I N T R O D U C T I O N

The majority of reactions that are of chemical or biological interest occur in solution. It was previously believed that solvent merely provides an inert medium for chemical reactions. The significance of solute-solvent interactions was realised only recently as a result of extensive studies in aqueous, non-aqueous and mixed solvents[1-10].

Water is the most abundant solvent in nature. In view of its extreme importance to chemistry, biology, agriculture, geology, etc., water has been extensively used in kinetic and equilibrium studies. Inspite of such extensive studies, our knowledge of molecular interactions in water is extremely limited. Moreover, the uniqueness of water as solvent has been questioned[11,12] in recent years and it has been realised that the studies in other solvent media (non-aqueous and mixed solvents) would be of great help in understanding different molecular interactions and a host of complicated phenomena[1-10].

Extensive studies on the physical properties of different solvent systems have been made but a lamentable gap still exists. Several classifications of organic solvent systems based on their dielectric constant, organic group type, acid-base properties or association through hydrogen-bonding[10] donor-acceptor-properties[13], hard and solft acid-base principles etc have been made, as a result, the properties of different solvent systems would show a wide divergence of properties which would naturally be reflected on the thermodynamic and transport properties of electrolytes and non-electrolytes etc in these solvents. The determination of thermodynamic and transport properties of different electrolytes in various solvents would thus provide an important step in this direction. Naturally, in the development of theories, dealing with electrolyte solutions, much attention has been devoted to ion-solvent interactions which are the "controlling forces" in infinitely dilute solutions where ion-ion interactions are absent. Ion-solvent interactions or broadly solute-solvent interactions are important in understanding the physico-chemical properties of solutions. It is very difficult to suggest the forces or factors involved in the solute (or ion) solvent interactions as most of the determining factors of solute-solvent interactions remain obscure. Ion-solvent (or solute-solvent) interactions manifest themselves in all thermodynamic and transport properties of electrolytes generally obtained by extrapolation to infinite dilution. By separating these functions into ionic contributions, it is possible to determine the contributions due to cations and anions in the solute-solvent interactions. These depend on the intrinsic solvent structure and on the nature of the ions (dimension, charge, charge-distribution in case of large ions, H-bonding etc.).

One of the reasons for the intracies in solution chemistry is that the structure of the solvent molecules are not known with certainty. The introduction of an ion or solute modifies the solvent structure to an uncertain magnitude whereas the solute molecules are also modified and the interplay of forces like solute-solute, solute-solvent and solvent-solvent interactions become predominant.

though the isolated picture of any of the forces is completely unknown.

The problem of ion-solvent interactions which are closely akin to ionic solvations can be studied from different angles using almost all the available physico-chemical techniques.

Ion-solvent interactions can be studied spectroscopically where the spectral solvent shifts or the chemical shifts determine the qualitative and quantitative nature of the ion-solvent interactions. But even qualitative or quantitative apportioning of the ion-solvent interactions into the various possible factors is still an uphill task.

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

Similarly, the ion-solvent interactions can be studied using solvational approaches involving the studies of the different transport properties such as viscosity, conductance and compressibility etc of electrolytes and derive the various factors associated with ionic solvation.

We shall particularly dwell upon the different aspects of these transport properties as the present dissertation is intimately related to the studies of viscosity, conductance and compressibilities of different tetraalkyl and related salts in dipolar aprotic solvent DMSO and DMSO + H_2O mixtures.

Viscosity:

Viscosity is one of the most important transport properties used for the determination of ion-solvent interactions and studied extensively[15,16]. Viscosity is not a thermodynamic quantity, but viscosity of an electrolytic solution together with the thermodynamic property $\bar{V}_2$, partial molal volume gives much information and insight regarding ion-solvent interactions and the structures of the electrolytic solutions. The viscosity relationships of electrolytic solutions are highly complicated. There are strong electrical forces between the ions and between the ions and solvent and separation of the forces are not really possible. But from careful analysis, valid conclusions can be drawn regarding the structure and the nature of the solvation of a particular system.

The 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 therefore, increase or decrease viscosity.

If large spheres are placed in the liquid, the planes will be keyed together 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 interplanar 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. The coloumb interaction of the ions also keys the plane together and gives a $C^{\frac{1}{2}}$ dependence on concentration, but the effect is small and will be swamped at moderate concentrations[16].

The first systematic measurements of viscosities of a number of electrolyte solutions over a wide concentration range was performed byGrüneisen[17] in 1905. He noted non-linearity and a negative curvature in the viscosity concentration curves (irrespective of low or high concentrations). In 1929, Jones and Dole[18] suggested an empirical equation (1), quantitatively correlating the relative viscosities of the electrolytes with molar concentrations C,

$$\frac{\eta}{\eta_0} = 1 + AC^{\frac{1}{2}} + BC \qquad \ldots (1)$$

The equation reduces to

$$\left(\frac{\eta}{\eta_0} - 1\right)/C^{\frac{1}{2}} = A + BC^{\frac{1}{2}} \qquad \ldots (2)$$

Where A and B are constants specific to ion and the solvent. The equation is applicable equally to aqueous and non-aqueous solvent systems and used extensively. The term $AC^{\frac{1}{2}}$, originally ascribed to Grüneisen effect, arose from the long-range coulomb forces between the ions. The significance of the term had since then been realized due to the development of Debye-Hückel theory of inter-ionic attractions (1923), Falkenhagen's[20-22] theoretical calculation of the constant A using the equilibrium theory and the theory of irreversible processes in electrolytes developed by Onsager and

Fuoss[23]. The A-coefficient depends on the ion-ion interactions and can be calculated from the physical properties of solvent and solution using the Falkenhagen-Vernon[22] equation.

$$A_{Theor} = \frac{0.2577\,\Lambda_0}{\eta_0 (\varepsilon T)^{1/2} \lambda_0^+ \lambda_0^-} \left[1 - 0.6863 \left(\frac{\lambda_0^+ - \lambda_0^-}{\Lambda_0}\right)^2\right] \quad \ldots (3)$$

where Λ_0, λ_0^+ and λ_0^- are the limiting equivalent conductances of the electrolyte and the ions respectively at temperature T. ε and η_0 are the dielectric constant and viscosity of the solvent. For most solutions, both aqueous and non-aqueous, the equation is valid upto 0.1M[15,24]. At higher concentrations, the extended Jones-Dole equation (4) involving an additional constant D, originally used by Kaminsky[25] has been used by several workers[26,27].

$$\frac{\eta}{\eta_0} = 1 + AC^{\frac{1}{2}} + BC + DC^2 \quad \ldots (4)$$

The constant D cannot be evaluated properly and the significance of the constant is also not always meaningful and therefore, the equation (1) is used by most of the workers.

The plots of $(\eta/\eta_0 - 1)/C^{\frac{1}{2}}$ against $C^{\frac{1}{2}}$ for the electrolytes should give the value of A but in general the values come out to be negative or considerable scatter and deviations from linearity occur[24,28,29]. Thus, instead of determining A-values from the plots or by least square method, the A-values are generally calculated using Falkenhagen-Vernon equation (3).

A-coefficient should be zero for non-electrolytes. According to Jones and Dole, the coefficient A probably represents the stiffering effect on the solution of the electric forces between the ions which tend to maintain a space-lattice structure[18].

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 which increase or decrease the viscosities of the solvent as enumerated at the beginning also condition the increase or decrease of B-values. The factors which influence B-values are[30,31]:

(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-values.

(2) The destruction of the three dimensional structure of solvent molecules (i.e. structure breaking effect or depolymerization effect) decreases η or B-values.

(3) High molal volume and low dielectric constant yield high B-values for similar solvents.

(4) Reduced B-values are obtained when the primary solvation of ions is sterically hindered in high molal volume solvents or if either ion of a binary electrolyte cannot be specifically solvated.

Viscosities at higher concentrations:

It had been found the viscosity values at high concentrations (1M to saturation) can be represented by the empirical formula suggested by Andrade[32]

$$\eta = A \exp b/T \qquad \ldots (5)$$

A number of alternative formulations have been proposed for representing results of viscosity measurements in the high concentration range[33-38] and the equation suggested by Angell[39,40] based on an extension of the free volume theory of transport phenomena in liquids and fused salts to ionic solutions, is particularly noteworthy.

The equation is

$$\frac{1}{\eta} = A \exp\left[-\frac{k'}{N_0 - N}\right] \qquad \ldots (6)$$

where N represents the concentration of the salt in equiv. lit^{-1}, A and k' 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 Majumdar et al[41-43] introducing the limiting condition that as $N \to 0$, $\eta \to \eta_0$, the viscosity of the pure solvent. Thus, we have

$$\ln \frac{\eta}{\eta_0} = \ln \eta_{rel} = \frac{k' N}{N_0 (N_0 - N)} \qquad \ldots (7)$$

The equation (7) predicts a straight line passing through the origin for the plot of $\ln \eta_{rel}$ vs $N/(N_0-N)$, if a suitable choice for N_0 is made. The equation (7) has been tested by Majumdar et al using the data from the literature and from their own experimental results. The best choice for N_o and k' was selected by a trial and error method. The set of k' and N_o which produce minimum deviation between η_{rel} (expt) and η_{rel} (theo) was accepted.

In dilute solutions, $N \ll N_o$, we have

$$\eta_{rel} = \exp\left(k'N/N_o^2\right) \approx 1 + \frac{k'N}{N_o^2} \quad \ldots (8)$$

which is nothing but the Jone-Dole equation with the ion-ion interaction term omitted and $B = \frac{k'}{N_o^2}$. The agreement between B values determined in this way and using Jones-Dole equation has been found to be good for several electrolytes.

Further the equation (7) written in the form

$$\frac{N}{\ln \eta_{rel}} = \frac{N_o^2}{k'} - \frac{N_o}{k'} N \quad \ldots (9)$$

closely resembles Vand's equation[36] for fluidity (reciprocal for viscosity) :

$$\frac{2.5\ C}{2.3 \log \eta_{rel}} = \frac{1}{V} - QC \quad \ldots (10)$$

where C is the molar concentration of the solute and V is the effective rigid molar volume of the salt and Q is the interaction constant.

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[29,44-74]. However, the B-coefficients, as determined experimentally using Jone-Doles equation, does not give any impression regarding ion-solvent interactions unless there is some way to identify the separate contributions of cations and anions in the total solute-solvent interactions. It is well known that no physico-chemical property of the total solute can reflect the properties of the individual ions and only ionic contributions may give insight on the intrinsic nature of the solvent structure and its modification by the ions (conditioned by the dimension, charge, charge distribution, H-bonding etc.) .

Fortunately for us, the B-coefficient is purely an additive functions of ionic B-values (in absence or in presence of insignificant ionic association) as will be apparent from the fact that the B-values for pairs of salts with the same anion but different cations have constant differences.

However, the division of B-values into ionic B^{+} or B^{-} values is quite arbitrary based on some approximations or assumptions, the validity of which may be questioned.

The following methods have been used for the division of B-values into ionic components (1) Cox and Wolfenden[75] 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 mobilites.

$$B_{NaBPh_4} + B_{Ph_4PBr} - B_{NaBr} = B_{BPh_4PPh_4} \quad \ldots (14)$$

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. Thus,

a) Criss and Mastroianni[47] assumed $B_{K^+} = B_{Cl^-}$ in methanol (based on equal mobilities of ions[79]). They also adopted $B^{25}_{Me_4N^+} = 0.25$ as the initial value for acetonitrile solutions.

b) For acetonitrile solutions, Tuan and Fuoss[80] proposed the equality $B_{Bu_4N^+} = B_{Ph_4B^-}$ (15), since they thought that these ions have similar mobilities. However, according to Springer et al[81], $\lambda^{25}_{0,Bu_4N^+} = 61.4$ and $\lambda^{25}_{0,Ph_4B^-} = 58.3$ in acetonitrile.

c) Gopal and Rastogi[45] resolved the B-coefficient in N-methyl propionamide solutions, assuming (without proof) that $B_{Et_4N^+} = B_{I^-}$ (16) at all temperatures. In dimethylsulphoxide, the division of B-coefficients were carried out by Yao and Bennion[20] assuming

$$B_{[(i\text{-}Pe)_3BuN^+]} = B_{[Ph_4B^-]} = \tfrac{1}{2}B_{[(i\text{-}Pe)_3BuNPh_4B]} \quad \ldots (17)$$

at all temperatures. (tri-isopentyl-n-butyl ammonium tetraphenyl borate) wide use of this method has been made by other authors for dimethylsulphoxide[27], sulpholane[55], hexamethylphosphotriamide[59] and ethylene carbonate[82] solutions.

The methods, however, have been strongly criticized by Krumgalz[83]. According to him, any method of resolution based on the equality of equivalent conductances for certain ions suffers from the drawback that it is impossible to select any two ions for which $\lambda_{o,+} = \lambda_{o,-}$ in all solvents at proper temperatures. Thus, though $\lambda_{o,K^+} = \lambda_{o,Cl^-}$ at 25°C in methanol, but not in ethanol or in other solvents. In addition, if the mobilities of some ions are even equal at infinite dilution, but it is not necessarily true at moderate concentrations for which the B-coefficient values are calculated. Further, according to him, equality of dimensions of $(i-Pe)_3BuN^+$ or $(i-am)_3BuN^+$ and Ph_4B^- does not necessarily imply equality of B-coefficients of these ions as they are likely to be solvent and ion-structure dependent.

Krumgalz[83] 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[85,86] in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic B-values for large tetra-alkyl ammonium ions R_4N^+ (where $R > Bu$) in organic solvents are proportional to their ionic dimensions.

Thus, we have

$$B_{R_4NX} = a + br^3_{R_4N^+} \qquad \ldots (18)$$

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

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

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

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \quad \ldots (19)$$

and

$$\frac{B_{R_4N^+}}{B_{R'_4N^+}} = \frac{r^3_{R_4N^+}}{r^3_{R'_4N^+}} \quad \ldots (20)$$

The radii of the tetraalkylammonium ion have been calculated from the accurate conductometric data[87].

Gill and Sharma[70] used Bu_4NBPh_4 as a reference electrolyte. The method of resolution of B is based on the assumption, like Krumgalz, that Bu_4N^+ and Ph_4B^- ions with large R-groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constant. The ionic radii of Bu_4N^+ (5.00 Å) and Ph_4B^- (5.35 Å) have, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers. They proposed the equations

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \left(\frac{5.35}{5.00}\right)^3 \quad \ldots (21)$$

and $$B_{Bu_4NBPh_4} = B_{Ph_4B^-} + B_{Bu_4N^+} \quad \ldots (22)$$

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

$$B_{i\text{-}Am_3BuN^+} = B_{Ph_4B^-} = B_{i\text{-}Am_3BuNBPh_4}/2 \quad \ldots (23)$$

Recently, Lawrence and Sacco[71,72a] used (tetrabutyl-ammonium tetrabutylborate) Bu_4NBBu_4 and tetraphenyl phosphonium tetraphenyl borate (Ph_4PBPh_4) as reference electrolytes because the cation and anion in each case are symmetrically shaped and have almost equal Vander Waals volumes. Thus, we have,

$$\frac{B(Bu_4N^+)}{B(Bu_4B^-)} = \frac{V_w(Bu_4N^+)}{V_w(Bu_4B^-)} \quad \ldots (24)$$

$$\text{or} \quad B(Bu_4B^-) = B(Bu_4NBBu_4) \Big/ \left[1 + \frac{V_w(Bu_4N^+)}{V_w(Bu_4B^-)}\right] \quad \ldots (25)$$

A similar division can be made for the Ph_4PBPh_4 system.

Recently, Lawrence et al[72b] determined the viscosity measurement of tetraalkyl (from propyl to heptayl) ammonium bromides in DMSO and HMPT. The B-coefficients

$$[B(R_4NBr) - B(Br^-) + a\,[f_{N}(R_4N^+)]]$$

were plotted as functions of the Vander Waals volumes, stokes radii and formula weight of the cations to get $B(Br^-)$ value. The $B(Br^-)$ values thus obtained were compared with the accurately determined $B(Br^-)$ value obtained using Bu_4NBu_4B and Ph_4PPh_4B as reference salts. They concluded that the 'reference salt' method is the best available method for the division into ionic contributions. Their analysis is in agreement with the conclusions made by Thomson et al[72c,d].

Jenkins and Pritchett[88] 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 Fajans' competition principle[89] and 'volcano plots' of Morris[90]. The principle was extended to derive absolute single ion B-coefficients for alkali metals and halides in water. They also observed that $B(Cs^+) \approx B(I^-)$ suggested by Krumgalz[85] to be more reliable than $B(K^+) = B(Cl^-)$ in aqueous solutions. However, we require more data to test the validity of this method.

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

Temperature dependence of B_{ion} - values:

A regularity in the behaviour of $B_{\pm}$ and $\frac{dB_{\pm}}{dT}$ has been observed both in aqueous and non-aqueous solvents[15] and useful generalisations have been made by Kaminsky[25]. 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 coefficient of B_{ion} values increases as the ionic radius increases. The results can be summarised as follows:

(i) A and $\frac{dA}{dT} > 0$ ... (26)

(ii) $B_{ion} < 0$ and $\frac{dB_{ion}}{dT} > 0$ ... (27)

characteristic of structure breaking ions.

(iii) $B_{ion} > 0$ and $\frac{dB_{ion}}{dT} < 0$, characteristic of structure making ions.

... (28)

It is well known that an ion is surrounded by a solvation sheath and the properties of the solvents which are different from those present in the bulk structure. This is well reflected in the 'co-sphere' model of Gurney[91], A,B,C zones of Frank and Wen[92] and hydrated radius of Nightingale[77].

Stokes and Mills[15] gave an analysis of viscosity 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 competition between various effects occurring in the ionic neighbourhood. Thus,

$$\eta = \eta^0 + \eta^* + \eta^E + \eta^A + \eta^D = \eta^0 + \eta^0 (A\sqrt{c} + Bc) \quad ... (29)$$

(Jones-Dole equation)

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

$$\eta^E + \eta^A + \eta^D = \eta^0 B C \qquad \ldots (30)$$

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

Following Stokes and Mills[15] and Krumgalz[83] we can write for B_{ion}

$$B_{ion} = B_{ion}^{Einst} + B_{ion}^{Orient} + B_{ion}^{Str} + B_{ion}^{reinf} \qquad \ldots (31)$$

whereas according to Lawrence and Sacco[71],

$$B_{ion} = B_W + B_{solv} + B_{shape} + B_{ord} + B_{disord} \qquad \ldots (32)$$

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 ionic co-sphere arising from the opposing tendencies of the ion to orientate the molecules round itself centrosymmetrically and solvent to keep its own structure. (This corresponds to η^D or B_{disord}).

B_{ion}^{reinf} is the positive increment conditioned by the effect of "reinforcement of the water structure" by large tetra-alkyl-ammonium ions due to hydrophobic hydration. The phenomenon is inherent in the intrinsic water structure and absent in organic solvents.

B_V and B_{Solv} account for viscosity increases 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}^{Einst} or η^E positive). At ordinary temperatures, alignment of the solvent molecules around the inner layer also causes increase in B_{ion}^{orient} (η^A) B_{ion}^{Str} (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. But 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. $B_{ion}^{Einst} + B_{ion}$ B_{ion}^{Str} so that B is close to zero.

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

The increase in temperature will have no effect on B_{ion}^{Einst} but the orientation of solvent molecules in the secondary layer will be decreased due to increased thermal motion leading to decrease in B_{ion}^{Str}. B_{ion}^{orient} will decrease slowly with temperature as there will be less competition between the ionic field and the reduced solvent structure. The positive or negative temperature coefficient will thus depend on the change of the relative magnitudes of $B_{ion}^{reorient}$ and B_{ion}^{Str}.

It is clear that 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 zones will be disordered leading to a decrease in B_{ion} values and increase in entropy 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 clear correlation between the viscosity, entropy of solvation and temperature dependent mobility of ions. Thus, the ionic B-coefficients and 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 characters 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[76,91] 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. He Ionic-B values show a linear relationship with the partial molar ionic entropies or partial molar entropies of hydration S_h°

$$S_h^\circ = S_{aq}^\circ - S_g^\circ \qquad \ldots (33)$$

where $\bar{S}_{aq}^\circ = \bar{S}_{ref}^\circ + \Delta S^\circ,$ $\bar{S}_g^\circ$ 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 monoatomic ions by equating the entropy of the hydrogen ion ($\bar{S}_{H^+}^0$) to - 5.5 cal $mole^{-1}deg^{-1}$. Asmus[93] used the entropy of hydration to correlate ionic B-values and Nightingale[77] showed that a single linear relationship can be obtained with it for both monoatomic and polyatomic ions.

The correlation was utilised by Abraham et al[94] to assign single-ion B-coefficients so that a plot of ΔS_e^o [95,96], the electrostatic entropy of solvation or $\Delta S_{I,II}^o$ [95,96], 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 or line. There are excellent linear correlations between ΔS_e^o and $\Delta S_{I,}^o$ and the single ion B-coefficients. Both entropy criteria (ΔS_e^o and $\Delta S_{I,II}^o$) and

B-ion values indicate that in water the ions Li^+, Na^+, Ag^+ and F^- are net structure-makers, the ions Rb^+, Cs^+, Cl^-, Br^-, I' and ClO_4^- are structure breakers and K^+ is a border-line case. [In non-aqueous solvents formamide, methanol, N-methyl-formamide, dimethyl formamide, dimethyl sulphoxide and acetonitrile, all the above ions are structure-makers with the exceptions of the weak structure-breaking ion ClO_4^- in formamide and the border line cases of ClO_4^- in methanol and I' in formamide].

Thermodynamics of Viscous flow:

Assuming viscous flow as a rate process, the viscosity η can be represented as using Eyring[97] approach

$$\eta = A\, e^{E_{vis}/RT} = \left(\frac{hN}{V}\right) \exp \Delta G^{*}/RT \qquad \ldots (34)$$
$$= \left(\frac{hN}{V}\right) \exp\left(\frac{\Delta H^{*}}{RT} - \frac{\Delta S^{*}}{R T}\right)$$

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

The problem is dealt in a different way by Nightingale and Benck[98] who calculated the thermodynamics of viscous flow of salts and ions in aqueous solution. E_{vis} value can be determined using the Jones-Dole equation neglecting the $AC^{\frac{1}{2}}$ term. Thus,

$$R \frac{d \ln \eta}{d(\frac{1}{T})} = R \frac{d \ln \eta_0}{d(\frac{1}{T})} + \frac{R}{1+BC} \frac{d(1+BC)}{d(\frac{1}{T})} \qquad \ldots (35)$$

$$\Delta E^{\neq}_{\eta\,(Soln)} = \Delta E^{\neq}_{\eta_0\,(Solv)} + \Delta E^{\neq}_{V} \quad 28 \qquad \ldots (36)$$

ΔE_v can be interpreted as the increase or decrease of the activation energies for viscous flow for the pure solvents due to the presence of ions i.e. effective influence of ions upon the viscous flow of the solvent molecules. The activation energy for viscous flow in a pure liquid can be interpreted as the energy required to occupy the volume into which the molecule jumps plus that required to break the bond with other molecules if the liquid is associated. Since the number of ions are generally very very small compared to the number of the solvent molecules, the contribution of the ions to the viscous flow of solvent molecules would be generally small.

Feakins et al[99] have suggested an alternative formulation based on the transition treatment of the relative viscosity of electrolytic solution. They suggested the following expression

$$B = \frac{(\bar{V}_1^\circ - \bar{V}_2^\circ)}{1000} + \frac{\bar{V}_1^\circ}{1000} \frac{(\Delta\mu_2^{\circ\neq} - \Delta\mu_1^{\circ\neq})}{RT} \quad \ldots (37)$$

$\bar{V}_1^\circ$ and $\bar{V}_2^\circ$ are the partial molal volumes of the solvent and solute respectively; $\Delta\mu_1^{\circ\neq}$ is the free energy of activation for viscous flow per mole of the solvent which is equal to

$$\Delta\mu_1^{\circ\neq} = \Delta G_1^{\neq} = RT \ln\left(\frac{\eta_1 V_1}{hN}\right) \quad \ldots (38)$$

The quantity $(\Delta\mu_2^{\circ\neq} - \Delta\mu_1^{\circ\neq})$ is the change in the activation energy per mole of the solute on replacing one mole of solvent by one mole of solute in an infinitely dilute solution. $\Delta\mu_2^{\circ\neq}$ is the ionic activation energy at infinite dilution. $\Delta\mu_2^{\circ\neq}$ has the same qualitative significance as that of $\Delta E_{\eta}^{\neq}$ but quantitatively different.

If D is known at various temperatures, we can calculate the ionic activation entropy and the ionic activation enthalpy :

$$d(\Delta\mu_2^{\circ\neq})/dT = -\Delta S_2^{\circ\neq} \qquad \ldots (39)$$

$$\Delta H_2^{\circ\neq} = \Delta\mu_2^{\circ\neq} + T\Delta S_2^{\circ\neq} \qquad \ldots (40)$$

The separation of the thermodynamic values into ionic values are based on equality effects for the K^+ and Cl^- ions or BPh_4^- and $(i\text{-}P_e)_3BuN^+$ ions. In aqueous solution, both $T\Delta S_2^{\circ\neq}$ and $\Delta H_2^{\circ\neq}$ are positive for Li^+ i.e. the formation of the transition state is associated with bond breaking and a decrease in order whereas for Cs^+, $\Delta H_2^{\circ\neq}$ and $T\Delta S_2^{\circ\neq}$ are negative i.e. the transition is associated with bond-making and increase in order.

Effects of Shape and Size:

This aspect of the problem has been dealt extensively by Stokes and Mills[15]. The ions in solution can be regarded to be rigid spheres suspended in continuum. The hydrodynamic treatment presented by Einstein[78] leads to the equation

$$\frac{\eta}{\eta_0} = 1 + 2.5\,\phi \qquad \ldots (41)$$

in case of small volume fractions of spherical particles where ϕ is the volume fraction occupied by the particles.

Modifications of the equation have been proposed by (i) Sinha[100] on the basis of departures from spherical shape and (ii) Vand[36] on the basis of the dependence of the flow patterns around the neighbouring particles at higher concentrations. However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monoatomic cations). Thus, we have from (1)

$$2.5\,\phi = A\sqrt{C} + BC \qquad \ldots (42)$$

Since $A\sqrt{C}$ term can be neglected in comparison with BC and $\phi = c\bar{V}_i$ where $\bar{V}_i$ is the partial molal volume of the ion. We get

$$2.5\,\bar{V}_i = B \qquad \ldots (43)$$

In the ideal case, the B-coefficient is a linear function of the solute partial molal volume ($\bar{V}_i$) with slope equal to 2.5.

The $B_\pm$ can be equated to

$$B_\pm = 2.5\bar{V} = 2.5 \times \frac{4}{3}\pi \frac{R_\pm^3 N}{1000} \qquad \ldots (44)$$

assuming that the ions behave like rigid spheres with an effective radii, $R_\pm$ moving in a continuum. $R_\pm$ calculated using the equation (44) 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 Einstein's equation[101]

$$B_{\pm} = \frac{2.5}{1000} (V_i + n_b V_s) \quad \ldots (45)$$

where V_i is the molar volume of the bare ion, V_s the molar volume of the solvent.

The equation (45) has been used by a number of workers to study the nature of solvation and solvation number.

Thus, it is apparent that the B_{ion}^{Einst} can be easily calculated leading to the determination of structural contributions to B_{ion}^{Str} as manifested in the change of solvation of ions.

Studies in mixed solvents:

Viscosity measurementsin mixed solvents are very few. But the viscosity measurements in mixed solvents may well throw much light on the nature of the solvation and ion-solvent interactions. In fact, in cases of binary mixtures the study of B-coefficients of electrolytes can provide useful information as regards to the structural changes in water when the co-solvent is added. In order to do this, it is worth obtaining the ionic values of the B-coefficients of the salts in mixed solvents. It would thus be possible to calculate the $B_{\pm}$ coefficients of transfer, defined as

$$\Delta B_{\pm} = B_{\pm} \text{(water + co-solvent mixtures)} - B_{\pm} \text{(water)} \quad \ldots (46)$$

Viscosity measurements in mixed solvents have been carried out in recent years[53,61-67].

Conductance:

Conductance measurement is one of most accurate and widely used physical methods for investigation of electrolyte solutions[102,103]. 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 most applicable. Fortunately for us accurate theories of electrolytic conductance are availble to explain the results even upto a concentration limit of kd (k = Debye-Huckel length, d = density of solution). Recent development of experimental technique provides an accuracy to the extent 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.

Two types of useful information can be obtained from conductance measurements

i) the mobility u, the velocity per unit field strength with which the ions move through solution.

ii) the variation of electrical mobility with concentrations.

These information together with theory enable us to calculate thermodynamic association or dissociation constants, ion-size parameters, solvation number, etc.

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[109-110]. The details are omitted for space economy.

Conductance measurements give us equivalent conductances of solutions which are dependent upon solvent, temperature, pressure and the strength of the electrical field.

The solvent affects conductance due to its viscosity (resists the motion of ions), dielectric constant (controls the effective field strength and interionic potential affecting ion velocities, attraction between ions thereby the extent of ion-pairing) and its specific interactions with ions (affecting both mobility and association).

Variation of temperature or pressure changes the viscosity, dielectric constant and density of the solvent. In addition, temperature is proportional to the thermal energy of both ions and solvent molecules and thus affects interactions among them. High pressure decreases free volume and forces the solution components closer together, thus changing interactions among them.

King[111] stressed the importance of the following aspects

i) Accurate temperature control — A temperature control of 0.005° is required for a precision of 0.01%.

Oil bath rather than water bath should be used to avoid capacitance coupling between the leads of electrodes, the solution and the bath,

ii) Exceptional purity of solute and solvents.

iii) Avoidance of polarisation errors and precision of the electrical measurements.

The important aspects such as preparation of solutions, bridges and conductance cells have been emphasised by a number of workers. The theory and design of alternating current bridges have been discussed in details by Jones and Joseph, etc[112,113]. Shedlovsky[106], Evans and Matesich[102].

Since the conductometric method primarily depends on the mobility of ions, it can be suitably utilised to determine the dissociation constants of weak acids and association constants of electrolytes in aqueous, mixed and non-aqueous solvents. The conductometric method in conjunction with viscosity measurements give us much information regarding the ion-ion and ion-solvent interactions.

The study of conductance measurements were persued vigorously both theoretically and experimentally during the last fifty years and a number of important theoretical equations have been derived. We shall dwell briefly on some of these aspects and our discussion will be limited to the studies in non-aqueous and mixed solvents.

The studies on the conductance of ionophones (completely dissociated in solutions) and ionogens (consisting of neutral molecules that yield ions by reacting with suitable solvents)[114,115] as a function of concentration gives the conductance at infinite dilution, the dissociation constants of ionogens, the association constants of ionophores and information about the structure of the solutions in the vicinity of the ion[109].

The successful application of the Debye-Hückel theory of interionic attraction was made by Onsager[116] in deriving the Kohlrausch's equation

$$\Lambda = \Lambda^0 - S\sqrt{C} \qquad \ldots (47)$$

where
$$S = \alpha \Lambda^{0} + \beta \qquad \ldots (48)$$

$$\alpha = \frac{(ze)^{2} k}{3(2+\sqrt{2})\varepsilon_{r} k T c^{\frac{1}{2}}} = 82.0460 \times 10^{4} \frac{z^{3}}{(\varepsilon_{r} T)^{3/2}} / mol^{-\frac{1}{2}} l^{\frac{1}{2}} \qquad \ldots (49)$$

and
$$\beta = \frac{z^{2} e F k}{3 \pi \eta c^{\frac{1}{2}}} = 82.487 \frac{z^{3}}{\eta (\varepsilon_{r} T)^{\frac{1}{2}}} / \Omega^{-1} cm^{2} mol^{-\frac{3}{2}} l^{\frac{1}{2}} \qquad \ldots (50)$$

η = viscosity in poise.

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[117]. In the subsequent years, Pitts (1953)[118] and Fuoss and Onsager (1957)[107,119] 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[117] from that obtained using Pitt's theory and the derivation of the Fuoss-Onsager equation was questioned[103,120,121]. The observation was confirmed by Fuoss-Hsia[122]. The original F.O. equation was modified by Fuoss and Hsia[122] who recalculated the relaxation field, retaining the terms which had previously been neglected. The equation usually employed is of the form[103]

$$\Lambda = \Lambda^{0} - \frac{\alpha \Lambda^{0} c^{\frac{1}{2}}}{(1+ka)(1+ka/\sqrt{2})} - \frac{\beta c^{\frac{1}{2}}}{1+ka} + G(ka) \qquad \ldots (51)$$

where G(Ka) is a complicated function of the variable. The simplified form

$$\Lambda = \Lambda^0 - S\sqrt{c} + Ec\ln c + J_1 c - J_2 c^{3/2} \quad \ldots (52)$$

is generally employed in the analysis of experimental resultswhere

$$ba = \frac{(ze)^2}{\varepsilon_r kT} = 16.7099 \times 10^4 \frac{Z^2}{\varepsilon_r T} / A^0 \quad \ldots (53)$$

$$k = 50.2916 \frac{Z\sqrt{c}}{(\varepsilon_r T)^{1/2}} / A^{0\,-1} \quad \ldots (54)$$

$$E = E_1 \Lambda^0 - E_2 \quad \ldots (55)$$

$$E_1 = \frac{(kab)^2}{24c} = 2.94257 \times 10^{12} \frac{Z^6}{(\varepsilon_r T)^3} / mol^{-1} \quad \ldots (56)$$

$$E_2 = \frac{kab\beta}{16c^{\frac{1}{2}}} = 4.33244 \times 10^7 \frac{Z^5}{(\varepsilon_r T)^2 \eta} / \Omega^{-1} cm^2 mol^{-2} \ldots (57)$$

The J_1 and J_2 can be written as

$$J_1 = 2E_1\Lambda^0 \left[\ln\left(\frac{ka}{c^{\frac{1}{2}}}\right) + \Delta_1 \right] + 2E_2 \left[\Delta_2 - \ln\left(\frac{ka}{c^{\frac{1}{2}}}\right) \right] \quad \ldots (58)$$

$$J_2 = \frac{kab}{c^{\frac{1}{2}}} \left[4E_1\Lambda^0 \Delta_3 + 2E_2\Delta_4 \right] - \Delta_5 \quad \ldots (59)$$

The values of Δ_i terms are different for different theoretical treatments derived by Pitts[123], Fuoss and Hsia[124] and Kraeft[125]. We are giving the values for Fuoss and Hsia treatment

$$\Delta_1 = \frac{1}{b^3} [2b^2 + 2b - 1] + 0.90735 \qquad \ldots (60)$$

$$\Delta_2 = \frac{22}{3b} + 0.01420 \qquad \ldots (61)$$

$$\Delta_3 = \frac{0.9571}{b^3} + \frac{1.1187}{b^2} + \frac{0.1523}{b} \qquad \ldots (62)$$

$$\Delta_4 = \frac{1}{b^3} [0.5738b^2 + 7.0572b - \frac{2}{3}] -0.6467 \qquad \ldots (63)$$

$$\Delta_5 = \frac{E_2 \beta}{\Lambda_0} [\frac{4}{3b} - 2.2194] \quad (-1.5527 \frac{E_2}{\Lambda_0}) \qquad \ldots (64)$$

b is equal to the Bjerrum distance.

However, it has been found that all the equations are incomplete and in some cases fail to fit experimental data. Some of these results have been discussed elaborately by Fernandez-Prini[103]. Further correction of the equation (52) was made by Fuoss and Accascina[107]. They took into consideration of the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation becomes

$$\Lambda = \Lambda^0 - S\sqrt{c} + Ec \ln c + J_1 c - J_2 c^{3/2} - B\Lambda_0 c \qquad \ldots (65)$$

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[126].

Ion -association:

The equation (65) as given above successfully represent the behaviour of completely dissociated electrolytes. The plot of Λ against $C^{\frac{1}{2}}$ (limiting Onsager equation) are used to assign the dissociation or association of electrolytes. Thus, if Λ^{o} (experimental) is greater than Λ^{o} (theoretical) i.e. if positive deviations occur (ascribed to short-range hard-core repulsive interaction between ions), the electrolyte may be regarded as completely dissociated but if negative deviations ($\Lambda^{o}_{expt} < \Lambda^{o}_{theo}$) or positive deviations from the Onsager limiting tangent -($\alpha\Lambda_o + \beta$) occur, the electrolytes 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^{o} (expt.) and Λ^{o} (theo) would be considerable with increasing association[127].

Conductance measurements helps us to determine the values of the ion-pair association constants K_A for the process

$$M^{z+} + A^{z-} \rightleftharpoons MA \qquad \ldots (66)$$

where

$$K_A = \frac{1 - \alpha}{\alpha^2 c \, \gamma_{\pm}^2} \qquad \ldots (67)$$

and

$$\alpha = 1 - \alpha^2 c \, K_A \gamma_{\pm}^2 \qquad \ldots (68)$$

For strong electrolytes, the constant K_A and Λ^0 has been determined using Fuoss-Kraus equation[128] or Shedlovsky's equation[129].

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda^0} + \frac{K_A}{(\Lambda^0)^2} \cdot \frac{c\gamma_\pm^2 \Lambda}{T(z)} \qquad \dots (69)$$

where $J(z) = F(z)$ (Fuoss -Kraus) and $\frac{1}{T(z)} = S(z)$ (Shedlovsky)

$$F(z) = 1 - z\left(1 - z\left(1 - \right)^{-\frac{1}{2}}\right)^{-\frac{1}{2}} \qquad \dots (69a)$$

and $$\frac{1}{T(z)} \equiv S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \dots \qquad \dots (69b)$$

The plot of $T(z)/\Lambda$ against $c\gamma_\pm^2\Lambda/T(z)$ should be a straight line having $\frac{1}{\Lambda^0}$ for its intercept and $K_A/(\Lambda^0)^2$ for its slope. When K_A is large, there will be considerable uncertainty in the determined values of Λ^0 and K_A from (69). The Fuoss-Hsia conductance equation for associated electrolytes is given by

$$\Lambda = \Lambda^0 - S\sqrt{(\alpha c)} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A \Lambda \gamma_\pm^2 (\alpha c) \qquad \dots (70)$$

The equation was modified by Justice[130]. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations

$$\Lambda = \alpha\left(\Lambda^0 - S\sqrt{(\alpha c)} + E(\alpha c)\ln(\alpha c) + J_1(R)\alpha c - J_2(R)(\alpha c)^{3/2}\right) \qquad \dots (71)$$

$$(1-\alpha)/\alpha^2 c\, \gamma_\pm^2 = K_A \qquad \dots (72)$$

$$\ln \gamma_{\pm} = -Kq^{1/2}/(1+KR\sqrt{\alpha c}) \quad \ldots (73)$$

The conductance parameters are obtained from a least square treatment after setting

$$R = q = \frac{e^2}{2\varepsilon kT} \quad \ldots (74)$$

(Bjerrum's critical distance).

According to Justice, the method of fixing the J-coefficient by setting $R = q$ clearly permits a better-defined value of K_A to be obtained. Since the equation (71) is a series expansion truncated at the $c^{3/2}$ term, it would be preferable that the resulting errors be absorbed as much as possible by J_2 rather than by K_A, whose theoretical interest is greater as it contains the information concerning short-range cation-anion interaction.

From the experimental values of the association constant K_A, one can use two methods in order to determine the distance of closest approach a^o of two free ions to form one ion-pair. The following equation has been proposed by Fuoss[131]

$$K_A = (4\pi N a^3/3000)\exp(e^2/a\varepsilon kT) \quad \ldots (75)$$

In some cases, the magnitude of K_A was too small to permit a calculation of a^o. The distance parameter was finally determined from the more general equation due to Bjerrum[132]

$$K_A = (4\pi N/1000)\int_0^{r=q} r^2 \exp(z^2e^2/r\varepsilon kT)\,dr \quad \ldots (76)$$

The equation neglects 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 utilised by Bouheret[133].

Ion-size parameter and ionic association

The equation (65) can be written as

$$\Lambda' = \Lambda + S\sqrt{c} - Ec \log c = \Lambda^0 + (J - B\Lambda^0)c = \Lambda^0 + J'c \qquad \ldots (82)$$

(with J_2 term omitted).

Thus, a plot of Λ' vs C gives a straight line with Λ^0 as intercept and J' or $(J-B\Lambda^0)$ as slope. Assuming B to be negligible, a^0 values can be calculated from J'. The a^0 values obtained by this method in DMSO were much smaller[127] than would be expected from sums of crystallographic radii. One of the reasons attributed to it is ion-solvent interactions which 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^0 values (much in conformity with the crystallographic radii) of alkali metal salts (having ions of high surface charge density) in sulpholane. The viscosity correction (which should be $B\Lambda C$ rather than $B\Lambda^0 C$) leads to a larger values of a^0[138], still the agreement is poor. However, little of real physical significance may be attached to the distance of closest approach derived from J[139].

For slightly associated salt, the slope of the Fuoss-Onsager equation, after correcting for viscosity, becomes $J-K_a\gamma^2\Lambda^\circ$ and Fuoss[140] has shown that an unattainable precision of ± 0.001% would be required to resolve the two terms. If we assume a 'reasonable' value for the ion-size parameter, we could calculate J and from the corrected slope obtain a rough value of the association constant[127].

Fuoss[134] in 1975 proposed a new conductance equation. He[134] subsequently put forward another conductance equation (in 1978) which replaces the old equations suggested by Fuoss and co-workers. He classified the ions of an electrolytic solutions in one of the three categories : (1) those which find 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 which form a cage around the pairs.

(2) Those with overlapping Gurney co-spheres (solvent separated pairs). For these $r_{ij} = (a+ns)$ where n is generally one but may be 2,3 etc; s is the diammeter of a sphere corresponding to the average volume (actual plus free) per solvent molecule, contact pairs form by a sequence of ion-solvent site interchanges inside the R-spheres, until two ions of opposite charge become nearest neighbours.

(3) Those which find no other unpaired ion in a surrounding sphere of radius R, where R is the diameter of the co-sphere (unpaired ions).

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

$$A^+ + B^- \rightleftharpoons (A^+ \cdots\cdots B^-) \rightleftharpoons A^+B^- \rightleftharpoons AB \quad \cdots (77)$$

Solvent-separated Pair   Contact Pair   Neutral Molecule

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

The equilibrium constants for (77) are

$$K_R = (1-\alpha)(1-\gamma)/C\gamma^2 f^2 \quad \text{---- (78a)}$$

$$K_S = \alpha/1-\alpha = \exp(-E_S/kT) = e^{-\varepsilon} \quad \text{---- (78b)}$$

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 calculable 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 measured in units kT.

Now, $$1 - \alpha = 1/(1 + K_S) \quad \cdots (78c)$$

and the conductometric pairing constant is given by

$$K_\Lambda = (1-\gamma)/c\gamma^2 f^2 = K_R/(1-\alpha) = K_R(1+K_S) \quad \cdots (79)$$

The equation determines the concentration of 'active ions' which 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 felt 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 all be reproduced by theoretical functions of the form

$$\Lambda = p\left[\Lambda_o\left(1+\Delta X/X\right) + \Delta\Lambda_e\right] \qquad \ldots (80)$$

$$= p\left[\Lambda^o\left(1+RX\right) + EL\right] \qquad \ldots (80a)$$

which is a three parameter equation $\Lambda = \Lambda(c, \Lambda_o, R, E_S)$. $\Delta X/X$ (<0, the relaxation field RX) and $\Delta\Lambda_e$ (<0, the electrophoretic counter current, EL) are long-range effects due to electrostatic interionic forces and p is the fraction of solute which contributes to conductance current. R is the diameter of the Gurney co-sphere. The parameter K_S (or E_S) is a catch-all for all short-range effects.

$$p \approx 1 - \alpha(1-\gamma) \qquad \ldots (80b)$$

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

$$\Lambda = \gamma\left[\Lambda^o\left(1+\Delta X/X\right) + \Delta\Lambda_e\right] \qquad \ldots (80c)$$

The equilibrium constant for the effective reaction

$A^{+} + B^{-} \rightleftharpoons AB$ is then

$$K_{\Lambda} = (1-\gamma)/c\gamma^{2}f^{2} \approx K_{R}K_{S} \qquad \text{... (80d)}$$

because $K_S \gg 1$.

The parameters and the variables are related by the set of equations

$$\gamma = 1 - K_{R}\,c\gamma^{2}f^{2}/(1-\alpha) \qquad \text{... (81)}$$

$$K_{R} = (4\pi NR^{3}/3000)\exp(\beta/R) \qquad \text{... (81a)}$$

$$-\ln f = \beta k/2(1+kR), \quad \beta = \frac{e^{2}}{DkT} \qquad \text{... (81b)}$$

$$k^{2} = 8\pi\beta\gamma n = \pi\beta N\gamma c/125 \qquad \text{... (81c)}$$

$$-\varepsilon = \ln[\alpha/(1-\alpha)] \qquad \text{... (81d)}$$

The details of the calculations are presented in the 1978 paper. The short comings of the previous equations have been rectified in the present equation which is more general than the previous equations and can be used in the higher concentration regions (0.1 N in aqueous solutions).

Limiting Equivalent Conductances:

The limiting equivalent conductance of an electrolyte can be easily determined from the theoretical equations and experimental observations. At infinite dilutions, the motion of an ion is limited solely by the interactions with the surrounding solvent molecules as the ions are infinitely apart. Under these conditions, the validity of Kohlrausch's law of independent migration of ions is almost axiomatic. Thus,

$$\Lambda^{o} = \lambda^{o}_{+} + \lambda^{o}_{-} \quad \text{... (83a)}$$

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

i.e

$$\lambda^{o}_{+} = t_{+}\Lambda^{o} \text{ and } \lambda^{o}_{-} = t_{-}\Lambda^{o} \quad \text{... (83b)}$$

Thus, from the accurate value of λ^{o} of ions, it is possible to separate the contributions due to cations and anions in the solute-solvent interactions[141]. However, accurate transference number determinations are limited to few solvents only. Spiro[142] and more recently Krumgalz[143] have made extensive reviews on the subject.

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

The methods as have been summarized by Krumgalz[143], are :

i) Walden equation[144]

$$(\lambda_{o,\pm})_{acetone} \cdot \eta_{o\,acetone} = (\lambda_{o,\pm})_{water} \cdot \eta_{o\,water} \quad \text{.. (84a)}$$

ii) $\lambda_{o,Pic^-} \cdot \eta_o = 0.267$ ⋮ [144,145] based on ⋮ $\Lambda^o_{,Et_4NPic} \cdot \eta_o = 0.563$ .. (84b)

$\lambda_{o,Et_4N^+} \cdot \eta_o = 0.296$

Walden considered the products to be independent of temperature and solvent. However, the Λ_{o,Et_4NPic} 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) $\lambda^{25}_o, Bu_4N^+ = \lambda^{25}_o, BPh_3F^-$ (based on the equality of the ... (85)

Λ^{25}_o Bu_4NBPh_3F and Λ^{25}_o $Bu_4NB(OH)Ph_3$ which is obviously wrong[146])

.. (86)

(iv) $\lambda^{25}_o, Me_3OctdN^+ = \lambda^{25}_o, OctdSO_4^-$. But this is not realised in practice[147] ... (87)

(v) $\lambda^{25}_o, Bu_4N^+ \cdot \eta_o$ [148-153] = 0.208 ± 0.009; 0.206 ± 0.008; 0.206; 0.209; 0.201; 0.233 ... (88)

But from precise transference number measurements, we obtain $\lambda^{25}_o, Bu_4N^+ \cdot \eta_o = 0.213 \pm 0.002$ and the method cannot be used for splitting Λ°-values.

(vi) λ_{o}^{25}, Me_3PhN^{+} = λ_{o}^{25}, $PhSO_3^{-}$ [154], The equality is observed in some solvents but not in others.

... (89)

(vii) λ_{o}^{25}, Bu_4N^{+} = λ_{o}^{25}, Ph_4B^{-} [155] ... (90)

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

(viii) λ°, Ph_4As^{+} = λ°, Ph_4B^{-} [156] ... (91)

may be applicable for the equal division of ΔG^{o}_{tr} (Ph_4AsBPh_4) but the method is not applicable to obtain the limiting equivalent conductances.

(ix) λ_{o}^{25}, Bu_4N^{+} = λ_{o}^{25}, Bu_4B^{-} [157] ... (92)

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^{-}. But the method could not be checked due to lack of accurate transference data.

(x) The equation suggested by Gill [158,158(a)]

$$\lambda_{o}^{25},\ R_4N^{+} = ZF^2 / 6\pi N \eta_o \left[r_i - (0.0103\, \varepsilon_o + r_y) \right] \quad \ldots (93)$$

z and r_i = charge and crystallographic radius of proper ion.

η_o and ε_o = solvent viscosity and static dielectric constant of the medium.

r_y = adjustable parameter taken equal to 0.85Å and 1.13Å for dipolar non-associated solvents and for hydrogen-bonded and other associated solvents.

However, large discrepancies were observed between the experimental and calculated values[143]. In a recent paper[143(a)], Krumgalz examined the Gill's approach more critically using conductance data in as many as 11 solvents and found the method reliable in three solvents e.g. buten-1-ol, acetonitrile and nitromethane.

(xi) λ_o^{25}, $i\text{-}Am_3BuN^+$ = λ_o^{25}, Ph_4B^- [159] ... (94)

It has been found from transference measurements that the λ_o^{25}, $i\text{-}Am_3BuN^+$ and λ_o^{25}, Ph_4B^- values differ from one another only by 1%.

(xii) λ_o^{25}, $i\text{-}Am_4N^+$ = λ_o^{25}, $i\text{-}Am_4B^-$ [160] ... (95)

The equality is not proved.

(xiii) λ_o^{25}, Bu_4N^+ = 1.08 λ_o^{25}, $i\text{-}Am_4N^+$ [160] ... (96)

The value differs from solvent to solvent.

(xiv) λ_o^{25}, Ph_4B^- = 1.01 λ_o^{25}, $i\text{-}Am_4B^-$ [160] ... (97)

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

(xv) $$\left(\lambda_{o}^{25},\ i\text{-}Am_3BuN^{+}\ \eta_o\right)_{n\text{-}ProH,\ n\text{-}BuOH} = \left(\lambda_{o}^{25},\ i\text{-}Am_3BuN^{+}\cdot\eta_o\right)^{161}_{EtOH} \quad \ldots (98)$$

$$\left(\lambda_{o}^{25},\ Hept_4N^{+},\ \eta_o\right)_{n\text{-}ProH,\ n\text{-}BuOH} = \left(\lambda_{o}^{25},\ Hept_4N^{+}\ \eta_o\right)^{161}_{EtOH} \quad \ldots (99)$$

The methods (xi), (xiv) and (xv) are regarded to be the methods which can give correct single ion values for any organic solvent[143].

Krumgalz[143] suggested a method for determining the limiting ion conductances in organic solvents or organic solvent mixtures. The method is based on the fact that large tetraalkyl (aryl) onium ions are not solvated in organic solvents in the kinetic sense (i.e. the mobility or concentration of solvent molecules around the ions is equal to the corresponding values in the body of the solvent, which are perturbed by the influence of foreign particles) due to impossibility of the formation of donor-acceptor complexes of the ions with the solvent molecules and the extremely weak electrostatic interactions between solvent molecules and the large ions with low surface charge density. The phenomenon of non-solvation is confirmed by N.M.R. measurement and is utilised as a suitable model for apportioning Λ^{0} values into ionic components for non-aqueous electrolyte solutions.

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

$$r_s = \frac{|z|\,F^2}{A\pi N\eta_o\lambda_{o,\pm}} \quad \ldots (100)$$

where A is a coefficient varying from 6 (in the case of perfect sticking) to 4 (in the 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

$$\lambda^{\circ}_{\pm} \eta_{o} = \text{Constant} \qquad \ldots (100a)$$

This relation has been verified using $\lambda^{\circ}_{\pm}$ values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i\text{-}Am_4B^-$, Ph_4As^+ and Ph_4B^- ions and for tetra-alkylammonium cations starting with $n\text{-}Pr_4N^+$. The relationship can be well utilised to determine $\lambda_{o,\pm}$ of ions in other organic solvents from the determined Λ° values.

Solvation Number[141]

If the limiting conductance of the ion i of charge z_i is known, the effective radius of the solvated ion can easily be determined from the Stokes law. The volume of the solvation shell Vs can be written as

$$V_s = \frac{4\pi}{3}\left(r_s^3 - r_c^3\right) \qquad \ldots (101)$$

where r_c is the crystal radius of the ion. n_s would then be obtained from

$$n_s = \frac{V_s}{V_o} \qquad \ldots (102)$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects[162] from

$$V_s^{\circ} = 4.35r_s^3 \qquad \ldots (103)$$

where V_s° is expressed in mol/litre and r_s in angstroms. However, the method of determination of solvation number is not applicable to ions of medium size though a number of empirical[22,77,108] and theoretical corrections[163-166] have been suggested to make the method general.

Stokes' law and Walden's Rule

The limiting conductance λ_i° of an spherical ion of radius R_i moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

$$\lambda_i^{\circ} = \frac{|z_i e|\tilde{e}F}{6\pi\eta_0 R_i} = \frac{0.819|z_i|}{\eta_0 R_i} \qquad \ldots (104)$$

where η_0 = macroscopic viscosity by the solvent in poise, R_i 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

$$\lambda_i^{\circ}\eta_0 = \frac{0.819|z_i|}{R_i} = \text{Constant} \qquad \ldots (105)$$

This is known as Walden's rule[167]. The effective radii obtained using the equation can be used to obtain solvation number. The failure of the Stokes' radii to give the effective size of the solvated ions for small ions is generally ascribed to the inapplicability of Stokes' law to molecular motions.

Robinson and Stokes[108], Nightingale[77] and others[168-170] plotted r_{eff}/r_s versus r_s, r_{eff} versus r_s and r_x versus r_s

where r_s is Stokes' radius, r_{eff} = effective radius of ion in solution which is equal to the crystal radii r_x of the large and unsolvated tetraalkylammonium ion and obtained by calibration curves for each solvent for correcting the Stokes' radii of ions. 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[171] was invoked without much success[172,173] but it has been found $\lambda_i^o \eta^p$ = constant (105a), where p is usually 0.7 for alkali metal or halide ions and p = 1 for the large ions[174,175].

Attempts to explain the change in the Stokes' radius R_i has been made. The apparent increase in the real radius r had been attributed to ion-dipole polarisation and the effect of dielectric saturation on R. The dependence of the Walden product $\Lambda^o \eta_o$ on the dielectric constant led Fuoss to consider the effect of the electrostatic forces on the hydrodynamics of the system, considering the excess frictional resistance caused by the dielectric relaxation in the solvent caused by ionic motion, Fuoss proposed the relation

$$\lambda_{i,o}^o = \frac{\bar{F} e |z_i|}{6\pi R_\infty (1 + A/\varepsilon R_\infty^2)} \qquad \ldots (106)$$

or

$$R_i = R_\infty + \frac{A}{\varepsilon} \qquad \ldots (107)$$

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

Boyd[164] gave the expression

$$\lambda_i^\circ = \frac{Fe|z_i|}{6\pi\eta_0 r_i}\left[1 + \frac{2}{27}\frac{1}{\pi\eta_0}\frac{z_i^2 e^2 \tau}{r_i^4 \varepsilon_0}\right] \quad \ldots (108)$$

considering the effect of dielectric relaxation on ionic motion τ is the Debye relaxation time for the solvent molecules.

Zwanzig[165] treated the ion as a rigid sphere of radius r_i moving with a steady state velocity v_i through a viscous incompressible dielectric continuum. The conductance equation suggested by Zwanzig is

$$\lambda_i^\circ = \frac{z_i^2 e F}{A_v \pi \eta_0 r_i + A_D\left[z_i^2 e^2(\varepsilon_r^\circ - \varepsilon_r^\infty)\tau / \varepsilon_r^\circ(2\varepsilon_r^\circ + 1) r_i^3\right]} \quad \ldots (109)$$

$\varepsilon_r^\circ, \varepsilon_r^\infty$ are the static and the limiting high-frequency (optical) dielectric constants, $A_v = 6$ and $A_D = \frac{3}{8}$ for perfect sticking and $A_v = 4$ and $A_D = \frac{3}{4}$ for perfect slipping,

$$\text{or} \quad \lambda_i^\circ = A r_i^3 / (r_i^4 + B) \quad \ldots (110)$$

The theory predicts[177] that λ_i° 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 of results in different solvents, the equation can be rearranged as[178]

$$\frac{z_i^2 eF}{\lambda_i^\circ \eta_\circ} = A_v \pi r_i + \frac{A_D z_i^2}{r_i^3} \cdot \frac{e^2(\varepsilon_r^\circ - \varepsilon_r^\infty)}{\varepsilon_r^\circ(2\varepsilon_r^\circ + 1)} \cdot \frac{T}{\eta_\circ} \quad \text{... (111)}$$

or

$$L^* = A_v \pi r_i + \frac{A_D z_i^2}{r_i^3} \cdot P^* \quad \text{... (112)}$$

In order to test Zwanzig's theory the equation (112) was applied to methanol, ethanol, acetonitrile, butanol and pentanol solutions where accurate conductance and transference data are available[177-182,161]. All the plots were found to be straight lines. But the radii calculated from the intercepts and slopes are far apart from equal except in some cases were moderate success is noted. It is noted that the relaxation effect is not the predominant factor affecting ionic mobilities and that these mobility differences could be explained qualitatively if the microscopic properties of the solvent, dipole moment and free electron pairs were considered the predominant factors in the deviation from Stokes's law[141].

It is noted that the Zwanzig theory is successful for large organic cations in aprotic media where solvation is likely to be minimal 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[183] e.g.

1) It does not allow for any correlation in the reorientation of the solvent molecules as the ion passes by and this may be the reason why the equations do not apply to hydrogen bonded solvents[184].

2) 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 conductances than the fastest cations[183].

The Walden product in case of mixed solvents do not show any constancy but the Walden product show a maximum in case of DMF+H_2O and DMA+H_2O[135-137] mixtures and other aqueous binary mixtures[185-188]. To derive expressions for the variation of the Walden product with the composition of mixed polar solvents, various attempts[164,165,189] has 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 as : (1) it is difficult to include all types of interactions between ions as well as solvents in a single mathematical expression; (2) it is not possible to account for some specific properties of different kinds of ions and solvent molecules[135]. Ions moving in a dielectric medium experience a friction force due to dielectric loss arising from ion-solvent interactions with the hydrodynamic force. Zwanzig's expression though account for a change in Walden product with solvent composition but does not account for the maxima. Hemmes[190] suggested that the major deviations in the Walden product is due to the variation of the electrochemical equilibrium between ions and solvent molecules with the composition of mixed polar solvents. In cases where more than one type of solvated complexes are formed, there should be a maximum and/or a minimum in the Walden product. This is supported from experimental observations. Habbard and Onsager[191] have developed the kinetic theory of ion-solvent interaction within the framework of continuum mechanics where the concept of kinetic polarisation deficiency has been introduced. Lal Bahadur and Ramanamurti[135-137] explained the variation of Walden product (in DMF+H_2O and DMA+H_2O mixtures) on the basis of hydrophobic dehydration of ions due to co-solvent DMF or DMA giving excess mobility of ions producing a maximum in Walden product in the water rich region whereas solvation of ions with DMF or DMA will be more effective in the DMF or DMA rich region resulting in further decrease of Walden product.

However, quantitative expression is still awaited. Further improvements naturally must be in terms of (1) sophisticated treatment of dielectric saturation, (2) specific structural effects involving ion-solvent interactions.

<u>Compressibility Methods</u>[198-201]

Another important method for the determination of ion-solvent interactions is based on compressibility method. The compressibility method may well be utilised to determine the solvation number of ions[192-201].

The compressibility is defined by

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \ldots (113)$$

Under the influence of pressure, the structure of the solvent molecules break down and the interstitial spaces are filled up so that the volume decreases.

Passynski[202] tried to explain the decrease in compressibility of electrolyte solutions with increasing concentration. He assumed that in presence of an electrolyte, the solvent molecules are firmly held and fully compressed by the electrical forces of the ions of the electrolyte. The phenomenon is known as 'electrostriction'. Thus, the solvent molecules in the 'primary solvation shells' of the ions are rendered incompressible.

Passynski[202] related the adiabatic compressibilities of solution β_{soln} and that of the solvent β_{soln} by the equation

$$\frac{\beta_{soln}}{\beta_{solv}} = 1 - S\,\frac{n_2}{n_1} \qquad \text{... (114)}$$

where S is the primary solvation number of electrolyte, n_1 and n_2 are the number of moles of solvent and solute present. The adiabatic compressibility is defined by

$$\beta = \frac{1}{C^2 \rho} \qquad \text{... (115)}$$

where C is the velocity of sound for a liquid of density ρ (all expressed in their appropriate units). By extrapolation of the graph of S versus n_2 to $n_2 = 0$, 'true' solvation number S_o may be obtained.

Allam and Lee[203] expressed the compressibilities of various electrolytes in water, methanol and ethanol by the equation

$$\beta_{soln} = \beta_{solv}\left[1 + n_2(S_0 + An_2 + Bn_2^2)/n_1\right]^{-1} \quad \cdots (116)$$

where A and B are constants.

The third and fourth terms represent contributions to the compressibility of the solution from the interactions of the solvated ions and solvent and of the solvated ions and solvated ions, assuming that th e solvated species retain part of the solvent compressibility. Thus,

$$\text{Limit} \quad \left(d\beta_{soln}/dn_2\right)_{n_2 \to 0} = -\beta_0\, S_0/(n_1)_0 \quad \cdots (117)$$

The limiting slope of the compressibility versus concentration plot is proportional to the limiting solvation number S_0. The method was utilised to obtain the solvation number of various electrolytes at 25°C in water, methanol and ethanol.

The parameter of hydration[203-206] may also be calculated assuming that the hydration shells, together with the central solute ions, are incompressible. The volume of water bound to one mole of solute in solution reduced to one atmosphere pressure P_0 to be

$$V_h = \left(n_1 \beta_1^{(P_0)} V_1^{(P_0)} - \beta^{(P_0)} \cdot V^{(P_0)}\right) = -K_2/\beta_1^{(P_0)} \quad \cdots (118)$$

where n_1 is the number of moles of water in the solution β_1 is the isothermal compressibility of the water, V_1 is the molar volume of water, P_0 is the one bar standard pressure, β is the isothermal compressibility of the solute.

Using compressibility and density data, the value of V_h and hence the average hydration number of a pair of solute ions can be calculated using the following relation:

$$n = \frac{V_1}{V_h(P_0)} \qquad \ldots (119)$$

The compressibility methods have been used by various workers[203-28] to determine the solvation number of electrolytes. Recently, Lahiri and co-workers[209,210] utilised this method to determine the solvation number of electrolytes and amino acids in aqueous and mixed solvents.

The solvation number of individual ions have generally been calculated assuming that in water, the hydration numbers of K^+ and Cl^- ions in KCl are equal. The solvation numbers of individual ions have also been calculated assuming that in water, methanol and ethanol, the nitrate ion owing to its configuration and size, has two solvent molecules[208]. The solvation numbers in water have also been calculated assuming zero solvation number of anions[193]. But the assumption of zero solvation of anions is incompatible with the theories of hydration of Buckingham[211], Eley and Evans[212] where similar hydration of anions and cations are assumed. Lahiri et al[209] used equal solvation of cations and anions in aqueous and mixed solvents.

However, further works are needed in this direction.

From the discussions it is apparent that the problem of ion-solvent interactions is intriguing as well as interesting. Inspite of extensive studies, the proper nature of the ion-solvent interactions is yet to be explored. Moreover, studies in mixed solvents are relatively few.

It is desirable to study the problem of ion-solvent interactions using the different experimental techniques and also utilize the different methods to calculate the single ion values so as to have a reasonably consistent set of values of ions. This may enable us to have a better understanding of the ion-solvent interactions both from theoretical and experimental points of view.

We have utilized the three important methods elaborately described before amongst the large number of different physico-chemical techniques to study the problem of ion-solvent interactions of tetraalkyl halides and related compounds in DMSO and DMSO + water mixtures. We have tried to determine the single ion values wherever possible.

Dimethyl Sulphoxide (DMSO)[10]

Dimethyl sulphoxide is a versatile and useful aprotic solvent with wide applications in organic syntheses and in electrochemical systems[213-215]. Its clinical applications particularly for the preparation of ointments used for topical applications are also noted[10]. It is a good nucleophilic agent and tends to enhance reaction rates and yields of many organic syntheses by stabilizing charged intermediates in the reaction[213].

The physical properties of DMSO suggest that it is highly associated in both liquid and solid states[216].

DMSO is pyramidal in shape with two C-atoms, the O-atom and the S-atom at the vertices[217,218]. The molecule has a dipole moment of 3.89D at 25°C. Both the sulphur and the oxygen atoms possess a lone pair of electrons and in sulphur the lone pair is tetrahedrally disposed to the methyl groups and the oxygen atom. A strong electrostatic interaction between the positive charge on a cation and the lone pair on the oxygen atom of each solvent molecule is envisaged when the cation-solvent complex is formed. Interaction between an anion and a DMSO molecule is difficult. The positive pole of the solvent dipole will be located on a plane that bisects the C-S-C bond angle between the methyl groups but the methyl groups may sterically hinder the close approach of an ion to the centre of the charge[27].

The results of our investigations have been described in subsequent chapters. A brief summary of the works done has been given in the preface.

Due to high dipole moment of the solvent, the intermolecular association of the solvent molecule is expected. Weak intermolecular bonding between methyl protons and oxygen atoms also makes a contribution of solvent association[219].

Dispersion forces are particularly responsible for cohesion of DMSO. Greater non-chemical interactions cause the dipolar aprotic solvents to be rigid. In terms of non-chemical structuring, the dipolar aprotic solvents are the most structured of all solvents[219].

The good dipolar and physical properties of DMSO coupled with the stability of some potentially useful electrode materials in DMSO make the solvent theoretically promising for high density battery application[28]. Transport behaviour of ions in DMSO as applied to battery application and the function of DMSO solvent molecules in organic reactions both require the understanding of the nature of ion-solvent interactions. Transport parameters of electrolyte solutions such as ionic conductance and viscosity can provide information concerning the nature of the kinetic entities from which the ion-solvent interaction can be inferred.

We have, therefore, devoted our attention to the study of the transport properties in DMSO and DMSO + water mixtures.

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