_i^2 \quad (9)$$

$$\text{And, } K = N^2 e^2 \left( \frac{8\pi}{1000 \epsilon^3 RT} \right)^{1/2} \left[ \left( \frac{\partial \ln \epsilon}{\partial p} \right)_T - \frac{\beta}{3} \right] \quad (10)$$

In equation (10),  $K$  is the compressibility of the solvent and the others signifying their usual meanings.

The Redlich-Meyer's extrapolation equation [62] effectively represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation. Thus, for polyvalent electrolytes, the more complete Owen-Brinkley equation [63] can be used to aid in the extrapolation to infinite dilution and to adequately represent the concentration dependency of  $\phi_v$ . The Owen-Brinkley equation which includes the ion-size parameter,  $a$  (cm), is:

$$\phi_v = \phi_v^0 + S_v \tau(\kappa a) \sqrt{c} + 0.5 w_v \theta(\kappa a) c + 0.5 K_v c \quad (11)$$

Where, the symbols have their usual significance. However, this equation is not widely used for non-aqueous solutions.

Recently, the Pitzer formalism has been used by Pogue and Atkinson [67] to fit the apparent molal volume data. The Pitzer equation for the apparent molar volume of a single salt  $M\gamma_M M\gamma_X$  is as follows & the symbols are of usual meaning :

$$\phi_V = \phi_V^0 + V |Z_M Z_X| A_V |2b \ln \left( I + bI^{\frac{1}{2}} \right) + 2\gamma_M \gamma_X RT \left[ mB_{MX}^2 + m^2 (\gamma_M \gamma_X)^{\frac{1}{2}} C_{MX}^V \right] | \quad (12)$$

### 2.6.2. LIMITING PARTIAL MOLAR VOLUMES

The calculation of the ionic limiting partial molar volumes in diverse solvents is, however, a difficult one. At present, however, most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods originally developed for aqueous solutions to non-aqueous electrolyte solutions. In the last few years, the way suggested by Conway *et al.* [68] has been used more often. These authors used the method to determine the limiting partial molar volumes of the anion for a series of homologous tetraalkylammonium chlorides, bromides and iodides in aqueous solution. They plotted the limiting partial molar volume  $\phi_{vR_4NX}^0$ , for a series of these salts with a halide ion in common as a function of the formula weight of the cation,  $M_{R_4N^+}$  and obtained straight-lines for each series in the given equation (13):

$$\phi_{vR_4NX}^0 = bM_{R_4N^+} + \phi_{vX^-}^0 \quad (13)$$

The extrapolation to zero cationic formula weight gave  $\phi_{vX^-}^0$  of the halide ions.

Uosaki *et al.* [69] used this method for the parting of some literature values and of their own  $\phi_{vR_4NX}^0$  values into ionic contributions in organic electrolyte solutions. Krumgalz [70] applied the similar method to a large number of partial molar volume data for non-aqueous electrolyte solutions in a wide temperature range.

### 2.6.3. EXCESS MOLAR VOLUMES

The excess molar volumes,  $V^E$  are calculated from the molar masses  $M_i$  and the densities of pure liquids and the mixtures by the following equation [71, 72]

$$V^E = \sum_{i=1}^n x_i M_i \left( \frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (14)$$

Where,  $\rho_i$  and  $\rho$  are the density of the  $i^{\text{th}}$  component and density of the solution mixture respectively.  $V^E$  is the resultant of contributions from several opposing effects, namely, chemical, physical and structural. Physical contributions, which are nonspecific interactions between the real species present in the mixture, contribute a positive term to  $V^E$ . The chemical or specific intermolecular interactions result in a volume decrease, thereby contributing negative  $V^E$  values. The structural contributions are mostly negative and arise from several effects.

## 2.7. VISCOSITY

Viscosity is the basic property of liquids. Viscosity and volume could also give a lot of information on the structures and molecular interactions of liquid mixtures. Viscosity and volume are different types of properties of one liquid, though there is a certain relationship between them. So by measuring and studying them together, relatively more realistic and comprehensive information could be expected to be gained. The viscometric information includes 'Viscosity' as a function of composition, on the basis of weight, volume and mole fraction; comparison of experimental viscosities with those calculated with several equations and excess Gibbs free energy of viscous flow. Viscosity, one of the most significant transport properties is used for the determination of ion-solvent interactions and studied widely [73, 74]. Viscosity is not thermodynamic quantity, but viscosity of an electrolytic solution along with the thermodynamic property,  $\phi_{v,2}^0$ , i.e., the partial molar volume, gives lot of information and insight regarding ion-solvent interactions and the nature of structures in the electrolytic solutions.

### 2.7.1. VISCOSITY OF PURE LIQUIDS AND LIQUID MIXTURES

The comparison of viscosity of pure liquids & liquid mixtures give the idea about the molecular motion in liquids and it is controlled by the influence of the neighbouring molecules. The actual movement of molecules depends on the

intermolecular force between the neighbouring molecules. Thus this aspect of the momentum transfer which forms the origin of the procedures for predicting the variations in the viscosity of liquids and also liquid mixtures.

### 2.7.2. THE REACTION RATE THEORY FOR VISCOUS FLOW

Considering viscous flow as a chemical reaction in which a molecule moving in a plane occasionally acquires the activation energy necessary to leap over the potential barrier to the next equilibrium position in the same plane. Eyring [78]

showed that the viscosity of the liquid is given by:

$$\eta = \frac{\lambda_i h F_n}{\kappa \lambda^2 \lambda_2 \lambda_3 F_a^*} \exp \frac{\Delta E_{act}}{kT} \quad (15)$$

Where  $\lambda$  is the average distance between the equilibrium positions in the direction of motion,  $\lambda_1$  is the perpendicular distance between two neighbouring layers of molecules in relative motion,  $\lambda_2$  is the distance between neighbouring molecules in the same direction and  $\lambda_3$  is the distance from molecule to molecule in the plane normal to the direction of motion. The transmission coefficient ( $\kappa$ ) is the measure of the chance that a molecule having once crossed the potential barrier will react and not cross in the reverse direction,  $F_n$  is the partition function of the normal molecules,  $F_a^*$  that of the activated molecule with a degree of freedom corresponding to flow,  $\Delta E_{act}$  is the energy of activation for the flow process,  $h$  is Planck's constant and  $k$  is Boltzmann constant. Ewell and Eyring argued that for a molecule to flow into a hole, it is not necessary that the latter be of the same size as the molecule. Consequently they assume that  $\Delta E_{act}$  is a function of  $\Delta E_{vap}$  for viscous flow because  $\Delta E_{vap}$  is the energy required to make a hole in the liquid of the size of a molecule.

Utilizing the idea and certain other relations [76] finally gets

$$\eta = \frac{N_A h (2\pi m k T)^{\frac{1}{2}}}{V h} \frac{b R T V^{\frac{1}{3}}}{N_A^{\frac{1}{3}} \Delta E_{vap}} \exp \frac{\Delta E_{vap}}{n R T} \quad (16)$$

Where,  $n$  and  $b$  are constants. It was found that the theory could reproduce the trend in temperature dependence of  $\eta$  but the computed values are greater than the

observed values by a factor of 2 or 3 for most liquids. Kincaid, Eyring and Stearn [80, 85] have summarized all the working relations.

### 2.7.3. THE SIGNIFICANT STRUCTURE THEORY AND LIQUID VISCOSITY

Eyring and co-workers [78-83] improved the "holes in solid" model theory to picture the liquid state by identifying three significant structures. In brief, a molecule has solid like properties for the short time it vibrates about an equilibrium position and then it assumes instantly the gas like behaviour on jumping into the neighbouring vacancy. The above idea of significant structures leads to the following relation for the viscosity of liquid [78-79].

$$\eta = \frac{V_s}{V} \eta_s + \frac{V - V_s}{V} \eta_g \quad (17)$$

Where,  $V_s$  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 while  $\eta_s$  and  $\eta_g$  are the viscosity contributions from the solid-like and gas-like degrees of freedom, respectively. The expressions for  $\eta_s$  and  $\eta_g$  are given by Carlson, Eyring and Ree [86]. Eyring and Ree [87] have discussed in detail the evaluation of  $\eta_s$  from the reaction rate theory of Eyring [88] assuming that a solid molecule can jump into all neighbouring empty sites. The expression for  $\eta_s$  takes the following form [89]

$$\eta_s = \frac{N_A h}{Z \kappa} \cdot \frac{V}{V_s} \cdot \frac{6}{2^{\frac{1}{2}}} \cdot \frac{1}{V - V_s} \cdot \frac{1}{1 - e^{-\theta/T}} \exp \frac{a' E_s V_s}{(V - V_s) R T} \quad (18)$$

Where  $N_A$  is Avogadro's number,  $Z$  is the number of nearest neighbours,  $\theta$  is the Einstein characteristic temperature,  $E_s$  is the energy of sublimation and  $a'$  is the proportionality constant. On the other hand, the term  $\eta_g$  is obtained from the kinetic theory of gases by the relation:

$$\eta_g = \frac{2}{3d^2} \left( \frac{mkT}{\pi^3} \right)^{\frac{1}{2}} \quad (19)$$

Where  $d$  is the molecular diameter and  $m$  is the molecular mass.

## 2.7.4. VISCOSITY OF ELECTROLYTIC SOLUTIONS

The viscosity relationships of electrolytic solutions are highly complicated. Because ion-ion and ion-solvent interactions are occurring in the solution and separation of the related forces is a difficult task. But, from careful analysis, vivid and valid conclusions can be drawn regarding the structure and the nature of the solvation of the particular system. As viscosity is a measure of the friction between adjacent, relatively moving parallel planes of the liquid, anything that increases or decreases the interaction between the planes will raise or lower the friction and thus, increase or decrease the viscosity. If large spheres are placed in the liquid, the planes will be keyed together in increasing the viscosity. Similarly, increase in the average degree of hydrogen bonding between the planes will increase the friction between the planes, thereby viscosity. An ion with a large rigid co-sphere for a structure-promoting ion will behave as a rigid sphere placed in the liquid and increase the inter-planar friction. Similarly, an ion increasing the degree of hydrogen bonding or the degree of correlation among the adjacent solvent molecules will increase the viscosity. Conversely, ions destroying correlation would decrease the viscosity. In 1905, Grüneisen [90] performed the first systematic measurement of viscosities of a number of electrolytic solutions over a wide range of concentrations. He noted non-linearity and negative curvature in the viscosity concentration curves irrespective of low or high concentrations. In 1929, Jones and Dole [91] suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations ( $c$ ):

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc \quad (20)$$

The above equation can be rearranged as:

$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} \quad (21)$$

Where  $A$  and  $B$  are constants specific to ion-ion and ion-solvent interactions. The equation is applicable equally to aqueous and non-aqueous solvent systems where there is no ionic association and has been used extensively. The term  $A\sqrt{c}$ , 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 [92] of inter-ionic attractions in 1923. The  $A$ -coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory [93] and is given by the Falkenhagen Vernon [94-95] equation:

$$A_{Theo} = \frac{0.2577 \Lambda_o}{\eta_o (\varepsilon T)^{0.5} \lambda_+^o \lambda_-^o} \left[ 1 - 0.6863 \left( \frac{\lambda_+^o \lambda_-^o}{\Lambda_o} \right)^2 \right] \quad (22)$$

Where, the symbols have their usual significance. In very accurate work on aqueous solutions [96], A-coefficient has been obtained by fitting  $\eta_r$  to equation (22) and compared with the values calculated from equation (23), the agreement was normally excellent. The accuracy achieved with partially aqueous solutions was however poorer [97].  $A$ -coefficient suggesting that should be calculated from conductivity measurements. Crudden *et al.* [98] suggested that if association of the ions occurs to form an ion pair, the viscosity should be analysed by the equation:

$$\frac{\eta_r - 1 - A\sqrt{\alpha c}}{\alpha c} = B_i + B_p \left( \frac{1-\alpha}{\alpha} \right) \quad (23)$$

Where  $A$ ,  $B_i$  and  $B_p$  are characteristic constants and  $\alpha$  is the degree of dissociation of ion pair. Thus, a plot of  $(\eta_r - 1 - A\sqrt{\alpha c}/\alpha c)$  against  $(1-\alpha)/\alpha$ , when extrapolated to  $(1-\alpha)/\alpha = 0$  gave the intercept  $B_i$ . However, for the most of the electrolytic solutions both aqueous and non-aqueous, the equation (22) is valid up to 0.1 (M) [100, 101] with in experimental errors.

At higher concentrations the extended equation (25), involving an additional coefficient  $D$ , originally used by Kaminsky, has been used by several workers [102, 104] and is given below:

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc + Dc^2 \quad (24)$$

The coefficient  $D$  cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, equation (21) is used by the most of the workers.

The plots of  $(\eta/\eta_o - 1)/\sqrt{c}$  against  $\sqrt{c}$  for the electrolytes should give the value of  $A$ -coefficient. But sometimes, the values come out to be negative or considerably scatter and also deviation from linearity occur [105-106]. Thus, instead of

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determining  $A$ - coefficient from the plots or by the least square method, the  $A$  - coefficient are generally calculated using Falkenhagen-Vernon equation (23). $A$  - coefficient should be zero for non-electrolytes. According to Jones and Dole, the  $A$ - coefficient probably represents the stiffening effect on the solution of the electric forces between the ions, which tend to maintain a space-lattice structure [107]. The  $B$  -coefficient may be either positive or negative and it is actually the ion-solvent interaction parameter. It is conditioned by the ions and the solvent and cannot be calculated a priori. The  $B$  –coefficients are obtained as slopes of the straight lines using the least square method and intercepts equal to the  $A$  values.

The factors influencing  $B$  - coefficients are:

- (1) The effect of ionic solvation and the action of the field of the ion in producing long-range order in solvent molecules, increase  $\eta$  or  $B$  -value.
- (2) The destruction of the three dimensional structure of solvent molecules (i.e., structure breaking effect or depolymeriation effect) decreases  $\eta$  values.
- (3) High molal volume and low dielectric constant, which yield high  $B$ -values for similar solvents.
- (4) Reduced  $B$ -values are obtained 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.

### **2.7.5. DIVISION OF $B$ -COEFFICIENT INTO IONIC VALUES**

The viscosity  $B$  -coefficients have been determined by a large number of workers in aqueous, mixed and non-aqueous solvents. However, the  $B$  -coefficients as determined experimentally using the Jones-Dole equation, does not give any impression regarding ion-solvent interactions unless there is some way to identify the separate contribution of cations and anions to the total solute-solvent interaction. The division of  $B$  -values into ionic components is quite arbitrary and based on some assumptions, the validity of which may be questioned. The following methods have been used for the division of  $B$  – values in the ionic components:

(1) Cox and Wolfenden [123] carried out the division on the assumption that  $B_{ion}$  values of  $\text{Li}^+$  and  $\text{IO}_3^-$  in  $\text{LiIO}_3$  are proportional to the ionic volumes which are proportional to the third power of the ionic mobilities. The method of Gurney [124] and also of Kaminsky is based on:

$$B_{K^+} = B_{Cl^-} \text{ (In water)} \quad (25)$$

The argument in favour of this assignment is based on the fact that the  $B$ -coefficients for KCl is very small and that the mobilities' of  $\text{K}^+$  and  $\text{Cl}^-$  are very similar over the temperature range 288.15 – 318.15 K. The assignment is supported from other thermodynamic properties. Nightingale [125], however preferred RbCl or CsCl to KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron is based on the assumption that the  $\text{Et}_4\text{N}^+$  ion in water is probably closest to be neither structure breaker nor a structure maker. Thus, they suggest that it is possible to apply with a high degree of accuracy of the Einstein's equation [126],

$$B = 0.0025\overline{V_o} \quad (26)$$

and by having an accurate value of the partial molar volume of the ion,  $V_o$ , it is possible to calculate the value of 0.359 for  $B_{Et_4N^+}$  in water at 298.15 K. Recently, Sacco *et al.* proposed the "reference electrolytic" method for the division of  $B$ -values.

Thus, for tetraphenyl phosphonium tetraphenyl borate in water, we have:

$$B_{BPh_4^-} = B_{PPh_4^+} + B_{BPh_4PPh_4}/2 \quad (27)$$

$B_{BPh_4PPh_4}$  (Scarcely soluble in water) has been obtained by the following method:

$$B_{BPh_4PPh_4} = B_{\text{NaBPh}_4} + B_{\text{PPh}_4\text{Br}} - B_{\text{NaBr}} \quad (28)$$

The values obtained are in good agreement with those obtained by other methods. The criteria adopted for the separation of  $B$ -coefficients in non-aqueous solvents differ from those generally used in water. However, the methods are based on the equality of equivalent conductance of counter ions at infinite dilutions.

- (a) Criss and Mastroianni assumed  $B_{K^+} = B_{Cl^-}$  in ethanol based on equal mobilities of ions [159]. They also adopted  $B_{Me_4N^+}^{25} = 0.25$  as the initial value for acetonitrile solutions.
- (b) For acetonitrile solutions, Tuan and Fuoss [160] proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer *et al.* [165],  $\lambda_{25}^o(Bu_4N^+) = 61.4$  and  $\lambda_{25}^o(Ph_4B^-) = 58.3$  in acetonitrile.

$$B_{Bu_4N^+} = B_{Ph_4B^-} \quad (29)$$

- (c) Gopal and Rastogi [115] resolved the  $B$ -coefficient in N-methylpropionamide solutions assuming that  $B_{Et_4N^+} = B_I$  at all temperatures.
- (d) In dimethyl sulphoxide, the division of  $B$ -coefficients were carried out by Yao and Beunion [154] assuming:

$$B_{[(i-pe)_3BuN^+]} = B_{Ph_4B^-} = 1/2B_{[(i-pe)_3BuNPh_4B]} \quad (30)$$

at all temperatures.

Wide use of this method has been made by other authors for dimethyl sulphoxide, sulpholane, hexamethyl phosphotriamide and ethylene carbonate [162] solutions. The methods, however, have been strongly criticized by Krumgalz [163]. According to him, any method of resolution based on the equality of equivalent conductance for certain ions suffers from the drawback that it is impossible to select any two ions for which  $\lambda_o^+ = \lambda_o^-$  in all solvents at all temperatures. Thus, though  $\lambda_K^+ = \lambda_{Cl^-}^-$  at 298.15 K in methanol, but is not so in ethanol or in any other solvents. In addition, if the mobilities of some ions are even equal at infinite dilution, but it is not necessarily true at moderate concentrations for which the  $B$ -coefficient values are calculated. Further, according to him, equality of dimensions of  $(i-pe)_3BuN^+$  or  $(i-Am)_3BuN^+$  and  $Ph_4B^-$  does not necessarily imply the equality of  $B$ -coefficients of these ions and they are likely to be solvent and ion-structure dependent. Krumgalz [158, 159] has recently proposed a method for the resolution of  $B$ -coefficients. The method is based on the fact that the large tetraalkylammonium cations are not solvated [159, 160] in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic  $B$ -values for large tetraalkylammonium

ions,  $R_4N^+$  (where  $R > Bu$ ) inorganic solvents are proportional to their ionic dimensions. So, we have:

$$B_{R_4NX} = a + br^3 R_4N^+ \quad (31)$$

$a=B_{X^-}$  and  $b$  is a constant dependent on temperature and solvent nature.

The extrapolation of the plot of  $B_{R_4NX}$  ( $R > Pr$  or  $Bu$ ) against  $r^3$  to  $R_4N$  to zero cation dimension gives directly  $B_{X^-}$  in the proper solvent and thus  $B$ -ion values can be calculated.

The  $B$ -ion values can also be calculated from the equations:

$$B_{R_4N^+} - B_{R_4'N^+} = B_{R_4NX} - B_{R_4'NX} \quad (32)$$

$$\frac{B_{R_4N^+}}{B_{R_4'N^+}} = \frac{r^3_{R_4N^+}}{r^3_{R_4'N^+}} \quad (33)$$

The radii of the tetraalkylammonium ions have been calculated from the conductometric data [167]. Gill and Sharma [165] used  $Bu_4NBPh_4$  as a reference electrolyte. The method of resolution is based on the assumption, like Krumgalz, that  $Bu_4N^+$  and  $Ph_4B^-$  ions with large R-groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constant. The ionic radii of  $Bu_4N^+$  (5 Å) and  $Ph_4B^-$  (5.35 Å) were, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers. They proposed the equations:

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \left(\frac{5.35}{5.00}\right)^3 \quad (34)$$

$$B_{Bu_4NBPh_4} = B_{Bu_4N^+} + B_{Ph_4B^-} \quad (35)$$

The method requires only the  $B$ -values of  $Bu_4NBPh_4$  and is equally applicable to mixed non-aqueous solvents. The  $B$ -ion values obtained by this method agree well with those reported by Sacco *et al.* in different organic solvents using the assumption as given below:

$$B_{[(i-Am)_3Bu_4N^+]} = B_{Ph_4B^-} = 1/2 B_{Bu_4NBPh_4} \quad (36)$$

Recently, Lawrence and Sacco and others [120-129] used tetrabutylammonium tetrabutylborate ( $Bu_4NBBu_4$ ) as reference electrolyte because the cation and anion

in each case are symmetrical in shape and have almost equal Vander Waal's volume. Thus, we have:

$$\frac{B_{\text{Bu}_4\text{N}^+}}{B_{\text{Bu}_4\text{B}^-}} = \frac{V_W(\text{Bu}_4\text{N}^+)}{V_W(\text{Bu}_4\text{B}^-)} \quad (37)$$

$$B_{\text{Bu}_4\text{N}^+} = \frac{B_{\text{Bu}_4\text{NBPh}_4}}{[1 + V_W(\text{Bu}_4\text{B}^-)/V_W(\text{Bu}_4\text{N}^+)]} \quad (38)$$

A similar division can be made for  $\text{Ph}_4\text{PBPh}_4$  system.

Recently, Lawrence *et al.* made the viscosity measurements of tetraalkyl (from propyl to heptyl) ammonium bromides in DMSO and HMPT.

The  $B$ -coefficients  $B_{\text{R}_4\text{NBr}} = B_{\text{Br}^-} + a[f_x R_4 N^+]$  were plotted as functions of the Vander Waal's volumes. The  $B_{\text{Br}^-}$  values thus obtained were compared with the accurately determined  $B_{\text{Br}^-}$  value using  $\text{Bu}_4\text{NBBu}_4$  and  $\text{Ph}_4\text{PBPh}_4$  as reference salts. They concluded that the 'reference salt' method is the best available method for division into ionic contributions.

Jenkins and Pritchett [130] suggested a least square analytical technique to examine additives relationship for combined ion thermodynamics data, to effect apportioning into single-ion components for alkali metal halide salts by employing Fajan's competition principle [169] and 'volcano plots' of Morris [132]. The principle was extended to derive absolute single ion  $B$ -coefficients for alkali metals and halides in water. They also observed that  $B_{\text{Cs}^+} = B_{\text{I}^-}$  suggested by Krumgalz to be more reliable than  $B_{\text{K}^+} = B_{\text{Cl}^-}$  in aqueous solutions. However, we require more data to test the validity of this method.

It is apparent that almost all these methods are based on certain approximations and anomalous results may arise unless proper mathematical theory is developed to calculate  $B$ -values.

## 2.7.6. TEMPERATURE DEPENDENCE OF B -ION VALUES cut

Regularity in the behaviour of  $B_\pm$  and  $dB_\pm/dT$  has been observed both in aqueous and non-aqueous solvents and useful generalizations have been made by Kaminsky. He observed that (i) within a group of the periodic table the  $B$ -ion values

decrease as the crystal ionic radii increase, (ii) within a group of periodic system, the temperature co-efficient of  $B_{Ion}$  values increase as the ionic radius. The results can be summarized as follows:

$$(i) A \text{ and } dA/dT > 0 \quad (39)$$

$$(ii) B_{Ion} < 0 \text{ and } dB_{Ion}/dT > 0 \quad (40)$$

Characteristics for the structure breaking of ions,

$$(iii) B_{Ion} > 0 \text{ and } dB_{Ion}/dT < 0 \quad (41)$$

Characteristics for the structure making of ions,

An ion when surrounded by a solvent sheath, the properties of the solvent in the solvation layer may be different from those present in the bulk structure. This is well reflected in the 'Co-sphere' model of Gurney [155], A, B, C Zones of Frank and Wen [134-139] and hydrated radius of Nightingale [140].

Stokes and Mills gave an analysis of the viscosity data incorporating the basic ideas presented before. The viscosity of a dilute electrolyte solution has been equated to the viscosity of the solvent ( $\eta_o$ ) in addition the viscosity changes resulting from the competition between various effects occurring in the ionic neighbourhood. Thus, the Jones-Dole equation:

$$\eta = \eta_o + \eta^* + \eta^E + \eta^A + \eta^D = \eta_o + \eta(A\sqrt{c} + Bc) \quad (42)$$

Where,  $\eta^*$ , the positive growth in viscosity is caused by columbic interaction. Thus,

$$\eta^E + \eta^A + \eta^D = \eta_o Bc \quad (43)$$

$B$ -coefficient can thus be explained in terms of the competitive viscosity effects.

Following Stokes, Mills & Krumgalz [173] we can write:

$$B_{Ion} = B_{Ion}^{Einst} + B_{Ion}^{Orient} + B_{Ion}^{Str} + B_{Ion}^{Reinf} \quad (44)$$

Whereas according to Lawrence and Sacco:

$$B_{Ion} = B_W + B_{Solv} + B_{Shape} + B_{Ord} + B_{Discord} \quad (45)$$

## General Introduction (Review of the Earlier Work)

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$B_{Ion}^{Einst}$  is the positive increment arising from the obstacle to the viscous flow of the solvent caused by the shape and dimension of the ions (the term corresponds to  $\eta^E$  or  $B_{Shape}$ ).  $B_{Ion}^{Orient}$  is the positive increment arising from the alignment or structure making action of the electric field of the ion on the dipoles of the solvent molecules (the term corresponds to  $\eta^A$  or  $B_{Ord}$ ).  $B_{Ion}^{Str}$  is the negative increment related to the destruction of the solvent structure in the region of the ionic co-sphere arising from the opposing tendencies of the ion to orientate the molecules round itself centro symmetrically and solvent to keep its own structure (this corresponds to  $\eta^D$  or  $B_{Disord}$ ).  $B_{Ion}^{Reinf}$  is the positive increment conditioned by the effect of reinforcement of the water structure' by large tetraalkylammonium ions due to hydrophobic hydration. The phenomenon is inherent in the intrinsic water structure and absent in organic solvents.  $B_W$  and  $B_{Solv}$  account for viscosity increases and attributed to the Van der Waals volume & the volume of the solvation of ions. Thus, small and highly charged cations like  $\text{Li}^+$  and  $\text{Mg}^{2+}$  form a firmly attached primary solvation sheath around these ions ( $B_{Ion}^{Orient}$  or  $\eta^E$  positive). At ordinary temperature, alignment of the solvent molecules around the inner layer also cause increase in  $B_{Ion}^{Orient}$  ( $\eta^A$ ),  $B_{Ion}^{Orient}$  ( $\eta^D$ ) is small for these ions. Thus,  $B_{Ion}$  will be large and positive as  $B_{Ion}^{Einst} + B_{Ion}^{Orient} > B_{Ion}^{Str}$  however,  $B_{Ion}^{Einst}$  and  $B_{Ion}^{Orient}$  would be small for ions of greatest crystal radii (within a group) like  $\text{Cs}^+$  or  $\text{I}^-$  due to small surface charge densities resulting in weak orienting and structure forming effect.  $B_{Ion}^{Str}$  would be large due to structural disorder in the immediate neighbourhood of the ion due to competition between the ionic field and the bulk structure. Thus,  $B_{Ion}^{Einst} + B_{Ion}^{Orient} < B_{Ion}^{Str}$  and  $B_{Ion}$  is negative. Ions of intermediate size (e.g.,  $\text{K}^+$  and  $\text{Cl}^-$ ) have a close balance of viscous forces in their vicinity, i.e.,  $B_{Ion}^{Einst} + B_{Ion}^{Orient} = B_{Ion}^{Str}$  so that  $B$  is close to zero.

Large molecular ions like tetraalkylammonium ions have large  $B_{Ion}^{Einst}$  because of large size but  $B_{Ion}^{Orient}$  and  $B_{Ion}^{Str}$  would be small, i.e.,  $B_{Ion}^{Einst} + B_{Ion}^{Orient} \gg B_{Ion}^{Str}$  would be positive and large. The value would be further reinforced in water arising from  $B_{Ion}^{Reinf}$  due to hydrophobic hydrations.

The increase in temperature will have no effect on  $B_{Ion}^{Einst}$ , but the orientation of solvent molecules in the secondary layer will be decreased due to increase in

thermal motion leading to decrease in  $B_{Ion}^{Str}$ .  $B_{Ion}^{Orient}$  will decrease slowly with temperature as there will be less competition between the ionic field and reduced solvent structure. The positive or negative temperature co-efficient will thus depend on the change of the relative magnitudes of  $B_{Ion}^{Orient}$  and  $B_{Ion}^{Str}$ .

In case of structure-making ions, the ions are firmly surrounded by a primary solvation sheath and the secondary solvation zone will be considerably ordered leading to an increase in  $B_{Ion}$  & related decrease in entropy of solvation & the mobility of ions. Structure breaking ions, on the other hand, are not solvated to a great extent and the secondary solvation zone will be disordered leading to a decrease in  $B_{Ion}$  values and increases in entropy of solvation & the mobility of ions. Moreover, the temperature induced change in viscosity of ions (or entropy of solvation or mobility of ions) would be more pronounced in case of smaller ions than in case of the larger ions. So, there is a correlation between the viscosity, entropy of solvation & temperature dependent mobility of ions. Thus, the ionic  $B$ -coefficient and the entropy of solvation of ions have rightly been used as probes of ion-solvent interactions & as a direct sign of structure making and structure breaking character of ions. The linear plot of ionic  $B$ -coefficients against the ratios of mobility viscosity products at two temperatures (a more sensitive variable than ionic mobility) by Gurney [180] clearly demonstrates a close relation between ionic  $B$ -coefficients and ionic mobilities. Gurney also demonstrated a clear correlation between the molar entropy of solution values with  $B$ -coefficient of salts. The ionic  $B$ -values show a linear relationship with the partial molar ionic entropies or partial molar entropies of hydration ( $\bar{S}_h^o$ ) as:

$$\bar{S}_h^o = \bar{S}_{aq}^o - \bar{S}_g^o \quad (46)$$

Where,  $\bar{S}_{aq}^o = \bar{S}_{ref}^o + \Delta S^o$ ,  $\bar{S}_g^o$ , is the calculated sum of the translational and rotational entropies of the gaseous ions. Gurney obtained a single linear plot between ionic entropies and ionic  $B$ -coefficients for all mono atomic ions by equating the entropy of the hydrogen ion ( $S_{H^+}^o$ ) to  $-5.5 \text{ cal.mol}^{-1} \text{ deg}^{-1}$ . Asmus [174] used the entropy of hydration to correlate ionic  $B$  values and Nightingale [167] showed that a single linear relationship could be obtained with it for both mono atomic and polyatomic ions. The correlation was utilized by Abraham *et al.* [174] to assign single ion  $B$ -

coefficients so that a plot of  $\Delta S_e^o$  [175, 176] the electrostatic entropy of solvation or  $\Delta S_{I,II}^o$  the entropic contributions of the first and second solvation layers of ions against  $B$  points (taken from the works of Nightingale) for both cations & anions lie on the same curve. There are brilliant linear correlations between  $\Delta S_e^o$  and  $\Delta S_I^o$  and the single ion  $B$ -coefficients. Both entropy criteria ( $\Delta S_e^o$  and  $\Delta S_{I,II}^o$ ) &  $B$ -ion values indicate that in H<sub>2</sub>O the ions Li<sup>+</sup>, Na<sup>+</sup>, Ag<sup>+</sup> & F<sup>-</sup> are not structure makers, & the ions Rb<sup>+</sup>, Cs<sup>+</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> & ClO<sub>4</sub><sup>-</sup> are structure breakers & K<sup>+</sup> is a border line case.

### 2.7.7. VISCOSITY DEVIATION

Viscosity of liquid mixtures can also provide information for the elucidation of the fundamental behaviour of liquid mixtures, aid in the correlation of mixture viscosities with those of pure components, and may provide a basis for the selection of physico-chemical methods of analysis. Quantitatively, as per the absolute reaction rates theory, the deviations in viscosities  $\Delta\eta$ , from the ideal mixture values can be calculated as:

$$\Delta\eta = \eta - \sum_{i=1}^j (x_i \eta_i) \quad (47)$$

Where  $\eta$  is the dynamic viscosities of the mixture and  $x_i \eta_i$  are the mole fraction and viscosity of i<sup>th</sup> component in the mixture, respectively.

### 2.7.8. GIBBS EXCESS ENERGY OF ACTIVATION FOR VISCOUS FLOW

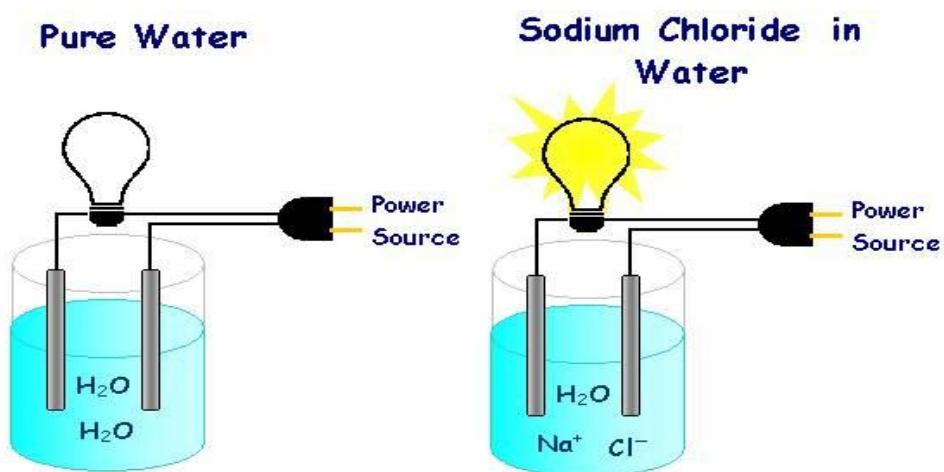
Quantitatively, the Gibbs excess energy of activation for viscous flow  $\Delta G^E$  can be designed as [182]:

$$\Delta G^E = RT \left[ \ln \eta V - \sum_{i=1}^j (x_i \ln \eta_i V_i) \right] \quad (48)$$

Where,  $\eta$  and  $V$  are the viscosity and molar volume of the mixture;  $\eta_i$  and  $V_i$  are the viscosity and molar volume of i<sup>th</sup> pure component, respectively.

## 2.8. CONDUCTANCE

One of the most precise and direct technique available to determine the extent of the dissociation constants of electrolytes in aqueous, mixed and non-aqueous solvents is the "conductometric method." Conductance data in conjunction with viscosity measurements, gives a large amount of information regarding ion-ion and ion-solvent interaction.



## 2.9. REFRACTIVE INDEX

Optical data (refractive index) of electrolyte mixtures 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 other properties [253].

The refractive index defined as the ratio of the speed of light in a vacuum with respect to the speed of light in other substance.

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

Whenever light changes speed as it travels a border from one solution into another medium, its movement of direction also changes, i.e., it is refracted. The relationship between light's speed in the two mediums ( $V_A$  and  $V_B$ ), the angles of incidence ( $\sin\theta_A$ ) and refraction ( $\sin\theta_B$ ) and the refractive indexes of the two mediums ( $n_A$  and  $n_B$ ) is shown below:

$$\frac{V_A}{V_B} = \frac{\sin \theta_A}{\sin \theta_B} = \frac{n_B}{n_A} \quad (49)$$

Thus, it is not necessary to measure the speed of light in a sample in order to measure its index of refraction. Refractive index or index of refraction of a molecule suggests the compactness of the sample; it is 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 [358] by using,  $n_D$  experimental data according to the following expression

$$R = [(n_D^2 - 1) / n_D^2 + 2] (M / \rho) \quad (50)$$

Where,  $M$  is the mean molecular weight of the mixture and  $\rho$  is the mixture density.  $n_D$  can be expressed as the following:

$$n_D = [(2A + 1) / (1 - A)]^{0.5} \quad (51)$$

Where,  $A$  is given by:

$$A = \left[ \left\{ \frac{(n_1^2 - 1)}{(n_1^2 + 2)} (1 / \rho_1) \right\} - \left\{ \frac{(n_1^2 - 1)}{(n_1^2 + 2)} (w_2 / \rho_1) \right\} + \left\{ \frac{(n_2^2 - 1)}{(n_2^2 + 2)} (w_2 / \rho_2) \right\} \rho \right] \quad (52)$$

Where,  $n_1$  and  $n_2$  are the pure component refractive indices,  $w_j$  the weight fraction,  $\rho$  the mixture density, and  $\rho_1$  and  $\rho_2$  the pure component densities.

The molar refractivity deviation is calculated by the following expression:

$$\Delta R = R - \phi_1 R_1 - \phi_2 R_2 \quad (53)$$

Where  $\phi_1$  and  $\phi_2$  are volume fractions and  $R$ ,  $R_1$ , and  $R_2$  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:

$$\Delta n_D = n_D - x_1 n_{D1} - x_2 n_{D2} \quad (54)$$

Where,  $\Delta n_D$  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 and  $x$  is the mole fraction.

The computed deviations of refractive indices of the binary mixtures are fitted using the following Redlich- Kister expression [254].

$$\Delta n_{Dew} = w_e w_w \sum_{P=0}^S B_p (w_e w_w)^p \quad (55)$$

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:

$$n_{Ds,sol} = n_{Dsol} + \sum_{i=1}^N A_i m^i \quad (56)$$

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

For the ternary systems of the salt + solvent-1 + solvent-2 solutions a polynomial expansion similar to that obtained for the salt + solvent solutions [130] was used to represent ternary refractive indices:

$$n_D = n_{Dw} + \sum_{i=1}^P C_i m^i \quad (57)$$

$n_D$  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 general rule that states how to calculate a refractivity deviation function. However, the molar refractivity is isomorphic to a volume for which the ideal behaviour may be expressed in terms of mole fraction: in this case smaller deviations occur but data are more spread because of the higher sensitivity of the expression to rounding errors in the mole fraction. For the sake of completeness,

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both calculations of refractivity deviation function, molar refractivity deviation was fitted to a Redlich and Kister-type expression and the adjustable parameters and the relevant standard deviation  $\sigma$  are calculated for the expression in terms of volume fractions and in terms of mole fractions, respectively.