

CHAPTER II

GENERAL INTRODUCTION

2.1 SOLUTION CHEMISTRY:

Solution Chemistry is an important branch of physical chemistry which studies the change in properties that arise when solute dissolves in solvent. The mixing of different solute or solvent with another solvent/solvent mixtures gives rise to solutions that generally do not behave ideally. This deviation from ideality is expressed in terms of many thermodynamic parameters. These thermodynamic properties of solution corresponds to the difference between the actual property and the property if the system behaves ideally and thus are useful in the study of molecular interactions and arrangements. Knowledge of the thermodynamic properties is essential for the proper design of industrial processes. Measurements of the bulk properties, such as viscosities and densities of liquids, measurement of refractive indices, sound velocity- provides insight into the molecular arrangement in liquids and help one to understand the thermodynamic properties of liquid mixtures.

Vitamins are organic compounds which are needed in small quantities to sustain life. We get vitamins from food, because the human body either does not produce enough of them, or not at all. Vitamin is a vital nutrient that an organism requires in limited amounts. They are essential precursors for various coenzymes. These coenzymes are therefore required in almost all metabolic pathways [1].

SOME WATER SOLUBLE VITAMINS:

Vitamin C is required for the synthesis of collagen, the intercellular "cement" which gives the structure of muscles, vascular tissues, bones, and tendon. Importantly Ascorbic acid (vitamin C) is also able to regenerate other antioxidants as vitamin E. Vitamin C with Zn is also important for the healing of wounds. It is also needed for the metabolism of bile acids which may have implications for blood



cholesterol levels and gallstones. Ascorbic acid and its sodium, potassium, and calcium salts are commonly used as antioxidants food additives. Vitamin C plays an important role for the synthesis of several important peptide hormones neurotransmitters and creatinine. It also enhances the eye's ability and delay the progression of advanced age related muscular degeneration.

Vitamin B3 is a water-soluble vitamin, an essential micronutrient and a reactive moiety of the coenzyme nicotinamide adenine dinucleotide (NAD).[2] It is sometimes referred to as nothing more than vitamin PP (Pellagra Preventive) [3,4], since its deficiency in human diet causes pellagra. It is an essential part of the coenzyme – nicotinamide adenine dinucleotide phosphate (NADP), its reduced form NADPH, NAD and its reduced form NADH. It also serves to maintain normal function of the digestive systems and cholesterol levels in human body [1].The combination of nicotinic acid and nicotinamide is clinically referred as niacin [3-5], since nicotinic acid is converted in the body into the amide very fast and for nutritional purposes both of them have equal biological activities. NA is an interesting molecule because of its two nitrogen atoms – one in the heterocyclic ring and the other as the amide group.

Folic acid (also known as folate, vitamin M, vitamin B9, vitamin B_c (or folacin), pteroyl-L-glutamic acid, pteroyl-L-glutamate, and pteroylmonoglutamic acid) is water-soluble vitamin. Folic acid (FA) is composed of three components: an aromatic pteridine ring system (Pteridine), a *p*-amino benzoic acid (PABA) portion and the amino acid glutamic acid (Glu).. It is an essential vitamin that is yellow-orange in color, is reported to be present in photosensitive organs, various mammalian metabolic pathways, and possibly involved in photosynthesis [6]. Folic acid is itself not biologically active, but its biological importance is due to tetrahydrofolate and other derivatives after its conversion to dihydrofolic acid in the liver [7]. Humans cannot synthesize folate *de novo*; therefore, folate has to be supplied through the diet to meet their daily requirements. The human body needs folate to synthesize DNA, repair DNA, and methylate DNA as well as to act as a cofactor in certain biological reactions [8]. It is especially important in aiding rapid cell division and growth, such as in infancy and pregnancy, and reproduction of cells, particularly red blood cells. Children and adults both require folic acid to produce healthy red blood cells and prevent anemia [9]. Folate is also necessary for the

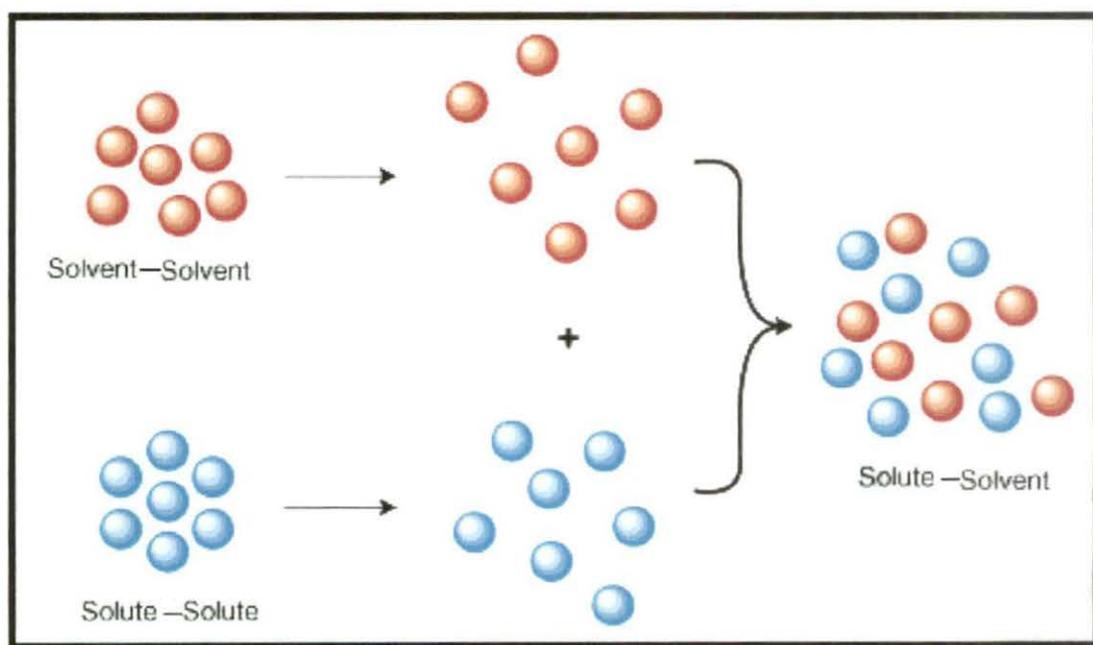
production and maintenance of new cells, for DNA synthesis and RNA synthesis, and for preventing changes to DNA, and, thus, for preventing cancer [10].

Bio-active solutes such as amino acids[11], carbohydrates also serve as adjusting factors in human body due to their physiological activity. Various methods have been developed to enhance the level of bioactive components in food materials, including thermal, alkali, acid and chemical treatments.

2.2 INTERACTIONS IN SOLUTION PHASE

There are three types of interactions in the solution process:

- a. **Solvent – solvent interactions:** energy required to break weak bonds between solvent molecules.
- b. **Solute – solute interactions:** energy required to break intermolecular bonds between the solute molecules.
- c. **Solute – solvent interactions:** ΔH is negative since bonds are formed between them.



For liquid systems, the macroscopic properties are usually quite well known, whereas the microscopic structure is often much less studied. The liquid phase is characterized by local order and long-range disorder, and to study processes in liquids, it is therefore valuable to use methods that probe the local surrounding of

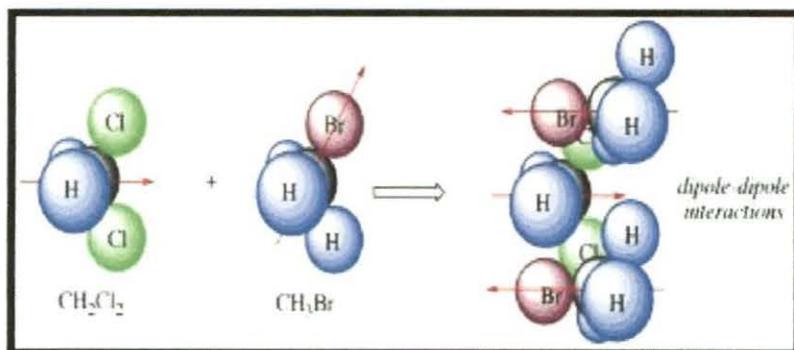
the constituent particles. The same is also true for solvation processes, a local probe is important to obtain insight into the occurring physical and chemical processes.

2.3 VARIOUS FORCES OF ATTRACTION

Intermolecular forces are forces of attraction or repulsion which act between surrounding particles (atoms, molecules or ions). In a molecule the forces binding atoms are due to chemical bonding. The energy required to break a 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 typical bond-energy, but intermolecular forces play important 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. This link gives an excellent introduction to the interactions between molecules.

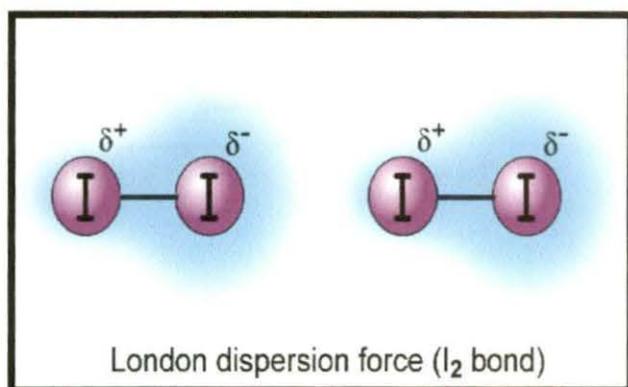
In general, intermolecular forces can be divided into several categories. The prominent types are:

Dipole-dipole forces: Substances, whose molecules have dipole moment have higher melting point or boiling point than those of similar molecular mass, having no dipole moment.

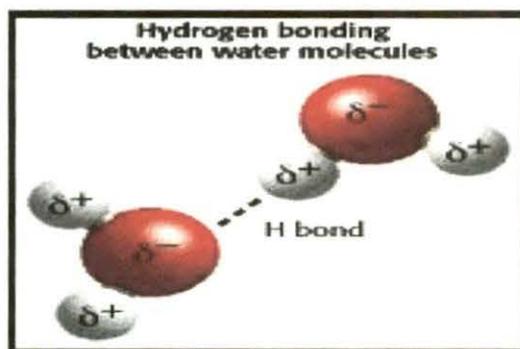


London dispersion forces or van der Waal's force: These forces always operate in any substance. The force arisen from induced dipole and the interaction is weaker than the dipole-dipole interaction. In general, the heavier the molecule, the stronger the van der Waal's force of interaction. For example, the boiling points of

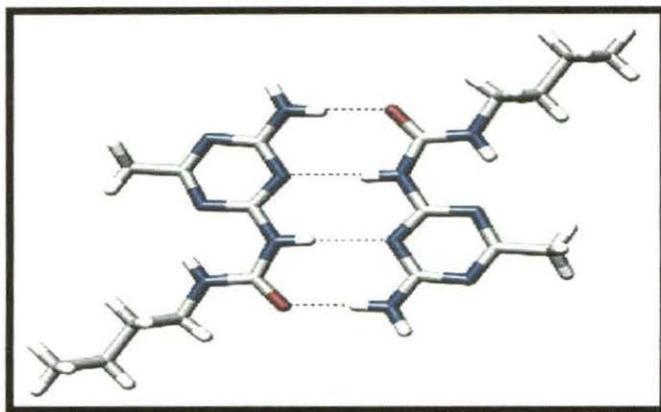
inert gases increase as their atomic masses increases due to stronger London dispersion interactions.



Hydrogen bond: Hydrogen bond is the attractive interactive force of a hydrogen atom with an electronegative atom, such as nitrogen, oxygen or fluorine. The hydrogen must be covalently bonded to another electronegative atom to create the bond. These bonds can occur between molecules (*intermolecularly*), or within different parts of a single molecule (*intramolecularly*). The hydrogen bond (5 to 30 kJ/mole) is stronger than a van der Waals interaction, but weaker than covalent or ionic bonds. This type of bond occurs in both inorganic molecules such as water and organic molecules such as DNA. 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 containing OH and NH_2 groups also form hydrogen bonds. Molecules of many organic compounds such as acids, alcohols, amines, and amino acids contain these groups, and thus hydrogen bonding plays an important role in biological science.



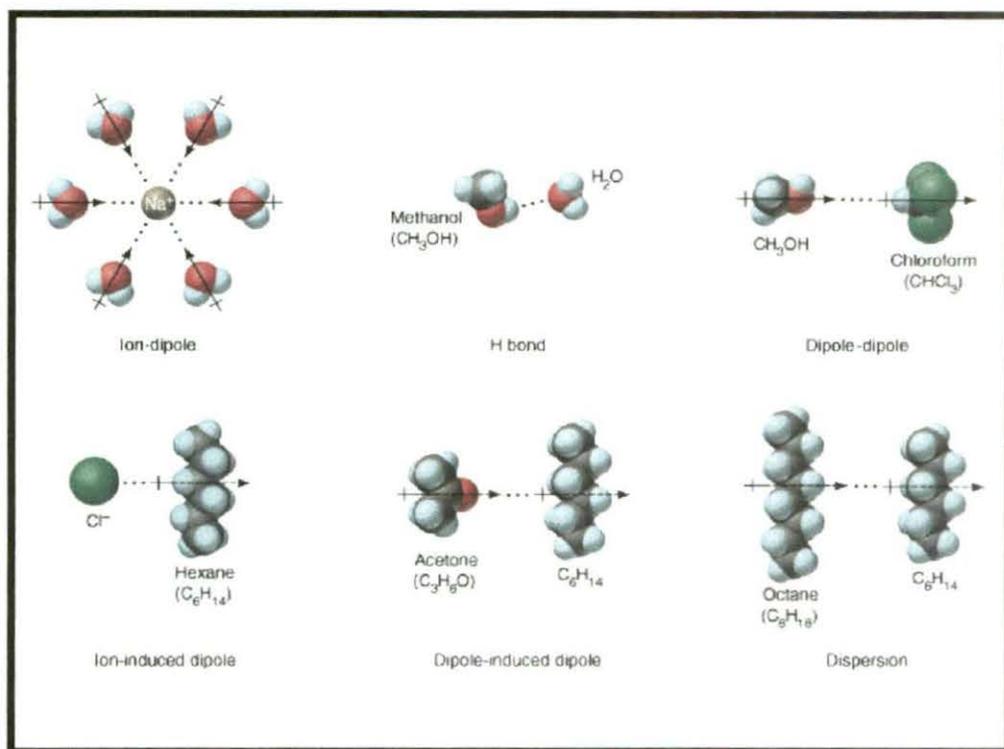
Intermolecular hydrogen bonding in a self-assembled dimer complex

Covalent bonding: Covalent is really intramolecular force rather than intermolecular force. It is mentioned here, because some solids are formed due to covalent bonding. For example, in diamond, silicon, quartz etc., the all atoms in the entire crystal are linked together by covalent bonding. These solids are hard, brittle, and have high melting points. Covalent bonding holds atoms tighter than ionic attraction.

Strong ionic attraction: It has relations to properties of solids. The more ionic compound has the higher lattice energy. The following result can be explained by way of ionic attraction: LiF, 1036; LiI, 737; KF, 821; MgF_2 , 2957 kJ/mol.

Metallic bonding: Forces between atom in metallic solids belong to another category. Valence electrons in metals are rampant. They are not restricted to certain atoms or bonds. Rather they run freely in the entire solid, providing good conductivity for heat and electric energy. These behaviours of electrons give special properties such as ductility and mechanical strength to metals.

All types can be present simultaneously for many substances. Usually, intermolecular forces are discussed together with "The States of Matter". Intermolecular forces also play important roles in solutions. A summary of the interactions is illustrated in the following diagram:



The majority of reactions occurring in solutions are of chemical or biological in nature. It was presumed earlier that the solvent only provides an inert medium for chemical reactions. The significance of solute-solvent interactions was realized after intensive studies in aqueous, non-aqueous and mixed solvents [12,13]. Intermolecular forces are also important in determining the solubility of a substance. “Like” intermolecular forces for solute and solvent will make the solute soluble in the solvent. In this regard ΔH_{soln} is sometimes negative and sometimes positive.

2.4 INVESTIGATION ON DIFFERENT KIND OF INTERACTIONS

One of the causes for the intricacies in solution chemistry is that the structure of the solvent molecule is not known with certainty. The introduction of a solute also modifies the solvent structure to an uncertain magnitude whereas the solute molecule is also modified and the interplay of forces like solute-solute, solute-solvent and solvent-solvent interactions become predominant though the **isolated** picture of any of the forces is still not known completely to the solution chemist.

The determination of thermodynamic, acoustic, transport and optical properties of different solutes in various solvents would thus provide an important

step in this direction. Naturally, in the development of theories, much attention has been devoted to solute-solvent interactions which are the controlling forces in infinitely dilute solutions where solute-solute interactions are absent.

The problems of solute-solvent interactions which are closely akin to solvation of solute can be studied from different angles using almost all the available physico-chemical techniques.

The solute-solvent interactions can also be studied from the thermodynamic point of view where the changes of free energy, enthalpy and entropy, etc. associated with a particular reaction can be qualitatively and quantitatively evaluated using various physico-chemical techniques from which conclusions regarding the factors associated with the solute-solvent interactions can be worked out.

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

We shall particularly reside upon the different aspects of these thermodynamic, transports, acoustic and optical properties as the present research work is familiarly related to the studies of solute-solute, solute-solvent and solvent-solvent interactions.

2.4.1 SOLUTE-SOLVENT INTERACTION

Solvation is a phenomenon of primary interest in many contexts of chemistry because solvated molecules/ions are omnipresent on Earth. Hydrated molecules/ions occur in aqueous solution in many chemical and biological systems [14]. Solvated molecules/ions appear in high concentrations in living organisms, where their presence or absence can fundamentally alter the functions of life. Solutes solvated in organic solvents or mixtures of water and organic solvents are also very common [15]. The exchange of solvent molecules around solutes in solutions is fundamental to the understanding of the reactivity of solutes in solution [16]. Solvated ions also play a key role in electrochemical applications, where for instance the conductivity of electrolytes depends on ion-solvent interactions [17].

The majority of reactions occurring in solutions are chemical or biological in nature. It was presumed earlier that the solvent only provides an inert medium for chemical reactions. The significance of ion-solvent interactions was realized after extensive studies in aqueous, non-aqueous and mixed solvents [18-27]. Most chemical processes of individual and biological importance occur in solution. The role of solvent is so great that million fold rate changes take place in some reactions simply by changing the reaction medium. Our bodies contain 65 to 70 % water, which acts as a lubricant, as an aid to digestion and more specifically as a stabilizing factor to the double helix conformations of DNA. With the exceptions of heterogeneous catalytic reactions most reactions in technical importance occur in solutions. In addition, molecules not only have to travel through a solvent to their reaction partner before reacting, but also need to present a sufficiently unsolvated rate for collision. The solvent governs the movement and energy of the reacting species to such an extent that a reaction suffers a several-million fold change in rate when the solvent is changed. As water is the most abundant solvent in nature and its major importance to chemistry, biology, agriculture, geology, etc., water has been extensively used in kinetic and equilibrium studies. But still our knowledge of molecular interactions in water is extremely limited.

Moreover, the uniqueness of water as a solvent has been questioned [28,29] 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 and a host of complicated phenomena. The organic solvents have been classified on the basis of dielectric constants, organic group types, acid base properties or association through hydrogen bonding [27] donor-acceptor properties [30,31] hard and soft acid-base principles [32] etc. As a result, the different solvents show a wide divergence of properties ultimately influencing their thermodynamic, transport and acoustic properties in presence of electrolytes and non electrolytes in these solvents. The determination of thermodynamic, transport and acoustic properties of different electrolytes or non electrolytes in various solvents would thus provide important information in this direction. Henceforth, in the development of theories of electrolytic solutions, much attention has been devoted to the controlling forces-'ion-solvent interactions' in infinitely dilute solutions wherein ion-ion interactions are almost absent. By separating these functions into

ionic contributions, it is possible to determine the contributions due to cations and anions in the solute-solvent interactions. Thus ion-solvent interactions play a key role to understand the physico-chemical properties of solutions. One of the causes for the intricacies in solution chemistry is the uncertainty about the structure of the solvent molecules in solution. The introduction of a solute modifies the solvent structure to an uncertain magnitude, the solvent molecule and the interplay of forces like solute-solute, solute-solvent also modify the solute molecule and solvent-solvent interactions become predominant, though the isolated picture of any of the forces is still not known completely to the solution chemist. Ion-solvent interactions can be studied by spectrometry [33,34]. The spectral solvent shifts or the chemical shifts are able determine the qualitative and quantitative nature of ion-solvent interactions. But even qualitative or quantitative apportioning of the solute-solvent interactions into the various possible factors is still an mounting task. It is thus apparent that the real understanding of the solute-solvent interaction is a tricky task. The aspect embraces a wide range of topics but we concentrated only on the measurement of transport properties like viscosity, conductance etc. and such thermodynamic properties as apparent and partial molar volumes and apparent molal adiabatic compressibility.

2.4.2 SOLVENT-SOLVENT INTERACTION

As the mixed and non-aqueous solvents are increasingly used in chromatography, solvent extraction, in the elucidation of reaction mechanism, in preparing high density batteries, etc. a number of molecular theories, based on either the radial distribution function or the choice of suitable physical model, have been developed for mixed solvents. Theories of perturbation type have been extended from their successful applicability in pure solvents to mixed solvents. L. Jones and Devonshire [35] 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 [36] extended the above approach to solvent mixtures. Random mixing of solvents was their main assumption provided the molecules have similar sizes. Prigogine and Bellemans [37] 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.* [38] 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 contribute a positive term to V^E . The chemical or specific intermolecular interactions result in a volume decrease and contribute negative values to V^E . The 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 deviation ($\Delta\eta$) may be positive and vice-versa. This assumption is not a concrete one, as evident from some studies [39,40]. It is observed in many systems that there is no simple correlation between the strength of interaction and the observed properties. Rastogi *et al.*[41] therefore suggested that the observed excess property is a combination of an interaction and non-interaction part. The non-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 [42], L. Huggins [43] 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.* [44-46] 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 [47]. A more successful approach is due to Flory who made the use of certain features of cell theory [48-50] 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 [51] 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 [52-54] and coworkers 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.* [40-42]. Subsequently the ERAS model has been successfully applied by many workers [55-57] 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[58]. 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 [58,59]. Gepert *et al.* [60] applied this model for studying some binary systems containing alcohols.

2.4.3 SOLUTE-SOLUTE INTERACTION

Solute-solute interaction in dilute solutions is now theoretically well understood, but solute-solvent interactions or solvation still remains a complex process. The degree of this interactions affects the properties of solution and depends on the nature of solute under investigation. While proton transfer reactions are particularly sensitive to the nature of the solvent, it has become cleared that the solvents significantly modify the majority of the solutes. Conversely, the nature of the strongly structured solvents, such as water, is substantially modified by the presence of solutes. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute, solute-solvent and solvent-solvent interactions are elucidated and thus the present dissertation is intimately related to the studies of solute-solute, solute-solvent and solvent-solvent interactions in some solvent media.

2.5. DENSITY

The physicochemical properties of liquid mixtures have attracted much attention from both theoretical and engineering applications points of view. Many engineering applications require quantitative data on the density of liquid mixtures. They also provide information about the nature and molecular interactions between liquid mixture components.

The volumetric information includes '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 fluids is the use of thermodynamic methods. Thermodynamic properties are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in the solution phase. Fundamental properties such as enthalpy, entropy and Gibbs energy represent the macroscopic state of the system as an average of numerous microscopic states at a given temperature and pressure. An interpretation of these macroscopic properties in terms of molecular phenomena is generally difficult. Sometimes higher derivatives of these properties can be interpreted more effectively in terms of molecular interactions. The volumetric information may be of immense importance in this regard. Various concepts regarding molecular processes in solutions like electrostriction [61], hydrophobic hydration [62], micellization [63] and co-sphere overlap during solute-solvent interactions [64] have been derived and interpreted from the partial molar volume data of many compounds.

2.5.1. APPARENT AND PARTIAL MOLAR VOLUMES

Density data can be used for the calculation of molar volume of a pure substance. However, the volume contributed to a solvent by the addition of one mole of solute is difficult to determine. This is so because, upon entry into the solvent, the solutes change the volume of the solution due to a break up of the solvent structure. 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 [65].

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

where M is the molar mass of the solute, c is the molarity of the solution; ρ_0 and ρ are the densities of the solvent and the solution respectively. The partial molar volumes, ϕ_{2v} can be obtained from the equation [66]:

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

The extrapolation of the apparent molar volume to infinite dilution and the expression of the concentration dependence of the apparent molar volume have been made by four major equations over a period of years – the Masson equation [67], the Redlich-Meyer equation [68], the Owen-Brinkley equation [69], and the Pitzer equation [31]. Masson found that the apparent molar volume of solute, ϕ_V , vary with the square root of the molar concentration by the linear equation:

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

where, ϕ_V^0 is the apparent molar volume (equal to the partial molar volume) at infinite dilution and S_V^* the experimental slope. The majority of ϕ_V data in water [70] and nearly all ϕ_V data in non-aqueous [71--75] solvents have been extrapolated to infinite dilution through the use of equation (3).

The temperature dependence of ϕ_V^0 or various investigated solutes in various solvents can be expressed by the general equation as follows:

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

where a_0 , a_1 , a_2 are the coefficients of a particular solute and T is the temperature in Kelvin.

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

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

The limiting apparent molar expansibilities (ϕ_E^0) change in magnitude with the change of temperature. During the past few years it has been emphasized by a

number of workers that S_v^* is not the sole criterion for determining the structure-making or breaking tendency of any solute. Helper [76] developed a technique of examining the sign of $(\delta\phi_E^0/\delta T)_p$ for the solute in terms of long-range structure-making and breaking capacity of the electrolytes in the mixed solvent systems. The general thermodynamic expression used is as follows:

$$(\delta\phi_E^0/\delta T)_p = (\delta^2\phi_v^0/\delta T^2)_p = 2a_2 \quad (6)$$

If the sign of $(\delta\phi_E^0/\delta T)_p$ is positive or small negative the electrolyte is a structure maker and when the sign of $(\delta\phi_E^0/\delta T)_p$ is negative, it is a structure breaker. Redlich and Meyer [68] 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 suggested the equation:

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

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

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

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

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

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

The Redlich-Meyer's extrapolation equation [68] adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies [60-71] 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 [69] 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 [69] which includes the ion-size parameter, a (cm), is given by:

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

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

Recently, the Pitzer formalism has been used by Pogue and Atkinson [77] 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 :

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

where the symbols have their usual significance.

2.5.2 LIMITING PARTIAL MOLAR VOLUMES

The individual partial molar volumes provide information relevant to the general question of the structure near the solute, i.e., its solvation. The calculation of the limiting partial molar volumes in organic solvents is, however, a difficult one. At present, however, most of the existing 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.* [78] has been used more frequently. These authors used the method to determine the limiting partial molar volumes of the anion for a series of homologous tetra alkyl ammonium chlorides, bromides and iodides in aqueous solution. They plotted the limiting partial molar volume ϕ_{V, R_4NX}^0 for a series of these salts with a halide ion in common as a function of the formula weight of the cation, $M_{R_4N^+}$ and obtained straight-lines for each series. Therefore, they suggested the following equation:

$$\phi_{V, R_4NX}^0 = b M_{R_4N^+} + \phi_{V, X^-}^0 \quad (13)$$

The extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions ϕ_{V, X^-}^0 . Uosaki *et al.* [79] used this method for the separation of some literature values and of their own ϕ_{V, R_4NX}^0 values into ionic contributions in organic electrolyte solutions. Krumgalz [80] applied the same method to a large number of partial molar volume data for non-aqueous electrolyte solutions in a wide temperature range.

2.5.3 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 [81,82]

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

where ρ_i and ρ are the density of the i^{th} component and density of the solution mixture respectively. V^E is the resultant of contributions from 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 [16]. These phenomena are the results of difference in energies of interaction between molecules being in solutions and packing effects. Disruption of the ordered structure of pure component during formation of the mixture leads to a positive effect observed on excess volume while an order formation in the mixture leads to negative contribution.

2.6. VISCOSITY

As fundamental and important 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 relationship between them could also be studied. 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 [83,84]. Viscosity is not a thermodynamic quantity, but viscosity of an

electrolytic solution along with the thermodynamic property, $\phi_{v,2}^0$, i.e., the partial molar volume, gives a lot of information and insight regarding ion-solvent interactions and the nature of structures in the electrolytic solutions.

2.6.1 VISCOSITY OF PURE LIQUIDS AND LIQUID MIXTURES

Since the molecular motion in liquids is controlled by the influence of the neighbouring molecules, the transport of momentum in liquids takes place, in sharp contrast with gases at ordinary pressures, not by the actual movement of molecules but by the intense influence of intermolecular force fields. It is this aspect of the mechanism of momentum transfer which forms the basis of the procedures for predicting the variations in the viscosity of liquids and liquid mixtures.

2.6.2 EARLY THEORETICAL CONSIDERATIONS ON LIQUID VISCOSITY

The theoretical development of liquid viscosity in early stages has been reviewed Andrade [85] and Frenkel [86]. 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 [85] developed equations which checked well against data on mono atomic metals at the melting point. Frenkel [86] 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 [87] assumed the momentum transfer to take place by the irregular Brownian movement of the holes [88] 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:

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

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 [85] and Ewell and Eyring [89] Auluck, De and Kothari [90]

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 [91].

2.6.3 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 [92,93] and further expanded by Pople [94]. Eisenschitz employing this model developed a theory of viscosity by considering the motion of the representative molecules to be Brownian and their distribution according to the Smoluchowski equation. Even with certain assumptions, the final expression showed shortcomings most of which were later overcome in a subsequent publication [95].

2.6.4 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 [96,97] Mayer and Montroll [98], Mayer [99], Born and Green [100] and the considerations on the basis of the general kinetic theory led Born and Green [100,101] to develop a viscosity equation which provided explanation for several empirical equations [84, 85, 87] proposed for liquid viscosity. In this connection the theoretical contributions of Kirkwood and coworkers [88, 102-108] Zwanzig *et al.*, [109] Rice and coworkers [110-113] Longuet- Higgins and Valleeu [114] and Davis and Coworkers [115, 116] are worth mentioning.

2.6.5 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 [117] 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 [118], Boon and Thomaes [119-120] Boon, Legros and Thomaes [121], and Hollman and Hijmans [122] are worth mentioning.

2.6.6 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 slip over the potential barrier to the next equilibrium position in the same plane. Eyring [123] showed that the viscosity of the liquid is given by:

$$\eta = \frac{\lambda_1 h F_n}{\kappa \lambda^2 \lambda_2 \lambda_3 F_a^*} \exp \frac{\Delta E_{act}}{kT} \quad (16)$$

where λ is the average distance between the equilibrium positions in the direction of motion, λ_1 is the perpendicular distance between two neighbouring layers of molecules in relative motion, λ_2 is the distance between neighbouring molecules in the same direction and λ_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 recross 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^{84, 120} finally gets

$$\eta = \frac{N_A h (2\pi m k T)^{\frac{1}{2}}}{V h} \frac{b R T V^{\frac{1}{3}}}{N_A^{\frac{1}{3}} \Delta E_{vap}} \exp \frac{\Delta E_{vap}}{n R T} \quad (17)$$

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 [124] have summarized all the working relations.

2.6.7 THE SIGNIFICANT STRUCTURE THEORY AND LIQUID VISCOSITY

Eyring and coworkers [125-128] improved the "holes in solid" model theory [124-129] 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 [130, 131].

$$\eta = \frac{V_s}{V} \eta_s + \frac{V - V_s}{V} \eta_g \quad (18)$$

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. Eyring and Ree [132] have discussed in detail the evaluation of η_s from the reaction rate theory of Eyring [123] assuming that a solid molecule can jump into all neighbouring empty sites. The expression for η_s takes the following form [133]

$$\eta = \frac{N_A h V}{Z \kappa} \frac{6}{V_s} \frac{1}{2^{\frac{1}{2}}} \frac{1}{V - V_s} \frac{1}{1 - e^{-\frac{\theta}{T}}} \exp \frac{a E_s V_s}{(V - V_s) RT} \quad (19)$$

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 [133] by the relation:

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

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

2.6.8 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 [134] 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 [135] suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations (c):

$$\frac{\eta}{\eta_0} = \eta_r = 1 + A\sqrt{c} + Bc \quad (21)$$

The above equation can be rearranged as:

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

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 coulombic forces between the ions. The significance of the term had since then been realized due to the development Debye-Hückel theory [136] of inter-ionic attractions in 1923. The A -coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory [137-139] and is given by the Falkenhagen Vernon [139] equation:

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

where the symbols have their usual significance. In very accurate work on aqueous solutions [140], 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 [141]. A-coefficient suggesting that should be calculated from conductivity measurements. Crudden *et al.* [142] suggested that if association of the ions occurs to form an ion pair, the viscosity should be analysed by the equation:

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

where A , B_i and B_p are characteristic constants and α is the degree of dissociation of ion pair. Thus, a plot of $(\eta_r - 1 - A\sqrt{\alpha c}/\alpha c)$ against $(1-\alpha)/\alpha$, when extrapolated to $(1-\alpha)/\alpha = 0$ gave the intercept B_i . However, for the most of the electrolytic solutions both aqueous and nonaqueous, the equation (22) is valid up to 0.1 (M) [143, 144] within experimental errors. At higher concentrations the extended Jones-Dole equation (25), involving an additional coefficient D , originally used by Kaminsky, [145] has been used by several workers [147, 148] and is given below:

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

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

The plots of $(\eta/\eta_o - 1)/\sqrt{c}$ against \sqrt{c} for the electrolytes should give the value of A - coefficient. But sometimes, the values come out to be negative or considerably scatter and also deviation from linearity occur [148,149]. 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 [135]. 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 [150, 151]:

- (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.

2.6.9 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:

$$\eta = A \exp^{\frac{b}{T}} \quad (26)$$

The several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration range [152-157] and the equation suggested by Angell [158-159] 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:

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

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.* [160-162] introducing the limiting condition, that is $N \rightarrow 0$, $\eta \rightarrow \eta_o$; which is the viscosity of the pure solvent.

Thus, we have:

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

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.* 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:

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

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:

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

It closely resembles the Vand's equation [152] for fluidity (reciprocal for viscosity):

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

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.

2.6.10 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 [163-193]. 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 [194] 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 mobilities. The method of Gurney [195] and also of Kaminsky [150] is based on:

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

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. Nightingale [196], however preferred RbCl or CsCl to KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron is based on the assumption that the Et_4N^+ ion in water is probably closest to be neither structure breaker nor a structure maker. Thus, they suggest that it is possible to apply with a high degree of accuracy of the Einstein's equation [197],

$$B = 0.0025\overline{V}_o \quad (33)$$

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

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

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

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

$$B_{BPh_4PPh_4} = B_{NaBPh_4} + B_{PPh_4Br} - B_{NaBr} \quad (35)$$

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

(a) Criss and Mastroianni assumed $B_{K^+} = B_{Cl^-}$ in ethanol based on equal mobilities of ions [198]. They also adopted $B_{Me_4N^+}^{25} = 0.25$ as the initial value for acetonitrile solutions.

(b) For acetonitrile solutions, Tuan and Fuoss [199] proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer *et al.* [197], $\lambda_{25}^{\circ}(Bu_4N^+) = 61.4$ and $\lambda_{25}^{\circ}(Ph_4B^-) = 58.3$ in acetonitrile.

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

(c) Gopal and Rastogi [164] resolved the B -coefficient in N-methyl propionamide solutions assuming that $B_{Et_4N^+} = B_{I^-}$ at all temperatures.

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

$$B_{[(i-pe)_3Bu_4N^+]} = B_{Ph_4B^-} = \frac{1}{2} B_{[(i-pe)_3BuNPh_4B]} \quad (37)$$

at all temperatures.

Wide use of this method has been made by other authors for dimethyl sulphoxide, sulpholane, hexamethyl phosphotriamide and ethylene carbonate [200] solutions. The methods, however, have been strongly criticized by Krumgalz [201]. According to him, any method of resolution based on the equality of equivalent conductances for certain ions suffers from the drawback that it is impossible to select any two ions for which $\lambda_o^+ = \lambda_o^-$ in all solvents at all temperatures. Thus, though $\lambda_K^+ = \lambda_{Cl^-}$ at 298.15 K in methanol, but is not so in ethanol or in any other solvents. In addition, if the mobilities of some ions are even equal at infinite dilution, but it is not necessarily true at moderate concentrations for which the B -coefficient values are calculated. Further, according to him, equality of dimensions of $(i-pe)_3BuN^+$ or $(i-Am)_3BuN^+$ and Ph_4B^- does not necessarily imply the equality of B -coefficients of these ions and they are likely to be solvent and ion-structure dependent. Krumgalz [202, 203] 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 [203, 204] in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic B -

values for large tetraalkylammonium ions, R_4N^+ (where $R > Bu$) in organic 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^3 to R_4N to zero cation dimension gives directly B_{X^-} in the proper solvent and thus B -ion values can be calculated.

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

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \quad (39)$$

$$\frac{B_{R_4N^+}}{B_{R'_4N^+}} = \frac{r^3_{R_4N^+}}{r^3_{R'_4N^+}} \quad (40)$$

The radii of the tetraalkylammonium ions have been calculated from the conductometric data [205]. Gill and Sharma [184] used Bu_4NBPh_4 as a reference electrolyte. The method of resolution is based on the assumption, like Krumgalz, that Bu_4N^+ and Ph_4B^- ions with large R -groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constant. The ionic radii of Bu_4N^+ (5.00 Å) and Ph_4B^- (5.35 Å) were, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers. They proposed the equations:

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

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

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:

$$B_{[(i-Am)_3Bu_4N^+]} = B_{Ph_4B^-} = \frac{1}{2} B_{[Bu_4NPh_4B]} \quad (43)$$

Recently, Lawrence and Sacco [187] used tetrabutylammonium tetrabutylborate

(Bu₄NBBu₄) as reference electrolyte because the cation and anion in each case are symmetrical in shape and have almost equal Van der Waal's volume. Thus, we have:

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

$$B_{Bu_4N^+} = \frac{B_{Bu_4NBPh_4}}{\left[1 + \frac{V_{W(Bu_4B^-)}}{V_{W(Bu_4N^+)}} \right]} \quad (45)$$

A similar division can be made for Ph₄PBPh₄ system.

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

The B -coefficients $B_{R_4NBr} = B_{Br^-} + a[f_x R_4N^+]$ 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 Bu₄NBBu₄ and Ph₄PBPh₄ as reference salts. They concluded that the 'reference salt' method is the best available method for division into ionic contributions.

Jenkins and Pritchett [206] suggested a least square analytical technique to examine additivity relationship for combined ion thermodynamics data, to effect apportioning into single-ion components for alkali metal halide salts by employing Fajan's competition principle [207] and 'volcano plots' of Morris [208]. The principle was extended to derive absolute single ion B coefficients for alkali metals and halides in water. They also observed that $B_{Cs^+} = B_{I^-}$ suggested by Krumgalz [203] to be more reliable 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.

2.6.11 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:

$$(i) A \text{ and } dA/dT > 0 \quad (46)$$

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

characteristic of the structure breaking ions.

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

characteristic of the structure making 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 [209], A, B, C Zones of Frank and Wen [210] and hydrated radius of Nightingale [196].

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 neighborhood. 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 coulombic 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 [201] we can write:

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

whereas according to Lawrence and Sacco:

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

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 centrosymmetrically 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 tetraalkylammonium ions due to hydrophobic hydration. The phenomenon is inherent in the intrinsic water structure and absent in organic solvents. B_W and B_{Solv} account for viscosity increases and attributed to the 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 be further reinforced in water arising from B_{Ion}^{Reinf} due to hydrophobic hydrations.

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

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

In case of structure-making ions, the ions are firmly surrounded by a primary solvation sheath and the secondary solvation zone will be considerably ordered leading to an increase in B_{Ion} 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 solvation 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 [195] clearly demonstrates a close relation between ionic B -coefficients and ionic mobilities. Gurney also demonstrated a clear correlation between the molar entropy of solution values with B -coefficient of salts. The ionic B -values show a linear relationship with the partial molar ionic entropies or partial molar entropies of hydration (\bar{S}_h^o) as:

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

Where, $\bar{S}_{aq}^o = \bar{S}_{ref}^o + \Delta S^o$, \bar{S}_g^o is the calculated sum of the translational and rotational entropies of the gaseous ions. Gurney obtained a single linear plot between ionic entropies and ionic B -coefficients for all mono atomic ions by equating the entropy of the hydrogen ion ($S_{H^+}^o$) to $-5.5 \text{ cal. mol}^{-1} \text{ deg}^{-1}$. Asmus [211] used the entropy of hydration to correlate ionic B values and Nightingale [196] 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.* [212] to assign single ion B -coefficients so that a plot of ΔS_e° [213, 214] the electrostatic entropy of solvation or $\Delta S_{I,II}^\circ$ the entropic contributions of the first and second solvation 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 ΔS_e° and ΔS_I° and the single ion B -coefficients. Both entropy criteria (ΔS_e° and $\Delta S_{I,II}^\circ$) 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.

2.6.12 THERMODYNAMICS OF VISCOUS FLOW

Assuming viscous flow as a rate process, the viscosity (η) can be represented from Eyring's [215] approaches as:

$$\eta = A e^{\frac{E_{vis}}{RT}} = \left(\frac{hN_A}{V} \right) e^{\frac{\Delta G^\ddagger}{RT}} = \left(\frac{hN_A}{V} \right) e^{\left(\frac{\Delta H^\ddagger}{RT} - \frac{\Delta S^\ddagger}{R} \right)} \quad (54)$$

where E_{vis} = the experimental entropy of activation determined from a plot of $\ln \eta$ against $1/T$. ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger are the free energy, enthalpy and entropy of activation, respectively

Nightingale and Benck [216] 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:

$$R \left[\frac{d \ln \eta}{d \left(\frac{1}{T} \right)} \right] = r \left[\frac{d \ln \eta_o}{d \left(\frac{1}{T} \right)} \right] + \frac{R}{1+Bc} \frac{d(1+Bc)}{d \left(\frac{1}{T} \right)} \quad (55)$$

$$\Delta E_{\eta(\text{Soln})}^\ddagger = \Delta E_{\eta(\text{Solv})}^\ddagger + \Delta E_V^\ddagger \quad (56)$$

ΔE_V^\ddagger 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.* [217] have suggested an alternative formulation based on the transition state

treatment of the relative viscosity of electrolytic solution. They suggested the following expression:

$$B = \frac{(\phi_{v,2}^0 - \phi_{v,1}^0)}{1000} + \phi_{v,2}^0 \frac{(\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#})}{1000RT} \quad (57)$$

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

$$\Delta\mu_1^{0\#} = \Delta G_1^{0\#} = RT \ln(\eta_0 \phi_{v,1}^0 / hN_A) \quad (58)$$

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:

$$\frac{d(\Delta\mu_2^{0\#})}{dT} = -\Delta S_2^{0\#} \quad (59)$$

$$\Delta H_2^{0\#} = \Delta\mu_2^{0\#} + T \Delta S_2^{0\#} \quad (60)$$

2.6.13 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 [197] leads to the equation:

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi \quad (61)$$

where ϕ is the volume fraction occupied by the particles. Modifications of the equation have been proposed by (i) Sinha [218] on the basis of departures from spherical shape and (ii) Vand on the basis of dependence of the flow patterns around the neighboring 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):

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

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

$$2.5\phi_{v,i}^0 = B \quad (63)$$

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

$$B_{\pm} = 2.5\phi_{\pm}^0 = \frac{2.5 \times 4 (\pi R_{\pm}^3 N)}{3 \times 1000} \quad (64)$$

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:

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

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.

2.6.14 VISCOSITY OF NON-ELECTROLYTIC SOLUTIONS

The equations of Vand [219], Thomas [220] 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 nonelectrolytes [221-223]. These equations are:

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

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

$$\text{Moulik equation:} \quad \eta^2 = I + Mc^2 \quad (68)$$

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; l 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. 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:

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

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

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

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

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

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

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 [224-230].

$$\begin{aligned}\eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] \\ & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_3 - x_1) + C_{31}(x_3 - x_1)^2]\end{aligned}\quad (76a)$$

The correlation of ternary is modified to the following form:

$$\begin{aligned}\eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] \\ & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_3 - x_1) + C_{31}(x_3 - x_1)^2] \\ & + A_{123}(x_1 x_2 x_3)\end{aligned}\quad (76b)$$

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

$$\begin{aligned}\eta_m = & \sum_i^3 x_i \eta_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] \\ & + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] \\ & + x_3 x_1 [A_{31} + B_{31}(x_3 - x_1) + C_{31}(x_3 - x_1)^2] \\ & + x_1 x_2 x_3 [A_{123} + B_{123} x_1^2 (x_2 - x_3)^2 + C_{123} x_1^3 (x_2 - x_3)^3]\end{aligned}\quad (76c)$$

where A_{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.

2.6.15 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 [231], the deviations in viscosities ($\Delta\eta$) from the ideal mixture values can be calculated as:

$$\Delta\eta = \eta - \sum_{i=1}^3 (x_i \eta_i) \quad (77)$$

where η is the dynamic viscosities of the mixture and $x_i\eta_i$ are the mole fraction and viscosity of i^{th} component in the mixture, respectively.

2.6.16 GIBBS EXCESS ENERGY OF ACTIVATION FOR VISCOUS FLOW

Quantitatively, the Gibbs excess energy of activation for viscous flow, ΔG^E can be calculated as [232]:

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

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 i^{th} pure component, respectively.

2.6.17 VISCOUS SYNERGY AND ANTAGONISM

Rheology is the branch of science that studies [233] material deformation and flow, and is increasingly applied to analyze the viscous behavior of many pharmaceutical products, [234-243] and to establish their stability and even bioavailability, since it has been firmly established that viscosity influences the drug absorption rate in the body [244, 245]. The study of the viscous behavior 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 [246, 247].

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 [248] 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, η_{exp} , with the viscosity expected in the absence of interaction, η_{cal} , as defined by the simple mixing rule as:

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

where w_i and η_i are the fraction by weight and the viscosity of the i^{th} 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 [249].

In order to secure more comparable viscous synergy results, the so-called synergic interaction index (I_s) as introduced by Howell [250] is taken into account:

$$I_s = \frac{\eta_{exp} - \eta_{mix}}{\eta_{mix}} = \frac{\Delta\eta}{\eta_{mix}} \quad (80)$$

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, ρ_{exp} , and a calculation is made for ρ_{cal} based on the expression:

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

where ρ_i is the experimentally measured density of the i^{th} 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.

2.7 ULTRASONIC SPEED

In recent years, there has been considerably progress in the determination of thermodynamic, acoustic and transport properties of working liquids from ultrasonic speeds, density and viscosity measurement. The study of ultrasonic

speeds and isentropic compressibilities of liquids, solutions and liquid mixtures provide useful information about molecular interactions, association and dissociation. Various parameters like molar isentropic and isothermal compressibilities, apparent molal compressibility, isentropic compressibility, deviation in isentropic compressibility from ideality, etc. can very well be evaluated and studied from the measurement of ultrasonic speeds and densities in solutions. Isentropic compressibilities play a vital role in characterization of binary and ternary liquid mixtures particularly in cases where partial molar volume data alone fail to provide an unequivocal interpretation of the interactions.

2.7.1 APPARENT MOLAL ISENTROPIC COMPRESSIBILITY

Although for a long time attention has been paid to the apparent molal isentropic compressibility for electrolytes and other compounds in aqueous solutions,[251-255] measurements in non-aqueous solvents are still scarce. It has been emphasized by many authors that the apparent molal isentropic compressibility data can be used as a useful parameter in elucidating the solute-solvent and solute-solute interactions. The most convenient way to measure the compressibility of a solvent/solution is from the speed of sound in it.

The isentropic compressibility (β) of a solvent/solution can be calculated from the Laplace's equation [256]:

$$\beta = \frac{1}{u^2 \rho} \quad (82)$$

where ρ is the solution density and u is the ultrasonic speed in the solvent/solution. The isentropic compressibility (β) determined by equation (82) is adiabatic, not an isothermal one, because the local compressions occurring when the ultrasound passes through the solvent/solution are too rapid to allow an escape of the heat produced.

The apparent molal isentropic compressibility (ϕ_k) of the solutions was calculated using the relation:

$$\phi_k = M\beta / \rho + 1000(\beta\rho_0 - \beta_0\rho) / m\rho\rho_0 \quad (83)$$

β_0 is the isentropic compressibility of the solvent mixture, M is the molar mass of the solute and m is the molality of the solution.

The limiting apparent isentropic compressibility ϕ_K^0 may be obtained by extrapolating the plots of ϕ_K versus the square root of the molal concentration of the solutes by the computerized least-square method according to the equation.

$$\phi_K = \phi_K^0 + S_K^* \sqrt{m} \quad (84)$$

The limiting apparent molal isentropic compressibility (ϕ_K^0) and the experimental slope S_K^* can be interpreted in terms of solute-solvent and solute-solute interactions respectively. It is well established that the solutes causing electrostriction leads to the decrease in the compressibility of the solution [257, 258]. This is reflected by the negative values of ϕ_K^0 of electrolytic solutions. Hydrophobic solutes often show negative compressibilities due to the ordering induced by them in the water structure. The compressibility of hydrogen-bonded structure, however, varies depending on the nature of the hydrogen bonding involved. However, the poor fit of the solute molecules [259, 260] as well as the possibility of flexible hydrogen bond formation appear to be responsible for causing a more compressible environment and hence positive ϕ_K^0 values have been reported in aqueous non-electrolyte [261] and non-aqueous non-electrolyte [262] solutions.

2.7.2 DEVIATION IN ISENTROPIC COMPRESSIBILITY

The deviation in isentropic compressibility (ΔK_S) can be calculated using the following equation [263-265]:

$$\Delta K_S = K_S - \sum_{i=1}^J x_i K_{S,i} \quad (85)$$

where $x_i, K_{S,i}$ are the mole fraction and isentropic compressibility of i^{th} component in the mixture, respectively. The observed values of ΔK_S can be qualitatively explained by considering the factors, namely (i) the mutual disruption of associated species present in the pure liquids, (ii) the formation of weak bonds by dipole-induced dipole interaction between unlike molecules, and (iii) geometrical fitting of component molecules into each other structure. The first factor contributes to positive ΔK_S values, whereas the remaining two factors lead to negative ΔK_S values

[266]. The resultant values of ΔK_s for the mixtures are due to the net effect of the combination of (i) to (iii) [267].

Moreover, the excess or deviation properties ($V_m^E, \Delta\eta, \Delta G^E$ and ΔK_s) have been fitted to Redlich-Kister [268] polynomial equation using the method of least squares involving the Marquardt algorithm [269] and the binary coefficients, α_i were determined as follows :

$$Y_{i,j}^E = x_1 x_2 \sum_{i=1}^j \alpha_i (x_1 - x_2)^i \quad (86)$$

where $Y_{i,j}^E$ refers to an excess or deviation property and x_1 and x_2 are the mole fraction of the solvent 1 and solvent 2, respectively. In each case, the optimal number of coefficients was ascertained from an approximation of the variation in the standard deviation (σ). The standard deviation (σ) was calculated using,

$$\sigma = \left[\frac{(Y_{\text{exp}}^E - Y_{\text{cal}}^E)^2}{n - m} \right]^{\frac{1}{2}} \quad (87)$$

where n is the number of data points and m is the number of coefficients.

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.

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 [270] 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:

$$\Lambda = \Lambda_0 - S\sqrt{c} \quad (88)$$

where, $S = \alpha\Lambda_0 + \beta \quad (89)$

$$\alpha = \frac{(z^2)k}{3(2+\sqrt{2})\epsilon_r kT\sqrt{c}} = \frac{82.406 \times 10^4 z^3}{(\epsilon_r T)^{\frac{3}{2}}} \quad (90a)$$

$$\beta = \frac{z^2 e F k}{3\pi\eta\sqrt{c}} = \frac{82.487 z^3}{\eta\sqrt{\epsilon_r T}} \quad (90b)$$

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 [271]. In the subsequent years, Pitts (1953) [272] and Fuoss and Onsager (1957) [273] independently worked out the solution of the problem of electrolytic conductance accounting for both long-range and short-range interactions. However, the Λ_0 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 [274,275]. The original Fuoss-Onsager equation was further modified by Fuoss and Hsia [276] 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:

$$\Lambda = \frac{\Lambda_0 - \alpha\Lambda_0\sqrt{c}}{(1+\kappa\alpha)} \left(\frac{1+\kappa\alpha}{\sqrt{2}} \right) - \frac{\beta\sqrt{c}}{(1+\kappa\alpha)} + G(\kappa\alpha) \quad (91)$$

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

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \ln c + J_1 c + J_2 \sqrt[3]{c} \quad (92)$$

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 [277,278]. Further correction of the equation (92) was made by Fuoss and Accascini. They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec \ln c + J_1 c + J_2 \sqrt[3]{c} - F\Lambda c \quad (93)$$

where, $Fc = \frac{4\pi R^3 N_A}{3} \quad (94)$

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 [279].

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 [280].

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



$$K_A = \frac{(1-\alpha)}{\alpha^2 c \gamma_{\pm}^2} \quad (96)$$

$$\alpha = 1 - \alpha^2 K_A c \gamma_{\pm}^2 \quad (97)$$

where γ_{\pm} is the mean activity coefficient of the free ions at concentration αc

For strongly associated electrolytes, the constant, K_A and Λ_o has been determined using Fuoss-Kraus equation [281] or Shedlovsky's equation [282].

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda_o} + \frac{K_A}{\Lambda_o^2} \cdot \frac{c \gamma_{\pm}^2 \Lambda}{T(z)} \quad (98)$$

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

$$F(z) = 1 - z(1 - z(1 - \dots)^{\frac{1}{2}})^{\frac{1}{2}} \quad (99a)$$

and

$$\frac{1}{T(z)} = S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \dots \quad (99b)$$

A plot of $T(z)/\Lambda$ against $cy_{\pm}^2\Lambda/T(z)$ should be a straight line having $1/\Lambda_0$ for its intercept and K_A/Λ_0^2 for its slope. Where K_A is large, there will be considerable uncertainty in the determined values of Λ_0 and K_A from equation (98).

The Fuoss-Hsia [276] conductance equation for associated electrolytes is given by:

$$\Lambda = \Lambda_0 - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A\Lambda\gamma_{\pm}^2(\alpha c) \quad (100)$$

The equation was modified by Justice [283]. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

$$\Lambda = \alpha(\Lambda_0 - S\sqrt{\alpha c} + E(\alpha c)\ln(\alpha c) + J_1R(\alpha c) - J_2R(\alpha c)^{3/2}) \quad (101)$$

$$\frac{(1-\alpha)}{\alpha^2 cy_{\pm}^2} = K_A \quad (102)$$

$$\ln \gamma_{\pm} = \frac{-k\sqrt{q}}{(1+kR\sqrt{\alpha c})} \quad (103)$$

The conductance parameters are obtained from a least square treatment after setting, $R = q = \frac{e^2}{2\epsilon kT}$ (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 (101) is a series expansion truncated at the $c^{3/2}$ term, it would be preferable that the resulting errors be absorbed as much as possible by J_2 rather than by K_A , whose theoretical interest is greater as it contains the information concerning short-range cation-anion interaction. 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 [284]:

$$K_A = \frac{4\pi N_A \alpha^3}{3000} \exp\left(\frac{e^2}{\alpha \epsilon kT}\right) \quad (104)$$

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 [285].

$$K_A = \frac{4\pi N_A \alpha}{1000} \int_{r=a}^{r=\infty} r^2 \exp\left(\frac{z^2 e^2}{r \epsilon k T}\right) dr \quad (105)$$

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 [286].

2.8.2 ION SIZE PARAMETER AND IONIC ASSOCIATION

For plotting, equation (93) can be rearranged to the 'A' function as:

$$\Lambda_1 = \Lambda + S\sqrt{c} - Ec \ln c = \Lambda_0 + J_1 c + J_2 \sqrt[3]{c} = \Lambda_0 + J_1 c \quad (106)$$

with J_2 term omitted.

Thus, a plot of Λ_0 vs. c gives a straight line with Λ_0 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' [287] 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 [288]. Fuoss [289] in 1975 proposed a new conductance equation. Later 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:



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. 107 are:

$$K_R = \frac{(1-\alpha)(1-\gamma)}{c\gamma^2 f^2} \quad (108)$$

$$K_S = \frac{\alpha}{1-\alpha} = \exp\left(\frac{-E_S}{kT}\right) = e^{-\epsilon} \quad (109)$$

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 is 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 ($r = a$); ϵ is E_S measured in units of kT .

Now,
$$(1-\alpha) = \frac{1}{1+K_S} \quad (110)$$

and the conductometric pairing constant is given by:

$$K_A = \frac{(1-\alpha)}{c\gamma^2 f^2} = \frac{K_R}{1-\alpha} = K_R(1+K_S) \quad (111)$$

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 $(\Delta X \Delta A_e)$). The various patterns can be reproduced by theoretical fractions in the form:

$$\Lambda = p \left[\Lambda_0 \left(\frac{1 + \Delta X}{X} \right) + \Delta \Lambda_e \right] = p \left[\Lambda_0 (1 + R_x) + E_L \right] \quad (112)$$

which is a three parameter equation $\Lambda = \Lambda(c, \Lambda_0, R, E_S), \Delta X / X$ (the relaxation field) and $\Delta \Lambda_e$ (the electrophoretic counter current) are long range effects due to electrostatic interionic forces and p is the fraction of Gurney co-sphere.

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

$$p = 1 - \alpha(1 - \gamma) \quad (113)$$

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

$$\Lambda = \gamma \left[\Lambda_0 \left(\frac{1 + \Delta X}{X} \right) \right] + \Delta \Lambda_e \quad (114)$$

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

$$K_A = \frac{(1 - \gamma)}{c\gamma^2 f^2} \approx K_R K_S \quad (115)$$

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

$$\gamma = 1 - \frac{K_R c \gamma^2 f^2}{(1 - \alpha)} \quad (116)$$

$$K_R = \left(\frac{4\pi N_A R^3}{3000} \right) \exp\left(\frac{\beta}{R}\right) \quad (117)$$

$$-\ln f = \frac{\beta \kappa}{2(1 + \kappa R)}, \quad \beta = \frac{e^2}{\epsilon \kappa T} \quad (118)$$

$$\kappa^2 = 8\pi\beta\gamma\eta = \frac{\pi\beta N_A \gamma c}{125} \quad (119)$$

$$-\epsilon = \ln \left[\frac{\alpha}{1 - \alpha} \right] \quad (120)$$

The details of the calculations are presented in the 1978 paper [287]. 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 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 surrounding 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:

$$\Lambda_0 = \lambda_o^+ + \lambda_o^- \quad (121a)$$

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.,

$$\lambda_o^+ = t_+ \Lambda_0 \quad \text{and} \quad \lambda_o^- = t_- \Lambda_0 \quad (121b)$$

Thus, from accurate value of λ_o 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 Krungalz [290] and some important points are mentioned as follows:

(i) Walden equation [291]

$$(\lambda_o^\pm)_{\text{water}}^{25} \cdot \eta_{o,\text{water}} = (\lambda_o^\pm)_{\text{acetone}}^{25} \cdot \eta_{o,\text{acetone}} \quad (122)$$

$$(ii) \quad (\lambda_{o,\text{pic}} \cdot \eta_o) = 0.267, \quad \lambda_{o,\text{Et}_4\text{N}^+} \cdot \eta_o = 0.269 \quad [301,302] \quad (123)$$

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

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.

$$(iii) \quad \lambda_o^{25}(\text{Bu}_4\text{N}^+) = \lambda_o^{25}(\text{Ph}_4\text{B}^-) \quad (124)$$

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

$$(iv) \quad \lambda_o^{25}(\text{Bu}_4\text{N}^+) = \lambda_o^{25}(\text{Bu}_4\text{B}^-) \quad [303] \quad (125)$$

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 [304] is:

$$\lambda_o^{25}(R_4N^+) = \frac{ZF^2}{6\pi N_A \eta_o [r_i - (0.0103\varepsilon_o + r_y)]} \quad (126)$$

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.

However, large discrepancies were observed between the experimental and calculated values [290(a)]. In a paper, [290(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.

$$(vi) \quad \lambda_o^{25}[(i-Am)_3 BuN^+] = \lambda_o^{25}(\text{Ph}_4\text{B}^-)^{[305]} \quad (127)$$

It has been found from transference number measurements that the $\lambda_o^{25}[(i-Am)_3 BuN^+]$ and $\lambda_o^{25}(\text{Ph}_4\text{B}^-)$ values differ from one another by 1%.

$$(vii) \quad \lambda_o^{25}(\text{Ph}_4\text{B}^-) = 1.01\lambda_o^{25}[(i-Am)_4 B^-]^{306} \quad (128)$$

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_0 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:

$$r_s = \frac{|z|F^2}{A\pi\eta_0\lambda_0^\pm} \quad (129)$$

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:

$$\lambda_0^\pm\eta_0 = \text{constant} \quad (130)$$

This relation has been verified using λ_0^\pm values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i\text{-Am}_4\text{B}^-$, Ph_4As^+ , Ph_4B^- ions and for tetraalkylammonium cation starting with Et_4N^+ . The relationship can be well utilized to determine λ_0^\pm of ions in other organic solvents from the determined Λ_0 values

2.8.4 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.

$$V_s = \left(\frac{4\pi}{3}\right)(r_s^3 - r_c^3) \quad (131)$$

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

$$n_s = \frac{V_s}{V_o} \quad (132)$$

Assuming Stokes' relation to hold well, the ionic solvated volume can be obtained, because of the packing effects [292], from

$$V_s^o = 4.35r_s^3 \quad (133)$$

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 [293-296] have been suggested in order to apply it to most of the ions.

2.8.5 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

$$\lambda_i^o = \frac{|z_i e| e F}{6\pi\eta_o R_i} = \frac{0.819|z_i|}{\eta_o R_i} \quad (134)$$

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:

$$\lambda_i^o \eta_o = \frac{0.819z_i}{R_i} = \text{constant} \quad (135)$$

This is known as the Walden rule [297]. 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 [298], Nightingale [196] and others [299-301] 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 [302] was invoked without much success [303, 304] but it has been found that:

$$\lambda'_o \eta_o = \text{constant} \quad (136)$$

where p is usually 0.7 for alkali metal or halide ions and $p = 1$ for the large ions [305, 306]. Gill [307] has pointed out the inapplicability of the Zwanzig theory [308] 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:

$$r_i = \frac{|z|F^2}{6\pi N \lambda'_o \eta_o} + 0.0103D + r_y \quad (137)$$

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 [307, 308].

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:

$$\lambda'_o = \frac{Fe|z_i|}{6\pi R_\infty} \left(\frac{1+A}{\epsilon R_\infty^2} \right) \quad (138)$$

or,
$$R_i = R_\infty + \frac{R}{\infty} \quad (139)$$

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.

It is found that the Zwanzig's 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, [309] 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 [310].

(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 [309-318] mixtures and other aqueous binary mixtures [319-322]. To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts [323] 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 [324] 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 [325] 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 [326, 327] 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 physico-chemical studies in different solvent media.

2.8.6 THERMODYNAMICS OF ION-PAIR FORMATION

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

$$\Delta G^\circ = -RT \ln K_A \quad (140)$$

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

$$\Delta H^\circ = -T^2 \left[\frac{d(\Delta G^\circ / T)}{dT} \right]_P \quad (141)$$

$$\Delta S^\circ = -T^2 \left[\frac{d(\Delta G^\circ)}{dT} \right]_P \quad (142)$$

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

$$\Delta G^\circ = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \quad (143)$$

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

$$\Delta G_{298.15}^\circ = c_0 \quad (144)$$

$$\Delta S_{298.15}^\circ = c_1 \quad (145)$$

$$\Delta H_{298.15}^\circ = c_0 + 298.15c_1 \quad (146)$$

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° can also be calculated using the following equation:

$$\Delta G^\circ = N_A W_\pm \quad (147)$$

$$K_A = \left(\frac{4\pi N_A}{1000} \right) \int_a^R r^2 \exp\left(\frac{2q}{r} - \frac{W_\pm}{kT} \right) dr \quad (148)$$

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.

2.8.7 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 SchÖdinger 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 [328-332]. 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 KJ/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.

A. Galindo *et al.* [333,334] 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 modeled 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.* [335] of the University of Barcelona, Spain, have compared several "Preferential Solvation Models".

2.9 REFRACTIVE INDEX

Refractive Index measurement data provides 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 [336].

The ratio of the speed of light in a vacuum to the speed of light in another substance is defined as the index of refraction (n_D) for the 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 crosses a boundary from one medium into another, its direction of travel also changes, i.e., it is refracted. The relationship between light's speed in the two mediums (V_A and V_B), the angles of incidence ($\sin\theta_A$) and refraction ($\sin\theta_B$) and the refractive indexes of the two mediums (n_A and n_B) is shown below:

$$\frac{V_A}{V_B} = \frac{\sin\theta_A}{\sin\theta_B} = \frac{n_B}{n_A} \quad (149)$$

By measuring the angle of refraction, and knowing the index of refraction of the layer that is in contact with 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 by using, n_D experimental data according to the following expression

$$R = [(n_D^2 - 1) / n_D^2 + 2](M / \rho) \quad (150)$$

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

$$n_D = [(2A + 1) / (1 - A)]^{0.5} \quad (151)$$

where A is given by:

$$A = \left[\left\{ \frac{(n_1^2 - 1)}{(n_1^2 + 2)} (1 / \rho_1) \right\} - \left\{ \frac{(n_1^2 - 1)}{(n_1^2 + 2)} (w_1 / \rho_1) \right\} + \left\{ \frac{(n_2^2 - 1)}{(n_2^2 + 2)} (w_2 / \rho_2) \right\} \rho \right] \quad (152)$$

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:

$$\Delta R = R - \phi_1 R_1 - \phi_2 R_2 \quad (153)$$

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:

$$\Delta n_D = n_D - x_1 n_{D1} - x_2 n_{D2} \quad (154)$$

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

The computed deviations of refractive indices of the binary mixtures are fitted using the following Redlich-Kister expression [337].

$$\Delta n_{Dew} = w_e w_w \sum_{P=0}^S B_p (w_e w_w)^P \quad (155)$$

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

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

$$n_{Ds,sol} = n_{Dsol} + \sum_{i=1}^N A_i m^i \quad (156)$$

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

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 behavior may be expressed in terms of mole fraction: in this case smaller deviations occur but data are more scattered 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 σ are calculated for the expression in terms of volume fractions and in terms of mole fractions, respectively.

From the discussion, it is apparent that the problem of molecular interactions is stimulating as well as interesting. It is desirable to attack this problem using different experimental techniques. We have, therefore, utilized five important methods, *viz.*, volumetric, viscometric, interferometric, conductometric and refractometric for the physico-chemical studies in different solution systems.