CHAPTER II

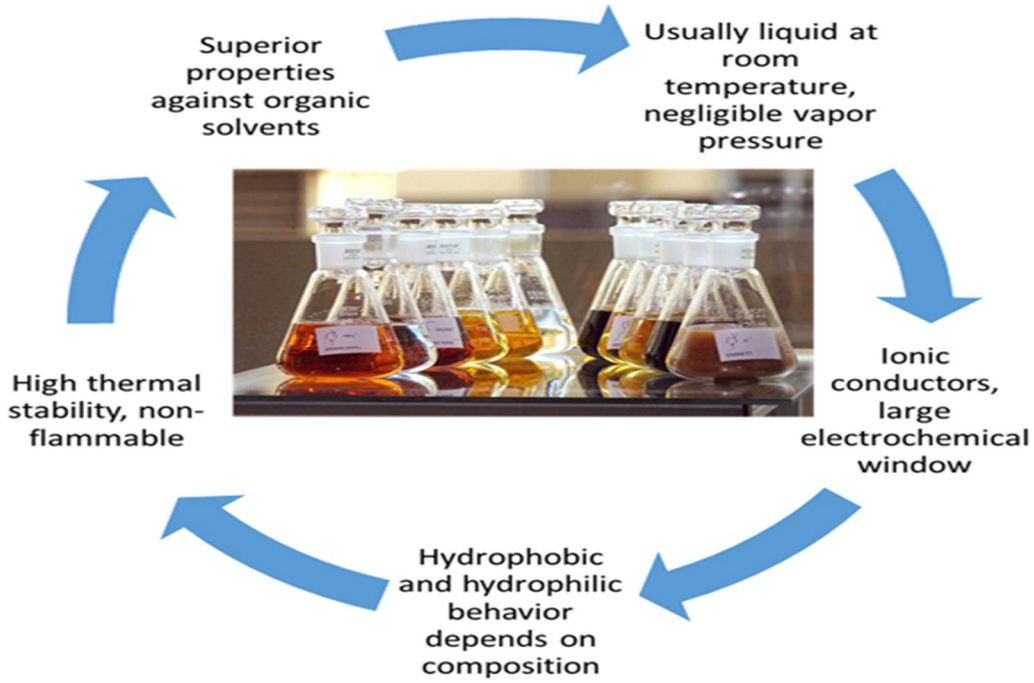
GENERAL INTRODUCTION (REVIEW OF THE EARLIER WORKS)

2.1. IONIC LIQUIDS

In the last few decades a new class of materials came into the focus of many research groups around the world: ionic liquids (IL). There physical and chemical characteristics are growing interests to modern scientists. A much more exhaustive overview 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]. 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 assorted 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[3]. Ionic liquids are salts with melting points below 373 K. They consist of an organic cation combined with an organic or inorganic anion [4]. The melting points of these organic salts are frequently found below 150 °C and occasionally as low as –96 °C. 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].

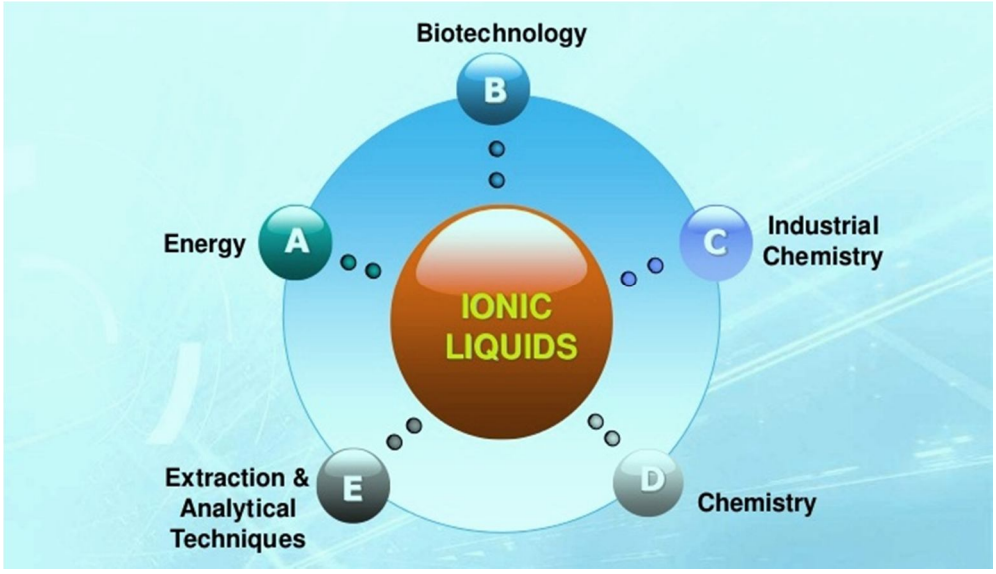
Room temperature ionic liquid (RTIL) are ILs which are liquid at room temperature. In the older (and some current) review, ionic liquids are occasionally called liquid organic salts, it may be fused salts or molten salts or ionic melts. RTIL have also termed as non-aqueous ionic liquids, room-temperature 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

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 $[C_n mim]^+$, where n = number of carbon atoms in a linear alkyl chain), *N*-alkylpyridinium (accordingly abbreviated $[C_n py]^+$), tetraalkylammonium (Bu_4N^+) or tetraalkylphosphonium (Bu_4P^+) cations, and many others; and inorganic anions such as hexafluorophosphate $[PF_6]^-$, tetrafluoroborate $[BF_4]^-$, some alkylsulfates $[RSO_4]^-$, alkylsulfonates $[RSO_3]^-$, halides as chloride $[Cl]^-$, bromide [Br]- or iodide [I]-, nitrate $[NO_3]$-, sulfate $[SO_4]$-, aluminum chloride $[AlCl_4]$-, triflate ($[CF_3SO_3]^-$ = $[TfO]^-$), bis(trifluoromethylsulfonyl)imide ($[(CF_3SO_2)_2N]^-$ = $[Tf_2N]^-$), etc.

Ionic liquids have wide applications in different industries, 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 great 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 the moment only about 300 ionic liquids are commercialized.

2.2. SOME BIOLOGICALLY ACTIVE MOLECULES

Biologically active molecules have at least one practical effect on living organism, tissue or cell of the human body. For this reason all the drug molecules are biologically active molecules including some vitamin, amino acid molecules. Basically they are organic molecules having carbon, hydrogen and oxygen and to lesser extent of nitrogen, phosphorus and sulphur. Other elements sometimes incorporate but are much less common. They include macromolecules such as polysaccharides, proteins, lipids and nucleic acids as well as small molecules such as natural products etc. Biologically active compounds are widely used as a drug, food or nutrients. These active molecules thus have direct effects on health. These will reduce the many hazards disease, like cancer, cardiovascular disease, 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

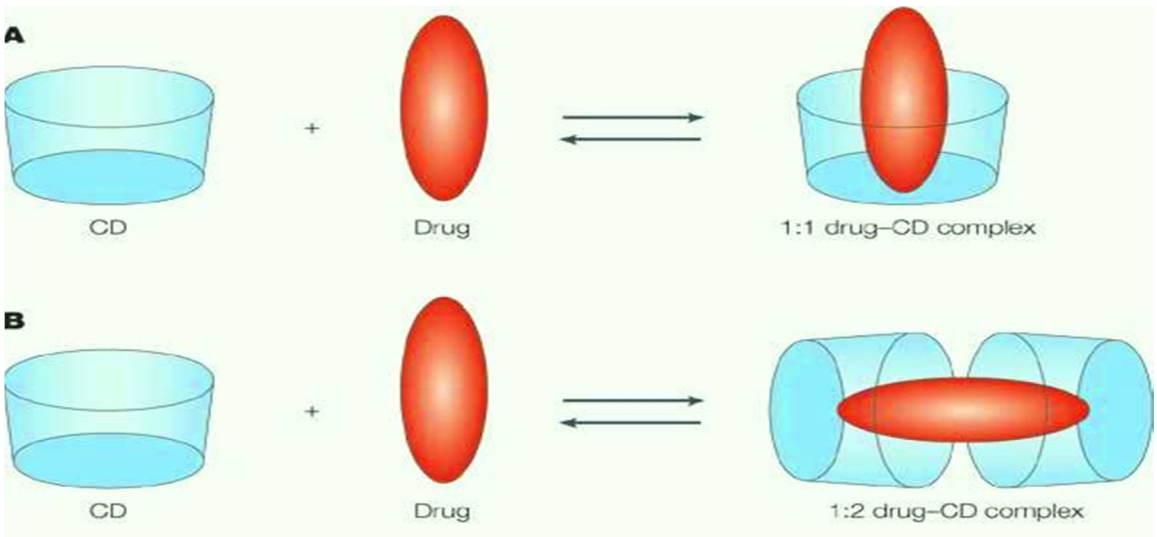
bio-active molecules are therefore required in almost all metabolic and therapeutic purposes.

α-Cyclodextrin and β-cyclodextrin are polysachharides, 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. α-cyclodextrin and β-cyclodextrin are most commonly used as a complexing agent in hormones, some vitamins, and many other compounds normally used in tissue and cell biology [9,10].

Dopamine hydrochloride is a naturally occurring catecholamine and it is a significant neurotransmitter in the mammalian central nervous system and is a member of catecholamine. It required for the treatment of Perkinson's disease. Tyramine hydrochloride is amino-acid derivative (tyrosine residue) acts as a catecholamine releasing agent. In food, it often is produced by the decarboxylation of tyrosine during fermentation decay. Epinephrine is known as adrenalin or adrenaline. It is also hormone and neurotransmitter, serves as chemical mediators for conveying the nerve impulses to effectors organs. Epinephrine is normally produced by both the adrenal glands and certain neurons. It plays an important role in increasing blood flow to muscles, output of the heart, pupil dilation, and blood sugar. Parlidoxime or 2-pyridine aldoxime methochloride is a drug molecule. In drug industry it has immense importance for nerve stimuli because of its prompt functionality. It is an important drug and acts as a nerve agent for the treatment of organophosphorus poisoning in the nervous system. It binds to the organophosphate; the organophosphate changes conformation, and loses its binding to the acetylcholinesterase enzyme. The conjoined poison antidote then unbinds from the site, and thus regenerates the desired enzyme, which is now active to function again.

2.3. INCLUSION COMPLEXES

Inclusion Complexes are those in which a guest molecule or part of the molecule is actually inserted into the host molecule. The interaction taking place for these host-guest complexes is non-covalent interactions. Cyclodextrin, crowns, cucurbitrils, porphyrins, calixarenes etc. are seems to be the host molecules. The guest molecules have suitable polarity and cavity dimensions. In host-guest chemistry, an inclusion complex is a complex in which one chemical compound ("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, vitamin, amino acid and amino acid derivatives are considered as guest molecules for inclusion complexes with cyclodextrins, calixarenes, cucurbitrils, crowns, etc.



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 and 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. CDs, act as the useful solubilizer enabling both solid and liquid oral and parenteral dosage forms. Solid binary system of drug and CDs are capable to modify the physicochemical properties of drugs such as solubility, particle size, crystal habit, thermal behaviour, and there by forming a highly water soluble amorphous forms. The CDs, due to their extreme 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- CD inclusion compounds [11, 12].

2.4. SOLUTION CHEMISTRY

Solution chemistry investigates the miscibility of substances and it deals with the change in propertis 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 [13], the second is the thermodynamic contribution by measuring the free energies, enthalpies and entropies of solvation of ions from which factors related with solvation can be exposed [14] and the third is to use spectroscopic

measurements where the spectral shifts or the chemical shifts find out their qualitative and quantitative nature[15].

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 thoroughly related to the studies of solute-solute, and solvent-solvent interactions in some industrially and biologically important liquid systems.

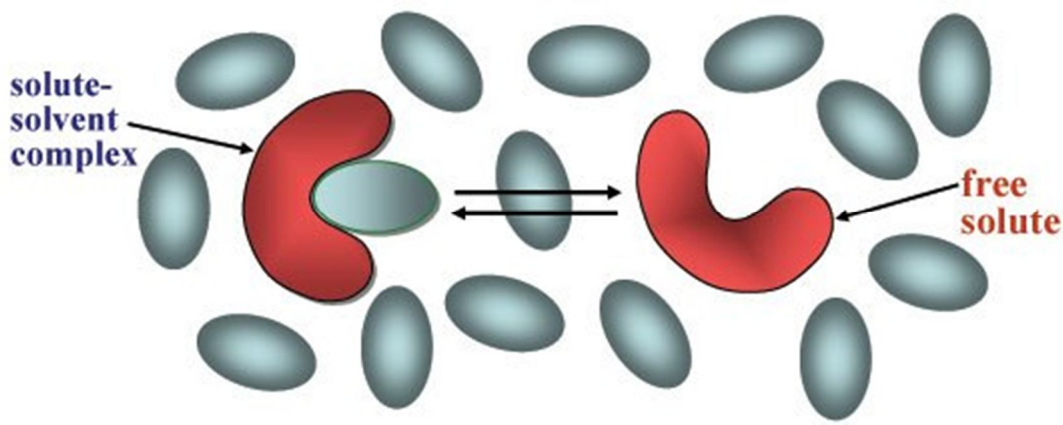
2.5. INTERACTIONS IN LIQUID PHASE

There three types of interactions in the liquid systems:

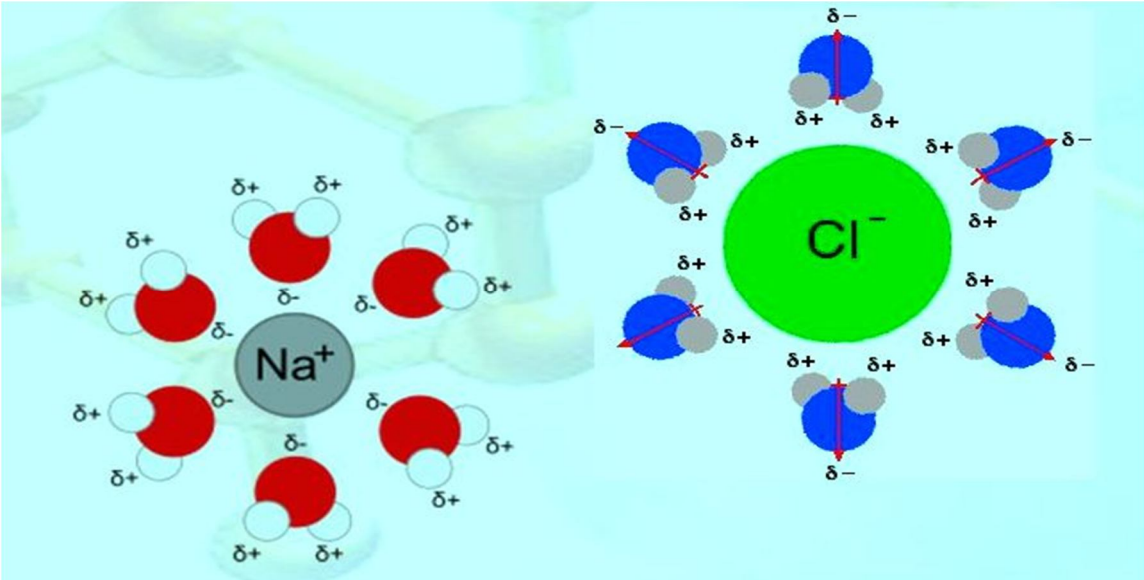
a. Solvent – solvent interactions: energy necessary to break weak bonds between solvent molecules.

b. Solute – solute interactions: energy necessary to break intermolecular bonds between the solute molecules.

c. Solute – solvent interactions: comprises ΔH 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 solvent media.



Schematic presentation of possible processes for solvation of a molecule.

2.5.1. VARIOUS KIND OF INTERACTIONS

The forces of interactions can be attractive or repulsive depending on whether like or unlike charges of the solute and solvent molecules are closer together. 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 shake 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. This separation of ions from each other 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 sodium chloride acts as a solution of sodium ions and chloride ions.

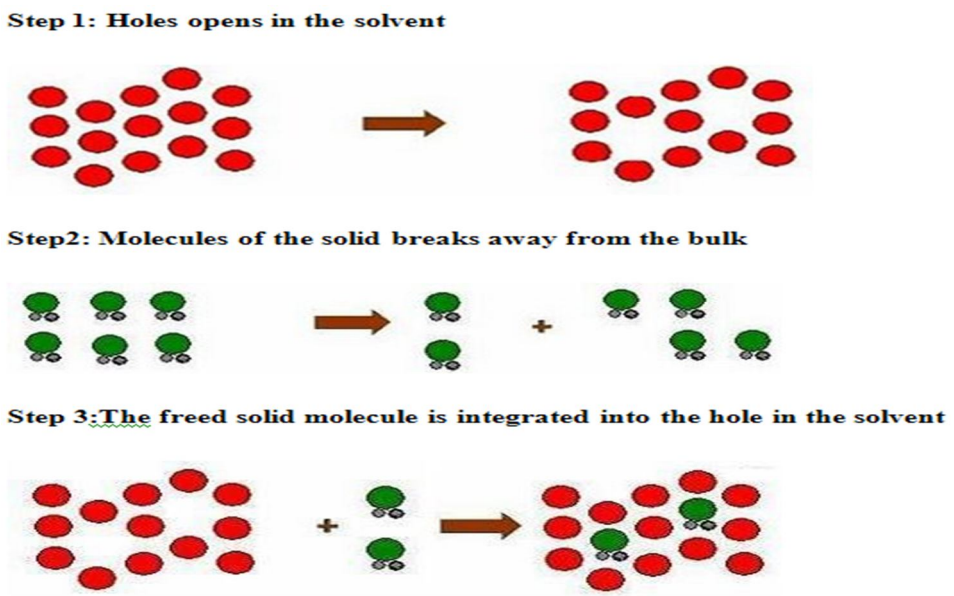
The determination of thermodynamic, transport and volumetric properties of different electrolytes in various solvents would thus give an essential step in this direction. Therefore, the development of theories, involving with electrolyte solutions, much interest has been devoted to ion-solvent interactions 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, such as, changes of free energy, enthalpy and entropy, etc. associated with a particular reaction.

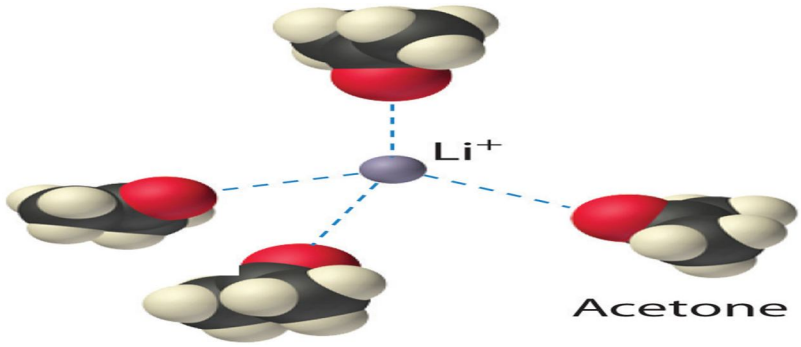
2.5.2. ION-SOLVENT INTERACTION

Every living organism has solvated ions with their optimum existence. Presence or absence of these solvated ions can vitally alter the functions of life. Ions solvated in organic solvents or mixtures of water and organic solvents are also very common [16]. The exchange of solvent molecules around ions in solutions is fundamental to the understanding of the reactivity of ions in solution [17]. Solvated ions also play a key function in electrochemical industries, where for instance the conductivity of electrolytes depends on ion-solvent relations [18].



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. These interactions are together termed as ion- solvent interactions.



Water is the universal solvent in nature and its major consequence to chemistry, biology, agriculture, geology, etc., water has been broadly used in kinetic and equilibrium studies. But still our knowledge of molecular interactions in water is tremendously limited. Moreover, the uniqueness of water as a solvent has been a subject of debate [19] and it has been realized that the studies of other solvent media like non-aqueous and mixed solvents would be of great help in understanding different molecular interactions.

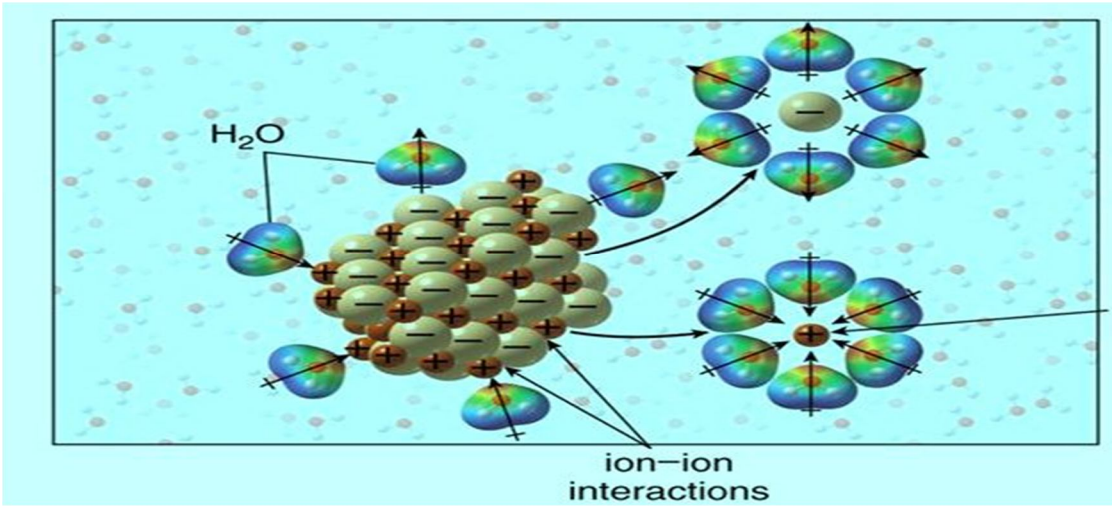
Organic solvents have common features such as dielectric constants, organic moieties, acid base properties or association through hydrogen bonding [20] donor-acceptor properties hard and soft acid-base characters etc. Organic solvents show a wide variance of properties influencing their thermodynamic, transport and volumetric properties in presence of solute particles. Thus, the resolve of physicochemical properties of different electrolytes or non-electrolytes in various solvents would thus afford significant information in this way [21].

Ion-solvent interactions can also be investigated by spectrometry [22]. The spectral shifts of solvent or the chemical shifts can determine the qualitative and quantitative nature of ion-solvent associations. But even qualitative or quantitative assign of the ion-solvent interactions into the various probable factors is still a rising task.

2.5.3. ION-ION INTERACTION

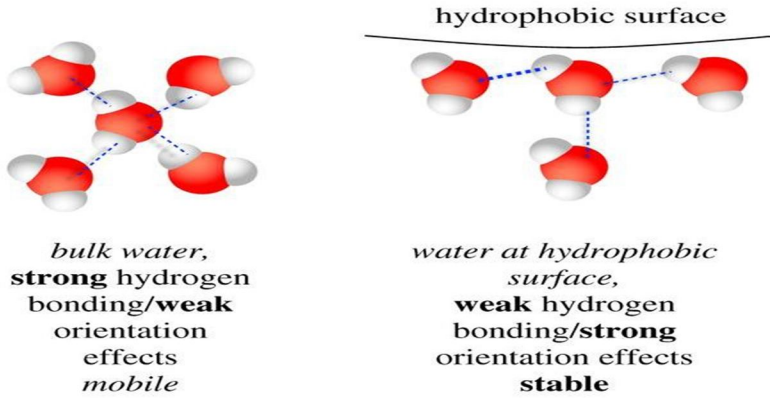
The surrounding of an ion sees not only solvent molecules but also other ions. The mutual interactions between these ions comprise the fundamental part- 'ion-ion interactions' or solute –solute interactions. The extent of ion-ion an interaction affects the properties of solution and depends on the nature of electrolyte under investigation. Ion-ion interactions are stronger than ion-solvent interactions. Ion-ion

interaction in dilute solutions is now theoretically well implicit, but ion-solvent interactions or ion-solvation still remains a complex practice. 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. 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. Theories of perturbation type have been extended from their successful applicability in pure solvents to mixed solvents. L. Jones and Devonshire [23] 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 [24] extended the above approach to solvent mixtures. Random mixing of solvents was their main assumption provided the molecules have similar sizes. Prigogine and Bellemans [25] 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*. [26] 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 or specific 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 assumption is not a concrete one, as evident from some studies [27, 28]. It is observed in many systems that there is no simple correlation between the strength of interaction and the observed properties. Rastogi *et al*. [29] 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 [30], L. Huggins [31] 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 thermodynamic properties of the pure components.

Recently, Rowlinson *et al.* [32-34] 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 [35]. A more successful approach is due to Flory who made the use of certain features of cell theory [36-38] 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 [39] combined both Prigogine and Flory theories to a unified one for rationalizing various contributions of free volume, internal pressure, etc. to the excess thermodynamic properties. Recently, Heintz[40-43] 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 [44] 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 [45]. The symmetrical-ERAS (S-ERAS) model makes it possible to describe excess molar enthalpies and excess molar 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 [46, 47]. Gepert *et al.*[48] applied this model for studying some binary systems containing alcohols.

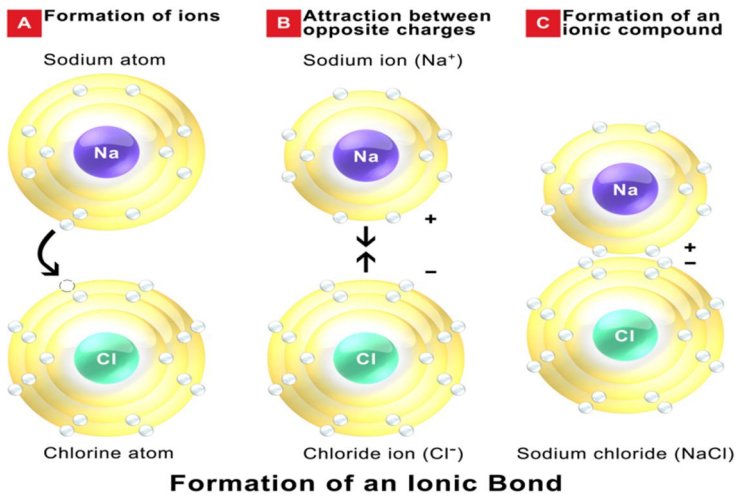
2.5.5. BINDING FORCES OF ATOMS IN A MOLECULE

Molecular interactions between two or more molecules are called 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. For example the average bond-energy for O-H bonds in water 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 particularly important in terms how molecules interact and form biological organisms or even life.

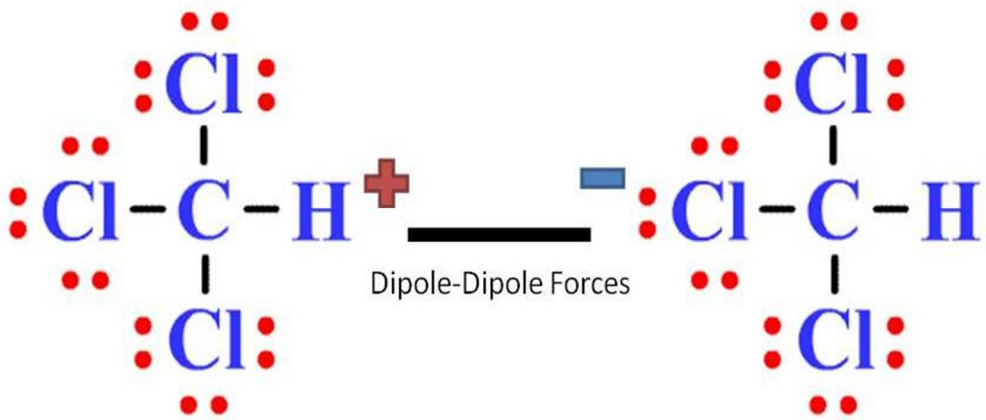
Various intermolecular forces of interactions are-

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_2, 2957 kJ/mol.



b. Dipole-dipole forces:

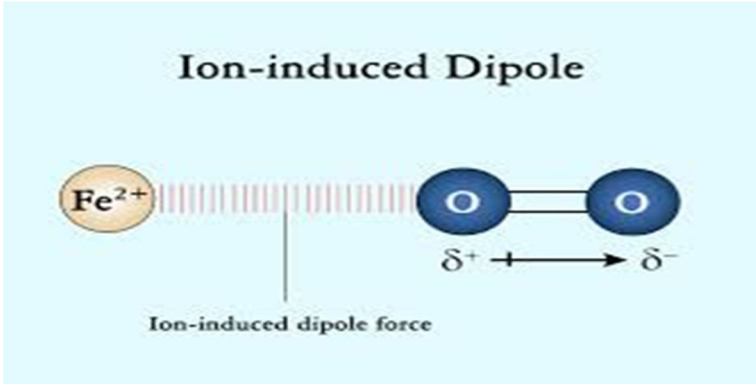
Molecules have permanent dipoles can interact with other polar molecules through dipole-dipole interactions and this type of interactions electrostatic in nature. Higher dipole moment material show greater melting and boiling point than lower dipole moment material.



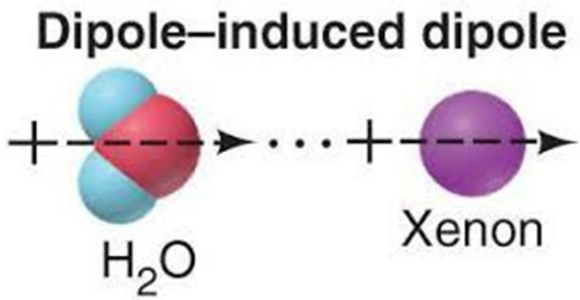
c. Ion-dipole forces: This is the attractive interaction between ion and a dipolar molecule.

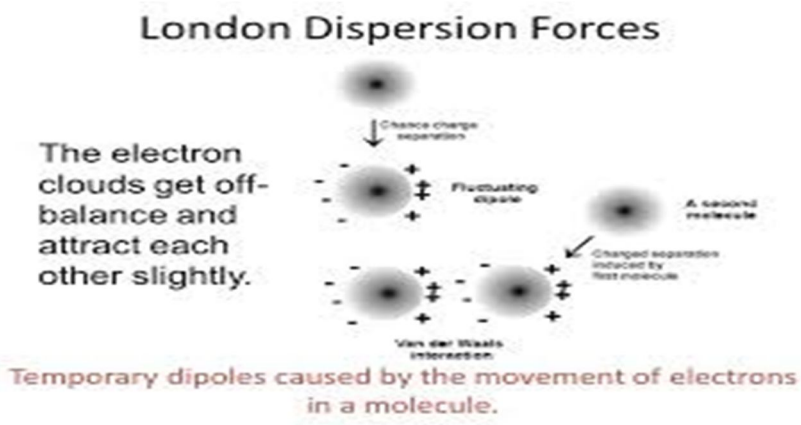
d. Weak London dispersion forces or van der Waal's force:

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.

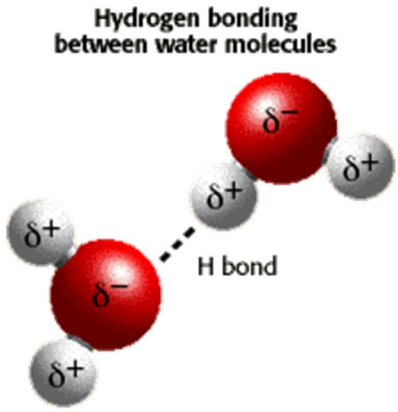


A permanent dipole molecule can induce a near about molecule and create a dipole in the second molecule that is located nearby in space. The strength of the interaction depends on the dipole moment of the first molecule and the polarizability of the second.



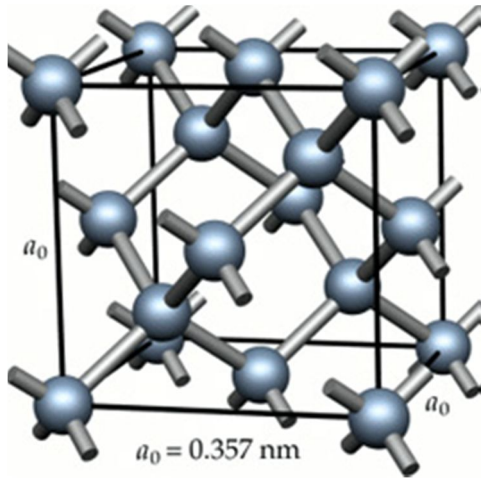


e. Hydrogen bond: Hydrogen bond is the attractive force of interaction between polar molecules in which hydrogen is bound to highly electronegative atom, such as nitrogen, oxygen or fluorine. The hydrogen atom so covalently bonded to other electronegative atoms of the other molecule or itself to create the new type of bond. This type of bond can occurs intermolecularly or intramolecularly between the molecules. The hydrogen bond (5 to 30 kJ/mole) is stronger than a van der Waals interaction, but weaker than covalent or ionic bonds. Certain substances such as H_2O, HF, NH_3 form hydrogen bonds, and the formation of which affects properties (m.p, b.p, solubility) of substance.



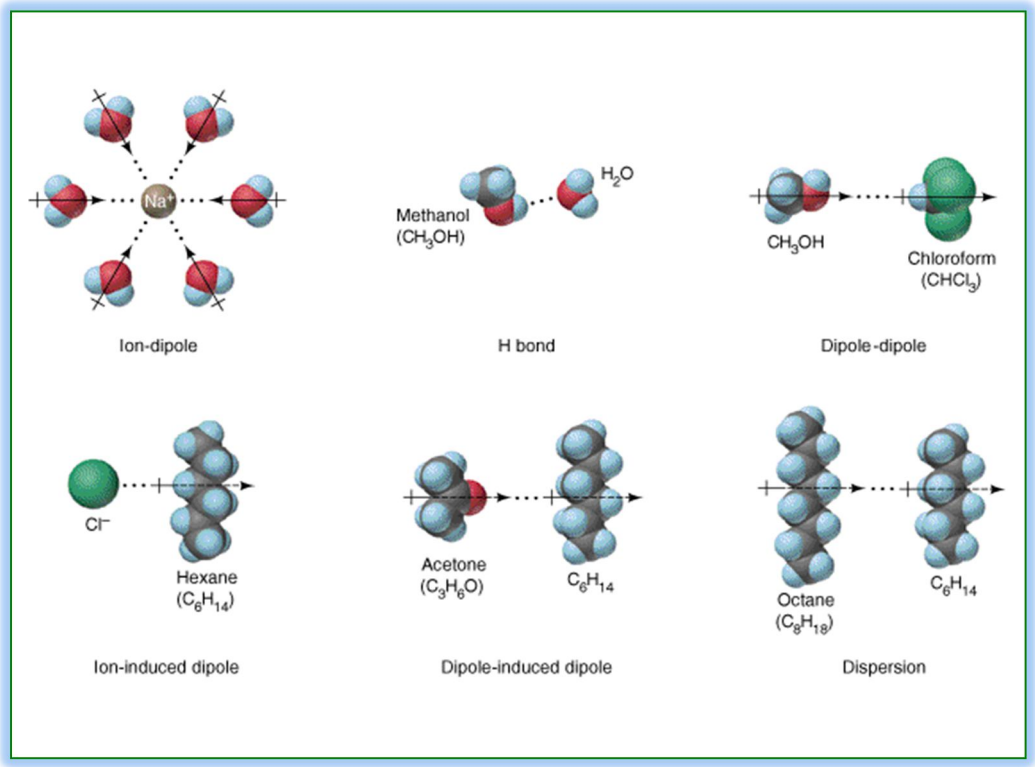
Other compounds, such as, OH and NH_2 addendum also form hydrogen bonds. Hence, molecules of many chemicals such as aliphatic or aromatic alcohols, esters, various acids, different amines, and also amino acids contain these groups, and thus finally hydrogen bonding plays an important role in biological science.

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 kcal per mole and weaker than ionic bond. It is declared here, because some solids are formed by the covalent interactions. For example, 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 points. Covalent bonding holds atoms tighter than ionic attraction.



Covalent Bonding in Diamond

g. Metallic bonding: The metallic bond involves the sharing of free electrons among a metal atoms lattice. The metallic bonds may be compared to molten compounds. The ions and the electrons in the pure metal have a heavy attractive force between metallic bond. Hence metals frequently have high point of boiling or melting and ductility in nature. The outer electrons are so weakly bound to metal atoms that they are free to roam across the entire metal.



Intermolecular interactions are important in decisive the solubility of a substance. “Like dissolve like” i.e., polar molecules dissolve in polar solvent and non-polar molecules dissolve i non-polar solvents.

2.6. DENSITY

The physicochemical properties of liquid systems have concerned much attention from both theoretical and engineering relevance. Many engineering

applications require quantitative data on the density of liquid mixtures. They also supply information about the nature and molecular interactions between liquid systems.

The volumetric properties include 'Density' as a function of weight, volume and mole fraction and excess volumes of mixing. One of the well-recognized approaches to the study of molecular interactions in liquids is the use 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 presentation of these macroscopic properties in terms of molecular phenomena is usually difficult. Sometimes higher derivatives of these properties can be interpreted more effectively in terms of molecular interactions. The volumetric information may be of enormous importance in this regard. Various concepts regarding molecular processes in solutions like electrostriction, hydrophobic hydrations, micellization and co-sphere overlap during solute-solvent interactions [49-51] have been derived and interpreted from the partial molar volume data.

2.6.1. APPARENT AND PARTIAL MOLAR VOLUMES

The molar volume data are useful interpret the solute-solvent interactions in dilute solutions. It obtained from the density measurements. Actually, the volume contributed to a solvent by the addition of one mole of an ion is difficult to understand. This is so 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. Electrostriction is a general phenomenon and whenever there are electric fields of the order of 10^9-10^{10} V m^{-1}, the compression of ions and molecules is likely to be significant. The effective volume of an ion in solution, the partial molar volume, can be determined from a directly obtainable quantity- apparent molar volume (ϕ_V). The apparent molar volumes, (ϕ_V), of the solutes can be calculated by using the following relation [52].

$$\phi_V = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \qquad (1)$$

where M is the molar mass of the solute, c is the molarities of the solution; $\rho_o$and ρ are the densities of the solvent and the solution respectively. The partial molar volumes, ϕ_{2v} can be obtained from the equation [52]:

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

The extrapolation of the apparent molar volume of electrolyte to infinite dilution solution obtained by four most important equations over a decades – the Masson equation [53], the Redlich-Meyer equation [54], the Owen-Brinkley equation[55], and the Pitzer equation. Masson found that the apparent molar volume of electrolyte, ϕ_V , vary with the square root of the molar concentration by the use of linear equation:

$$\phi_V = \phi_V^0 + S_V^* \sqrt{c} \qquad (3)$$

where, ϕ_V^0 is the apparent molar volume or the partial molar volume at infinite dilution and S_V^* the experimental slope. The majority of ϕ_V data in water and nearly all ϕ_V data in non-aqueous [44-55] solvents have been extrapolated to infinite dilution through the use of equation (3).

The temperature dependence of ϕ_V^0 or various investigated electrolytes in various solvents can be expressed as follows:

$$\phi_V^0 = a_0 + a_1 T + a_2 T^2 \qquad (4)$$

Where a_0, a_1 and a_2 are the coefficients of a particular electrolyte and *T* is the absolute temperature.

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

$$\phi_E^0 = \left(\delta\phi_V^0 / \delta T\right)_P = a_1 + 2a_2 T \qquad (5)$$

The limiting apparent molar expansibilities (ϕ_E^0) change in magnitude withthe change of temperature. Different workers emphasized that S_V^* is not the sole criterion for determining the structure-making or breaking tendency of any solute. So, Helper [57] developed a technique of examining the sign of $\left(\delta\phi_E^0 / \delta T\right)_P$ 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:

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

If the sign of $\left(\delta\phi_E^0/\delta T\right)_P$ is positive or small negative the electrolyte is a structure maker and when the sign of $\left(\delta\phi_E^0/\delta T\right)_P$ is negative, it is a structure breaker. Redlich and Meyer [55] have shown that an equation (3) cannot be any more than 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:

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

$$\text{where } S_v = Kw^{3/2} \qquad (8)$$

S_V is the theoretical slope, based on molar concentration, including the valence factor where

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

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

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

The Redlich-Meyer's extrapolation equation [54] adequately 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 [55] can be used to aid in the extrapolation to infinite dilution and to adequately represent the concentration dependency of ϕ_V . The Owen-Brinkley equation which includes the ion-size parameter, a (cm), is given by:

$$\phi_V = \phi_V^0 + S_V\tau(\kappa a)\sqrt{c} + 0.5w_V\theta(\kappa a)c + 0.5K_V c \qquad (11)$$

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

In recent times, the Pitzer formalism has been used by Pogue and Atkinson [59] 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 and the symbols are usual meaning :

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

2.6.2. LIMITING PARTIAL MOLAR VOLUMES

The calculation of the ionic limiting partial molar volumes in diverse solvents is, however, a complicated 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 method suggested by Conway *et al.* [60] 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 $\phi^0_{\mathrm{v}\,\mathrm{R_4NX}}$, for a series of these salts with a halide ion in common as a function of the formula weight of the cation, M_{R4N+} and obtained straight-lines for each series in the given equation (13):

$$\phi^0_{v\,R_4NX} = bM_{R_4N^+} + \phi^0_{v\,X^-} \qquad (13)$$

The extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions $\phi^0_{V_{X^-}}$.

Uosaki *et al.*[61] used this method for the separation of some literature values and of their own $\phi^0_{V\,R_4NX}$ values into ionic contributions in organic electrolyte solutions. Krumgalz [62] applied the same 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 according to the following equation [63, 64]

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

Where, ρ_i and ρ are the density of the ith component and density of the solution mixture respectively. V^E is the resultant of contributions from several opposing effects. These may be divided arbitrarily into three types, 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, especially from interstitial accommodation and changes of free volume.

2.7. VISCOSITY

Viscosity is the fundamental properties of liquids. Viscosity and volume could also provide a lot of information on the structures and molecular interactions of liquid mixtures. Viscosity and volume are different types of properties of one liquid, and 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 important transport properties is used for the determination of ion-solvent interactions and studied extensively [65, 66]. 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 and 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 basis of the procedures for predicting the variations in the viscosity of liquids and also liquid mixtures.

2.7.2. EARLY THEORETICAL CONSIDERATIONS ON LIQUID VISCOSITY

The theoretical development of liquid viscosity in early stages has been reviewed Andrade [67] and Frenkel [68]. By considering the forces of collision to be the only important factor and assuming 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. Andrade developed equations which checked well against data on mono atomic metals at the melting point. Frenkel considered the molecules of a liquid to be spheres moving with an average velocity with respect to the surrounding medium and using Stokes' law and Einstein's relation for self-diffusion-coefficient, arrived at a complicated expression for liquid viscosity with only limited applicability. Furth [69] assumed the momentum transfer to take place by the irregular Brownian movement of the holes [70] which were linked to clusters in a gas and thus, in analogy with the gas theory of viscosity and with assumption of the equipartition law of energy, showed that for liquids:

$$\eta = 0.915\frac{RT}{V}\left(\frac{m}{\sigma}\right)e^{\frac{A}{RT}} \qquad (15)$$

Where, η, V and m are viscosity, volume and mass, respectively, T is the temperature, R is the universal gas constant, σ is the surface tension and A is the work function at the melting point. He compared his theory with experiment as well as with the theories of Andrade [67] and Ewell and Eyring [70] Auluck, De and Kothari [71] further modified the theory and successfully explained the variations of the viscosity with pressure. A critical review of these simple theories and their abilities to explain momentum transport in liquids is given by Eisenschitz [72].

2.7.3. THE CELL LATTICE THEORY AND LIQUID VISCOSITY

A model related to in the literature by various names such as cell, lattice, cage, free volume or one particle model was introduced by Lennard-Jones and Devonshire [73, 74] and further expanded by Pople [75]. Eisenschitzemploying this

model developed a theory of viscosity by considering themotion of the representative molecules to be Brownian and theirdistribution according to the Smoluchowski equation. Even with certain assumptions, the final expression showed shortcomings most of which were later overcome in a subsequent publication [76].

2.7.4. STATISTICAL MECHANICAL APPROACH TO LIQUID VISCOSITY

The distribution functions for the liquid molecules were obtained on the basis of statistical mechanical theory mainly by the efforts of Kirkwood [77, 78] Mayer and Montroll [79], Mayer [80], Born and Green [81] and the considerations on the basis of the general kinetic theory led Born and Green [81, 82] to develop a viscosity equation which provided explanation for several empirical equations [80, 81, 83] proposed for liquid viscosity. In this connection the theoretical contributions of Kirkwood and coworkers [84-89] Zwanzig *et al.*,[90] Rice and coworkers [91-94] Longuet-Higgins and Valleau[95] and Davis and Co-workers[96, 97] are worth mentioning.

2.7.5. PRINCIPLE OF CORRESPONDING STATES AND LIQUID VISCOSITY

The principle of the corresponding states has been applied to liquids in the same way as to gases [98] the basic assumption being that the intermolecular potential between two molecules is a universal function of the reduced intermolecular separation. This assumption is a good approximation for spherically symmetric mono atomic non-polar molecules. For complicated molecules, the principle becomes increasingly crude. In general, more parameters are introduced in the corresponding state correlations on somewhat empirical grounds in the hope that such modification in some way compensates the shortcomings of the above stated assumption. In this connection the studies by Rogers and Brickwedde [99], Boon and Thomaes [101-103] Boon, Legros and Thomaes, and Hollman and Hijmans [104] are worth mentioning.

2.7.6. 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 sleep over the

potential barrier to the next equilibrium position in the same plane. Eyring [105] showed that the viscosity of the liquid is given by:

$$\eta = \frac{\lambda_i h F_n}{\kappa \lambda^2 \lambda_2 \lambda_3 F_a^*} \exp \frac{\Delta E_{act}}{kT} \qquad (16)$$

Where λ 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 (κ) 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, ΔE_{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 ΔE_{act} is a function of ΔE_{vap} for viscous flow because ΔE_{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 [106] finally gets

$$\eta = \frac{N_A h (2\pi mkT)^{\frac{1}{2}}}{Vh} \frac{bRTV^{\frac{1}{3}}}{N_A^{\frac{1}{3}} \Delta E_{Vap}} \exp \frac{\Delta E_{Vap}}{nRT} \qquad (17)$$

Where, n and b are constants. It was found that the theory could reproduce the trend in temperature dependence of η but the computed values are greater than the observed values by a factor of 2 or 3 for most liquids. Kincaid, Eyring and Stearn [107, 112] have summarized all the working relations.

2.7.7. THE SIGNIFICANT STRUCTURE THEORY AND LIQUID VISCOSITY

Eyring and co-workers [105-110] 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 [111-112].

$$\eta = \frac{V_s}{V}\eta_S + \frac{V - V_s}{V}\eta_g \qquad (18)$$

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 η_S and η_g are the viscosity contributions from the solid-like and gas-like degrees of freedom, respectively. The expressions for η_S and η_g are given by Carlson, Eyring and Ree [113]. Eyring and Ree [114] have discussed in detail the evaluation of η_S from the reaction rate theory of Eyring [115] assuming that asolid molecule can jump into all neighbouring empty sites. The expressionfor η_S takes the following form [116]

$$\eta_S = \frac{N_A h}{Z\kappa} \cdot \frac{V}{V_S} \cdot \frac{6}{2^{\frac{1}{2}}} \cdot \frac{1}{V - V_S} \cdot \frac{1}{1 - e^{\frac{\theta}{T}}} exp \frac{\acute{a} E_S V_S}{(V - V_S)RT} \qquad (19)$$

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

$$\eta_g = \frac{2}{3d^2}\left(\frac{mkT}{\pi^3}\right)^{\frac{1}{2}} \qquad (20)$$

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

2.7.8. 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 [117] 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 [118] suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations (*c*):

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc \qquad (21)$$

The above equation can be rearranged as:

$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} \qquad (22)$$

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 [119] of inter-ionic attractions in 1923. The *A* -coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory [120] and is given by the Falkenhagen Vernon [121-122] equation:

$$A_{Theo} = \frac{0.2577\Lambda_o}{\eta_o(\varepsilon T)^{0.5}\lambda_+^o\lambda_-^o}\left[1 - 0.6863\left(\frac{\lambda_+^o\lambda_-^o}{\Lambda_o}\right)^2\right] \qquad (23)$$

Where, the symbols have their usual significance. In very accurate work on aqueous solutions [123], A-coefficient has been obtained by fitting η_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 [124]. *A*-coefficient suggesting that should be calculated from conductivity measurements. Crudden *et al.* [125] suggested that if association of the ions occurs to form an ion pair, the viscosity should be analysed by the equation:

$$\frac{\eta_r - 1 - A\sqrt{\alpha c}}{\alpha c} = B_i + B_P\left(\frac{1-\alpha}{\alpha}\right) \qquad (24)$$

Where A , B_i and B_P are characteristic constants and a is the degree of dissociation of ion pair. Thus, a plot of (η_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)[127, 128]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 [129, 131] and is given below:

$$\frac{\eta}{\eta_o} = \eta_r = 1 + A\sqrt{c} + Bc + Dc^2 \qquad (25)$$

The coefficient *D* cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, equation (22) is usedby the most of the workers.

The plots of (η/η_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 [132-133]. Thus, instead of determining *A*- coefficient from the plots or by the least square method, the *A* -coefficient are generally calculated using Falkenhagen-Vernon equation (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 [134]. 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 η or *B* -value.

(2) The destruction of the three dimensional structure of solvent molecules (i.e., structure breaking effect or depolymeriation effect) decreases η 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.

2.7.9. VISCOSITIES AT HIGHER CONCENTRATION

It had been found that the viscosity at high concentrations (1M to saturation) can be represented by the empirical formula suggested by Andrade:

$$\eta = Aexp^{\frac{b}{T}} \qquad (26)$$

The several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration range [135-138]and the equation suggested by Angell [139-140] based on an extension of the free volume theory of transport phenomena in liquids and fused salts to ionic solutions is particularly noteworthy. The equation is:

$$\frac{1}{\eta} = A\exp\left[-\frac{K_1}{N_o - N}\right] \qquad (27)$$

Where, *N* represents the concentration of the salt in eqv. litre^{-1}, *A* and $K_1$are constants supposed to be independent of the salt composition and N_o is the hypothetical concentration at which the system becomes glass. The equation was recast by Majumder *et al.* introducing the limiting condition, that is $N \rightarrow 0$, $\eta \rightarrow \eta_o$; which is the viscosity of the pure solvent. Thus, we have:

$$\ln \eta / \eta_o = \ln \eta_{Rel} = \frac{K_1 N}{N_o(N_o - N)} \qquad (28)$$

Equation (28) predicts a straight line passing through the origin for the plot of $ln\,\eta_{Rel}$ vs. $N/(N_o-N)$if a suitable choice for $N_o$is made. Majumder *et al.* [141-143] tested the equation (28) by using literature data as well as their own experimental data. The best choice for $N_o$and $K_1$was selected by a trial and error methods. The set of $K_1$and N_o producing minimum deviations between η_{Rel}^{Exp} and η_{Rel}^{Theo} was accepted. In dilute solutions, $N \ll N_o$and we have:

$$\eta_{Rel} = \exp\left(\frac{K_1 N}{N_o^2}\right) \cong 1 + \frac{K_1 N}{N_o^2} \qquad (29)$$

Equation (29) is nothing but the Jones-Dole equation with the ion-solvent interaction term represented as $B=K_1/N_o^2$.The arrangement between *B*-values determined in this way and using Jones-Dole equation has been found to be good for several electrolytes. Further, the equation (28) can be written in the form:

$$\frac{N}{ln\eta_{Rel}} = \frac{N_0^2}{K_1} - \left(\frac{N_0}{K_1}\right)N \qquad (30)$$

It closely resembles the Vand's equation [153] for fluidity (reciprocal for viscosity):

$$\frac{2.5c}{2.3\log\eta_{Rel}} = \frac{1}{V_h} - Qc \qquad (31)$$

Where, *c* is the molar concentration of the solute and $V_h$is the effective rigid molar volume of the salt and *Q* is the interaction constant.

2.7.10. 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 [144] carried out the division on the assumption that B_{ion} values of Li^+ and IO_3^-in $LiIO_3$are proportional to the ionic volumes which are proportional to the third power of the ionic nobilities. The method of Gurney [145] and also of Kaminsky is based on:

$$B_{K^+} = B_{Cl^-} \text{ (In water)} \qquad (32)$$

The argument in favour of this assignment is based on the fact that the *B* -coefficients for KCl is very small and that the motilities' of $K^+$and $Cl^-$are very similar over the temperature range 288.15 – 318.15 K. The assignment is supported from other thermodynamic properties. Nightingle [146], however preferred RbCl or CsCl to KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron is based onthe assumption that the Et_4N^+ion in water is probably closest to be neither structure breaker not a

structure maker. Thus, they suggest that it is possible to apply with a high degree of accuracy of the Einstein's equation [147],

$$B = 0.0025\overline{V_o} \qquad (33)$$

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 at298.15 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:

$$B_{\mathrm{BPh_4}^{-}} = B_{\mathrm{PPh_4}^{+}} + B_{\mathrm{BPh_4PPh_4}}/2 \qquad (34)$$

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

$$B_{\mathrm{BPh_4PPh_4}} = B_{\mathrm{NaBPh_4}^{+}} B_{\mathrm{PPh_4Br}} - B_{\mathrm{NaBr}} \qquad (35)$$

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 [186]. They also adopted $B^{25}_{\mathrm{Me_4N^+}} = 0.25$ as the initial value for acetonitrile solutions.

(b) For acetonitrile solutions, Tuan and Fuoss [187] proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer *et* al.[198], $\lambda^o_{25}(Bu_4N^+) = 61.4$ and $\lambda^o_{25}(Ph_4B^-) = 58.3$ in acetonitrile.

$$B_{\mathrm{Bu_4N^+}} = B_{\mathrm{Ph_4B^-}} \qquad (36)$$

(c) Gopal and Rastogi [148] resolved the *B* -coefficient in N-methylpropionamide solutions assuming that $B_{\mathrm{Et_4N^+}} = B_{\mathrm{I^-}}$ at all temperatures.

(d) In dimethyl sulphoxide, the division of *B* -coefficients were carried out by Yao and Beunion [187] assuming:

$$B_{[(\mathrm{i-pe})_3\mathrm{BuN^+}]} = B_{\mathrm{Ph_4B^-}} = 1/2 B_{[(\mathrm{i-pe})_3\mathrm{BuNPh_4B}]} \qquad (37)$$

at all temperatures.

Wide use of this method has been made by other authors for dimethyl sulphoxide, sulpholane, hexamethyl phosphotriamide andethylene carbonate [189] solutions. The methods, however, have been strongly criticized by Krumgalz [190].

According to him, any method of resolution based on the equality of equivalent conductance for certain ions suffers from the drawback that itis 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 $(i-pe)_3 BuN^+$ or $(i-Am)_3 BuN^+$ 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[191, 192] 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 [192, 193] 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:

$$B_{R_4NX} = a + br^3 R_4N^+ \quad (38)$$

a=B_{X^-} *B*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^3toR_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:

$$B_{R_4N^+} - B_{R_4'N^+} = B_{R_4NX} - B_{R_4'NX} \quad (39)$$

$$\frac{B_{R_4N^+}}{B_{R_4'N^+}} = \frac{r^3{}_{R_4N^+}}{r^3{}_{R_4'N^+}} \quad (40)$$

The radii of the tetraalkylammonium ions have been calculated from the conductometric data [194]. Gill and Sharma [192]used Bu_4NBPh_4as 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^+(5.00Å) 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:

$$\frac{B_{\mathrm{Ph_4B^-}}}{B_{\mathrm{Bu_4N^+}}} = \frac{r^3{}_{\mathrm{Ph_4B^-}}}{r^3{}_{\mathrm{Bu_4N^+}}} = \left(\frac{5.35}{5.00}\right)^3 \qquad (41)$$

$$B_{\mathrm{Bu_4NBPh_4}} = B_{\mathrm{Bu_4N^+}} + B_{\mathrm{Ph_4B^-}} \qquad (42)$$

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:

$$B_{[(\mathrm{i-Am})_3\mathrm{Bu_4N^+}]} = B_{\mathrm{Ph_4B^-}} = 1/2B_{\mathrm{Bu_4NBPh_4}} \qquad (43)$$

Recently, Lawrence and Sacco and others [147-156] used tetrabutylammonium tetrabutylborate (Bu_4NBBu_4) as reference electrolyte because the cation andanion in each case are symmetrical in shape and have almost equal Vander Waal's volume. Thus, we have:

$$\frac{B_{\mathrm{Bu_4N^+}}}{B_{\mathrm{Bu_4B^-}}} = \frac{V_{W(\mathrm{Bu_4N^+})}}{V_{W(\mathrm{Bu_4B^-})}} \qquad (44)$$

$$B_{\mathrm{Bu_4N^+}} = \frac{B_{\mathrm{Bu_4NBPh_4}}}{[1 + V_{W(\mathrm{Bu_4B^-})}/V_{W(\mathrm{Bu_4N^+})}]} \qquad (45)$$

A similar division can be made for Ph_4PBPh_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 $B_{\mathrm{R_4NBr}} = B_{\mathrm{Br^-}} + a[f_x R_4 N^+]$were plotted as functions of the Vander Waal's volumes. The B_{Br^-} values thus obtained were compared with the accurately determined B_{Br^-} value using $Bu_4NBBu_4$and Ph_4PBPh_4 as reference salts. They concluded that the 'reference salt'method is the best available method for division into ionic contributions.

Jenkins and Pritcheit[157] 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[196]and 'volcano plots' of Morris [159]. The principle was extended to derive absolute single ion *B*-coefficients for alkali metals and halides in water. They also observed that $B_{\mathrm{Cs^+}} = B_{\mathrm{I^-}}$suggested by Krumgalz to be

morereliable than $B_{K^+} = B_{Cl^-}$ 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.

2.7.11. TEMPERATURE DEPENDENCE OF B - ION VALUES

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 and $dA/dT>0$ (46)

(ii) $B_{Ion}<0$ and $dB_{Ion}/dT>0$ (47)

characteristics for the structure breaking of ions.

(iii) $B_{Ion}>0$ and $dB_{Ion}/dT<0$ (48)

characteristics for the structure making of ions.

An ion when surrounded by a solvent sheath, the properties of the solvent in the solvational layer may be different from those present in the bulk structure. This is well reflected in the 'Co-sphere' model of Gurney[160], A, B, C Zones of Frank and Wen[161-166] and hydrated radius of Nightingle [167].

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 (η_o) plus the viscosity changes resulting from the competition between various effects occurring in the ionic neighbourhood. Thus, the Jones-Dole equation:

$$\eta = \eta_o + \eta^* + \eta^E + \eta^A + \eta^D = \eta_o + \eta(A\sqrt{c} + Bc) \quad (49)$$

Where, η^*, the positive increment in viscosity is caused by columbic interaction. Thus,

$$\eta^E + \eta^A + \eta^D = \eta_o Bc \quad (50)$$

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

Following Stokes, Mills and Krumgalz [200] we can write:

$$B_{Ion} = B_{Ion}^{Einst} + B_{Ion}^{Orient} + B_{Ion}^{Str} + B_{Ion}^{Reinf} \qquad (51)$$

Where, as according to Lawrence and Sacco:

$$B_{Ion} = B_W + B_{Solv} + B_{Shape} + B_{Ord} + B_{Discord} \qquad (52)$$

B_{Ion}^{Einst} is the positive increment arising from the obstruction to the viscous flow of the solvent caused by the shape and size of the ions (the term corresponds to η^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 η^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 centrosymetrically and solvent to keep its own structure (this corresponds to η^D or B_{Disord}). B_{Ion}^{Reinf} is the positive increment conditioned by the effect of'reinforcement of the water structure' by large tetraalkylammoniumionsdue 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 Vander Waals volume and the volume of the solvation of ions. Thus, small and highly charged cations like Li^+ and Mg^{2+} form a firmly attached primary solvation sheath around these ions (B_{Ion}^{Orient} or η^E positive). At ordinary temperature, alignment of the solvent molecules around the inner layer also cause increase in B_{Ion}^{Orient} (η^A), B_{Ion}^{Orient} (η^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 Cs^+ or 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., K^+ and 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 befurther reinforced in water arising from B_{Ion}^{Reinf} due to hydrophobichydrations.

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} and concomitant decrease in entropy of solvation and 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 and 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 and temperature dependent mobility of ions. Thus, the ionic *B* -coefficient and the entropy of salvation of ions have rightly been used as probes of ion-solvent interactions and as a direct indication 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 [207] 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:

$$\bar{S}_h^o = \bar{S}_{aq}^o - \bar{S}_g^o \qquad (53)$$

Where, $\bar{S}^o_{aq} = \bar{S}^o_{ref} + \Delta S^o$, $\bar{S}^o_g$, 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 monoatomicions by equating the entropy of the hydrogen ion ($S^o_{H^+}$) to –5.5 cal.mol^{-1}deg^{-1}. Asmus[201] used the entropy of hydration to correlate ionic *B* values and Nightingale [194] showed that a single linear relationship could be obtained with it for both monoatomic and polyatomic ions. The correlation was utilized by Abraham *et al.* [201] to assign single ion *B* -coefficients so that a plot of ΔS^o_e [202, 203] the electrostatic entropy of solvation or$\Delta S_{I,II}{}^o$the entropic contributions of the first and secondsolvation layers of ions against *B* points (taken from the works of Nightingale) for both cations and anions lie on the same curve. There are excellent 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 $\Delta S_{I,II}{}^o$) and *B* -ion values indicate that in water the ions Li^+, Na^+, Ag^+ and F^- are not structure makers, and the ions Rb^+, Cs^+, Cl^-, Br^-, $I^-$and $ClO_4^-$are structure breakers and $K^+$is a border line case.

2.7.12. THERMODYNAMICS OF VISCOUS FLOW

Assuming viscous flow as a rate process, the viscosity (η) can be represented from Eyring's approaches as:

$$\eta = Ae^{\frac{E_{vis}}{RT}} = \left(\frac{hN_A}{V}\right)e^{\frac{\Delta G^*}{RT}} = \left(\frac{hN_A}{V}\right)e^{\left(\frac{\Delta H^*}{RT} - \frac{\Delta s}{R}\right)} \qquad (54)$$

Where E_{vis} = the experimental entropy of activation determined from a plot of lnη against 1/T . ΔG^*, $\Delta H^*$and $\Delta S^*$are the free energy, enthalpy and entropy of activation, respectively.

Nightingale and Benck [167] dealt in the problem in a different way and calculated the thermodynamics of viscous flow of salts in aqueous solution with the help of the Jones-Dole equation (neglecting the *A c* term).Thus, we have:

$$R\left[\frac{dln\eta}{d(1/T)}\right] = r\left[\frac{dln\eta_o}{d(1/T)}\right] + \frac{R}{(1+Bc)}.\frac{d(1+Bc)}{d(1/T)} \qquad (55)$$

$$\Delta E^{\neq}_{\eta(Soln)} = \Delta E^{\neq}_{\eta_o(Solv)} + \Delta E^{\neq}_V \qquad (56)$$

$\Delta E^{\neq}_V$can be interpreted as the increase or decrease of the activation energies for viscous flow of the pure solvents due to the presence of ions, i.e., the effective

influence of the ions upon the viscous flow of the solvent molecules. Feakins *et al.*[168] have suggested an alternative formulation based on the transition state treatment of the relative viscosity of electrolytic solution. They suggested the following expression:

$$B = \frac{\left(\phi_{V,2}^{0} - \phi_{V,1}^{0}\right)}{1000} + \phi_{v,2}^{0}\frac{\left(\Delta\mu_{2}^{0\neq} - \Delta\mu_{1}^{0\neq}\right)}{1000RT} \qquad (57)$$

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

$$\Delta\mu_{1}^{0\neq} = \Delta G_{1}^{0\neq} = RT\ln(\eta_{0}\phi_{v,1}^{0}/hN_{A}) \qquad (58)$$

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:

$$\frac{d(\Delta\mu_{2}^{o\neq})}{dT} = -\Delta S_{2}^{o\neq} \qquad (59)$$

$$\Delta H_{2}^{o\neq} = \Delta\mu_{2}^{o\neq} + T\Delta S_{2}^{o\neq} \qquad (60)$$

2.7.13. EFFECTS OF SHAPE AND SIZE

Stokes and Mills have dealt in the aspect of shape and size extensively. The ions in solution can be regarded to be rigid spheres suspended in continuum. The hydrodynamic treatment presented by Einstein leads to the equation:

$$\frac{\eta}{\eta_{0}} = 1 + 2.5\phi \qquad (61)$$

Where, ϕ is the volume fraction occupied by the particles. Modifications of the equation have been proposed by (i) Sinha[169]on the basis of departures from spherical shape and (ii) Vand on the basis of dependence of the flow patterns around the neighbouring particles at higher concentrations. However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monatomic cations). Thus, we have from equation (61):

$$2.5\phi = A\sqrt{c} + Bc \qquad (62)$$

Since $A\sqrt{c}$ term can be neglected in comparison with *Bc* and ϕ = c$\phi^0_{v,1}$ where $\phi^0_{v,1}$ is the partial molar volume of the ion, we get:

$$2.5\phi^0_{v,1} = B \qquad (63)$$

In the ideal case, the *B* -coefficient is a linear function of partial molar volume of the solute, $\phi^0_{v,1}$ with slope to 2.5. Thus, $B_\pm$ can be equated to:

$$B_\pm = 2.5\phi^0_\pm = \frac{2.5\times 4}{3}\frac{\left(\pi R^3_\pm N\right)}{1000} \qquad (64)$$

Assuming that the ions behave like rigid spheres with a effective radii, $R_\pm$ moving in a continuum. $R_\pm$, calculated using the equation (64) should be close to crystallographic radii or corrected Stoke's radii if the ions are scarcely solvated and behave as spherical entities. But, in general, $R_\pm$ values of the ions are higher than the crystallographic radii indicating appreciable solvation.

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

$$B_\pm = \frac{2.5}{1000\left(\phi_i + n_b\phi_s\right)} \qquad (65)$$

Where, ϕ_i is the molar volume of the base ion and ϕ_s, the molar volume of the solvent. The equation (65) has been used by a number of workers to study the nature of solvation and solvation number.

2.7.14. VISCOSITY OF NON-ELECTROLYTIC SOLUTIONS

The equations of Vand [170], Thomas [171] and Moulik proposed mainly to account for the viscosity of the concentrated solutions of bigger spherical particles have been also found to correlate the mixture viscosities of the usual non electrolytes [172-173]. These equations are:

Vand equation: $\ln\eta_r = \frac{\alpha}{1-Q} = \frac{2.5V_h c}{1-QV_h c}$ (66)

Thomas equation: $\eta_r = 1 + 2.5V_h + 10.05cV_h^2 c$ (67)

Moulik equation: $\eta^2 = I + Mc^2$ (68)

where η_r is the relative viscosity, *a* is constant depending on axial ratios of the particles, *Q* is the interaction constant, V_h is the molar volume of the solute including rigidly held solvent molecules due to hydration, *c* is the molar concentration of the solutes; *I* and *M* are constants. The viscosity equation proposed by Eyring and coworkers for pure liquids on the basis of pure significant liquid structures theory, can be extended to predict the viscosity of mixed liquids also[173-184]. The final expression for the liquid mixtures takes the following form:

$$\eta_m = \frac{6N_A h}{\sqrt{2} r_m (V_m - V_{Sm})}\left[\sum_i^n \left\{1 - \exp\left(\frac{-\theta_i}{T}\right)\right\}^{-x_i}\right]\exp\left[\frac{a_m E_{Sm} V_{Sm}}{RT(V_m - V_{Sm}}\right] + \frac{V_m - V_{Sm}}{V_m}\left[\sum_i^n \frac{2}{3d_i^2}\left(\frac{m_i kT}{\pi^3}\right)^{\frac{1}{2}} x_i\right] \quad (69)$$

Where *n* is 2 for binary and 3 for ternary liquid mixtures. The mixture parameters, r_m, E_{Sm}, V_m, V_{Sm} and a_m were calculated from the corresponding pure component parameters by using the following relations :

$$r_m = \sum_i^n x_i^2 r_i + \sum_{i \neq j} 2x_i x_j r_{ij} \quad (70)$$

$$E_{Sm} = \sum_i^n x_i^2 E_{Si} + \sum_{i \neq j} 2x_i x_j E_{Sij} \quad (71)$$

$$V_m = \sum_i^n x_i V_i V_{Sm} = \sum_i^n x_i V_{Si} a_m = \sum_i^n x_i a_i \quad (72)$$

$$r_{ij} = (r_i r_j)^{\frac{1}{2}} \text{ and } E_{Sij} = (E_{Si} E_{Sj})^{\frac{1}{2}} \quad (73)$$

$$\theta = \frac{h}{\kappa 2\pi}\left(\frac{b}{m}\right)^{\frac{1}{2}} \quad (74)$$

$$b = 2Z\varepsilon\left[22.106\left(\frac{N_A\sigma^2}{V_S}\right)^4 - 10.559\left(\frac{N_A\sigma^3}{V_S}\right)^2\right]\frac{1}{\sqrt{2}\sigma^2}\left(\frac{N_A\sigma^3}{V_S}\right)^{\frac{2}{3}} \quad (75)$$

Here σ and ε are Lennard-Jones potential parameters and the other symbols have their usual significance.

For interpolation and limited extrapolation purposes, the viscosities of ternary mixture can be correlated to a high degree of accuracy in terms of binary contribution by the following equations.

$$\eta_m = \sum_i^3 x_i\eta_i + x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] + x_2x_3\,[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] + x_3x_1[A_{31} + B_{31}(x_1 - x_2) + C_{31}(x_1 - x_2)^2] \quad (76a)$$

The correlation of ternary is modified to the following form:

$$\eta_m = \sum_i^3 x_i\eta_i + x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] + x_2x_3\,[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] + x_3x_1[A_{31} + B_{31}(x_1 - x_2) + C_{31}(x_1 - x_2)^2] + A^*_{123}x_1x_2x_3 \quad (76b)$$

However,a better result may be obtained using the following relation:

$$\eta_m = \sum_i^3 x_i\eta_i + x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] + x_2x_3\,[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] + x_3x_1[A_{31} + B_{31}(x_1 - x_2) + C_{31}(x_1 - x_2)^2] + x_1x_2x_3[A_{123} + B_{123}x_1^2(x_2 - x_3)^2 + C_{123}x_1^3(x_2 - x_3)^3] \quad (76c)$$

whereA_{12}, B_{12}, C_{12}, A_{23}, B_{23}, C_{23}, A_{31}, B_{31} and C_{31}, are constants for binary mixtures; A_{123}, B_{123} and $C_{123}$are constants for the ternaries; and the other symbols have their usual significance.

2.7.15. 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:

$$\Delta\eta = \eta - \sum_{i=1}^{j}(x_i\eta_i) \qquad (77)$$

Where η is the dynamic viscosities of the mixture and $x_i\eta_i$ are the mole fraction and viscosity of ith component in the mixture, respectively.

2.7.16. GIBBS EXCESS ENERGY OF ACTIVATION FOR VISCOUS FLOW

Quantitatively, the Gibbs excess energy of activation for viscous flow ΔG^E can be calculated as [215]:

$$\Delta G^E = RT\left[\ln\eta V - \sum_{i=1}^{j}(x_i \ln\eta_i V_i)\right] \qquad (78)$$

Where, η and V are the viscosity and molar volume of the mixture; η_i and V_i are the viscosity and molar volume of ith pure component, respectively.

2.7.17. VISCOUS SYNERGY AND ANTAGONISM

Rheology is the branch of science that studies [185] material deformation and flow, and is increasingly applied to analyze the viscous behaviour of many pharmaceutical products, [186-200] and to establish their stability and even bioavailability, since it has been firmly established that viscosity influences the drug absorption rate in the body. The study of the viscous behaviour of pharmaceutical, foodstuffs, cosmetics or industrial products, etc., is essential for conforming that their viscosity is appropriate for the contemplated use of the products.

Viscous synergy is the term used in the application to the interaction between the components of a system that causes the total viscosity of the system to be greater than the sum of the viscosities of each component considered separately. In contraposition to viscous synergy, viscous antagonism is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each component considered separately. If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is said to lack interaction.

The method most widely used to analyze the synergic and antagonic behavior of the ternary liquid mixtures used here is that developed by Kaletunc- Gencer and Peleg allowing quantification of the synergic and antagonic interactions taking place in the mixtures involving variable proportions of the constituent components. The method compares the viscosity of the system, determined experimentally, $\eta_{\exp}$, with the viscosity expected in the absence of interaction, η_{cal}, as defined by the simple mixing rule as:

$$\eta_{cal} = \sum_{i=1}^{j} w_i \eta_i \qquad (79)$$

where w_i and η_i are the fraction by weight and the viscosity of the ith component, measured experimentally and *i* is an integer.

Accordingly, when $\eta_{exp} > \eta_{cal}$, viscous synergy exists, while, when $\eta_{\exp} < \eta_{cal}$, the system is said to exhibit viscous antagonism. The procedure is used when Newtonian fluids are involved, since in non-synergy indices are defined in consequence.

In order to secure more comparable viscous synergy results, the so-called synergic interaction index (I_S) as introduced by Howell [201]is taken into account:

$$I_S = \frac{\eta_{\exp} - \eta_{mix}}{\eta_{mix}} = \frac{\Delta\eta}{\eta_{mix}} \qquad (80)$$

When the values of $I_S$are negative, it is concerned as antagonic interaction index (I_A).

The method used to analyze volume contraction and expansion is similar to that applied to viscosity, i.e., the density of the mixture is determined experimentally, $\rho_{\exp}$, and a calculation is made for ρ_{cal} based on the expression:

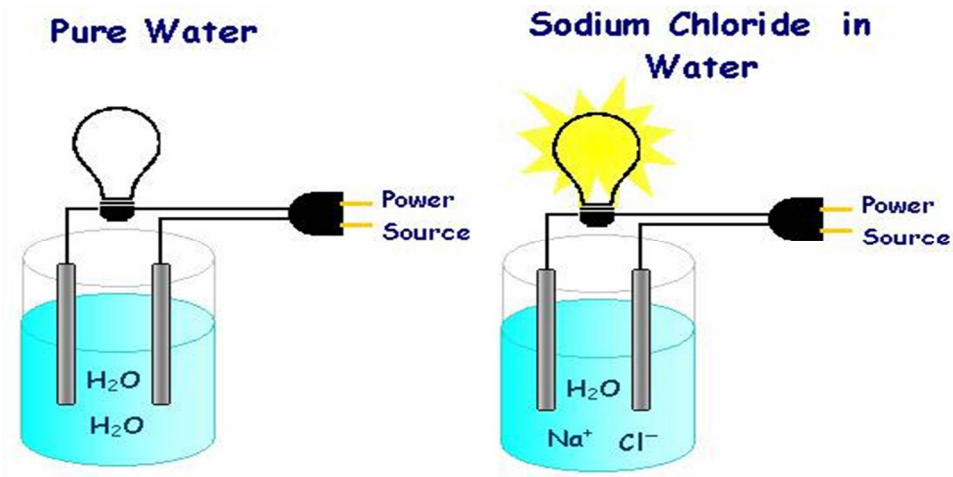
$$\rho_{cal} = \sum_{i=1}^{j} w_i \rho_i \qquad (81)$$

where ρ_i is the experimentally measured density of the ith component. Other symbols have their usual significance.

Accordingly, when $\rho_{\exp} > \rho_{cal}$, volume contraction occurs, but when $\rho_{\exp} < \rho_{cal}$, there is volume expansion in the system.

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 much information regarding ion-ion and ion-solvent interaction.



Dissolved Ions Conduct Electricity

The measurements can be made in a variety of solvents over wide ranges of temperature and pressure and in dilute solutions where interionic theories are not applicable. Conductance measurements together with transference number determinations provide an unequivocal method of obtaining single-ion values. The chief limitations, however, is the colligative-like nature of the information obtained.

The studies of conductance measurements were pursued vigorously during the last five decades, both theoretically and experimentally and a number of important theoretical equations have been derived. We shall dwell briefly on some of these aspects in relation to the studies in aqueous, non-aqueous, pure and mixed solvents. The successful application of the Debye-Hückel theory of interionic attraction was made by Onsager [202] to derive the Kohlrausch's equation representing the molar conductance of an electrolyte. For solutions of a single symmetrical electrolyte the equation is given by:

$$\Lambda = \Lambda_o - S\sqrt{c} \qquad (82)$$

where,

$$S = \alpha\Lambda_o + \beta \qquad (83)$$

$$\alpha = \frac{(z^2)k}{3(2+\sqrt{2})\varepsilon_r kT\sqrt{c}} = \frac{82.406\times10^4 z^3}{(\varepsilon_r T)^{\frac{3}{2}}} \qquad (84a)$$

$$\beta = \frac{z^2 eFk}{3\pi\eta\sqrt{c}} = \frac{82.487 z^3}{\eta\sqrt{\varepsilon_r T}} \qquad (84b)$$

The equation took no account for the short-range interactions and also of shape or size of the ions in solution. The ions were regarded as rigid charged spheres in an electrostatic and hydrodynamic continuum, i.e., the solvent. In the subsequent years, Pitts (1953) and Fuoss and Onsager (1957) [203-207] independently worked out the solution of the problem of electrolytic conductance accounting for both long-range and short-range interactions.

However, the Λ_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 was questioned. The original Fuoss-Onsager equation was further modified by Fuoss and Hsia [207-208] who recalculated the relaxation field, retaining the terms which had previously been neglected.

The results of conductance theories can be expressed in a general form:

$$\Lambda = \frac{\Lambda_o - \alpha\Lambda_o\sqrt{c}}{(1+\kappa\alpha)}\left(\frac{1+\kappa\alpha}{\sqrt{2}}\right) - \frac{\beta\sqrt{c}}{(1+\kappa\alpha)} + G(\kappa\alpha) \qquad (85)$$

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

$$\Lambda = \Lambda_o - S\sqrt{c} + Ec\,lnc + J_1 c - J_2\sqrt[3]{c} \qquad (86)$$

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 discussed elaborately by Fernandez-Prini [209-210]. Further correction of the equation (86) was made by Fuoss and Accascin. They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes:

$$\Lambda = \Lambda_o - S\sqrt{c} + Ec\ln c + J_1 c + J_2\sqrt[3]{c} - F\Lambda c \qquad (87)$$

where,

$$Fc = \frac{4\pi R^3 N_A}{3} \qquad (94a)$$

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.

2.8.1. IONIC ASSOCIATION

The equation (93) successfully represents the behaviour of completely dissociated electrolytes. The plot of Λ against $\sqrt{c}$ (limiting Onsager equation) is used to assign the dissociation or association of electrolytes. Thus, if $\Lambda_{o\,exp}$ is greater than $\Lambda_{o\,theo}$, i.e., if positive deviation occurs (ascribed to short range hard core repulsive interaction between ions), the electrolyte may be regarded as completely dissociated but if negative deviation ($\Lambda_{o\,exp} < \Lambda_{o\,theo}$) or positive deviation from the Onsager limiting tangent ($\alpha\Lambda_o + \beta$)occurs, the electrolyte may be regarded to be associated. Here the electrostatic interactions are large so as to cause association between cations and anions. The difference in $\Lambda_{o\,exp}$ and $\Lambda_{o\,theo}$ would be considerable with increasing association [211-212].

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

$$M^{z+} + A^{z-} = MA \qquad (88)$$

$$K_A = \frac{(1-\alpha)}{\alpha^2 c\gamma_\pm^2} \qquad (89)$$

$$\alpha = 1 - \alpha^2 K_A c\gamma_\pm^2 \qquad (90)$$

Where $\gamma_\pm$ is the mean activity coefficient of the free ions at concentration $\alpha\, c$

For strongly associated electrolytes, the constant, K_A and Λ_o has been determined using Fuoss-Kraus equation [213]or Shedlovsky's equation [214].

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda_o} + \frac{K_A}{{\Lambda_o}^2} \cdot \frac{c\gamma_\pm^2 \Lambda}{T(z)} \qquad (91)$$

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

$$F(z) = 1 - z(1 - z(1 - \ldots)^{-\frac{1}{2}})^{-\frac{1}{2}} \qquad (92a)$$

and

$$\frac{1}{T(z)} = S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \ldots. \qquad (92b)$$

A plot of $T(z)/\Lambda$ against $c\gamma_{\pm}^2\Lambda/T(z)$ should be a straight line having $1/\Lambda_o$ for its intercept and K_A/Λ_o^2 for its slope. Where K_A is large, there will be considerable uncertainty in the determined values of Λ_o and K_A from equation (91).

The Fuoss-Hsia conductance equation for associated electrolytes is given by:

$$\Lambda = \Lambda_o - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{\frac{3}{2}} - K_A\Lambda\gamma_{\pm}^2(\alpha c) \quad (93)$$

The equation was modified by Justice [215]. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

$$\Lambda = \alpha(\Lambda_o - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1R(\alpha c) - J_2R(\alpha c)^{\frac{3}{2}} \qquad (94b)$$

$$\frac{(1-\alpha)}{\alpha^2 c\gamma_{\pm}^2} = K_A \qquad (95)$$

$$\ln\gamma_{\pm} = \frac{-k\sqrt{q}}{(1+kR\sqrt{\alpha c})} \qquad (96)$$

The conductance parameters are obtained from a least square treatment after setting, $R = q = \frac{e^2}{2\varepsilon kT}$ (Bjerrum's critical distance).

According to Justice the method of fixing the J-coefficient by setting, $R = q$ clearly permits a better value of K_A to be obtained. Since the equation (96) is a series expansion truncated at the $c^{3/2}$ term, it would be preferable that the resulting errors be absorbed as must as possible by J_2 rather than by K_A, whose theoretical interest is greater as it contains the information concerning short-range cation-anion interaction. 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. The following equation has been proposed by Fuoss [216]:

$$K_A = \frac{4\pi N_A\alpha^3}{3000}\exp\left(\frac{e^2}{\alpha\varepsilon kT}\right) \qquad (97)$$

In some cases, the magnitude of K_A was too small to permit a calculation of *a*. The distance parameter was finally determined from the more general equation due to Bjerrum [274].

$$K_A = \frac{4\pi N_A \alpha}{1000} \int_{r=a}^{r=q} r^2 \exp\left(\frac{z^2 e^2}{r\varepsilon kT}\right) dr \qquad (98)$$

The equations neglect specific short-range interactions except for solvation in which the solvated ion can be approximated by a hard sphere model. The method has been successfully utilized by Douheret [217-218].

2.8.2. ION SIZE PARAMETER AND IONIC ASSOCIATION

For plotting, equation (87) can be rearranged to the 'Λ' function as:

$$\Lambda_1 = \Lambda + S\sqrt{c} - Ec\ln c = \Lambda_o + J_1 c + J_2 \sqrt[3]{c} = \Lambda_o + J_1 c \qquad (99)$$

with J_2 term omitted.

Thus, a plot of Λ_o vs. *c* gives a straight line with Λ_o as intercept and J_1 as slope and '*a*' values can be calculated from J_1 values. The '*a*' values obtained by this method for DMSO were much smaller than would be expected from sums of crystallographic radii. One of the reasons attributed to it is that ion-solvent interactions are not included in the continuum theory on which the conductance equations are based. The inclusion of dielectric saturation results in an increase in '*a*' values (much in conformity with the crystallographic radii) of alkali metal salts (having ions of high surface charge density) in sulpholane. The viscosity correction leads to a larger value of '*a*' but the agreement is still poor. However, little of real physical significance may be attached to the distance of closest approach derived from J_1 [219]. Fuoss [220] in 1975 proposed a new conductance equation. Latter he subsequently put forward another conductance equation in 1978 replacing the old one as suggested by Fuoss and co-workers. He classified the ions of electrolytic solutions in one of the three categories.

(i) Ions finding an ion of opposite charge in the first shell of nearest neighbours (contact pairs) with $r_{ij}=a$. The nearest neighbours to a contact pair are the solvent molecules forming a cage around the pairs.

(ii) Ions with overlapping Gurney's co-spheres (solvent separated pairs). For them r_{ij}= *a+ns*, where *n* is generally 1 but may be 2, 3 etc.;'s' is the diameter of sphere corresponding to the average volume (actual plus free) per solvent molecule.

(iii) Ions finding no other unpaired ion in a surrounding sphere of radius *R*, the diameter of the co-sphere (unpaired ions). Thermal motions and interionic forces establish a steady state, represented by the following equilibria:

$$A^+ + B^- \quad = \quad (A^+ \cdots\cdots\cdots\cdots B^-) \quad = \quad A^+ + B^- \quad = \quad AB \qquad (100)$$

Solvent separated ion-pair Contact ion-pair Neutral molecule

Contact pairs of ionogens may rearrange to neutral molecules $A^+B^- = AB$, e.g., H_3O^+ and CH_3COO^-. Let γ be the fraction of solute present as unpaired (r>R) ions. If $c\gamma$ is the concentration of unpaired ion and α is the fraction of paired ions($r \leq R$), then the concentration of unpaired ion and $c(1-\alpha)(1-\gamma)$ and that of contact pair is $\alpha c(1-\gamma)$.

The equation constants for eq. 100 are:

$$K_R = \frac{(1-\alpha)(1-\gamma)}{c\gamma^2 f^2} \qquad (101)$$

$$K_S = \frac{\alpha}{1-\alpha} = \exp\left(\frac{-E_S}{kT}\right) = e^{-\varepsilon} \qquad (102)$$

Where K_R describes the formation and separation of solvent separated pairs by diffusion in and out of spheres of diameter *R* around cations and can be calculated by continuum theory; K_S s the constant describing the specific short-range ion-solvent and ion-ion interactions by which contact pairs form and dissociate. E_S is the difference in energy between a pair in the states (*r* = *R*) and (*r* = *a*); $\varepsilon$is $E_S$measured in units of *kT*.

Now,

$$(1-\alpha) = \frac{1}{1+K_S} \qquad (103)$$

And the conductometric pairing constant is given by:

$$K_A = \frac{(1-\alpha)}{c\gamma^2 f^2} = \frac{K_R}{1-\alpha} = K_R(1+K_S) \qquad (104)$$

The equation determines the concentration, $c\gamma$ of active ions that produce long-range interionic effects. The contact pairs react as dipoles to an external field, *X* and contribute only to changing current. Both contact pairs and solvent separated pairs are left as virtual dipoles by unpaired ions, their interaction with unpaired ions is,

therefore, neglected in calculating long-range effects (activity coefficients, relaxation field ΔX and electrophoresis ($\Delta X \Delta \Lambda_e$). The various patterns can be reproduced by theoretical fractions in the form:

$$\Lambda = p\left[\Lambda_o\left(\frac{1+\Delta X}{X}\right)+\Delta\Lambda_e\right] = p\left[\Lambda_o\left(1+R_X\right)+E_L\right] \qquad (105)$$

Which is a three parameter equation $\Lambda = \Lambda(c, \Lambda_o, R, E_S), \Delta X / X$ (therelaxation field) and $\Delta\Lambda_e$ (the electrophoretic counter current) are longrangeeffects due to electrostatic interionic forces and *p* is the fraction of Gurney co-sphere.

The parameter K_R (or E_S) is a catch-all for all short range effects:

$$p = 1-\alpha(1-\gamma) \qquad (106)$$

In case of ionogens or for ionophores in solvents of low dielectric constant, α is very near to unity ($-E_S/kT$) >> 1 and the equation becomes:

$$\Lambda = \gamma\left[\Lambda_o\left(\frac{1+\Delta X}{X}\right)\right]+\Delta\Lambda_e \qquad (107)$$

The equilibrium constant for the effective reaction, $A^+ + B^- + AB$, is then

$$K_A = \frac{(1-\gamma)}{c\gamma^2 f^2} \approx K_R K_S \qquad (108)$$

as $K_S >> 1$. The parameters and the variables are related by the set of equations:

$$\gamma = 1-\frac{K_R c\gamma^2 f^2}{(1-\alpha)} \qquad (109)$$

$$K_R = \left(\frac{4\pi N_A R^3}{3000}\right)\exp\left(\frac{\beta}{R}\right) \qquad (110)$$

$$-\ln f = \frac{\beta\kappa}{2(1+\kappa R)}, \quad \beta = \frac{e^2}{\varepsilon\kappa T} \qquad (111)$$

$$\kappa^2 = 8\pi\beta\gamma\eta = \frac{\pi\beta N_A \gamma c}{125} \qquad (112)$$

$$-\varepsilon = \ln\left[\frac{\alpha}{1-\alpha}\right] \qquad (113)$$

The details of the calculations are presented in the 1978 paper [221]. The shortcomings of the previous equations have been rectified in the present equation

that is also more general than the previous equations and can be used for higher concentrations (0.1 N in aqueous solutions).

2.8.3. LEE-WHEATON CONDUCTANCE EQUATION

As Fuoss 1978 conductance equation contained a boundary condition error,[222, 224] Fuoss introduced a slight modification to his model [225]. According to him, the ion pairs (ion approaching with their Gurney co-sphere) are divided into two categories- contact pairs (with no contribution to conductance) and solvent separated ion pairs (which can only contribute to the net transfer of charge). To rectify the boundary errors contained in Fuoss 1978 conductance equation, Lee-Wheaton [226(a)] in the same year described in the derivation of a new conductance equation, based on the Gurney co-sphere model and henceforth the new equation is referred to as the Lee-Wheaton equation [226(b)]. The conductance data were analyzed by means of the Lee-Wheaton conductance equation [227] in the form:

$$\Lambda = \alpha_i \left[\begin{array}{l} \Lambda_o \left\{ 1 + C_1 \beta\kappa + C_2 (\beta\kappa)^2 + C_3 (\beta\kappa)^3 \right\} \\ -\dfrac{\rho\kappa}{1+\kappa R} \left\{ 1 + C_4 \beta\kappa + C_5 (\beta\kappa)^2 + \dfrac{\kappa R}{12} \right\} \end{array} \right] \tag{114}$$

The mass action law association [285] is

$$K_{A,c} = \frac{(1-\alpha_i)\gamma_A}{\alpha_i^2 c_i \gamma_\pm^2} \tag{115}$$

and the equation for the mean ionic activity coefficient:

$$\gamma_\pm = \exp\left[-\frac{q\kappa}{1+\kappa R} \right] \tag{116}$$

where $C_1$to $C_5$are least square fitting coefficients as described by Pethybridge and Taba[228], Λ_o is the limiting molar conductivity, $K_{A,c}$, is the association constant, α_i is the dissociation degree, q is the Bjerrum parameter and γ the activity coefficient and $\beta = 2q$. The distance parameter R is the least distance that two free ions can approach before they merge into ion pair. The Debye parameter κ, the Bjerrum parameter q and ρ are defined by the expressions [229]:

$$\kappa = 16000\pi N_A q c_i \alpha_i \tag{117}$$

$$q = \frac{e^2}{8\varepsilon_o \varepsilon_r \kappa T} \tag{118}$$

$$\rho = \frac{F\,e}{299.79 \times 3\pi\eta} \qquad (119)$$

Where, the symbols have their usual significance [230].

The equation (118) was resolved by an iterative procedure. For a definite *R* value the initial value of Λ_o and $K_{A,c}$, were obtained by the Kraus-Bray method. The parameter Λ_o and $K_{A,c}$, were made to approach gradually their best values by a sequence of alternating linearization and least squares optimizations by the Gauss-Siedel method [228]until satisfying the criterion for convergence. The best value of a parameter is the one when equation (118) is best fitted to the experimental data corresponding to minimum standard deviation (σ_A) for a sequence of predetermined *R* value and standard deviation (σ_A) was calculated by the following equation:

$$\sigma_A^2 = \sum_{i=1}^{n} \frac{[\Lambda_{i(calc)} - \Lambda_{i(obs)}]^2}{n-m} \qquad (120)$$

Where *n* is the number of experimental points and *m* is the number of fitting parameters. The conductance data were analyzed by fixing the distance of closest approach *R* with two parameter fit (*m*=2). For the electrolytes with no significant minima observed in the σ_A versus *R* curves, the *R* values were arbitrarily preset at the centre to centre distance of solvent-separated pair:

$$R = a + d \qquad (121)$$

Where, $a = r_c^+ + r_c^-$, i.e., the sum of the crystallographic radii of the cation and anion and *d* is the average distance corresponding to the side of a cell occupied by a solvent molecule. The definitions of *d* and related terms are described in the literature [229-233].

2.8.4. LIMITING EQUIVALENT CONDUCTANCE

The limiting equivalent conductance of an electrolyte can be easily determined from the theoretical equations and experimental observations. At infinite dilutions, the motion of an ion is limited solely by the interactions with the surroundings solvent molecules as the ions are infinitely apart. Under these

conditions, the validity of Kohlrausch's law of independent migration of ions is almost axiomatic. Thus:

$$\Lambda_0 = \lambda_o^+ + \lambda_o^- \qquad (122a)$$

At present, limiting equivalent conductance is the only function which can be divided into ionic components using experimentally determined transport number of ions, i.e.,

$$\lambda_o^+ = t_+ \Lambda_0 \text{ and } \lambda_o^- = t_- \Lambda_0 \qquad (122b)$$

Thus, from accurate value of λ_0 of ions it is possible to separate the contributions due to cations and anions in the solute-solvent interactions. However, accurate transference number determinations are limited to few solvents only.

In the absence of experimentally measured transference numbers it would be useful to develop indirect methods to obtain the ionic limiting equivalent conductances in solvents for which experimental transference numbers are not yet available. Various attempts were made to develop indirect methods to obtain the limiting ionic equivalent conductance, in ionic solvents for which experimental transference numbers are not yet available.

The method has been summarized by Krumgalz [234] and some important points are mentioned as follows:

(i) Walden equation [235]

$$(\lambda_o^{\pm})^{25}_{\text{water}} \cdot \eta_{o,\text{water}} = (\lambda_o^{\pm})^{25}_{\text{acetone}} \cdot \eta_{o,\text{acetone}} \qquad (123)$$

(ii) $(\lambda_{o,\text{pic}} \cdot \eta_o) = 0.267, \quad \lambda_{o,\text{Et}_4\text{N}^+} \cdot \eta_o = 0.269$ [301,302] (124)

based on $\Lambda_{o,\text{Et}_4\text{N}_{\text{pic}}} = 0.563$

Walden considered the products to be independent of temperature and solvent. However, the $\Lambda_{o,\text{Et}_4\text{N}_{\text{pic}}}$ values used by Walden were found to differ considerably from the data of subsequent more precise studies and the values of (ii) are considerably different for different solvents.

(iii) $\lambda_o^{25}(\text{Bu}_4\text{N}^+) = \lambda_o^{25}(\text{Ph}_4\text{B}^-)$ (125)

The equality holds well in nitrobenzene and in mixture with CCl_4 but not realized in methanol, acetonitrile and nitromethane.

(iv) $\lambda_o^{25}(\text{Bu}_4\text{N}^+) = \lambda_o^{25}(\text{Bu}_4\text{B}^-)$ [293,294] (126)

The method appears to be sound as the negative charge on boron in the Bu_4B^- ion is completely shielded by four inert butyl groups as in the Bu_4N^+ ion while this phenomenon was not observed in case of Ph_4B^-.

(v) The equation suggested by Gill [295] is:

$$\lambda_o^{25}(R_4N^+) = \frac{zF^2}{6\pi N_A \eta_o [r_i - (0.0103\varepsilon_o + r_y)]} \qquad (127)$$

Where Z and r_i are the charge and crystallographic radius of proper ion, respectively: η_o and ε_o are solvent viscosity and dielectric constant of the medium, respectively; r_y= adjustable parameter taken equal to 0.85 Å and 1.13 Å for dipolar non-associated solvents and for hydrogen bonded and other associated solvents respectively [236-237].

However, large discrepancies were observed between the experimental and calculated values [238(a)]. In a paper,[238(b)]Krumgalz examined the Gill's approach more critically using conductance data in many solvents and found the method reliable in three solvents e.g. butan-1-ol, acetonitrile and nitromethane.

(vi) $$\lambda_o^{25}\left[(i-Am)_3 BuN^+\right] = \lambda_o^{25}\left(Ph_4B^-\right) \qquad (128)$$

It has been found from transference number measurements that the $\lambda_o^{25}\left[(i-Am)_3 BuN^+\right]$ and $\lambda_o^{25}\left(Ph_4B^-\right)$ values differ from one another by 1%.

(vii) $$\lambda_o^{25}\left(Ph_4B^-\right) = 1.01\lambda_o^{25}\left[(i-Am)_4 B^-\right] \qquad (129)$$

The value is found to be true for various organic solvents.

Krumgalz suggested a method for determining the limiting ion conductance in organic solvents. The method is based on the fact that large tetraalkyl (aryl) onium ions are not solvated in organic solvents due to the extremely weak electrostatic interactions between solvent molecules and the large ions with low surface charge density and this phenomenon can be utilized as a suitable model for apportioning Λ_o values into ionic components for non-aqueous electrolytic solutions.

Considering the motion of solvated ion in an electrostatic field as a whole, it is possible to calculate the radius of the moving particle by the Stokes equation:

$$r_S = \frac{|z|F^2}{A\pi\eta_o\lambda_o^{\pm}} \qquad (130)$$

Where, *A* is a coefficient varying from 6 (in the case of perfect sticking) to 4 (in case of perfect slipping). Since the r_S values, the real dimension of the non-solvated tetraalkyl (aryl) onium ions must be constant, we have:

$$\lambda_o^{\pm}\eta_0 = \text{constant} \qquad (131)$$

This relation has been verified using $\lambda_o^{\pm}$ values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the i-Am_4B^-, Ph_4As^+, Ph_4B^- ions and for tetraalkylammonium cation starting with Et_4N^+. The relationship can be well utilized to determine $\lambda_o^{\pm}$ of ions in other organic solvents from the determined Λ_o values.

2.8. 5. SOLVATION

Various types of interactions exist between the ions in solutions. These interactions result in the orientation of the solvent molecules towards the ion. The number of solvent molecules that are involved in the solvation of the ion is called solvation number. If the solvent is water, this is called hydration number. Solvation region can be classified as primary and secondary solvation regions. Here we are concerned with the primary solvation region. The primary solvation number is defined as the number of solvent molecules which surrender their own translational freedom and remain with the ion, tightly bound, as it moves around, or the number of solvent molecules which are aligned in the force field of the ion.

If the limiting conductance of the ion *i* of charge $Z_i$is known, the effective radius of the solvated ion can be determined from Stokes' law. The volume of the solvation shell is given by the equation.

$$V_S = \left(\frac{4\pi}{3}\right)\left(r_S^3 - r_C^3\right) \qquad (132)$$

where r_c is the crystallographic radius of the ion. The solvation number n_s would then be obtained from

$$n_S = \frac{V_S}{V_0} \qquad (133)$$

Assuming Stokes' relation to hold well, the ionic solvated volume can be obtained, because of the packing effects [239-241], from

$$V_S^o = 4.35 r_S^3 \qquad (134)$$

Where V_S^o is expressed in mol/lit. and r_S in angstroms. However, this method is not applicable to ions of medium size though a number of empirical and theoretical corrections [242-245] have been suggested in order to apply it to most of the ions.

2.8.6. STOKES' LAW AND WALDEN'S RULE

The starting point for most evaluations of ionic conductances is Stokes' law that states that the limiting Walden product (the limiting ionic conductance-solvent viscosity product) for any singly charged, spherical ion is as function only of the ionic radius and thus, under normal conditions, is constant. The limiting conductances λ_i^o of a spherical ion of radius R_i moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

$$\lambda_o^i = \frac{|z_i e| eF}{6\pi\eta_o R_i} = \frac{0.819|z_i|}{\eta_o R_i} \qquad (135)$$

Where η_o = macroscopic viscosity by the solvent in poise, R_i is in angstroms. If the radius R_i is assumed to be the same in every organic solvent, as would be the case, in case of bulky organic ions, we get:

$$\lambda_o^i \eta_o = \frac{0.819 z_i}{R_i} = constant \qquad (136)$$

This is known as the Walden rule [246]. The effective radii obtained using this equation can be used to estimate the solvation numbers. However, Stokes' radii failed to give the effective size of the solvated ions for small ions.

Robinson and Stokes [247], Nightingale and others [248-251] have suggested a method of correcting the radii. The tetraalkylammonium ions were assumed to be not solvated and by plotting the Stokes' radii against the crystal radii of those large ions, a calibration curve was obtained for each solvent. However, the experimental results indicate that the method is incorrect as the method is based on the wrong assumption of the invariance of Walden's product with temperature. The idea of

microscopic viscosity [318] was invoked without much success [252] but it has been found that:

$$\lambda_o^i \eta_0 = \text{constant} \qquad (137)$$

Where p is usually 0.7 for alkali metal or halide ions and *p* = 1 for the large ions [253, 254,255]. Gill [256] has pointed out the inapplicability of the Zwanzig theory [257] of dielectric friction for some ions in non-aqueous and mixed solvents and has proposed an empirical modification of Stokes' Law accounting for the dielectric friction effect quantitatively and predicts actual solvated radii of ions in solution. This equation can be written as:

$$r_i = \frac{|z| F^2}{6\pi N_A \eta_o \lambda_o^i} + 0.0103D + r_y \qquad (138)$$

Where, r_i is the actual solvated radius of the ion in solution and r_y is an empirical constant dependent on the nature of the solvent [258-259].

The dependence of Walden product on the dielectric constant led Fuoss to consider the effect of the electrostatic forces on the hydrodynamics of the system. Considering the excess frictional resistance caused by the dielectric relaxation in the solvent caused by ionic motion, Fuoss proposed the relation:

$$\lambda_o^i = \frac{Fe|z_i|}{6\pi R_\infty}\left(\frac{1+A}{\varepsilon R_\infty^2}\right) \qquad (139)$$

or, $$R_i = R_\infty + \frac{R}{\infty} \qquad (140)$$

where R_∞ is the hydrodynamic radius of the ion in a hypothetical medium of dielectric constant where all electrostatic forces vanish and *A* is an empirical constant.

Boyd [243] gave the expression:

$$\lambda_o^i = \frac{Fe|z_i|}{6\pi\eta_o r_i\left[\left(1+\frac{2}{27}\pi\eta_o\right)\cdot\left(\frac{z_i^2 e^2 \tau}{r_i^4 \varepsilon_o}\right)\right]} \qquad (141)$$

by considering the effect of dielectric relaxation in ionic motion; τ is the Debye relaxation time for the solvent dipoles. Zwanzig [244] treated the ion as a rigid sphere of radius r_i moving with a steady state viscosity, V_i through a viscous

incompressible dielectric continuum. The conductance equation suggested by Zwanzig is:

$$\lambda_o^i = \frac{z_i^2 eF}{\left[A_V \pi \eta_o r_i + A_D \left\{ \frac{z_i^2 e^2 (\varepsilon_r^o - \varepsilon_r^\infty)\tau}{\varepsilon_r^o (2\varepsilon_r^o + 1) r_i^3} \right\} \right]} \qquad (142)$$

where ε_r^o and ε_r^∞ are the static and limiting high frequency (optical) dielectric constants. $A_V = 6$ and $A_D = 3/8$ for perfect sticking and $A_V = 4$ and $A_V = 3/4$ foe perfect slipping. It has been found that Born's and Zwanzig's equations are very similar and both may be written in the form:

$$\lambda_o^i = \frac{A r_i^3}{r_i^4 + B} \qquad (143)$$

The theory predicts that λ_o^i passes through a maximum of $27^{\frac{1}{4}} A / 4B^{\frac{1}{4}}$ at $r_i = (3B)^{1/4}$ The phenomenon of maximum conductance is well known. The relationship holds good to a reasonable extent for cations in aprotic solvents but fails in case of anions. The conductance, however, falls off rather more rapidly than predicted with increasing radius. For comparison with results in different solvents, the equation (142) can be rearranged as :

$$\frac{z_i^2 eF}{\lambda_o^i \eta_o} = \frac{A_V \pi r_i + A_D z_i^2}{r_i^3} \cdot \frac{e^2 (\varepsilon_r^o - \varepsilon_r^\infty)}{\varepsilon_r^o (2\varepsilon_r^o + 1)} \left(\frac{\tau}{\eta_o} \right) \qquad (144)$$

$$L^* = A_V \pi r_i + \frac{A_D z_i^2}{r_i^3 P^*} \qquad (145)$$

In order to test Zwanzig's theory, the equation (145) was applied for $Me_4N^+$and Et_4N^+ in pure aprotic solvents like methanol, ethanol, acetonitrile, butanol and pentanol [325-330]. Plots of L^* against the solvent function P^* were found to be straight line. But, the radii calculated from the intercepts and slopes are far apart from equal except in some cases where moderate success is noted. It is noted that relaxation effect is not the predominant factor affecting ionic mobility and these mobility differences could be explained quantitatively if the microscopic properties of the solvent, dipole moment and free electron pairs were considered the predominant factors in the deviation from the Stokes' law.

It is found that the Zwanzig's [257] theory is successful for large organic cations in aprotic media where solvation is likely to be minimum and where viscous friction predominates over that caused by dielectric relaxation. The theory breaks down whenever the dielectric relaxation term becomes large, i.e., for solvents of high P^* and for ions of small r_i. Like any continuum theory Zwanzig has the inherent weakness of its inability to account for the structural features [260-273],e.g.,

(i) It does not allow for any correlation in the orientation of the solvent molecules as the ion passes by and this may be the reason why the equation is not applicable to the hydrogen-bonded solvents.

(ii) The theory does not distinguish between positively and negatively charged ions and therefore, cannot explain why certain anions in dipolar aprotic media possess considerably higher molar concentrations than the fastest cations.

The Walden product in case of mixed solvents does not show any constancy but it shows a maximum in case of DMF + water and DMA +water mixtures and other aqueous binary mixtures. To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts have been made with different models for ion-solvent interactions but no satisfactory expression has been derived taking into account all types of ion-solvent interactions because

(i) it is difficult to include all types of interactions between ions as well as solvents in a single mathematical expression, and

(ii) it is not possible to account for some specific properties of different kinds of ions and solvent molecules.

Ions moving in a dielectric medium experience a frictional force due to dielectric loss arising from ion-solvent interactions with the hydrodynamic force. Though Zwanzig's expression accounts for a change in Walden product with solvent composition but does not account for the maxima. According to Hemmes [274] the major deviations in the Walden products are due to the variation in the electrochemical equilibrium between ions and solvent molecules of mixed polar solvent composition. In cases where more than one types of solvated complexes are formed, there should be a maximum and/or a minimum in the Walden product. This is supported from experimental observations. Hubbard and Onsager [275] have developed the kinetic theory of ion-solvent interaction within the framework of

continuum mechanics where the concept of kinetic polarization deficiency has been introduced. However, quantitative expression is still awaited. Further, improvements [276-277] naturally must be in terms of (i) sophisticated treatment of dielectric saturation, (ii) specific structural effects involving ion-solvent interactions. From the discussion, it is apparent that the problem of molecular interactions is intriguing as well as interesting. It is desirable to explore this problem using different experimental techniques. We have, therefore, utilized four important methods, viz., volumetric, viscometric, interferometric and conductometric for the physicochemical studies indifferent solvent media.

2.8.7. THERMODYNAMICS OF ION-PAIR FORMATION

The standard Gibbs energy changes (ΔG^o) for the ion- association process can be calculated from the equation

$$\Delta G^o = -RT \ln K_A \qquad (146)$$

The values of the standard enthalpy change, ΔH^o and the standard entropy change, ΔS^o, can be evaluated from the temperature dependence of values as follows,

$$\Delta H^o = -T^2 \left[\frac{d(\Delta G^o / T)}{dT} \right]_P \qquad (147)$$

$$\Delta S^o = -T^2 \left[\frac{d(\Delta G^o)}{dT} \right]_P \qquad (148)$$

The values can be fitted with the help of a polynomial of the type:

$$\Delta G^o = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \qquad (149)$$

And the coefficients of the fits can be compiled together with the σ% values of the fits. The standard values at 298.15 K are then:

$$\Delta G^o_{298.15} = c_0 \qquad (150)$$

$$\Delta S^o_{298.15} = c_1 \qquad (151)$$

$$\Delta H^o_{298.15} = c_o + 298.15 c_1 \qquad (152)$$

The main factors which govern the standard entropy of ion-association of electrolytes are: (i) the size and shape of the ions, (ii) charge density on the ions, (iii) electrostriction of the solvent molecules around the ions, and (iv) penetration of the solvent molecules inside the space of the ions, and the influence of these factors are discussed later.

The non-columbic part of the Gibbs energy ΔG^o can also be calculated using the following equation:

$$\Delta G^o = N_A W_{\pm} \tag{153}$$

$$K_A = \left(\frac{4\pi N_A}{1000}\right)\int_a^R r^2 \exp\left(\frac{2q}{r} - \frac{W_{\pm}}{kT}\right) dr \tag{154}$$

Where, the symbols have their usual significance.

The quantity 2q/r is Columbic part of the interionic mean force potential and $W_{\pm}$ is its non-columbic part.

2.8.8. SOLVATION MODELS—SOME RECENT TRENDS

The interactions between particles in chemistry have been based upon empirical laws- principally on Coulomb's law. This is also the basis of the attractive part of the potential energy used in the Schrödinger equation. Quantum mechanical approach for ion-water interactions was begun by Clementi in 1970. A quantum mechanical approach to salvation can provide information on the energy of the individual ion-water interactions provided it is relevant to solution chemistry, because it concerns potential energy rather than the entropic aspect of salvation. Another problem in quantum approach is the mobility of ions in solution affecting salvation number and coordination number. However, the Clementi calculations concerned stationary models and cannot have much to do with the dynamic salvation numbers. Covalent bond formation enters little into the aqueous calculations; however, with organic solvents the quantum mechanical approaches to bonding may be essential. The trend pointing to the future is thus the molecular dynamics technique. In molecular dynamic approach, a limited number of ions and molecules and Newtonian mechanics of movement of all particles in solution is concerned. The foundation of such a approach is the knowledge of the

intermolecular energy of interactions between a pair of particles. Computer simulation approaches may be useful in this regard and the last decade (1990-2000) witnessed some interesting trends in the development of solvation models and computer software. Based on a collection of experimental free energy of solvation data, C.J. Cramer, D.G. Truhlar and co-workers from the University of Minnesota, U.S.A. constructed a series of solvation models (SM1-SM5 series) to predict and calculate the free energy of solvation of a chemical compound. These models are applicable to virtually any substance composed of H, C, N, O, F, P, S, Cl, Br and/or I. The only input data required are, molecular formula, geometry, refractive index, surface tension, Abraham's a (acidity parameter) and b (basicity parameter) values, and, in the latest models, the dielectric constants. The advantage of models like SM5 series is that they can be used to predict the free energy of self-solvation to better than 1 KCl/mole. These are especially useful when other methods are not available. One can also analyze factors like electrostatics, dispersion, hydrogen bonding, etc. using these tools. They are also relatively inexpensive and available in easy to use computer codes.

Galindo *et al.*[350,351] have developed Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to model the thermodynamics and phase equilibrium of electrolytic aqueous solutions. The water molecules are modelled as hard spheres with four short-range attractive sites to account for the hydrogen-bond interactions. The electrolyte is modeled as two hard spheres of different diameter to describe the anion and cation. The Debye-Hückel and mean spherical approximations are used to describe the interactions. Good agreement with experimental data is found for a number of aqueous electrolyte solutions. The relative permittivity becomes very close to unity, especially when the mean spherical approximation is used, indicating a good description of the solvent. E. Bosch *et al.*[352]of the University of Barcelona, Spain, have compared several "Preferential Solvation Models" specially for describing the polarity of dipolar hydrogen bond acceptor-cosolvent mixture.

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 [280].

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:

$$\frac{V_A}{V_B} = \frac{sin\theta_A}{sin\theta_B} = \frac{n_B}{n_A} \qquad (155)$$

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

$$R = [(n_D^2 - 1)/n_D^2 + 2](M/\rho) \qquad (156)$$

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

$$n_D = [(2A+1)/(1-A)]^{0.5} \qquad (157)$$

Where, A is given by:

$$A = [\{\frac{(n_1^2-1)}{(n_1^2+2)}(1/\rho_1)\} - \{\frac{(n_1^2-1)}{(n_1^2+2)}(w_2/\rho_1)\} + \{\frac{(n_2^2-1)}{(n_2^2+2)}(w_2/\rho_2)\}\rho] \qquad (158)$$

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

The molar refractivity deviation is calculated by the following expression:

$$\Delta R = R - \phi_1 R_1 - \phi_2 R_2 \qquad (159)$$

where ϕ_1 and ϕ_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:

$$\Delta n_D = n_D - x_1 n_{D1} - x_2 n_{D2} \qquad (160)$$

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 and x is the mole fraction.

The computed deviations of refractive indices of the binary mixtures are fitted using the following Redlich-Kister expression [281].

$$\Delta n_{Dew} = w_e w_w \sum_{P=0}^{S} B_p (w_e w_w)^p \qquad (161)$$

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:

$$n_{Ds,sol} = n_{Dsol} + \sum_{i=1}^{N} A_i m^i \qquad (162)$$

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, Ai 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[360].Similar to that obtained for the salt + solvent solutions was used to represent ternary refractive indices:

$$n_D = n_{Dw} + \sum_{i=1}^{P} C_i m^i \qquad (163)$$

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, 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 *ó* are calculated for the expression in terms of volume fractions and in terms of mole fractions, respectively.