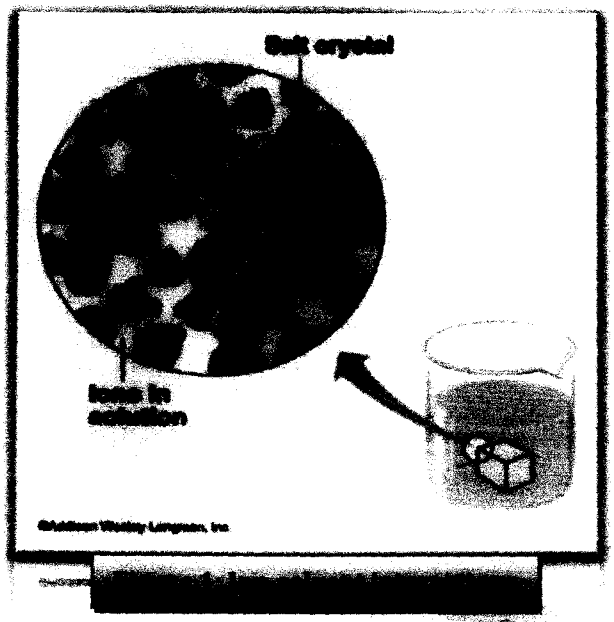
CHAPTER-II

GENERAL INTRODUCTION

The branch of physical chemistry that studies the change in properties that arise when one substance dissolves is termed as solution chemistry. It investigates the solubility of substances and how it is affected by the chemical nature of both the solute and the solvent. One of the interesting facts of solution chemistry is that the exact structure of the solvent molecule in a solution is not known with certainty. The introduction of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The interactions between solute and solute, solute and solvent, and solvent and solvent molecules and the resulting ion-solvation become predominant. The assessment of ion pairing in these systems is important because of its effect on the ionic conductivity and hence the mobility of the ions in solution. This explains the spurt in research in solution chemistry to elucidate the exact nature of these interactions through experimental studies involving conductometric, viscometric, densitometry, spectroscopy, ultrasonic interferometer and other suitable methods and to interpret the experimental data collected [1-7].



The majority of the reactions occurring in solutions are of either chemical of biological in nature. The solvent only provides an inert medium for chemical reactions previously presumed. The significance of solute-solvent interactions was realized only recently as a result of extensive studies in aqueous, non-aqueous and mixed solvents [8-13].

The behavior of electrolytes in solution depends mainly on ion-ion and ion-solvent interactions. The former interaction, in general, is stronger than the latter. Ion-ion interaction in dilute electrolytic solutions is now theoretically well understood, but the ion-solvent interaction or ion-solvation still remains a complex process.

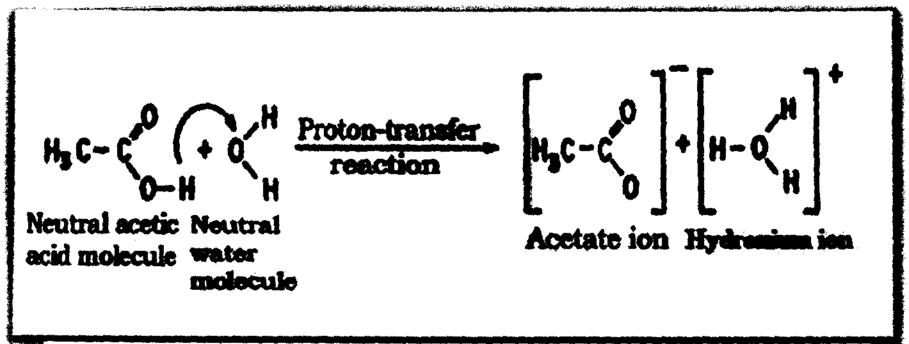


Figure 2: The chemical method of producing ionic solutions

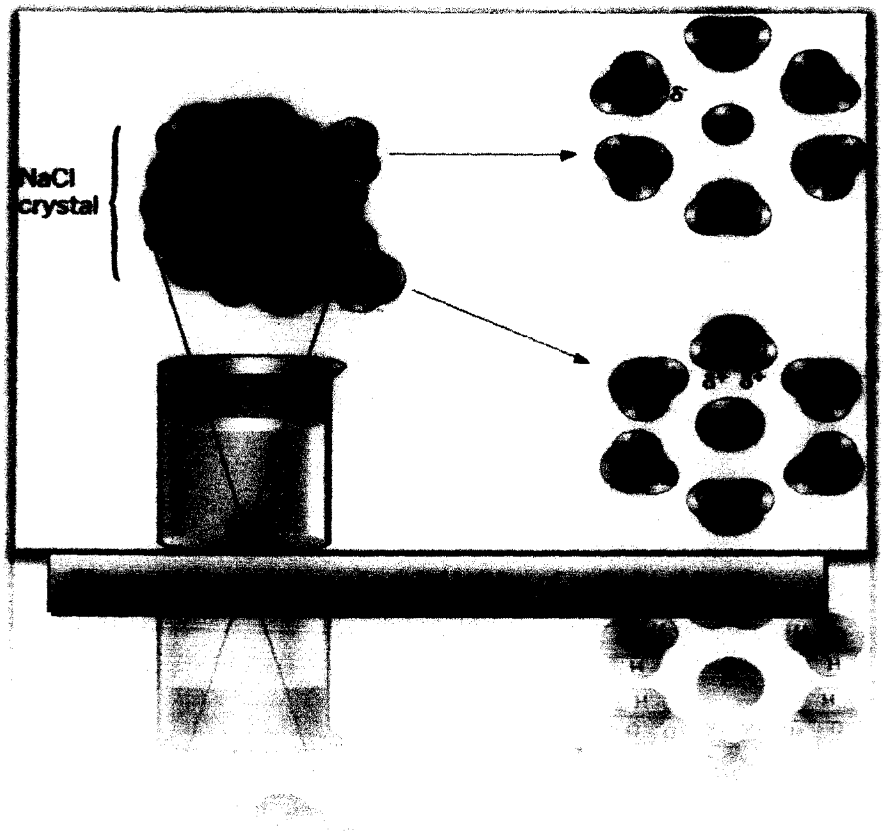
In the last few decades, considerable emphasis has been placed on research in the behavior of electrolytes in non-aqueous and mixed solvents to investigate the ion-ion (solute-solute) and ion-solvent (solute-solvent) interactions under varied conditions. Different sequences of solubility, differences in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have opened new vistas for physical chemists and interest in these organic solvents transcends traditional boundaries of inorganic, organic, physical, analytical and electrochemistry [10].

II.1. Ion-Solvent Interaction

Ion solvation is a phenomenon of primary interest in many contexts of chemistry because solvated ions are omnipresent on Earth. Hydrated ions occur in aqueous solution in many chemical and biological systems [14,15]. Solvated ions appear in high concentrations in living organisms, where their presence or absence can fundamentally alter the functions of life. Ions solvated in organic solvents or mixtures of water and organic solvents are also very common [16,17]. The exchange of solvent molecules around ions in solutions is fundamental to the understanding of the reactivity of ions in solution [18]. Solvated ions also play a key role in electrochemical applications, where for instance the conductivity of electrolytes depends on ion-solvent interactions [19].

The formation of mobile ions in solution is a basic aspect to electrochemistry. There are two distinct ways that mobile ions form in solution to create ionically conducting phases. The first one is illustrated for aqueous acetic acid in **Figure 2** [20].

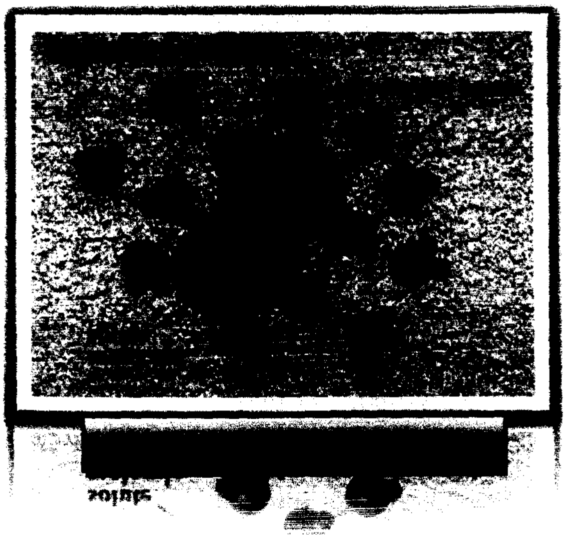
The second one involves dissociation of a solid lattice of ions such as the lattice of sodium chloride. The ion formation, as shown in **Figure 3** [20], is as if the solvent colliding with the walls of the crystal gives the ions in the crystal lattice a better deal energetically than they have within the lattice. It entices them out and into the solution. Thus there is a considerable energy of interaction between the ions and the solvent molecules. These interactions are collectively termed as ion- solvent interactions.



Ions orient dipoles. The spherically symmetrical electric field of the ion may tear solvent dipoles out of the solvent lattice and orient them with appropriate charged end toward the central ion. Thus, viewing the ion as a point charge and the solvent molecules as electric dipoles, ion-dipole forces become the principal source of ion-solvent interactions. 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 [2,4,9,11-13,21-24].

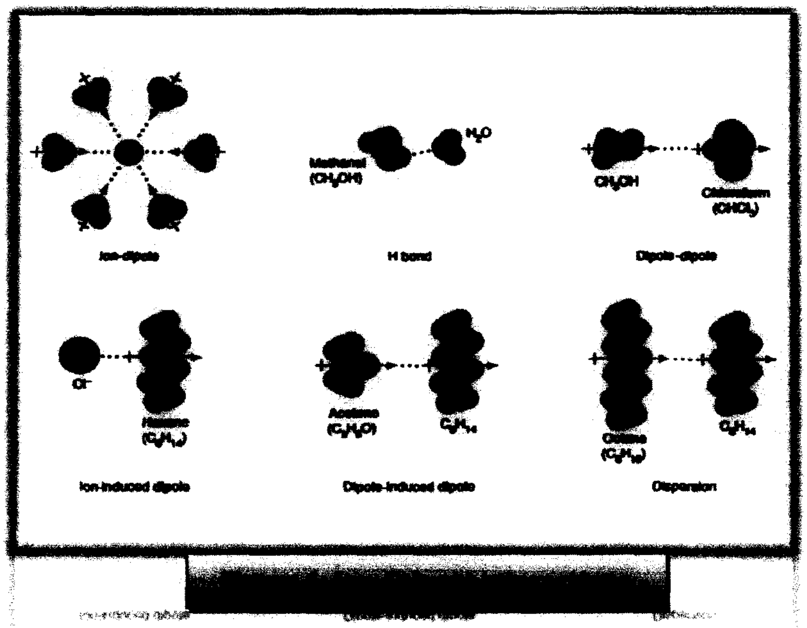
Most chemical processes of individual and biological importance occur in solution. The role of solvent is so great that million fold rate changes take place in some reactions simply by changing the reaction medium. Our bodies contain 65 to 70 % water, which acts as a lubricant, as an aid to digestion 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 [25,26] 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 [9] donor-acceptor properties [27,28] hard and soft acid-base principles [29] 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, modify also 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 [30,31]. The spectral solvent shifts or the chemical shifts can determine the qualitative and quantitative nature of ion-solvent interactions. But even qualitative or quantitative apportioning of the ion-solvent interactions into the various possible factors is still an uphill task.

In ion-solvation studies, broadly three types of approaches have been made to estimate the extent of solvation. The first is the solvational approach involving the studies of viscosity, conductance, etc., of electrolytes and the derivation of various factors associated with ionic solvation [32], the second is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated with solvation can be elucidated [33], and the third is to use spectroscopic measurements where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature [34].

It is thus apparent that the real understanding of the ion-solvent interaction is a difficult 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.

II.2. Ion-Ion Interaction

Ion-solvent interactions are only a part of the story of an ion related to its environment. The surrounding of an ion sees not only solvent molecules but also other ions. The mutual interactions between these ions constitute the essential part- 'ion-ion interactions'. The degree of ion-ion interactions affects the properties of solution and depends on the nature of electrolyte under investigation. Ion-ion interactions, in general, are stronger than ion-solvent interactions. Ion-ion interaction in dilute electrolytic solutions is now theoretically well understood, but ion-solvent interactions or ion-solvation still remains a complex process. While proton transfer reactions are particularly sensitive to the nature of the solvent, it has become cleared that the solvents significantly modify the majority of the solutes. Conversely, the nature of the strongly structured solvents, such as water, is substantially modified by the presence of solutes. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute, 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.

II.3. Theory of Mixed Solvents

As the mixed and non-aqueous solvents are increasingly used in chromatography, solvent extraction, in the elucidation of reaction mechanism, in preparing high density batteries, etc. a number of molecular theories, based on either the radial distribution function or the choice of suitable physical model, have been developed for mixed solvents. 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.* [48-50]. 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.

II.4. Density

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.

II.4.1. Apparent and Partial Molar Volumes

The molar volume of a pure substance can be calculated using density data. However, the volume contributed to a solvent by the addition of 1 mole of an ion is difficult to determine. This is so because, upon entry into the solvent, the ions change the volume of the solution due to a breakup of the solvent structure near the ions and the compression of the solvent under the influence of the ion's electric field, i.e., electrostriction. The effective volume of an ion in solution, the partial molar volume, can be determined from a directly obtainable quantity-apparent molar volume (V_ϕ). The apparent molar volumes, (V_ϕ), of the solutes can be calculated by using the following relation [24].

$$V_\phi = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \qquad (1)$$

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, $\overline{V_2}$, can be obtained from the equation [65]:

$$\overline{V_2} = \frac{V_\phi + (1000 - cV_\phi)}{\left(2000 + c^{3/2} \cdot \partial V_\phi / \partial\sqrt{c}\right)\sqrt{c} \cdot \left(\partial V_\phi / \partial\sqrt{c}\right)} \qquad (2)$$

The extrapolation of the apparent molar volume of electrolyte 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 [66], the Redlich-Meyer equation [67], the Owen-Brinkley equation [68], and the Pitzer equation[42]. Masson found that the apparent molar volume of electrolyte, V_ϕ, vary with the square root of the molar concentration by the linear equation:

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

where V_ϕ^0 is the apparent molar volume (equal to the partial molar volume, $\overline{V}_2^0$) at infinite dilution and S_V^* the experimental slope. The majority of V_ϕ data in water [69] and nearly all V_ϕ data in non-aqueous [65,70-73] solvents have been extrapolated to infinite dilution through the use of Eq. (3).

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

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \tag{4}$$

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

The limiting apparent molar expansibilities (ϕ_E^0) can be calculated from the general Eq. (5). Thus,

$$\phi_E^0 = \left(\frac{\partial V_\phi^0}{\partial T}\right)_P = a_1 + 2a_2 T \tag{5}$$

The limiting apparent molar expansibilities (ϕ_E^0) change in magnitude with the change of temperature. During the past few years, different workers emphasized that S_V^* is not the sole criterion for determining the structure-making or structure-breaking nature of any solute. Hepler [74] developed a technique of examining the sign of $\left(\frac{\partial^2 V_\phi^0}{\partial T^2}\right)_P$ for various solutes in terms of long range structure-making and breaking capacity of the solutes in solution using the general thermodynamic expression:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = \left(\frac{\partial^2 V_\phi^0}{\partial T^2}\right)_P \tag{6}$$

On the basis of this expression, it has been deduced that structure-making solutes should have positive value, whereas structure-breaking solutes should have negative value. However, Redlich and Meyer [66] have shown that Eq. (3) cannot be more than a limiting law and for a given solvent and temperature the slope, S_V^* should depend only upon the valence type. They suggested an equation for representing V_ϕ as follows:

$$V_\phi = V_\phi^0 + S_V\sqrt{c} + b_V c \qquad (7)$$

where,

$$S_V = K_w^{1/2} \qquad (8)$$

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

$$w = 0.5\sum_i^j \gamma_i z_i^2 \qquad (9)$$

and,

$$K = N^2 e^2 \left(\frac{8\pi}{1000\varepsilon^3 RT}\right)^{1/2} \left[\left(\frac{\partial \ln \varepsilon}{\partial P}\right)_T - \frac{\kappa_S}{3}\right] \qquad (10)$$

where κ_S is the compressibility of the solvent. But the variation of dielectric constant with pressure was not known accurately enough, even in water, to calculate accurate values of the theoretical limiting slope.

The Redlich-Meyer's extrapolation equation[66] adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies [75-77] 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 [68] can be used to aid in the extrapolation to infinite dilution and to adequately represent the concentration dependency of V_ϕ. The Owen-Brinkley equation [68] which includes the ion-size parameter, a (cm), is given by

$$V_\phi = V_\phi^0 + S_V \tau(Ka)\sqrt{c} + 0.5 w_V \theta(Ka) + 0.5 K_V c \qquad (11)$$

where the symbols have their usual significance. However, this Eq. (11) is not widely used for non-aqueous solutions.

Recently, Pogue and Atkinson [78] used the Pitzer formalism to fit the apparent molal volume data. The Pitzer equation for the apparent molar volume of a single salt $M_{\gamma M} X_{\gamma X}$ is:

$$V_\phi = V_\phi^0 \left| z_M z_X \right| A_V \left| 2b In(I + bI^{0.5}) + 2\gamma_M \gamma_X RT[mB_{MX}^2 + m^2(\gamma_M \gamma_X)^{0.5} C_{MX}^V] \qquad (12)$$

where the symbols have their usual significance.

II.4.2. Ionic Limiting Partial Molar Volumes

The individual partial ionic volumes provide information relevant to the general question of the structure near the ion, i.e., its solvation. The calculation of the ionic limiting partial molar volumes in organic solvents is, however, a difficult one. At present, however, most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods originally developed for aqueous solutions to non aqueous electrolyte solutions. In the last few years, the method suggested by Conway *et al.* [79] 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 tetraalkylammonium chlorides, bromides and iodides in aqueous solution. They plotted the limiting partial molar volume, $\overline{V}^0_{\mathrm{R_4NX}}$, for a series of these salts with a halide ion in common as a function of the formula weight of the cation, $M_{\mathrm{R_4N^+}}$ and obtained straight-lines for each series. Therefore, they suggested the following equation:

$$\overline{V}^0_{\mathrm{R_4NX}} = \overline{V}^0_{\mathrm{X^-}} + bM_{\mathrm{R_4N^+}} \qquad (13)$$

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

Uosaki *et al.* [80] used this method for the separation of some literature values and of their own $\overline{V}^0_{\mathrm{R_4NX}}$ values into ionic contributions in organic electrolyte solutions. Krumgalz [81] applied the same method to a large number of partial molar volume data for non-aqueous electrolyte solutions in a wide temperature range.

II.5. Excess Molar Volumes

The study has been carried out with the binary and ternary aqueous and non-aqueous solvent mixtures. The excess molar volumes (V^{E}) are calculated from density of these solvent mixtures according to the following equation: [82,83]

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

where, ρ is the density of the mixture and M_i, x_i and ρ_i are the molecular weight, mole fraction and density of ith component in the 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 [11]. 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.

II.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 [84,85]. Viscosity is not a thermodynamic quantity, but viscosity of an electrolytic solution along with the thermodynamic property, $\overline{V}_2^0$, 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.

II.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.

II.6.1.1. Early theoretical considerations on liquid viscosity

The theoretical development of liquid viscosity in early stages has been reviewed Andrade [86,87] and Frenkel [88]. 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 [92] developed equations which checked well against data on monoatomic metals at the melting point. Frenkel [88] 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 [89] assumed the momentum transfer to take place by the irregular Brownian movement of the holes [90] 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,

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

where η, V and m are viscosity, volume and mass, respectively, T is the temperature, R is the universal gas constant, s 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 [87] and Ewell and Eyring [91] Auluck, De and Kothari [92] 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 [93].

II.6.1.2. 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 [94,95] and further expanded by Pople [96]. Eisenschitz [93] 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 [97].

II.6.1.3. 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 [98,99] Mayer and Montroll [100], Mayer [101], Born and Green [102] and the considerations on the basis of the general kinetic theory led Born and Green [102,103] to develop a viscosity equation which provided explanation for several empirical equations [86,87,89] proposed for liquid viscosity. In this connection the theoretical contributions of Kirkwood and coworkers [90,104-110] Zwanzig *et al.*, [111] Rice and coworkers [112-115] Longuet-Higgins and Valleau [116] and Davis and Coworkers [117,118] are worth mentioning.

II.6.1.4. 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 [119] 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 [120], Boon and Thomaes [121-123] Boon, Legros and Thomaes [124], and Hollman and Hijmans [125] are worth mentioning.

II.6.1.5. The reaction rate theory for viscous flow

Considering viscous flow as a chemical reaction in which a molecule moving in a plane occasionally acquires the activation energy necessary to sleep over the potential barrier to the next equilibrium position in the same plane. Eyring [126] showed that the viscosity of the liquid is given by

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

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 [91] 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 [91, 127] finally gets

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

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 [128] have summarized all the working relations and the underlying

II.6.1.6. The significant structure theory and liquid viscosity

Eyring and coworkers [126-132] improved the "holes in solid" model theory [128-133] to picture the liquid state by identifying three significant structures - (i) solid like degrees of freedom because of the confinement of a molecule to an equilibrium position as a result of its binding by its neighbour, (ii) positional degeneracy in the solid like structure due to the availability of vacant sites to a molecule in addition to its equilibrium position and (iii) gas like degrees of freedom for a molecule which escapes from the solid lattice. 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 [134,135].

$$\eta = \frac{V_S}{V}\eta_S + \frac{V - V_S}{V}\eta_g \tag{18}$$

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 [136]. Eyring and Ree [136] have discussed in detail the evaluation of η_S from the reaction rate theory of Eyring [126] assuming that a solid molecule can jump into all neighbouring empty sites. The expression for η_S takes the following form [137]

$$\eta_S = \frac{N_A h}{Z\kappa} \cdot \frac{V}{V_S} \cdot \frac{6}{2^{1/2}} \cdot \frac{1}{V - V_S} \cdot \frac{1}{1 - e^{\theta/T}} exp \frac{a' E_S V_S}{(V - V_S) RT} \tag{19}$$

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 [137] by the relation:

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

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

II.6.2. 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 [138] 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 [139] suggested an empirical equation quantitatively correlating the relative viscosities of the electrolytes with molar concentrations (c):

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

The above equation can be rearranged as:

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

where A and B are constants specific to ion-ion and ion-solvent interactions. The equation is applicable equally to aqueous and non aqueous solvent systems where there is no ionic association and has been used extensively. The term $A\sqrt{c}$, originally ascribed to Grüneisen effect, arose from the long-range coulombic forces between the ions. The significance of the term had since then been realized due to the development Debye-Hückel theory [140] of inter-ionic attractions in 1923. The A-coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory [141-143] and is given by the Falkenhagen Vernon [143] equation:

$$A_{Theo} = \frac{0.2577\Lambda_0}{\eta_0(\varepsilon T)^{0.5}\lambda_+^0\lambda_-^0}\left[1 - 0.6863\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda_0}\right)^2\right] \qquad (23)$$

where the symbols have their usual significance. In very accurate work on aqueous solutions [144], A-coefficient has been obtained by fitting η_r to Eq. (22) and compared with the values calculated from Eq. (23), the agreement was normally excellent. The accuracy achieved with partially aqueous solutions was however poorer [145]. A-coefficient suggesting that should be calculated from conductivity measurements. Crudden *et al.* [146] suggested that if association of the ions occurs to form an ion pair, the viscosity should be analysed by the equation:

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

where A, B_i and B_p are characteristic constants and a is the degree of dissociation of ion pair. Thus, a plot of $(\eta_r - 1 - A\sqrt{\alpha c}/\alpha c)$ 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 Eq. (22) is valid up to 0.1 (M) [84,147,148] within experimental errors.

At higher concentrations the extended Jones-Dole Eq. (25), involving an additional coefficient D, originally used by Kaminsky, [149] has been used by several workers [150,151] and is given below:

$$\eta/\eta_0 = \eta_r = 1 + A\sqrt{c} + Bc + Dc^2 \qquad (25)$$

The coefficient D cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, Eq. (22) is used by the most of the workers. The plots of $(\eta/\eta_0 - 1)/\sqrt{c}$ 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 [148,152,153]. Thus, instead of determining A-coefficient from the plots or by the least square method, the A-coefficient are generally calculated using Falkenhagen-Vernon Eq. (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 [139]. The B-coefficient may be either positive or negative and it is actually the ion-solvent interaction parameter. It is conditioned by the ion size 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 [154,155]:

(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 depolymerisation 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.

II.6.3. 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 [87]:

$$\eta = Aexp^{b/T} \tag{26}$$

The several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration range [156-161] and the equation suggested by Angell [162,163] 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:

$$1/\eta = Aexp\left[-K_1/(N_0 - N)\right] \tag{27}$$

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_0 is the hypothetical concentration at which the system becomes glass. The equation was recast by Majumder *et al.* [164-166] introducing the limiting condition, that is $N \to 0$, $\eta \to \eta_0$; which is the viscosity of the pure solvent.

Thus, we have:

$$\ln \eta/\eta_0 = \ln \eta_{\mathrm{Rel}} = K_1 N/N_0 (N_0 - N) \tag{28}$$

The Eq. (28) predicts a straight line passing through the origin for the plot of $\ln \eta_{\mathrm{Rel}}$ vs. $N/N_0 (N_0 - N)$ if a suitable choice for N_0 is made. Majumder *et al.* tested the Eq. (28) by using literature data as well as their own experimental data. The best choice for N_0 and K_1 was selected by a trial and error methods. The set of K_1 and N_0 producing minimum deviations between $\eta_{\mathrm{Rel}}^{\mathrm{Exp}}$ and $\eta_{\mathrm{Rel}}^{\mathrm{Theo}}$ was accepted.

In dilute solutions, $N << N_0$ and we have:

$$\eta_{\mathrm{Rel}} = exp\left(K_1 N / N_0^2\right) \cong 1 + K_1 N / N_0^2 \tag{29}$$

Eq. (29) is nothing but the Jones-Dole equation with the ion-solvent interaction term represented as $B = K_1 / N_0^2$. 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 Eq. (28) can be written in the form:

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

It closely resembles the Vand's equation [156] for fluidity (reciprocal for viscosity):

$$2.5c / 2.3 \log \eta_{\mathrm{Rel}} = 1/V_{\mathrm{h}} - Qc \tag{31}$$

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.

II.6.4. 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 [153,167-196]. 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 [197] 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 [198] and also of Kaminsky [149] is based on:

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

The argument in favour of this assignment is based on the fact that the *B*-coefficients for KCl are very small and that the motilities' of K^+ and Cl^- are very similar over the temperature range 288.15–318.15 K. The assignment is supported from other thermodynamic properties. Nightingle [199], however preferred RbCl or CsCl to KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron [150] is based on the assumption that the Et_4N^+ ion in water is probably closest to be neither structure breaker not a structure maker. Thus, they suggest that it is possible to apply with a high degree of accuracy of the Einstein's equation [200],

$$B = 0.0025\overline{V}_0 \tag{33}$$

and by having an accurate value of the partial molar volume of the ion, $\overline{V}_0$, 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:

$$B_{BPh_4^-} = B_{PPh_4^+} + B_{BPh_4PPh_4}/2 \tag{34}$$

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

$$B_{BPh_4PPh_4} = B_{NaBPh_4} + B_{PPh_4Br} - B_{NaBr} \tag{35}$$

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

(a) Criss and Mastroianni assumed $B_{K^+} = B_{Cl^-}$ in ethanol based on equal mobilities of ions [168,201]. They also adopted $B^{25}_{Me_4N^+}$ = 0.25 as the initial value for acetonitrile solutions.

(b) For acetonitrile solutions, Tuan and Fuoss [202] proposed the equality, as they thought that these ions have similar mobilities. However, according to Springer *et al.*, [203] λ^0_{25} (Bu_4N^+) = 61.4 and λ^0_{25} (Ph_4B^-) = 58.3 in acetonitrile.

$$B_{Bu_4N^+} = B_{Ph_4B^-} \tag{36}$$

(c) Gopal and Rastogi [73] resolved the B-coefficient in N-methyl propionamide solutions assuming that $B_{Et_4N^+} = B_{I^-}$ at all temperatures.

(d) In dimethylsulphoxide, the division of B-coefficients was carried out by Yao and Beunion [153] assuming:

$$B_{[(i-pe)_3BuN^+]} = B_{Ph_4B^-} = 1/2B_{[(i-pe)_3BuNPh_4B]} \tag{37}$$

at all temperatures.

Wide use of this method has been made by other authors for dimethylsulphoxide, sulpholane, hexamethyl phosphotriamide and ethylene carbonate [204] solutions. The methods, however, have been strongly criticized by Krumgalz [205]. 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 $\lambda_+^0 = \lambda_-^0$ in all solvents at all temperatures. Thus, though $\lambda_{K^+}^0 = \lambda_{Cl^-}^0$ 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 $(i\text{-pe})_3BuN^+$ or $(i\text{-Am})_3BuN^+$ 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 [205,206] 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 [207,208] 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:

$$B_{R_4NX} = a + br^3R_4N^+ \tag{38}$$

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

The extrapolation of the plot of B_{R_4NX} (R > Pr or Bu) against $r^3R_4N^+$ 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:

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

$$B_{R_4N^+} / B_{R'_4N^+} = r^3_{R_4N^+} / r^3_{R'_4N^+} \tag{40}$$

The radii of the tetraalkylammonium ions have been calculated from the conductometric data [209]. Gill and Sharma [187] 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^+ (5.00Å) and Ph_4B^- (5.35 Å) were, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers. They proposed the equations:

$$B_{Ph_4B^-} / B_{Bu_4N^+} = r^3_{Ph_4B^-} / r^3_{Bu_4N^+} = (5.35/5.00)^3 \tag{41}$$

$$B_{Bu_4NBPh_4} = B_{Bu_4N^+} + B_{Ph_4B^-} \tag{42}$$

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.* [188,189] in different organic solvents using the assumption as given below:

$$B_{[(i-Am)_3Bu_4N^+]} = B_{Ph_4B^-} = 1/2B_{[(i-Am)_3Bu_4NBPh_4)]} \tag{43}$$

Recently, Lawrence and Sacco [190] used tetrabutylammonium tetrabutylborate (Bu_4NBBu_4) as reference electrolyte because the cation and anion in each case are symmetrical in shape and have almost equal Vander Waals volume. Thus, we have:

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

$$B_{\mathrm{Bu_4N^+}} = \frac{B_{\mathrm{Bu_4NBBu_4}}}{[1 + V_{W(\mathrm{Bu_4B^-})} / V_{W(\mathrm{Bu_4N^+})}]} \tag{45}$$

A similar division can be made for Ph_4PBPh_4 system.

Recently, Lawrence *et al.* made the viscosity measurements of tetraalkyl (from propyl to heptyl) ammonium bromides in DMSO and HMPT. The *B*-coefficients $B_{\mathrm{R_4NBr}} = B_{\mathrm{Br^-}} + a\left[f_x R_4 N^+\right]$ were plotted as functions of the Vander Waals volumes. The $B_{\mathrm{Br^-}}$ values thus obtained were compared with the accurately determined $B_{\mathrm{Br^-}}$ value using Bu_4NBBu_4 and Ph_4PBPh_4 as reference salts. They concluded that the 'reference salt' method is the best available method for division into ionic contributions.

Jenkins and Pritcheit [210] 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 [211] and 'volcano plots' of Morris [212]. The principle was extended to derive absolute single ion *B*-coefficients for alkali metals and halides in water. They also observed that $B_{\mathrm{Cs^+}} = B_{\mathrm{I^-}}$ suggested by Krumgalz [207] to be more reliable than $B_{\mathrm{K^+}} = B_{\mathrm{Cl^-}}$ 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.

II.6.5. Temperature Dependence of *B*-ion Values

Regularity in the behaviour of $B_\pm$ and $dB_\pm/dT$ has been observed both in aqueous and non-aqueous solvents and useful generalizations have been made by Kaminsky. He observed that (i) within a group of the periodic table the *B*-ion values decrease as the crystal ionic radii increase, (ii) within a group of periodic system, the temperature co-efficient of B_{ion} values increase as the ionic radius. The results can be summarized as follows:

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

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

characteristic of the structure breaking ions.

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

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 [213], A, B, C Zones of Frank and Wen [214] and hydrated radius of Nightingle [199].

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_0) plus the viscosity changes resulting from the competition between various effects occurring in the ionic neighborhood. Thus, the Jones-Dole equation:

$$\eta = \eta_0 + \eta^* + \eta^E + \eta^A + \eta^D = \eta_0 + \eta(A\sqrt{c} + Bc) \quad (46)$$

where η^*, the positive increment in viscosity is caused by coulombic interaction. Thus,

$$\eta^E + \eta^A + \eta^D = \eta_0 BC \quad (47)$$

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

Following Stokes, Mills and Krumgalz [205] we can write for B_{Ion} as:

$$B_{Ion} = B_{Ion}^{Einst} + B_{Ion}^{Orient} + B_{Ion}^{Str} + B_{Ion}^{Reinf} \quad (48)$$

whereas according to Lawrence and Sacco:

$$B_{Ion} = B_W + B_{Solv} + B_{Shape} + B_{Ord} + B_{Disord} \quad (49)$$

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 centro-symetrically 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.*, $B_{Ion}^{Einst} + B_{Ion}^{Orient} >> B_{Ion}^{Str}$ 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 $B_{\text{Ion}}^{\text{Einst}}$. But the orientation of solvent molecules in the secondary layer will be decreased due to increase in thermal motion leading to decrease in $B_{\text{Ion}}^{\text{Str}}$. $B_{\text{Ion}}^{\text{Orient}}$ 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 $B_{\text{Ion}}^{\text{Orient}}$ and $B_{\text{Ion}}^{\text{Str}}$.

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 [213] 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 $(\overline{S}_h^0)$ as:

$$\overline{S}_{\text{h}}^0 = \overline{S}_{\text{aq}}^0 - \overline{S}_{\text{g}}^0 \tag{50}$$

where, $\overline{S}_{\text{aq}}^0 = \overline{S}_{\text{ref}}^0 + \Delta S^0$, $\overline{S}_{\text{g}}^0$ 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 ($\overline{S}^{0}_{\mathrm{H}^+}$) to −5.5 cal. mol^{-1} deg^{-1}. Asmus [215] used the entropy of hydration to correlate ionic B-values and Nightingale [199] 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.* [216] to assign single ion B-coefficients so that a plot of ΔS^0_e [217,218] the electrostatic entropy of solvation or $\Delta S^0_{\mathrm{I,II}}$ 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 and ΔS^0_{I} and the single ion B-coefficients. Both entropy criteria (ΔS^0_e and $\Delta S^0_{\mathrm{I,II}}$) and B-ion values indicate that in water the ions Li^+, Na^+, Ag^+ and F^- are not structure makers, and the ions Rb^+, Cs^+, Cs^+, Cl^-, Br^-, I^- and ClO_4^- are structure breakers and K^+ is a border line case.

II.6.6. Thermodynamics of Viscous Flow

Assuming viscous flow as a rate process, the viscosity (η) can be represented from Eyring's [219] approaches as:

$$\eta = Ae^{E_{vis}/RT} = \left(hN_A/V\right)e^{\Delta G^*/RT} = \left(hN_A/V\right)e^{\left(\Delta H^*/RT - \Delta S^*/R\right)} \quad (51)$$

where E_{vis} = the experimental entropy of activation determined from a plot of ln $\eta = Ae^{E_{vis}/RT} = \left(hN_A/V\right)e^{\Delta G^*/RT} = \left(hN_A/V\right)e^{\left(\Delta H^*/RT - \Delta S^*/R\right)}$ against $1/T$. ΔG^*, ΔH^* and ΔS^* are the free energy, enthalpy and entropy of activation, respectively.

Nightingale and Benck [220] 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 $A\sqrt{c}$ term).

Thus, we have:

$$R\left[d\ln\eta/d(1/T)\right] = r\left[d\ln\eta_0/d(1/T)\right] + \frac{R}{(1+Bc)}\cdot\frac{d(1+Bc)}{d(1/T)} \quad (52)$$

$$\Delta E^{\neq}_{\eta(\mathrm{Soln})} = \Delta E^{\neq}_{\eta_0(\mathrm{Solv})} + \Delta E^{\neq}_{\mathrm{V}} \quad (53)$$

$\Delta E_{\mathrm{V}}^{\neq}$ 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.* [221] have suggested an alternative formulation based on the transition state treatment of the relative viscosity of electrolytic solution. They suggested the following expression:

$$B = (\overline{V}_1^0 - \overline{V}_2^0)/1000 + \overline{V}_1^0(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})/1000RT \qquad (54)$$

where $\overline{V}_1^0$ and $\overline{V}_2^0$ 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:

$$\Delta\mu_1^{0*} = \Delta G_1^{0*} = RTln\eta_1\overline{V}_1^0/hN_A \qquad (55)$$

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:

$$d(\Delta\mu_2^{0*})/dT = -\Delta S_2^{0*} \qquad (56)$$

$$\Delta H_2^{0*} = \Delta\mu_2^{0*} + T\Delta S_2^{0*} \qquad (57)$$

II.6.7. 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 [200] leads to the equation:

$$\eta/\eta_0 = 1 + 2.5\phi \qquad (58)$$

where ϕ is the volume fraction occupied by the particles.

Modifications of the equation have been proposed by (i) Sinha [222] 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 Eq. (58):

$$2.5\phi = A\sqrt{c} + Bc \tag{59}$$

Since $A\sqrt{c}$ term can be neglected in comparison with Bc and $\phi = c\overline{V}_1$ where $\overline{V}_1$ is the partial molar volume of the ion, we get:

$$2.5\overline{V}_1 = B \tag{60}$$

In the ideal case, the *B*-coefficient is a linear function of partial molar volume of the solute, $\overline{V}_1$, with slope to 2.5. Thus, $B_{\pm}$ can be equated to:

$$B_{\pm} = 2.5\overline{V}_{\pm} = 2.5 \times 4/3\left(\pi R_{\pm}^3 N_A/1000\right) \tag{61}$$

assuming that the ions behave like rigid spheres with a effective radii, $R_{\pm}$ moving in a continuum. $R_{\pm}$, calculated using the Eq. (61) 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 [160]:

$$B_{\pm} = 2.5/1000(V_i + n_b V_S) \tag{62}$$

where V_i is the molar volume of the base ion and V_S , the molar volume of the solvent. The Eq. (62) has been used by a number of workers to study the nature of solvation and solvation number.

II.6.8. Viscosity of Non-electrolytic Solutions

The equations of Vand [156], Thomas [223] and Moulik proposed mainly to account for the viscosity of the concentrated solutions of bigger spherical particles have been also found to correlate the mixture viscosities of the usual non-electrolytes [224-226]. These equations are:

Vand equation:
$$ln\,\eta_r = \frac{a}{1-Q} = \frac{2.5V_h c}{1-QV_h c} \quad (63)$$

Thomas equation:
$$\eta_r = 1 + 2.5V_h + 10.05cV_h^2 c \quad (64)$$

Moulik equation:
$$\eta^2 = I + Mc^2 \quad (65)$$

where η_r is the relative viscosity, a is constant depending on axial ratios of the particles, Q is the interaction constant, V_h is the molar volume of the solute including rigidly held solvent molecules due to hydration, c is the molar concentration of the solutes; I and M are constants. The viscosity equation proposed by Eyring and coworkers for pure liquids on the basis of pure significant liquid structures theory, can be extended to predict the viscosity of mixed liquids also. The final expression for the liquid mixtures takes the following form [137]:

$$\eta_m = \frac{6N_A h}{\sqrt{2}r_m(V_m - V_{Sm})}\left[\sum_i^n\left\{1-exp\left(\frac{-\theta_i}{T}\right)\right\}^{-x_i}\right]exp\left[\frac{a_m E_{Sm} V_{Sm}}{RT(V_m - V_{Sm})}\right] + \frac{V_m - V_{Sm}}{V_m}\left[\sum_i^n \frac{2}{3d_i^2}\left(\frac{m_i kT}{\pi^3}\right)^{1/2} x_i\right] \quad (66)$$

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 [137]:

$$r_m = \sum_i^n x_i^2 r_i + \sum_{i\neq j} 2x_i x_j r_{ij} \quad (67)$$

$$E_{Sm} = \sum_i^n x_i^2 E_{Si} + \sum_{i\neq j} 2x_i x_j E_{Sij} \quad (68)$$

$$V_m = \sum_i^n x_i V_i, \qquad V_{Sm} = \sum_i^n x_i V_{Si},\ a_m = \sum_i^n x_i a_i, \quad (69)$$

$$r_{ij} = (r_i r_j)^{1/2} \quad \text{and} \quad E_{Sij} = (E_{Si} E_{Sj})^{1/2} \quad (70)$$

$$\theta = \frac{h}{\kappa 2\pi}\left(\frac{b}{m}\right)^{1/2} \tag{71}$$

$$b = 2Z\varepsilon\left[22.106\left(\frac{N_A\sigma^3}{V_S}\right)^4 - 10.559\left(\frac{N_A\sigma^3}{V_S}\right)^2\right]\frac{1}{\sqrt{2}\sigma^2}\left(\frac{N_A\sigma^3}{V_S}\right)^{2/3} \tag{72}$$

where 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 [227-233].

$$\begin{aligned}\eta_m = \sum_i^3 x_i\eta_i &+ x_1x_2\left[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2\right] \\ &+ x_2x_3\left[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2\right] \\ &+ x_3x_1\left[A_{31} + B_{31}(x_1 - x_2) + C_{31}(x_1 - x_2)^2\right]\end{aligned} \tag{73a}$$

The correlation of ternary is modified to the following form:

$$\begin{aligned}\eta_m = \sum_i^3 x_i\eta_i &+ x_1x_2\left[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2\right] \\ &+ x_2x_3\left[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2\right] \\ &+ x_3x_1\left[A_{31} + B_{31}(x_1 - x_2) + C_{31}(x_1 - x_2)^2\right] \\ &+ A_{123}^{*}x_1x_2x_3\end{aligned} \tag{73b}$$

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

$$\begin{aligned}\eta_m = \sum_i^3 x_i\eta_i &+ x_1x_2\left[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2\right] \\ &+ x_2x_3\left[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2\right] \\ &+ x_3x_1\left[A_{31} + B_{31}(x_1 - x_2) + C_{31}(x_1 - x_2)^2\right] \\ &+ x_1x_2x_3\left[A_{123} + B_{123}x_1^2(x_2 - x_3)^2 + C_{123}x_1^3(x_2 - x_3)^3\right]\end{aligned} \tag{73c}$$

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; $A_{123}^{*}, A_{123}, B_{123}$ and C_{123} are constants for the ternaries; and the other symbols have their usual significance.

II.6.9. 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 [234], the deviations in viscosities $\Delta\eta$, from the ideal mixture values can be calculated as:

$$\Delta\eta = \eta - \sum_{i=1}^{j}(x_i\eta_i) \tag{74}$$

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

II.6.10. Gibbs Excess Energy of Activation for Viscous Flow

Quantitatively, the Gibbs excess energy of activation for viscous flow G^{*E}, can be calculated as [235]:

$$G^{*E} = RT\left[\ln\eta V - \sum_{i=1}^{j}x_i\ln\eta_i V_i\right] \tag{75}$$

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.

II.6.11 Molecular interactions in terms of Viscous Synergy and Antagonism

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 [236,237].

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 [238] 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:

$$\eta_{cal} = \sum_{i=1}^{j} w_i \eta_i \tag{76}$$

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 $\eta_{cal} > \eta_{exp}$, 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 [239].

In order to secure more comparable viscous synergy results, the so-called synergic interaction index (I_S) as introduced by Howell [240] is taken into account:

$$I_S = \frac{\eta_{exp} - \eta_{cal}}{\eta_{mix}} = \frac{\Delta\eta}{\eta_{mix}} \tag{77}$$

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:

$$\rho_{cal} = \sum_{i=1}^{j} w_i \eta_i \tag{78}$$

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 $\rho_{cal} > \rho_{exp}$, there is volume expansion in the system.

We extended our studies [241] to the ternary mixtures formed from 1,3-dioxolane represented as (A), water represented as (B) and monoalkanols represented as (C). The monoalkanols include methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), 1-butanol (1-BuOH), 2-butanol (2-BuOH), *t*-butanol (*t*-BuOH) and *i*-amyl alcohol (*i*-AmOH). It is observed that $\eta_{exp} > \eta_{cal}$ for the ternary mixtures, thus indicating synergy as mentioned earlier. The value gradually decreases with increasing amount of the cyclic diether. So, it has been observed that when (B) and (C) are in maximum proportion in absence of (A) in the mixture, there is maximum mutual interaction. As (A) comes into play, there is self-interaction and gradual breaking of the mutual interactions, thus causing decrease in viscosity for the ternary mixtures. Pure liquids thus have easier flow than the system. Further, it has been also observed that with increasing proportion of (A), antagonism comes into play which is quite evident for higher series of (C). Methanol and ethanol mixtures exhibit synergy over the whole composition range, but as the chain length increases the interaction between the unlike solvent molecules decreases and finally at a particular weight fraction the repulsion factor comes into play.

II.7. Ultrasonic Speed

The acoustic property- 'ultrasonic speed' is a sensitive indicator of molecular interactions and can provide useful information about these phenomena, particularly in cases where partial molar volume data alone fail to provide an unequivocal interpretation of the interactions.

II.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 [242-246] 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 (κ_S) of a solvent/solution can be calculated from the Laplace's equation [247,248]:

$$\kappa_S = 1/u^2\rho \tag{79}$$

where ρ is the solution density and u is the ultrasonic speed in the solvent/solution. The isentropic compressibility (κ_S) determined by Eq. (79) 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 (κ_ϕ) of the solutions was calculated using the relation:

$$\kappa_\phi = \frac{M\kappa_S}{\rho} + \frac{1000\left(\kappa_S\rho_0 - \kappa_S^0\rho\right)}{m\rho\rho_0} \tag{80}$$

κ_S^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 κ_ϕ^0 may be obtained by extrapolating the plots of κ_ϕ versus the square root of the molal concentration of the solutes by the computerized least- square method according to the equation [243,246].

$$\kappa_\phi = \kappa_\phi^0 + S_K^* \sqrt{m} \tag{81}$$

The limiting apparent molal isentropic compressibility (κ_{ϕ}^{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 [249,250]. This is reflected by the negative values of κ_{ϕ}^{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 [74,251] as well as the possibility of flexible hydrogen bond formation appear to be responsible for causing a more compressible environment and hence positive κ_{ϕ}^{0} values have been reported in aqueous non-electrolyte [252] and non-aqueous non-electrolyte [253] solutions.

II.7.2. Deviation in Isentropic Compressibility

The deviation in isentropic compressibility ($\Delta\kappa_S$) can be calculated using the following equation [254-256]:

$$\Delta\kappa_S = \kappa_S - \sum_{i=1}^{j} x_i \kappa_{S,i} \tag{82}$$

where x_i, $\kappa_{S,i}$ are the mole fraction and isentropic compressibility of i^{th} component in the mixture, respectively. The observed values of $\Delta\kappa_S$ 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 $\Delta\kappa_S$ values, whereas the remaining two factors lead to negative $\Delta\kappa_S$ values [257]. The resultant values of $\Delta\kappa_S$ for the present mixtures are due to the net effect of the combination of (i) to (iii) [258].

II.7.3. Excess isentropic compressibility

The excess isentropic compressibility, κ_S^E, were calculated from,

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{83}$$

where the isentropic compressibility term κ_S^{id} was computed using the relation [259,261]

$$\kappa_S^{id} = \sum_{i=1}^{2} \phi_i \left[\kappa_{S,i} + \frac{TV_i(\alpha_i^2)}{C_{P,i}} \right] - \left\{ \frac{T\left(\sum_{i=1}^{2} x_i V_i\right)\left(\sum_{i=1}^{2} \phi_i \alpha_i\right)^2}{\sum_{i=1}^{2} x_i C_{P,i}} \right\} \tag{84}$$

where V_i is the molar volume, α_i is the isobaric thermal expansion coefficient, $C_{P,i}$ is the isobaric molar heat capacity, and $\kappa_{S,i}$ is the isentropic compressibility of the i^{th} component.

The thermal expansion coefficients, α, have been calculated from the equation [261]

$$\alpha = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{85}$$

The volume fraction, ϕ_i was calculated as

$$\phi_i = \frac{x_i V_i}{\sum_{i=1} x_i V_i} \tag{86}$$

II.8. Correlating Equations

Several correlating equations and semi-empirical models have been proposed to estimate the properties of binary liquid mixtures in terms of pure-component data.

II.8.1. Density Correlations for Liquid Mixtures

The densities for the liquid mixtures can be determined by using the densities of the pure components and by employing the following relations:

$$\rho_m = \sum_i x_i \rho_i \tag{87}$$

$$\rho_m = \sum x_i^2 \rho_i + \sum_{i \neq j} 2x_i x_j (\rho_i \rho_j)^{1/2} \tag{88}$$

The densities of pure components can be determined experimentally.

Another appropriate approach for the prediction of mixture densities is based on the multi fluid model [262,263] which leads to the following equation:

$$\left(\frac{Z_C}{\rho_P V_C}\right)_{1,2\ldots\ldots n} = \left(\frac{Z_{Cn}}{\rho_{Pn} V_{Cn}}\right) - \left[\frac{\left(\sum_i^n x_i \omega_i \Big/ \sum_i^n x_i\right) - \omega_n}{\left(\sum_i^n x_i \omega_i \Big/ \sum_i^n x_i\right) - \omega_n}\right] \cdot \left[\frac{Z_{Cn}}{\rho_{Pn} V_{Cn}} - \left(\frac{Z_C}{\rho_P V_C}\right)_{1,2\ldots\ldots(n-1)}\right] \tag{89}$$

where Z_C and V_C are the critical compressibility and critical molar volume, respectively, ρ_P is the predicted density and ω is the acentric factor. For interpolation and limited extrapolation purposes the binary mixture densities can also be correlated to a high degree of accuracy using equations obtained by replacing ρ by η in equations (73a), (73b) and (73c).

II.8.2. Correlative Procedures for the Viscosity of Liquid Mixtures

Several semi-empirical models have been proposed to estimate the dynamic viscosity (η_m) of the binary liquid mixtures in terms of pure component data [264,265]. Some of them we examined are as follows:

a. The viscosity values can be further used to determine the Grunberg-Nissan parameter, d_{12} as [266]

$$\eta_m = exp\left[\sum_{i=1}^{n}(x_i \ln \eta_i) + d_{12}\prod_{i=1}^{n} x_i\right] \tag{90}$$

and d_{12} is proportional to the interchange energy. It may be regarded as an approximate measure of the strength of molecular interactions between the mixing components. The negative values of d_{12} indicate the presence of dispersion forces [227] between the mixing components in the mixtures while its positive values indicate the presence of specific interactions [227] between them.

b. Tamura-Kurata [267] put forward the following equation for the viscosity of the binary liquid mixtures:

$$\eta_m = \sum_{i=1}^{n} x_i \phi_i \eta_i + 2T_{12} \prod_{i=1}^{n} [x_i \phi_i]^{1/2} \tag{91}$$

where T_{12} is the interaction parameter and ϕ_i is the volume fraction of i^{th} pure component in the mixture.

c. Molecular interactions may also be interpreted by the following viscosity model of Hind *et al.*: [268]

$$\eta_m = \sum_{i=1}^{n} x_i^2 \eta_i + 2H_{12} \prod_{i=1}^{n} x_i \tag{92}$$

where H_{12} is Hind interaction parameter, which may be attributed to unlike pair interaction [269]. It has been observed that for a given binary mixture T_{12} and H_{12} do not differ appreciably from each other, this is in agreement with the view put forward by Fort and Moore [227] in regard to the nature of parameter T_{12} and H_{12}.

d. McAllister's three-body model:

McAllister [270] assumed that (i) the interactions in liquid mixtures are mostly three-body type, (ii) the probability of their occurrence is concentration dependent only and (iii) the free energy of activation terms are additive. With these assumptions, the McAllister equation involving 3-body interactions for multi component mixtures takes the following form:

$$\ln \nu_m = \sum_{i=1}^{n} x_i^3 \ln \nu_i M_i - \ln M_{av} + 3\sum_{i=1}^{n}\sum_{j=1}^{n} x_i^2 x_j \ln \nu_{ij} M_{ij} + 6\sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} x_i x_j x_k \ln \nu_{ijk} M_{ijk} \tag{93}$$

where

$$M_{av} = \sum_{i=1}^{n} x_i M_i \tag{94}$$

$$M_{ij} = \left(\frac{2M_i + M_j}{3}\right) \tag{95}$$

$$M_{ijk} = \left(\frac{M_i M_j M_k}{3}\right) \tag{96}$$

For binary liquid mixtures, the equation reduces to:

$$\begin{aligned}\ln \nu_m = {} & x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3x_1^2 x_2 \ln \nu_{12} + 3x_2^3 x_1 \ln \nu_{21} - \ln\left[x_1 + \frac{x_2 M_2}{M_1}\right] \\ & + 3x_1^2 x_2 \ln\left[\frac{2}{3} + \frac{M_2}{3M_1}\right] + 3x_2^2 x_1 \ln\left[\frac{1}{3} + \frac{2M_2}{3M_1}\right] + x_2^3 \ln\left[\frac{M_2}{M_1}\right]\end{aligned} \tag{97}$$

e. McAllister's four-body model:

The viscosities of the liquid mixtures are also correlated by using the McAllister equation based on four-body interactions [271] when hydrogen bondings are included in the systems and the behaviour of the systems becomes complex. McAllister equation for n-component mixture considering four-body interactions is given below:

$$\begin{aligned}\ln \nu_m = {} & \sum_{i-1}^{n} x_i^4 \ln(\nu_i M_i) + 4\sum_{i=1}^{n}\sum_{i=1}^{n} x_i^3 x_j \ln\left[\nu_{iiij}\left(\frac{3M_i + M_j}{4}\right)\right] \\ & + 6\sum_{i}^{n}\sum_{j}^{n} x_i^2 x_j \ln\left[\nu_{iijj}\left(\frac{M_i + M_j}{2}\right)\right] \\ & + 12\sum_{i}^{n}\sum_{j}^{n}\sum_{k}^{n} x_i^2 x_j x_k \ln\left[\nu_{iijk}\left(\frac{2M_i + M_j + M_k}{4}\right)\right]_{i \neq j, j \neq k, j<k} \\ & - \ln\left(\sum_{i}^{n} x_i M_i\right)\end{aligned} \tag{98}$$

For binary liquid mixtures, the equation reduces to:

$$\begin{aligned}\ln \nu_m = {} & x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 \\ & - \ln\left[x_1 + \frac{x_2 M_2}{M_1}\right] + 4x_1^3 x_2 \ln\left[\frac{3}{4} + \frac{M_2}{4M_1}\right] + 6x_1^2 x_2^2 \ln\left[\frac{1}{2} + \frac{M_2}{2M_1}\right] \\ & + 4x_1 x_2^3 \left[\frac{1}{3} + \frac{3M_2}{4M_1}\right] + x_2^4 \ln\left[\frac{M_2}{M_1}\right]\end{aligned} \quad (99)$$

where ν_i and M_i are the kinematic viscosity and the molecular mass of i^{th} pure component in the mixtures, respectively; and ν_{iiij}, ν_{iijj} and ν_{iijk} are the ternary adjustable parameters based on the four-body interaction approach to be evaluated from experimental data by least square method.

f. Heric-Brewer model:

Heric and Brewer [272] made provision for the excess viscosity in the ideal form of kinematic viscosity equations and used the following relations:

$$\nu_m = x_1\nu_1 + x_2\nu_2 + x_1x_2\left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \ldots\ldots\right] \quad (100a)$$

and

$$\begin{aligned}\ln \nu_m = {} & x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1 M_1 + x_2 M_2) \\ & + x_1 x_2\left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \ldots\ldots\right]\end{aligned} \quad (100b)$$

where A, B, C and D are constants.

Moreover, the excess or deviation properties (V^E, $\Delta\eta$, G^{*E}, $\Delta\kappa_S$ and κ_S^E) have been fitted to Redlich-Kister [229] polynomial equation using the method of least squares involving the Marquardt algorithm [273] and the binary coefficients, a_i were determined as follows :

$$Y_{ij}^E = x_1 x_2 \sum_{i=1}^{j} a_i (x_1 - x_2)^i \quad (101)$$

where Y_{ij}^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,

$$\sigma = \left[\frac{\left(Y^{E}_{exp} - Y^{E}_{cal}\right)^{2}}{\left(n-m\right)} \right]^{1/2} \tag{102}$$

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

II.9. Molecular interactions in terms of conductance

Conductance measurement is considered to be one of the most accurate and widely used physical methods for investigation of electrolyte of solution [274,275]. The measurements can be made in a variety of solvents over wide ranges of temperature and pressure and in dilute solutions where interionic theories are not applicable. Fortunately, accurate theories of electrolytic conductances are available to explain the results even up to a concentration limit of κd (κ = Debye-Hückel length, d = distance of closest approach of free ions). Recently developed experimental techniques provide an accuracy of ±0.01 % or even more. Conductance measurements together with transference number determinations provide an unequivocal method of obtaining single-ion values. The chief limitation, however, is the colligative-like nature of the information obtained.

Since the conductometric method primarily depends on the mobility of ions, it can be suitably utilized to determine the dissociation constants of electrolytes in aqueous, mixed and non-aqueous solvents. The conductometric method in conjunction with viscosity measurements gives us much information regarding the ion-ion and ion-solvent interactions. However, the choice and application of theoretical equations as well as equipment and experimental techniques are of great importance for precise measurements. These aspects have been described in details in a number of authoritative books and reviews [274-287].

The study of conductance measurements were pursued vigorously both theoretically and experimentally during the last five decades 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 [288] 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:

$$\Lambda = \Lambda_0 - S\sqrt{c} \tag{103}$$

where

$$S = \alpha\Lambda_0 + \beta \tag{104}$$

$$\alpha = \frac{(ze^2)\kappa}{3(2+\sqrt{2})\varepsilon_r kT\sqrt{c}} = \frac{82.406\times 10^4 z^3}{(\varepsilon_r T)^{3/2}} \tag{105}$$

$$\beta = \frac{z^2 eF\kappa}{3\pi\eta\sqrt{c}} = \frac{82.487z^3}{\eta\sqrt{\varepsilon_r T}} \tag{106}$$

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 [289]. In the subsequent years, Pitts (1953) [290] and Fuoss and Onsager (1957) [252,291] 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 [291] from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation was questioned [249,292,293]. The original Fuoss-Onsager equation was further modified by Fuoss and Hsia [294] 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:

$$\Lambda = \Lambda_0 - \alpha\Lambda_0\sqrt{c}/(1+\kappa a)(1+\kappa a/\sqrt{2}) - \beta\sqrt{c}/(1+\kappa a) + G(\kappa a) \tag{107}$$

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

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec\ln c + J_1 c - J_2\sqrt[3]{c} \tag{108}$$

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 [295,296]. Further correction of the Eq. (108) was made by Fuoss and Accascina [279]. They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes:

$$\Lambda = \Lambda_0 - S\sqrt{c} + Ec\ln c + J_1 c - J_2 \sqrt[3]{c} - F\Lambda c \tag{109}$$

where,

$$Fc = 4\pi R^3 N_A / 3 \tag{110}$$

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 [297].

II.9.1. Ionic Association

The Eq. (109) 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 Λ^0_{expt} is greater than Λ^0_{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 ($\Lambda^0_{expt} < \Lambda^0_{theo}$) or positive deviation from the Onsager limiting tangent ($\alpha\Lambda_0 + \beta$)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 Λ^0_{expt} and Λ^0_{theo} would be considerable with increasing association [298].

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

$$M^{z+} + A^{z-} = MA \tag{111}$$

$$K_A = (1-\alpha)/\alpha^2 c \gamma_{\pm}^2 \tag{112}$$

$$\alpha = 1 - \alpha^2 K_A c \gamma_\pm^2 \tag{113}$$

where $\gamma_\pm$ is the mean activity coefficient of the free ions at concentration αc.

For strongly associated electrolytes, the constant, K_A and Λ_0 has been determined using Fuoss-Kraus equation [299] or Shedlovsky's equation [300].

$$T(z)/\Lambda = 1/\Lambda_0 + K_A/\Lambda_0^2 \cdot c\gamma_\pm^2 \Lambda/T(z) \tag{114}$$

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

$$F(z) = 1 - z\left(1 - z(1 - ....)^{-1/2}\right)^{-1/2} \tag{115a}$$

$$1/T(z) = S(z) = 1 + z + z^2/2 + z^3/8 + ... \tag{115b}$$

A plot of $T(z)/\Lambda$ against $c\gamma_\pm^2\Lambda/T(z)$ 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 Eq. (114).

The Fuoss-Hsia [294] conductance equation for associated electrolytes is given by:

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

(116)

The equation was modified by Justice [301]. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations:

$$\Lambda = \alpha\left(\Lambda_0 - S\sqrt{\alpha c}\right) + E(\alpha c)\ln(\alpha c) + J_1(R)\alpha c - J_2(R)(\alpha c)^{3/2} \tag{117}$$

$$(1-\alpha)/\alpha^2 c\gamma_\pm^2 = K_A \tag{118}$$

$$\ln\gamma_\pm = -k\sqrt{q}/(1 + kR\sqrt{\alpha c}) \tag{119}$$

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

According to Justice the method of fixing the J-coefficient by setting, $R = q$ clearly permits a better value of K_A to be obtained. Since the Eq. (117) is a series expansion truncated at the $c^{3/2}$ term, it would be preferable that the resulting errors be absorbed as must as possible by J_2 rather than by K_A , whose theoretical interest is greater as it contains the information concerning short-range cation-anion interaction. From the experimental values of the association constant K_A, one can use two methods in order to determine the distance of closest approach, *a*, of two free ions to form an ion-pair. The following equation has been proposed by Fuoss [279]:

$$K_A = \left(4\pi N_A a^3/3000\right) exp\left(e^2/a\varepsilon KT\right) \tag{120}$$

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 [302].

$$K_A = \left(4\pi N_A a/1000\right) \int_{r=a}^{r=q} r^2 exp\left(z^2 e^2/r\varepsilon KT\right) dr \tag{121}$$

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 [303].

II.9.2. Ion size Parameter and Ionic Association

For plotting, Eq. (109) can be rearranged to the 'Λ' function as:

$$\Lambda_1 = \Lambda + S\sqrt{c} - Ec\ln c = \Lambda_0 + J_1 c + J_2 \sqrt[3]{c} = \Lambda_0 + J_1 c \tag{122}$$

with J_2 term omitted.

Thus, a plot of Λ_1 versus *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 [298] 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' [304] but the agreement is still poor. However, little of real physical significance may be attached to the distance of closest approach derived from J [305].

Fuoss [306] in 1975 proposed a new conductance equation. Latter he subsequently put forward another conductance equation in 1978 [307,308] replacing the old one as suggested by Fuoss and co-workers. He classified the ions of electrolytic solutions in one of the three categories.

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

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

(iii) Ions finding no other unpaired ion in a surrounding sphere of radius R, the diameter of the co-sphere (unpaired ions).

Thermal motions and interionic forces establish a steady state, represented by the following equilibria:

$$A^+ + B^- = \underset{\text{Solvent separated pair}}{(A^+ \ldots\ldots\ldots B^-)} = \underset{\text{Contact pair}}{A^+B^-} = \underset{\text{Neutral molecule}}{AB} \qquad (123)$$

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$(r \le R)$, 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 [175] are:

$$K_R = (1-\alpha)(1-\gamma)/c\gamma^2 f^2 \qquad (124)$$

$$K_S = \alpha/(1-\alpha) = exp(-E_S/kT) = e^{-\varepsilon} \qquad (125)$$

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, $$1-\alpha = 1/(1+K_S) \tag{126}$$

and the conductometric pairing constant is given by:

$$K_A = (1-\alpha)/c\gamma^2 f^2 = K_R/(1-\alpha) = K_R(1+K_S) \tag{127}$$

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

$$\Lambda = p\left[\Lambda_0\left(1+\Delta X/X\right)+\Delta\Lambda_e\right] = p\left[\Lambda_0\left(1+R_X\right)+E_L\right] \tag{128}$$

which is a three parameter equation $\Lambda = \Lambda(c, \Lambda_0, R, E_S)$ and $\Delta X/X$ (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:

$$p = 1-\alpha(1-\gamma) \tag{129}$$

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

$$\Lambda = \gamma\left[\Lambda_0\left(1+\Delta X/X\right)+\Delta\Lambda_e\right] \tag{130}$$

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

$$K_A = (1-\gamma)/c\gamma^2 f^2 \approx K_R K_S \tag{131}$$

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

$$\gamma = 1 - K_R c\gamma^2 f^2/(1-\alpha) \tag{132}$$

$$K_R = (4\pi N_A R^3/3000)\, exp(\beta/R) \tag{133}$$

$$-\ln f = \beta_\kappa/2(1+\kappa R), \qquad \beta = e^2/\varepsilon kT \tag{134}$$

$$\kappa^2 = 8\pi\beta\gamma n = \pi\beta N_A \gamma c/125 \tag{135}$$

$$-\varepsilon = \ln[\alpha/(1-\alpha)] \tag{136}$$

The details of the calculations are presented in the 1978 paper [307,308]. 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).

II.9.3. 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 surroundings solvent molecules, as the ions are infinitely apart. Under these conditions, the validity of Kohlrausch's law of independent migration of ions is almost axiomatic. Thus:

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0 \tag{137}$$

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

$$\lambda_+^0 = t_+ \Lambda_0 \qquad \text{and} \qquad \lambda_-^0 = t_- \Lambda_0 \tag{138}$$

Thus, from accurate value of λ^0 of ions it is possible to separate the contributions due to cations and anions in the solute-solvent interactions [309]. However, accurate transference number determinations are limited to few solvents only. Spiro [310] and Krumgalz [311] have made extensive reviews on the subject.

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

The method has been summarized by Krumgalz [311] and some important points are mentioned below:

(i). Walden equation, [312] $\left(\lambda_{\pm}^{0}\right)_{\text{water}}^{25} \cdot \eta_{0,\text{water}} = \left(\lambda_{\pm}^{0}\right)_{\text{acetone}}^{25} \cdot \eta_{0,\text{acetone}}$ (139)

(ii). $$\left.\begin{aligned} \lambda_{\text{pic}}^{0} \cdot \eta_0 &= 0.267 \\ \lambda_{\text{Et}_4\text{N}^+}^{0} \cdot \eta_0 &= 0.296 \end{aligned}\right|_{\text{based on } \Lambda_{\text{Et}_4\text{N}_{\text{pic}}}^{0} = 0.563}^{[312,313]} \qquad (140)$$

Walden considered the products to be independent of temperature and solvent. However the $\Lambda_{\text{Et}_4\text{N}_{\text{pic}}}^{0}$ values used by Walden was found to differ considerably from the data of subsequent more precise studies and the values of (ii) are considerably different for different solvents.

(iii). $$\lambda_{25}^{0}\left(\text{Bu}_4\text{N}^+\right) = \lambda_{25}^{0}\left(\text{Ph}_4\text{B}^-\right)^{[313]} \qquad (141)$$

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

(iv). $$\lambda_{25}^{0}\left(\text{Bu}_4\text{N}^+\right) = \lambda_{25}^{0}\left(\text{Bu}_4\text{B}^-\right)^{[314]} \qquad (142)$$

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 [315] is:

$$\lambda_{25}^{0}\left(\text{R}_4\text{N}^+\right) = zF^2/6\pi N_A \eta_0 \left[r_i - \left(0.0103\varepsilon_0 + r_y\right)\right] \qquad (143)$$

where z and r are charge and crystallographic radius of proper ion, respectively; η_0 and ε_0 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 [311(a)]. In a paper, [311(b)] Krumgalz examined the Gill's approach more critically using conductance data in many solvents and found the method reliable in three solvents e.g. butan-1-ol, acetonitrile and nitromethane.

(vi). $$\lambda_{25}^{0}\left[(i-\text{Am})_3\,\text{Bu}_4\text{N}^+\right]=\lambda_{25}^{0}\left(\text{Ph}_4\text{B}^-\right)^{[316]} \quad (144)$$

It has been found from transference number measurements that the $\lambda_{25}^{0}\left[(i-\text{Am})_3\,\text{Bu}_4\text{N}^+\right]$ and $\lambda_{25}^{0}\left(\text{Ph}_4\text{B}^-\right)$ values differ from one another by 1 %.

(vii). $$\lambda_{25}^{0}\left(\text{Ph}_4\text{B}^-\right)=1.01\lambda_{25}^{0}\left(i-\text{Am}_4\text{B}^-\right)^{[317]} \quad (145)$$

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:

$$r_S = |z|F^2 / A\pi\eta_0\lambda_{\pm}^{0} \quad (146)$$

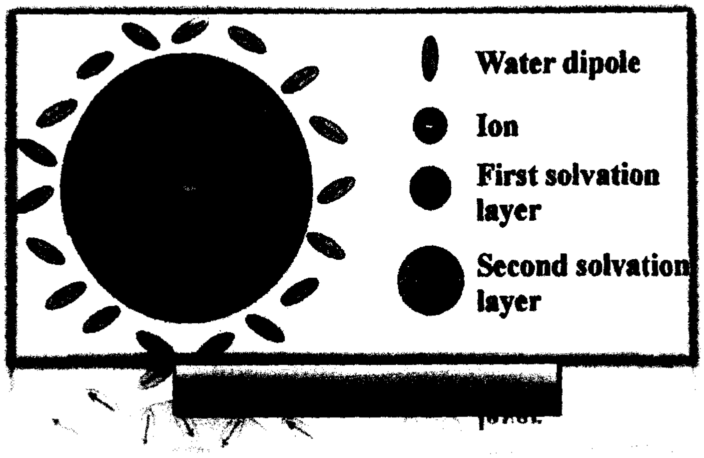
where A is a coefficient varying from 6 (in the case of perfect sticking) to 4 (in case of perfect slipping). Since the r_S values, the real dimension of the non-solvated tetraalkyl (aryl) onium ions must be constant, we have:

$$\lambda_{\pm}^{0}\eta_0 = \text{constant} \quad (147)$$

This relation has been verified using $\lambda_{\pm}^{0}$ values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i-\text{Am}_4\text{B}^-, \text{Ph}_4\text{As}^+, \text{Ph}_4\text{B}^-$ ions and for tetraalkylammonium cation starting with Et_4N^+. The relationship can be well utilized to determine $\lambda_{\pm}^{0}$ of ions in other organic solvents from the determined Λ_0 values.

II.9.4. 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, then this is called the 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.

$$-V_S = (4\pi/3)(r_S^3 - r_C^3) \qquad (148)$$

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

$$n_S = V_S/V_0 \qquad (149)$$

Assuming Stokes' relation to hold well, the ionic solvated volume can be obtained, because of the packing effects [318], from

$$V_S^0 = 4.35 r_S^3 \tag{150}$$

where V_S^0 is expressed in mol·lit^{-1} and r_S in angstroms. However, this method is not applicable to ions of medium size though a number of empirical and theoretical corrections [319-322] have been suggested in order to apply it to most of the ions.

II.9.5. 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^0 of a spherical ion of radius R_i moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

$$\lambda_i^0 = \frac{|z_i e| \hat{e} F}{6\pi\eta_0 R_i} = \frac{0.819|z_i|}{\eta_0 R_i} \tag{151}$$

where η_0 = 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:

$$\lambda_i^0 \eta_0 = 0.819|z_i|/R_i = \text{constant} \tag{152}$$

This is known as the Walden rule [323]. 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 [280], Nightingale [199] and others [324-326] 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 [327] was invoked without much success [328,329] but it has been found that:

$$\lambda_i^0 \eta^p = \text{constant} \tag{153}$$

where p is usually 0.7 for alkali metal or halide ions and p = 1 for the large ions [330,331]. Gill [315] has pointed out the inapplicability of the Zwanzig theory [332] 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:

$$r_i = |z| F^2 / (6\pi N_A \eta_0 \lambda_i^0) + 0.0103D + r_y \tag{154}$$

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 [315,332].

The dependence of Walden product on the dielectric constant led Fuoss [307] 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:

$$\lambda_{i,0}^0 = Fe|z_i| / 6\pi R_\alpha (1 + A/\varepsilon R_\infty^2) \tag{155}$$

or,

$$R_i = R_\infty + A/\varepsilon \tag{156}$$

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

Boyd [320] gave the expression:

$$\lambda_i^0 = Fe|z_i| / 6\pi\eta_0 r_i \left[1 + \left(2/27\pi\eta_0 \cdot z_i^2 e^2 \tau / r_i^4 \varepsilon_0\right)\right] \tag{157}$$

by considering the effect of dielectric relaxation in ionic motion; τ is the Debye relaxation time for the solvent dipoles. Zwanzig [321] treated the ion as a rigid sphere of radius r_i moving with a steady state viscosity, V_i, through a viscous incompressible dielectric continuum. The conductance equation suggested by Zwanzig is:

$$\lambda_i^0 = z_i^2 eF \Big/ \left\{ A_V \pi \eta_0 r_i + A_D \left[z_i^2 e^2 \left(\varepsilon_r^0 - \varepsilon_r^\infty \right) \tau / \varepsilon_r^0 \left(2\varepsilon_r^0 + 1 \right) r_i^3 \right] \right\} \tag{158}$$

where ε_r^0 and ε_r^∞ are the static and limiting high frequency (optical) dielectric constants. $A_V = 6$ and $A_D = 3/8$ for perfect sticking and $A_V = 4$ and $A_D = 3/4$ for perfect slipping. It has been found that Born's [319] and Zwanzig's [321] equations are very similar and both may be written in the form:

$$\lambda_i^0 = A r_i^3 \Big/ \left(r_i^4 + B \right) \tag{159}$$

The theory predicts [333] that λ_i^0 passes through a maximum of $27^{1/4} A/4B^{1/4}$ at $r_i = (3B)^{1/4}$. The phenomenon of maximum conductance is well known. The relationship holds good to a reasonable extent for cations in aprotic solvents but fails in case of anions. The conductance, however, falls off rather more rapidly than predicted with increasing radius. For comparison with results in different solvents, the Eq. (158) can be rearranged as [334]:

$$z_i^2 eF / \lambda_i^0 \eta_0 = A_V \pi r_i + A_D z_i^2 / r_i^3 \cdot e^2 \left(\varepsilon_r^0 - \varepsilon_i^\infty \right) \Big/ \varepsilon_r^0 \left(2\varepsilon_r^0 + 1 \right) \cdot \tau / \eta_0 \tag{160}$$

$$L^* = A_V \pi r_i + A_D z_i^2 / r_0^3 \, P^* \tag{161}$$

In order to test Zwanzig's theory, the Eq. (161) was applied for Me_4N^+ and Et_4N^+ in pure aprotic solvents like methanol, ethanol, acetonitrile, butanol and pentanol [333-338]. Plots of L^* against the solvent function P^* were found to be straight line. But, the radii calculated from the intercepts and slopes are far apart from equal except in some cases where moderate success is noted. It is noted that relaxation effect is not the predominant factor affecting ionic mobility and these mobility differences could be explained quantitatively if the microscopic properties of the solvent, dipole moment and free electron pairs were considered the predominant factors in the deviation from the Stokes' law.

It is found that the Zwanzig's 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, [334] 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 [335].

(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 [3357].

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) [310,333-342] mixtures and other aqueous binary mixtures [343-346]. To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts [320,321,347] 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 [348] 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 [349] 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 [350, 351] 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.

II.9.6. Thermodynamics of ion-pair formation

The standard Gibbs energy changes (ΔG^0) for the ion- association process can be calculated from the equation,

$$\Delta G^0 = -RT \ln K_A \tag{162}$$

The values of the standard enthalpy change, ΔH^0 nd the standard entropy change, ΔS^0 can be evaluated from the temperature dependence of ΔG^0 values as follows,

$$\Delta H^0 = -T^2\left[d\left(\Delta G^0/T\right)/dT\right]_P \tag{163}$$

$$\Delta S^0 = -T^2\left[d\left(\Delta G^0\right)/dT\right]_P \tag{164}$$

The ΔG^0 values can be fitted with the help of a polynomial of the type.

$$\Delta G^0 = c_0 + c_1(298.15 - T) + c_2(298.15 - T)^2 \tag{165}$$

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

$$\Delta G^0_{298.15} = c_0 \tag{166}$$

$$\Delta S^0_{298.15} = c_1 \tag{167}$$

$$\Delta H^0_{298.15} = c_0 + 298.15c_1 \tag{168}$$

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^0, can also be calculated using the following equation:

$$\Delta G^0 = N_A W_{\pm} \tag{169}$$

$$K_A = (4\pi N_A/1000)\int_a^R r^2 exp(2q/r - W_{\pm}/kT))\,dr \tag{170}$$

where the symbols have their usual significance. The quantity $2q/r$ is the Columbic part of the interionic mean force potential and $W_{\pm}$ is its non-columbic part. The procedure for the evaluation of the non-columbic part of the entropy and enthalpy (and ΔS^* and ΔH^* respectively) is the same as that used for obtaining ΔS^0 and ΔH^0.

II.10. 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 Schrodinger equation. Quantum mechanical approach for ion-water interactions was begun by Clementi in 1970s. 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, [20] 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 an 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 [352-356]. These models are applicable to virtually any substance composed of H, C, N, O, F, P, S, Cl, Br and/or I. The only input data required are, molecular formula, geometry, refractive index, surface tension, Abraham's a (acidity parameter) and b (basicity parameter) values, and, in the latest models, the dielectric constants. The advantage of models like SM5 series is that they can be used to predict the free energy of self-solvation to better than 1 KCl/mole. These are especially useful when other methods are not available. One can also analyze factors like electrostatics, dispersion, hydrogen bonding, etc. using these tools. They are also relatively inexpensive and available in easy to use computer codes.

A. Galindo *et al.* [357,358] 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.* [359] of the University of Barcelona, Spain, have compared several "Preferential Solvation Models" specially for describing the polarity of dipolar hydrogen bond acceptor-co solvent mixture.

II.11. Conductance - Some Recent Trends

Recently Blum, Turq and coworkers [360,363] have developed a mean spherical approximation (MSA) version of conductivity equations. Their theory starts from the same continuity and hydrodynamic equations used in the more classical treatment; however, an important difference exists in the use of MSA expressions for the equilibrium and structural properties of the electrolytic solutions. Although the differences in the derivation of the classical and MSA conductivity theories seem to be relatively small, it has been claimed that the performance of MSA equation is better with a much wider concentration range than that covered by the classical equations. However, no through study of the performance of the new equation at the experimental uncertainty level of conductivity measurement is yet available in the literature, except the study by Bianchi *et al.* [362]. They compared the results obtained using the old and new equations in order to evaluate their capacity to describe the conductivity of different electrolytic solutions. In 2000, Chandra and Bagchi [363] developed a new microscopic approach to ionic conductance and viscosity based on the mode coupling theory. Their study gives microscopic expressions of conductance and viscosity in terms of static and dynamic structural factors of charge and number density of the electrolytic solutions. They claim that their new equation is applicable at low as well as at high concentrations and it describes the cross over from low to high concentration smoothly. Debye-Huckel, Onsager and Falkenhagen expressions can be derived from this self-consistent theory at very low concentrations. For conductance, the agreement seems to be satisfactory up to 1 (M).

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