CHAPTER I

Introduction

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 realized only recently as a result of extensive studies in aqueous, non-aqueous and mixed solvents[1-13].

Water is the most abundant solvent in nature. In view of its extreme importance in chemistry, biology, agriculture, geology etc. water has been extensively used in kinetic and equilibrium studies. In spite of such extensive studies, our knowledge of molecular interactions in water is extremely limited. Moreover the uniqueness of water as solvent has been questioned[14,15] in recent years and it has been realized 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[1-13].

Extensive studies on the physical properties of different solvent systems have been made but a lamentable gap still exists. Several classifications of organic solvents based on their dielectric constant, organic group type, acid-base properties or association through hydrogen-bonding[10], donor-acceptor properties[16], hard and soft acid-base principles[17] etc. have been made; the properties of different solvent systems show a wide divergence of properties which would naturally be reflected on the thermodynamic and transport properties of electrolytes and nonelectrolytes 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 (or broadly speaking 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. Thus ion-solvent (or solute-solvent) interactions play very important role in understanding the physicochemical properties of solutions.

One of the reasons for the intricacies in solution chemistry is that the structure of the solvent molecule is 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 becomes predominant though the isolated picture of any of them is still not known completely to the solution chemists.

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

Ion-solvent interactions can be studied spectroscopically where special solvent shifts or the chemical shifts determine their qualitative and quantitative nature. 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 changes in free energy, enthalpy and entropy 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 different properties e.g., viscosity, conductance etc. of electrolytes and hence to derive the various factors associated with ionic solvation.

We shall particularly dwell upon the different aspects of transport and thermodynamic properties as the present dissertation is intimately related to the studies of viscosities, conductance of different tetraalkylammonium bromide salts in 2-ethoxyethanol and its binary mixtures with water.

Viscosity

Viscosity is one of the most important transport properties used for the determination of ion-solvent interactions and it has been studied extensively[18-21]. Viscosity is not a thermodynamic quantity, but viscosity of an electrolytic solution together with the thermodynamic property, $\bar{V}_2$, the partial molar 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 solvent, and the separation of these forces is not really possible. But from careful analysis, valid conclusion can be drawn as to the structure and the nature of solvation.

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 the viscosity.

The first systematic measurements of viscosities of a number of electrolyte solutions over a wide concentration range were attempted by Gruneisen[22] in 1905. He noted nonlinearity and negative curvature in the viscosity-concentration curves (irrespective of low or high concentration). In 1929, Jones and Dole[23] suggested an empirical equation (1), quantitatively correlating the relative viscosities (η_ρ) of the electrolytes with molar concentration (c):

$$\eta_r = 1 + Ac^{1/2} + Bc \qquad (1)$$

The equation reduces to

$$(\eta_r - 1)/c^{½} = A + Bc^{½} \tag{2}$$

where A and B are constants specific to ion-ion and ion-solvent interactions respectively. The equation is applicable equally to aqueous and non-aqueous solvent systems where there is no ion association and has been used extensively. The term $Ac^{½}$ originally ascribed to Gruneisen 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 of Debye Huckel theory[24] of interionic attractions (1923), Falkenhagen's[25-27] theoretical calculation of the constant A, using the equilibrium theory and the theory of irreversible process in electrolytes developed by Onsager and Fuoss[28]. The A-coefficient depends on the ion-ion interactions and can be calculated from the physical properties of the solvent and solution using the Falkenhagen-Vernon[27] equation.

$$A_{\text{theo}} = \frac{0.2577\Lambda^0}{\eta_0(\varepsilon T)^{½}\lambda_+^0\lambda_-^0}\left[1 - 0.6863\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0}\right)^2\right] \tag{3}$$

For most solutions, both aqueous and non-aqueous, the equation is valid upto 0.1M[18,29]. At higher concentrations, the extended Jones- Dole equation (4) involving an additional constant D, originally used by Kaminsky [30], has been used by several workers [31,32].

$$\eta_r = 1 + Ac^{½} + Bc + Dc^2 \tag{4}$$

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

The plots of $(\eta_r - 1)/c^{½}$ against $c^{½}$ for the electrolytes should give the value of A but in general the values come out to be negative or considerable scatter or deviation from linearity occur[29,33,34]. Thus, instead of determining the A-values from the plots or by least squares method, the *A* values are generally calculated using the Falkenhagen-Vernon equation (3).

In some solvents with very low relative permittivities (ε<20) even at the low concentrations at which *B* is determined, partial association takes place. Only the fraction α is then in the form of "free" ions; the rest, $1-\alpha$ being ion-paired. This can be taken into account, by modifying equation (2) to

$$[\eta_r - 1 - A(\alpha c)^{1/2}]/\alpha c = B_i + B_p(1-\alpha)/\alpha \qquad (4a)$$

where B_i pertains to the free ions and B_p to the ion pairs. A plot of the left hand side of the above equation against $(1-\alpha)/\alpha$ yields B_i as the intercept.

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 squares method and the intercepts being equal to the A-values. The factors which influence *B*-values are[35,36].

(1) The effect of ionic solvation and the action of the field of the ion in producing long range order in solvent increase η or *B*-values.
(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 relative permittivity, which 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 that the viscosity values at high concentrations (1M to saturation) can be represented by the empirical formula suggested by Andrade[37].

$$\eta = A\exp(b/T) \tag{5}$$

Several alternative formulations have been proposed for representing the result of viscosity measurements in the high concentration range[38-43] and the equation suggested by Angell[44,45] 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

$$l/\eta = A\exp[-K'/(N_0 - N)] \tag{6}$$

where N represents the concentration of the salt in eqv.litre^{-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.* a*l.*[46-48], introducing the limiting condition that as $N \rightarrow 0, \eta \rightarrow \eta_0$, the viscosity of the pure solvent. Thus we have

$$\ln(\eta/\eta_0) = \ln\ \eta_{rel} = \frac{K'N}{N_0(N_0 - N)} \tag{7}$$

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

$$\eta_{rel} = \exp\left(K'N/N_0^2\right) \simeq 1 + K'N/N_0^2 \tag{8}$$

which is nothing but the Jones-Dole equation with the ion-ion interaction term represented as $B = K'/N_0^2$. The agreement between B-values determined in this way and those obtained using the Jones-Dole equation has been found to be good for several electrolytes.

Further, equation (7) written in the form

$$\frac{N}{\ln \eta_{rel}} = \frac{N_0^2}{K'} - \frac{N_0}{K'} N \qquad (9)$$

closely resembles the Vand's equation (41) for fluidity (reciprocal of viscosity)

$$\frac{2.5c}{2.3 \log \eta_{rel}} = \frac{1}{V} - Qc \qquad (10)$$

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[24, 34, 49-97]. However, the B-coefficients as determined experimentally using Jones-Dole equation, do 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. The division of B-values into ionic components is quite arbitrarily based on some approximation 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[98] 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

212067
02 FEB 2009

again proportional to the third power of the ionic mobilities. The method of Gurney[99] and also of Kaminsky[30] is based on

$$B_{K^+} = B_{Cl^-} \text{ (in water)} \tag{11}$$

The argument in favour of this assignment is based on the fact that the *B*-coefficient for KCl is very small and that the mobilities of K^+ and Cl^- are very similar over the temperature range 15-45^{0}C.The assignment is supported from other thermodynamic properties[18]. Nightingale[100], however, preferred RbCl or CsCl rather than KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron[31] is based on the assumption that the ion Et_4N^+ in water is probably closest to being neither structure breaker nor a structure maker. Thus they suggest that it is possible to apply, with a high degree of accuracy, Einstein's equation[101].

$$B = 0.0025\,\overline{V}^{0} \tag{12}$$

and by having an accurate value of the partial molal volume of the ion $\overline{V}^{0}$ it is possible to calculate a value of 0.359 for $B(Et_4N^+)$ in water at 298.15 K.

On the other hand, Sacco *et. al.*[75], proposed the widely used "reference electrolyte" method. Thus for tetraphenylphosphonium tetraphenylborate in water, we have

$$B(Ph_4B^-) = B(Ph_4P^+) = B(Ph_4PBPh_4)/2 \tag{13}$$

$B(Ph_4PBPh_4)$ (since Ph_4PBPh_4 is scarcely soluble in water) has been obtained

$$B(NaBPh_4) + B(Ph_4PBr) - B(NaBr) = B(Ph_4PBPh_4) \tag{14}$$

The ionic *B*-values obtained by these methods 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 dilution. Thus

(a) Criss and Mastroianni[52] assumed $B(K^+) = B(Cl^-)$ in methanol (based on equal mobilities of ions[102]). They also adopted $B(Me_4N^+) = 0.25$ at 298.15 K as the initial value for acetonitrile solutions.

(b) For acetonitrile solutions. Tuan and Fuoss[103] proposed the equality

$$B\ (Bu_4N^+) = B(Ph_4B^-) \tag{15}$$

since they thought that these ions have similar mobilities. However, according to Springer *et.al.*[104], $\lambda^0(Bu_4N^+) = 61.4$ and $\lambda^0(Ph_4B^-) = 58.3$ at 298.15 K in acetonitrile.

(c) Gopal and Rastogi[50] resolved the B-coefficients in N-methylpropionamide solutions assuming that

$$B(Et_4N^+) = B(I^-) \tag{16}$$

at all temperatures. In dimethylsulphoxide, the divisions of B-coefficients were carried out by Yao and Bennion[33] assuming

$$B[(i-Pe)_3BuN^+] = B[Ph_4B^-] = 0.5\ B[(i-Pe)_3BuNPh_4B] \tag{17}$$

at all temperatures. Wide use of this method has been made by other authors for dimethylsulphoxide[32], sulpholane[60], hexamethylphosphotriamide[64] and ethylene carbonate[105] solutions.

The methods, however, have been strongly criticized by Krumgalz[106]. According to him, any method of resolution based on the equality of limiting equivalent conductance for certain ion suffers from the drawback that it is impossible to select any two ions for which $\lambda_{+}^{0} = \lambda_{-}^{0}$ in all solvents at proper temperatures. Thus, though $\lambda^{0}(K^{+}) = \lambda^{0}(Cl^{-})$ at 298.15 K in methanol, but not in ethanol and in other solvents. In addition, if the mobilities of some ions are even equal at infinite dilution, it is not necessarily true at moderate concentrations for which *B*-coefficient values are calculated. Further, according to him, equality of dimensions of $(i\text{-}Pe)_3\,BuN^+$ or $(i\text{-}Am)_3\,BuN^+$ and Ph_4B^- does not necessarily imply equality of *B*-coefficients of these ions and they are likely to be solvent and ion-structure dependent.

Krumgalz[106,107] later on proposed a method for the resolution of *B*-coefficients. The method is based on the fact that the large tetraalkylammonium ions are not solvated[108,109] in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic *B*-values for large R_4N^+ ions ($R \geq Bu$) in organic solvents are proportional to their ionic dimensions. Thus we have

$$B(R_4NX) = a + b\left[r(R_4N^+)\right]^3 \tag{18}$$

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 $[r(R_4N^+)]^3$ to zero cation dimension given directly $B(X^-)$ in the proper solvent from which other ionic *B*-values can be calculated.

The ionic *B*-values can also be calculated from the equations

$$B(R_4N^+) - B\left(R'_4N^+\right) = B(R_4NX) - B(R'_4NX) \tag{19}$$

and

$$B(R_4N^+) / B'\left(R'_4N^+\right) = \left[r(R_4N^+)\right]^3 / \left[r\left(R'_4N^+\right)\right]^3 \tag{20}$$

The radii of the tetraalkylammonium ions have been calculated from the accurate conductometric data[110].

Gill and Sharma[76] 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^+(5.00Å) and of Ph_4B^-(5.35Å) have been, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers. They proposed the equation

$$B(Ph_4B^-)/B(Bu_4N^+) = [r(Ph_4B^-)]^3/[r(Bu_4N^+)]^3 = (5.35/5.00)^3 \qquad (21)$$

and

$$B\ (Bu_4NBPh_4) = B(Bu_4N^+) + B(Ph_4B^-) \qquad (22)$$

The method requires only the *B*-values of $B(Bu_4NBPh_4)$ and is equally applicable to mixed non-aqueous solvents. The ionic *B*-values obtained by this method agree well with those reported by Sacco *et.al.*[75] in different organic solvents using the assumption

$$B(i-Am_3BuN^+) = B(Ph_4B^-) = 0.5\ \ B(i-Am_3BuNBPh_4) \qquad (23)$$

Lawrence and Sacco[71,72a] and Sacco *at.al.*[78] employed Bu_4NBBu_4 (tetrabutylammonium tetrabutylborate) and Ph_4PBPh_4 (tetraphenylphosphonium trtraphenylborate) as reference electrolytes because the cation and anion in each case are symmetrically shaped and have almost equal van der Waals' volumes. Thus, We have,

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

or,

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

A similar division can be made for the Ph_4PBPh_4 system.

Lawrence *et.at.*[79] reported the viscosity measurements of tetraalkylammonium bromides in DMSO and HMPT. The *B*-coefficients were plotted as functions of the van der Waals volumes, Stokes' radii and formula weights of the cations, and the linear portions of the graphs were extrapolated to the zero value of each property. The intercepts thus obtained were compared with the ionic $B\ (Br^-)$ values obtained using Bu_4NBBu_4 and Ph_4PBPh_4 as reference salts. They concluded that the 'reference salt' method is the best available method for the separation of viscosity *B*-coefficients into ionic contributions. Their analysis is in agreement with the conclusions made by Thomson *et.al.*[80, 81].

Jenkins and Pritcheit[111] suggested a least square analytical technique to examine additivity relationship for combined ion thermodynamics data, to effect apportioning into single-ion components for alkali halides by employing Fajans' competition principle[112] and 'volcano plots' of Morris[113]. The principle was extended to derive absolute single ion *B*-values for alkali metals and halides in water. They also observed that $B(Cs^+)=B(I^-)$ suggested by Krumgalz[108] 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 most of these methods are based on certain approximations and anomalous results may arise unless proper mathematical theory is developed to calculate the *B*-values.

Temperature dependence of B_{ion}- values

A regularity in the behaviour of $B_\pm$ and $dB_\pm/dT$ has been observed both in aqueous and non-aqueous solvents[18] and useful generalization have been made by Kaminsky[30]. He observed that

(a) Within a group of the periodic table, the B_{ion}-values decrease as the crystal ionic radii increase.

(b) Within a group of periodic system, the temperature coefficient of B_{ion} values increases as the ionic radius increases. The results can be summarized as follows:

$$\text{(i) } A \text{ and } dA/dT>0 \tag{26}$$

$$\text{(ii) } B_{ion}<0 \text{ and } dB_{ion}/dT>0 \tag{27}$$

are characteristic of structure breaking ion, and

$$\text{(iii) } B_{ion}>0 \text{ and } dB_{ion}/dT<0 \tag{28}$$

are characteristic of structure making ions.

When an ion is surrounded by a solvation sheath, the properties of the solvent molecules within this sheath may be different from those present in the bulk structure. This is well reflected in the 'Cosphere' model of Gurney[114].A, B, C zone of Frank and Wen[115] and hydrated radius of Nightingale[100].

Stokes and Mills[18] 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 effect occurring in the ionic neighborhood.Thu

$$\eta = \eta_0 + \eta^* + \eta^E + \eta^A + \eta^D = \eta_0^* + \eta_0(A\sqrt{c} + Bc) \tag{29}$$

(Jones-Dole equation)

η_0* is the positive increment in viscosity caused by Coulombic interaction. Thus,

$$\eta^E + \eta^A + \eta^D = \eta_0 Bc \tag{30}$$

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

Following Stokes and Mills[18] and Krumgalz[106], we can write B_{ion} as

$$B_{ion} = B_{ion}^{Einst} + B_{ion}^{Orient} + B_{ion}^{str} + B_{ion}^{\text{Reinf}} \tag{31}$$

whereas according to Lawrence and Sacco[77],

$$B_{ion} = B_w + B_{solv} + B_{shape} + B_{ord} + B_{Disord} \tag{32}$$

B^{Einst}_{ion} is defined as 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_{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^{str}_{ion} is the negative increment related to the destruction of the solvent structure in the region of ionic cosphere arising from the opposing tendencies of the ion to orientate the solvent molecules around itself centrosymmetrically and solvent to keep its own structure (this corresponds to η^D or B_{Disord}). B^{reinf}_{ion} 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 attributed to the van der Waals volume and the volume of the solvated ions.

Thus, small and highly charged cations like Li^+ and Mg^{+2} from a firmly attached primary solvation sheath around these ions ($B^{\text{Einst}}_{\text{ion}}$ or η^E positive).

At ordinary temperatures, alignment of the solvent molecules around the inner layer also causes increase in $B^{\text{orient}}_{\text{ion}}$ (η^A), $B^{\text{str}}_{\text{ion}}(\eta)$ is small for the ions. Thus B_{ion} will be larger and positive as $B^{\text{Einst}}_{\text{ion}} + B^{\text{orient}}_{\text{ion}} > B^{\text{str}}_{\text{ion}}$. However, $B^{\text{Einst}}_{\text{ion}}$ and $B^{\text{orient}}_{\text{ion}}$ would be small for ions of largest crystal radii (within a group) like Cs^+ or I^- due to small surface charge densities resulting in weak orienting and structure forming effect. $B^{\text{str}}_{\text{ion}}$ would be large due to structural disorder in the immediate neighborhood of the ion due to competition between the ionic field and the bulk B^{orien}_{ion} < structure. Thus $B^{\text{einst}}_{\text{ion}} + B^{orient}_{iion} = B^{str}_{ion}$ and B_{ion} is negative.

Ions of intermediate size (e.g., K^+ and Cl^-) have a close balances of viscous forces in their vicinity,i.e., $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{orient}} = B_{\text{ion}}^{\text{str}}$ 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 $B_{\text{ion}}^{\text{str}}$ would be small i.e., $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{orient}}$

$>> B_{\text{ion}}^{\text{str}}$ and B-would be positive and large. The values would be further reinforced in water arising from $B_{\text{ion}}^{\text{Reinf}}$ 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 increasing thermal motion leading to decrease in $B_{\text{ion}}^{\text{str}}$ will decrease slowly with the increase in 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 $B_{\text{ion}}^{\text{orient}}$ and $B_{\text{ion}}^{\text{str}}$.

It is clear that in case of structure-making ions, the ions are firmly surrounded by a 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 increase 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 ion than in case of larger ions. So there is a clear correlation between the viscosity, entropy of solvation and the 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[99,114] 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*-coefficients of salts. The ionic B-values show a linear relationship with the partial molar ionic entropies of hydration $\overline{S_h^0}$

$$\overline{S_h^0} = \overline{S_{aq}^0} - \overline{S_g^0} \tag{33}$$

where $\overline{S_{aq}^0} = \overline{S_{ref}^0} + \overline{\Delta S^0}$, $\overline{S_g^0}$ is the calculated sum of the rotational and translational entropies of the gaseous ions. Gurney obtained a single linear plot between ionic entropies and ionic *B*-coefficients for all monatomic ions by equating the entropy of the hydrogen ion (S_{H+}^0) to -5.5 cal mole^{-1} deg^{-1}. Asmus[116] used the entropy of hydration to correlate ionic *B*-values and Nightingale[100] showed that a single linear relationship can be obtained with it for both monatomic and polyatomic ions.

The correlation was utilized by Abraham *et. al.*[117] to assign single-ion B-coefficients so that a plot of ΔS_e^0[118,119], the electrostatic entropy of solvation or $\Delta S_{i,ii}^0$[118,119], 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 of the line. There are excellent linear correlations between ΔS_e^0 and ΔS_1^0, and the single-ion *B*-coefficients. Both entropy criteria (ΔS_e^0 and $\Delta S_{i,ii}^0$) 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 e.g., formamide, methanol, N-methylformamide, dimethylformamide, dimethylsulfoxide, acetonitrile, all the above ions are structure-makers with the exception of weakly structure-breaking ion ClO_4^- in formamide and the border line cases of ClO_4^- in methanol and I^- in formamide].

Themodynamics of viscous flow

Assuming viscous flow as a rate process, the viscosity can be represented by using the Eyring approach[120]

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

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

The problem was dealt in a different way by Nightingale and Benck[121] who studied 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 term $Ac^{1/2}$. Thus,

$$R\frac{d\ln\,\eta}{d(1/T)} = R\frac{d\ln\,\eta_0}{d(1/T)} + \frac{R}{1+Bc}\,\frac{d(1+Bc)}{d(1/T)} \quad (35)$$

$$\Delta E_{\eta\ (soln)}^{\neq 0} = \Delta E_{\eta\ (solv)}^{\neq 0} = \Delta E_{v}^{*} \quad (36)$$

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

Feakins *et.al.*[122] have suggested an alternative formulation based on the transition state treatment of the relative viscosity of the electrolytic solutions. They suggested the following expression.

$$B = \frac{\overline{V}_1^0 - \overline{V}_2^0}{1000} + \frac{\overline{V}_1^0}{1000}\,\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT} \tag{37}$$

where $\overline{V}_1^0$ and $\overline{V}_2^0$ are the partial molar volumes of the solvent and solute respectively; $\Delta\mu_1^{0\neq}$ is the free energy of activation for viscous flow per mole of the solvent which is given by[120]

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT \ln\,\left(\eta_1 V_1/hN\right) \tag{38}$$

and $\Delta\mu_2^{0\neq}$ is the contribution per mole of solute to the free energy of activation for viscous flow of solution.

The entropy (ΔS) and enthalpy (ΔH) of activation of viscous flow for the solvents and solutions (subscripts 1 and 2 respectively) can be calculated using the following equations

$$\Delta S_2^{0\neq} = -d\left(\Delta\mu_2^{0\neq}\right)\Big/dT \text{ and } \Delta S_1^{0\neq} = -d\left(\Delta\mu_1^{0\neq}\right)\Big/dT \tag{39}$$

$$\Delta H_2^{o\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \text{ and } \Delta H_1^{0\neq} = \Delta\mu_1^{0\neq} + T\Delta S_1^{0\neq} \tag{40}$$

The separation of the thermodynamic parameters are based on the equality of effects for K^+ and Cl^- or BPh_4^- and $(i\text{-}Pe)_3BuN^+$ ions. In aqueous solution, both $T\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ 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^+, $\Delta H_2^{0\neq}$ and $T\Delta S_2^{0\neq}$ are negative *i.e.*, the transition state is associated with bond-making and an increase in order.

Effects of shape and size

This aspect has been dealt extensively by Stokes and Mills[18]. The ions in solution can be regarded as rigid spheres suspended in a continuum. The hydrodynamic treatment presented by Einstein[101] leads to the equation

$$\eta/\eta_0 = 1 + 2.5\varphi \tag{41}$$

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

Modifications of the equation have been proposed by (i) Sinha[123] on the basis of departures from spherical shape and (ii) Vand[41] on the basis of the dependence of the flow patterns around the neighbouring particles at higher concentrations. However, considering in 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 (1) and (41)

$$2.5\,\varphi = A\sqrt{c} + Bc \tag{42}$$

since the term $A\sqrt{c}$ can be neglected in comparison with Bc and $\varphi = c\overline{V_i}$ where $\overline{V}_i$ is the partial molar volume of the solute, we get

$$2.5\overline{V_i} = B \tag{43}$$

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

$B_{\pm}$ can be equated to

$$B_{\pm} = 2.5\overline{V}_{\pm} = 2.5x\,(4/3)\pi\left(R_{\pm}^3 N/1000\right) \tag{44}$$

assuming that the ions behave like rigid spheres with an effective radii $R_{\pm}$ moving in a continuum. $R_{\pm}$ calculated using equation (44) should be close to crystallographic radii or corrected Stokes radii if the ions are scarcely solvated and behave as spherical entities. But $R_{\pm}$ values of the ions, which are higher than the crystallographic radii indicate solvation.

The number (n) of solvent molecules bound to the ion in the primary solvation shell can be calculated by comparing the Jones-Dole equation with that of *Einstein*[101]

$$B_{\pm} = \frac{2.5}{1000}\left(V_i + n\, V_s\right) \tag{45}$$

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

The above equation has been used by a number of workers to study the nature of solvation. A literature survey reveals that although viscosity measurements in pure nonaqueous solvents as well as in their aqueous mixtures have been frequently reported, such studies in mixed nonaqueous solvents are relatively scarce. But the viscosity measurements in mixed solvents may well throw much light on the nature of solvation and ion-solvent interactions. In fact, in case of binary mixtures when one of the components has H-bonded network, such study can provide useful information on the effects induced by the cosolvent on its structure.

Conductance

Electrolytic conductivity is a very useful classical experimental technique to determine transport as well as equilibrium properties of dilute electrolyte solution[125,126]. Because of its relative simplicity and versatility, the measurement of the conductivity of electrolyte solutions, which can be carried out to a very high precision, remains an important goal to obtain information about electrolytes in different solvents. Conductivity of aqueous systems has recently provided valuable information about the influence of the solvent's number-density in the low fluid-density regime and its effect on the ion pairing equilibrium[127-129]. Accurate theories of electrolytic conductance are available to explain the result even upto a concentration limit of *Kd* (*K*= Debye-Huckle length, *d* = distance of closest approach of free ions). 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 weak acids and association constants of electrolytes in aqueous, mixed and non-aqueous solvents. This method in conjunction with the viscosity measurements gives us much information regarding the ion-ion and ion- solvent interactions.

However, the choice and application of theoretical as well as equipments and experimental techniques are of great importance for obtaining an accurate information from such studies. These aspects have been described in details in a number of authoritative books and reviews[11b,125,126,130-143].

The studies on electrical conductances were persued extensively 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 ionophores (completely dissociated in solutions) and ionogens (consisting of neutral molecules that yield ions by reacting with suitable solvents[140,141]) as a function of concentration give the equivalent conductances at infinite dilution, the dissociation of ionogens, the association constants of ionophores and information about the structure of solutions in the vicinity of the ion[135].

The successful application of the Debye-Huckle theory of interionic attractions was made by Onsager[144] in deriving the Kohlrausch's equation.

$$\Lambda = \Lambda^0 - S\sqrt{c} \qquad (46)$$

where

$$S = \alpha\Lambda^0 + \beta \qquad (47)$$

$$\alpha = \frac{(2e)^2 K}{3\left(2+\sqrt{2}\right)\varepsilon_1 RTc^{1/2}} = 82.406 \text{ X } 10^4 \frac{Z^3}{\eta(\varepsilon_1 T)^{3/2}} /mol^{-1/2} l^{1/2} \qquad (48)$$

and

$$\beta = \frac{Z^2 eFK}{3\pi\eta c^{1/2}} = 82.487 \frac{Z^3}{\eta(\varepsilon_1 T)^{3/2}} /S\, cm^2 mol^{-3/2} l^{1/2} \qquad (49)$$

η = viscosity in poise and Z = ionic valence.

The equation took no account for the short range interactions and 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[145]. In the subsequent years Pitts (1953)[146] and Fuoss and Onsager (1957)[133,147] 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 equivalent conductances at infinite dilution using Fuoss-Onsager theory differed considerably[145] from those obtained using Pitts theory and the derivation of the Fuoss-Onsager equation was questioned[126,148,149]. The observation was confirmed by Fuoss-Hsia[150]. The original Fuoss-Onsager equation was modified by Fuoss and Hsia[150] who recalculated the relaxation field, retaining the terms had previously been neglected. The equation usually employed is of the form[126]

$$\Lambda = \Lambda^0 - \frac{\alpha\Lambda^0\sqrt{c}}{(1+Ka)(1+Ka/\sqrt{z})} - \frac{\beta\sqrt{c}}{1+Ka} + G\,(Ka) \qquad (50)$$

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

$$\Lambda = \Lambda^0 - S\sqrt{c} + Ec\ \ln\ c + J_1 c - J_2 c^{3/2} \qquad (51)$$

is generally employed in the analysis of experimental results.

However, it has been found that these equations have certain limitations and in some case fail to fit the experimental data. Some of these results have been discussed elaborately by Fernandez-Prini[126,151,152]. Further correction of equation (51) was made by Fuoss and Accascina[133]. They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation is

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

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 Pitts equation gives better fit to the experimental data in aqueous solutions[153].

Ion-association

The equation (52) given above 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 (experimental) is greater than Λ^0 (theoretical) i.e., if positive deviations occur (ascribed to short range hard-core repulsive interactions between ions), the electrolyte may be regarded as completely dissociated but if negative deviations $(\Lambda^0_{\text{expt}} < \Lambda^0_{\text{theo}})$ or positive deviations from the Onsager limiting tangent, 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^0_{expt} and Λ^0_{theo} would be considerable with increasing association[154].

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

$$M^{z+} + A^{z-} \leftrightarrows MA \tag{53}$$

where $$K_A = (1-\alpha)/(\alpha^2\, c\, \gamma_\pm^2) \tag{54}$$

and $$\alpha = 1 - \alpha^2 c K_A \gamma_\pm^2 \tag{55}$$

For strongly associated electrolytes, K_A and Λ^0 have been determined using Fouss-Kraus equation[155] or Shedlovsky's equation[156]

$$\frac{T(Z)}{\Lambda} = \frac{1}{\Lambda^0} + \frac{K_A}{(\Lambda^0)^2}\frac{c\gamma_\pm^2 \Lambda}{T(Z)} \tag{56}$$

where $T(Z) = F(Z)$ (Fuoss-Kraus)

and $1/T(Z) = S(Z)$ (Shedlovsky)

$$F(Z) = 1\text{-}Z\,(1\text{-}Z(1\text{-}Z(1\text{-}\ldots\ldots\ldots\ldots)^{-\frac{1}{2}})^{-\frac{1}{2}})^{-\frac{1}{2}} \tag{57}$$

And $$S(Z) = 1 + Z + Z^2/2 + Z^3/8 + \ldots\ldots\ldots\ldots \tag{58}$$

The plot of $T(Z)/\Lambda$ against $c\gamma_\pm^2\Lambda/T(Z)$ should be a straight line having an intercept of $1/\Lambda^0$ and a slope of $K_A/(\Lambda^0)^2$ when K_A is large, there will be considerable uncertainty in the determined values of Λ^0 and K_A from equation (56). The Fuoss-Hsia conductance equation for associated electrolytes is given by

$$\Lambda = \Lambda^0 - S\sqrt{\alpha c} + E(\alpha c)\,\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A \Lambda \gamma_\pm^2(\alpha c) \tag{59}$$

This equation was modified by Justice[157]. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations

$$\Lambda = \alpha[\Lambda^0 - S\sqrt{\alpha c} + E(\alpha c)\ \ln(\alpha c) + J_1(R)(\alpha c) - J_2(R)(\alpha c)^{3/2}] \quad (60)$$

$$(1-\alpha)/(\alpha^2 c\gamma_\pm^2) = K_A \quad (61)$$

$$\ln\ \gamma_\pm = -Kq^{1/2}/(1 + K_R\sqrt{\alpha c}) \quad (62)$$

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

$$R = q = e^2/(2 \in kT) \quad (63)$$

(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 (60) 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 importance 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^0 of two free ions to from an ion-pair. The following equation has been proposed by Fuoss[158].

$$K_A = (4\pi N a^3/3000)\ \exp\ (e^2/a^0 \in RT) \quad (64)$$

In some cases, the magnitude of K_A was too small to permit a calculation of a^0. The distance parameter was finally determined from the more general equation due to Bjerrum[159]

$$K_A = (4\pi N/1000)\int_{r=a}^{r=q} r^2 \exp(z^2e^2/r \in kT)dr \qquad (65)$$

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 utilized by Douheret[160].

Ion-size parameter and ionic association

The equation (52) can be written as

$$\Lambda' = \Lambda + S\sqrt{c} - Ec\ln c = \Lambda^0 + (J - B\Lambda^0)c = \Lambda^0 + J'c \qquad (66)$$

(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 $B\Lambda^0$ to be negligible, a^0 values can be calculated from J'. The a^0 values obtained by this method in dimethylsulfoxide were much smaller[154] than would be expected from the sums of the crystallographic radii of the ions. 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 value of a^0 [161], still the agreement is poor. However, little of real physical significance may be attached to the distance of closest approach derived from J[162].

Fuoss[163] in 1975 proposed a new conductance equation. He[163] subsequently put forward another conductance equation in 1978 which replaced the old one. He classified the ion of 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 contact-pair are the solvent molecules forming 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 1 but may be 2, 3 etc., 's' is the diameter of a sphere corresponding to the average volume (actual plus free) per solvent molecule, and contact pairs form by a sequence of ion-solvent site interchanges inside the *R*-spheres, until two ions of opposite charges 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:

$$A^+ + B^- \leftrightarrows (A^+ \ldots\ldots\ldots B^-) \leftrightarrows A^+\ B^- \quad \leftrightarrows \quad AB \tag{67}$$

(solvent-separated pair) contact pair neutral molecule

Contact pairs of ionogens may rearrange to neutral molecules $A^+B^- \leftrightarrows AB$ e.g., H_3O^+ and CH_3COO^-. Let ν be the fraction of solute present as unpaired ($r>R$) ions. The concentration of unpaired ions is $c\nu$. If α be the fraction of paired ions($r \leq R$), the concentration of solvent-separated pair is $c(1-\nu)(1-\alpha)$and that of contact pair is a $c(1\text{-}\alpha)$.

The equilibrium constants for (67) are

$$K_R = (1-\alpha)(1-\gamma)/\left(c\nu^2 f^2\right) \tag{68}$$

$$K_s = \alpha/(1-\alpha) = \exp(-E_s/kT) = e^{-\in} \tag{69}$$

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 ($r = a$), $\in$ is measured in units of kT. From (69)

$$1-\alpha = 1/(1+Ks) \tag{70}$$

Substitution in equation (68) gives the conductometric pairing constant

$$K_A = (1-\gamma)c\gamma^2 f^2 = K_R/(1-\alpha) = K_R(1+K_s) \tag{71}$$

which determines the concentration $c\gamma$ of active ions, 'active' in the sense that they produce the long-range interionic effects. That contact pairs behave like electrical dipoles to an external field X, contributing only to charging 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 $\Delta X/X < 0$, the relaxation field and $\Delta\Lambda_c < 0$, the electrophoretic countercurrent). The various patterns can be reproduced by theoretical functions of the form

$$\Lambda = p[\Lambda^0(1+\Delta X/X) + \Delta\Lambda_c] \tag{72}$$

$$= p[\Lambda^0(1+R_x) + E_L] \tag{73}$$

where R_x and E_L are relaxation and hydrodynamic terms respectively. The quantity p is the fraction of solute which contributes to conductance current and is given by

$$p = 1-\alpha(1-\gamma) \tag{74}$$

In case of ionogens or for ionophores in solvents of low relative permittivity α is very near to unity ($-E_s/kT >> 1$) and the equation becomes

$$\Lambda = \gamma[\Lambda^0(1+R_x) + E_L] \tag{75}$$

The equilibrium constant for the effective reaction

$$A^+ + B^- \leftrightarrows AB$$

is then

$$K_\Lambda = (1-\gamma)/c\gamma^2 f^2 \approx K_R K_S \tag{76}$$

because $K_s >> 1$.

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

$$r = 1 - K_\Lambda c\gamma^2 f^2 \tag{77}$$

$$-\ln\, f = \beta k/2(1+kR), \qquad \beta = e^2 / \in kT \tag{78}$$

$$-\in = \ln[\alpha/(1-\alpha)] \tag{79}$$

The details of the calculations are presented in the 1978 paper[163]. The shortcomings of the previous equations have been rectified in the present set of equations which are more general than the previous equations and can be used in the higher concentration regions (0.1N in aqueous solutions).

From 1992 to 1995, Blum, Turk, and co-workers[164-166] have developed a mean spherical approximation (MSA) version of conductivity equations. Their theory starts from some continuity and hydrodynamic equations used in the more classical treatments, however, an important difference consists in the use of the MSA expressions for the equilibrium and structural properties of the electrolyte solutions. Although the difference in the derivation of the classical and MSA conductivity theories seem relatively small, it has been claimed the performance of the MSA equation is good over a much wider concentration range than that covered by the classical equations. However, no thorough study of the performance of the new equation at the level of the experimental uncertainty of conductivity measurement is yet available in the literature, with the exception of a very recent study by Bianchi *et. al.*[167] who compared the results obtained using the old and new equations in order to evaluate their capacity in describing the conductivity of different electrolyte solution. Their investigation is too limited only to three aqueous salt solutions and the picture is consistent showing a better performance for the classical equations as far as system electrolytes are concerned.

Limiting ionic equivalent conductances

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

$$\Lambda^0 = \lambda_+^0 + \lambda_-^0 \tag{80}$$

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

$$\lambda_+^0 = t_+\Lambda^0 \quad \text{and} \quad \lambda_-^0 = t_-\Lambda^0 \tag{81}$$

Thus from the accurate values of λ^0 of ions, it is possible to separate the contribution due to cations and anions in the solute-solvent interactions[168]. However, accurate transference number determinations are limited to few solvents only. Spiro[169]and more recently Krumgalz[170a] 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 limiting ionic equivalent conductances in organic solvents for which experimental transference numbers are not yet available.

The methods have been summarized by Krumgalz[170a] and some important points are mentioned below:

(i) Walden equation[171]

$$\lambda_{\pm}^{0}.\eta_0(acetone) = \lambda_{\pm}^{0}.\eta_0(water) \quad (82)$$

at 298.15 K

(ii) $\lambda^0(Pic)\eta_0 = 0.267$

$$\lambda^0(Et_4N^+)\eta_0 = 0.296 \text{ based on } \Lambda^0(Et_4NPic) = 0.563^{171,172} \quad (83)$$

Walden considered the products to be independent of temperature and solvent. However, the $\Lambda^0(Et_4NPic)$ values used by Walden were found to differ considerably from the data of subsequent more precise studies and the values of (ii) are considerably different for different solvents.

(iii) $\lambda_{25}^{0}(Bu_4N^+) = \lambda_{25}^{0}(Ph_4B^-)$[173] (84)

(this equality holds good in nitrobenzene and its mixture with CCl_4 but is not realized in methanol, acetonitrile and nitromethane).

(iv) $\lambda_{25}^{0}(Bu_4N^+) = \lambda_{25}^{0}(Bu_4B^-)$[174] (85)

The method appears to be sound as the negative charge on boron in 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.

(v) $\lambda_{25}^{0}(R_4N^+) = ZF^2/\left[6\,\pi N\,\eta_0\left\{r_i - \left(0.0103\,\epsilon_0 + r_y\right)\right\}\right]$[175] (86)

where Z and r_1 are the charge and crystallographic radius of the relevant ion; η_0 and ϵ_0 are the viscosity and relative permittivity of the medium; r_y is an adjustable parameter taken to be equal to 0.85 for dipolar non-associated solvents and 1.13 for hydrogen-bonded and other associated solvent.

However, large discrepancies were observed between the experimental and calculated values[170a]. In a later paper[170b] Krumgalz examined Gill's approach more critically using conductance values in a number of solvents and found the method to be reliable in three solvents e.g., 1-butanol, acetonitrile and nitromethane.

$$\text{(vi)} \qquad \lambda_{25}^{0}\left(i-Am_3BuN^{+}\right)=\lambda_{25}^{0}\left(Ph_4B^{-}\right)^{176} \qquad (87)$$

It has been found from transference measurements that the $\lambda_{25}^{0}\left(i-Am_3BuN^{+}\right)$ and $\lambda_{25}^{0}\left(Ph_4B^{-}\right)$values differ from each other by 1%.

$$\text{(vii)} \qquad \lambda_{25}^{0}\left(Ph_4B^{-}\right)=1.01\lambda_{25}^{0}\left(i-Am_4B^{-}\right)^{177} \qquad (88)$$

The equality is found to be true for various organic solvents. Krumgalz[170a] suggested a method for determining the limiting ion conductnces in organic solvents or mixtures of organic solvents. The method is based on the fact that the large tetraalkyl (aryl) onium ions are not solvated in organic solvents in the kinetic sense due to the extremely weak electrostatic interactions between the solvent molecules and the large ions with low surface charge density. The phenomenon of non-solvation is confirmed by N.M.R. measurements and is utilized as a suitable model for apportioning Λ^0 values into ionic components for non-aqueous electrolytic 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

$$r_s = |Z| F^2 A \pi N \eta_0 \lambda_{\pm}^0 \qquad (89)$$

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

Since the r_s values, the real dimension of the non-solvated tetraalky (aryl) onium ions, must be constant, we have

$$\lambda_{\pm}^0 \eta_0 = \text{constant} \qquad (90)$$

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 $i-Am_4B^-, Ph_4As^+$ and Ph_4B^- ions and for tetraalkylammonium cations starting from Et_4N^+. The relationship can be well utilized to determine $\lambda_{\pm}^0$ values of ions in other organic solvents from the determined Λ^0 values.

We have used Bu_4NBPh_4 as the 'reference electrolyte', but instead of equal division, we divided the Λ_0 values using the method similar to that proposed by Krumgalz[106] for division of viscosity B-values

$$\frac{\lambda^0(Bu_4N^+)}{\lambda^0(Ph_4B^-)} = \frac{r(Ph_4B^-)}{r(Bu_4N^+)} = \frac{5.35}{5.00} = 1.07 \qquad (91)$$

The r-values have been taken from the works of Gill *et.al.*[178,179].

Though nothing can be said definitely regarding the accuracy of the method, some indirect evidences regarding the reliability of the values may be provided. The values of the ratio $\lambda^0(BPh_4^-)/\lambda^0(Bu_4N^+)$becomes 1.06 if we choose $r\ (Bu_4N^+) = 3.85\ \mathring{A}$ and $r(BPh_4^-) = 4.08\,\mathring{A}$ as suggested by Krumgalz[106,180].

Fuoss *et. al*[180-184] assumed, from extensive measurements Λ^0 values of R_4NBPh_4 salts in various mixed organic solvents, that the limiting transference number of Bu_4N^+ in Bu_4NBPh_4 is 0.519 independent of the solvent (this is claimed to be valid within $\pm 1\%$). This gives 1.079 for $\lambda^0(Bu_4N^+)/\lambda^0(Ph_4B^-)$ which is close to 1.07.

D'Aprano and Fuoss[184] used Bu_4NBPh_4 to calculate single-ion conductance in mixed organic solvents applying the relations $\lambda^0(Bu_4N^+) = 0.213/\eta_0$ and $\lambda^0(Ph_4B^-) = 0.201/\eta_0$ which means $\lambda^0(Bu_4N^+)/\lambda^0(Ph_4B^-) = 1.06$.

Moreover, since the charge is equal to the number of ions, the equivalent conductances of these ions depends on their mobilities, the division may be in terms of the reciprocal of their vander Waal's volume i.e.,

$$\lambda^0(Bu_4N^+)\,/\lambda^0(Ph_4B^-) = 186.8/179.1 = 1.04 \qquad (92)$$

The van der Waal's volumes have been taken from the works of Lawerence and Sacco[77]. However, the ratio comes out to be slightly lower than the usual 1.06-1.08.

In absence of accurate transference data in binary mixtures of organic solvents, it is difficult to compare the single-ion values and to test the validity of equation (91), but the values calculated by this method appear to be correct in different organic or mixed organic solvents. However, in aqueous binary mixtures the solvation pattern may be different and the validity of this method may be questioned. In absence of a suitable method, nothing can be said conclusively.

Recently, Gill *et. al.*[185] proposed the following equation

$$\lambda^0(Bu_4N^+)/\lambda^0(Ph_4B^-) = [5.35 - (0.0103\varepsilon_0 + r_y)]/[5.00 - (0.0103\varepsilon_0 + r_y)] \qquad (93)$$

and the ratio is to 1.07 as used by us.

Solvation number[168]

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 V_s can be written as

$$V_s^s = (4/3)\pi\left(r_s^3 - r_c^3\right) \tag{94}$$

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

$$n_s = V_s / \overline{V}_0 \tag{95}$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects[186], from

$$V_s^0 = 4.35 r_s^3 \tag{96}$$

when V_s^0 is expressed in mol/mole and r_s in Angstroms. However, this method of determination of solvation numbers is not applicable to ions of medium size though a number of empirical[27,32,134] and theoretical corrections[187-190] have been suggested in order to apply it to most of ions.

Stokes' law and Walden's rule

The limiting conductance 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

$$\lambda_i^0 = 0.819|Z_i| / \eta_0 R_i \tag{97}$$

where λ_0, the macroscopic viscosity of the solvent, is expressed in poise and R_i in Angstroms. If the radius R_i is assumed to be the same in every organic solvent, as would be the case of bulky organic ions, we get

$$\lambda_i^0 \eta_0 = 0.819\, Z_i / R_i = \text{constant} \tag{98}$$

This is known as Walden rule[191]. The effective radii obtained using this equation can be used to estimate the solvation numbers. The failure of the Stokes' radii to give effective size of the solvated ions for small ions is often attributed to the inapplicability of Stokes' law to molecular motion.

Robinson and Stokes[134], Nightingale[100] and others[192-194] 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 these large ions, a calibration curve was obtained for each solvent. This approach, however, suffers from one serious flaw. The basic assumption on which this approach rests is that the Walden product is invariant with temperature. Experimental results[154] indicate that his assumption is incorrect and that the resulting solvation numbers obtained from this type of correction to Stokes' law are meaningless. The idea of microscopic viscosity[195] was invoked without much success[196,197] but it has been found that

$$\lambda_i^0 \eta^p = \text{constant} \tag{99}$$

where $p = 0.7$ for alkali metal or halide ions and $p = 1$ for the large ions[198,199].

Attempts to explain the change in the Stokes' radius R_i have been made. The apparent increse in the real radius r has been attributed to ion-dipole polarization and the effect of dielectric saturation on R. Fuoss noticed[200] the dependence of the Walden product, $\Lambda^0 \eta_0$ on the relative permittivity and considered the effect of electrostatic forces on the hydrodynamics of the system.

He proposed that the dielectric relaxation in the solvent caused by ion motion leads to excess frictional resistance. He proposed the relation:

$$\lambda_{i,0}^{0} = Fe\left|Z_i\right|/6\pi R_\alpha\left(1 - A/\in R_\alpha^2\right) \tag{100}$$

from which the classical Stokes' radius, may be derived as

$$R_i = R_\alpha + A/\in \tag{101}$$

where R is the hydrodynamic radius of the ion in a hypothetical medium of relative permittinty where all electrostatic forces vanish and A is an empirical constant.

In 1961, Boyd[188] gave the expression

$$\lambda_i^0 = Fe\left|Z_i\right|/6\pi\eta_0 r_i\left[1 + 2/27.1/\pi\eta_0.Z_i^2 e^2 t/r_i^4 \in_0\right] \tag{102}$$

considering the effect of dielectric relaxation on ionic motion; t is the Debye relaxaton time for the solvent dipoles.

Zwanzig[189] treated the ion as a rigid sphere of radius r_i moving with a steady velocity v_i through a viscous incompressible dielectric continuum. The conductance equation suggested by Zwanzig is

$$\lambda_i^0 = \frac{Z_i^2 eF}{A_v \pi\eta_0 r_i + A_D\left[Z_i^2 e^2\left(\in_r^0 - \in a_r\right)\tau/\in_r^0\left(Z \in^0 r + 1\right)r_i^3\right]} \tag{103}$$

where $\in_r^0, \in a_r$ are the static and the limiting high frequency (optical) dielectric constants respectively, $A_v = 6$ and $A_D = 3/8$ for perfect sticking and $A_v = 4$ and $A_D = 3/4$ for perfect slipping. The above equation can be written as

$$\lambda_i^0 = Ar_i^3/(r_i^4 + B) \tag{104}$$

The theory predicts[201] that λ_i^0 passes through a maximum of (27/4)B at $r_i =$ (3B). 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, fails off rather more rapidly than predicted with increasing radius.

For comparison of the results in different solvents, equation (103) can be rearranged as[202]

$$\frac{Z_i^2 eF}{\lambda_i^0 \eta_0} = A_v \pi r_i + \frac{A_D Z_i^2 e^2 \left(\varepsilon_r^0 - \varepsilon_r^a\right)\tau}{\lambda_i^3 \varepsilon_r \left(2\varepsilon_r^0 + 1\right)\eta_0} \qquad (105)$$

$$L^* = A_v \pi r_i + \left(A_D Z_i^2 / r_i^3\right) P^* \qquad (106)$$

In order to test the Zwanzig's theory, the equation (106) was applied to methanol, ethanol, acetonitrile, butanol and pentanol solutions where accurate conductance and transference data are available[201-206]. All the plots were found to be linear. 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 the relaxation effect is not the predominant factor in affecting ionic mobilities and that these mobility differences could be explained qualitatively if the microscopic properties of the solvation from Stokes' law[168] is taken into account.

It is noted 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 solvent of high P^* and for ions of small r_i. Like any continuum theory, Zwanzig's theory has the inherent weakness of its ability to account for the structural features[207] 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 equation does not apply to hydrogen bonded solvents[208].

(2) The theory does not distinguish between positively and negatively charged ions and therefore cannot explain why certain anions in dipolar aprotic media posses considerably higher molar conductances than the fastest cations[207].

The Walden product in case of mixed solvents does not show any constancy but it passes through a maximum in case of DMF – H_2O, DMA –H_2O, mixtures[209-212] and other aqueous binary mixtures[213-218]. To derive expressions for the variation of the Walden products with the composition of mixed polar solvents, various attempts have been made[188,189,219] with different models for ion-solvent interactions but no satisfactory expression has been derived taking into account all types of ion-solvent interactions because:

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

(2) it is not possible to account for some specific properties of different kinds of ions and solvent molecules[209]. Ions moving in a dielectric medium experience a frictional force due to dielectric loss arising from ion-solvent interaction with the hydrodynamic force. Zwanig's expression though account for a change in Walden product with solvent composition does not account for the maxima. Hemmes[220] suggested that the major deviations in the Walden product are due to the variation of the electrochemical equilibrium between ions and solvent molecules with the composition of mixed polar solvents. In case 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 by experimental observations. Hubbard and Onsager[221] have developed the kinetic theory of ion-solvent interaction within the frame work of continuam mechanics where the concept of kinetic polarization deficiency has been introduced.

However, quantitative expression is still awaited. Further improvements[222,223] naturally must be in terms of (1) sophisticated treatment of dielectric saturation, and (2) Specific structural effects involving ion-solvent interactions.

References

1. R. G. Bates, *J. Electroanal. Chem.*, **29**, 1 (1972).
2. G. S. Kell, C. M. Davies and J. Jarzynski, in *Water and Aqueous Solutions: Structure, Thermodynamic and Transport Processes,* Ed. R.A. Horne, Willy-Interscience, New York, 1972, Chapters 9 and 10.
3. J. S. Muirhead-Gould and K. J. Laidler in *Chemical Physics of Ionic Solutions*, Eds. B. E. Conway and R. G. Barradas, John Wiley and Sons Inc., New York, 1966, pp. 75-86.
4. *Solute-Solvent Interactions*, Eds. J. F. Coetzee and C. D. Ritchie, Marcell Dekkar, New York, 1969.
5. *The Chemistry of Non-aqueous Solvents,* Ed. J. J. Lagowski, Academic Press, New York, 1966.
6. E. S. Amis and J. F. Hinton, *Solvent Effects on Chemical Phenomena,* Academic Press, New York, 1973.
7. *The Organic Chemistry of Electrolyte Solution*, Ed. J. E. Gordon, Wiley-Interscience, New York, 1975.
8. H. S. Harned and B. B. Owen, *The Physical Chemistry Of Electrolytic Solution*, Reinhold Publishing Corporation, New York, 3rd Ed, 1958.
9. *Chemical Physics of Ionic Solution*, Eds. B.E. Conway And R. G. Barradas, Wiley, New York, 1966.
10. *Physical Chemistry of Organic Solvent System,* Eds. A. K. Covington And T. Dickinson, Plenum Press, New York, 1973.
11. a) Y. Marcus, *Ion Solvation*, Wiley-Interscience, Chichester, 1986.
    b) Y. Marcus, *Ion Properties,* Dekker, New York, 1973.
12. G. A. Krestov, *Thermodynamics of Solvation,* Ellis Horwood, Chichester, 1991
13. R. Fernandez-Prini, H. Corti and M. Japas, *High-Temperature Aqueous Solutions: Thermodynamic Properties,* C R C Press, Boca Raton, FL, 1992.
14. F. Franks, in *Water-A Comprehensive Treatise*, Ed. F. Franks, Vol. 1, Plenum Press, New York, 1973.

15. F. Franks in Physico-Chemical Processes in Mixed Aqueous Solvents, Ed. F. Franks, Heinmann Educational Book Ltd., 1967, Pp 141-157

16. a) V. Gutmann, *Electrochim. Acts*, **21**, 661 (1976).

    b) V. Meyer and V. Gutmann, *Adv. Inorg. Chem. Radiochem.*, **17**, 189, (1975).

17. R. G. Pearson, *Hard and Soft Acids and Bases*, Dowdon, Hutchinson and Ross, Stroudsburgh, 1973.

18. R. H. Stokes and R. Mills, *Viscosity of Electrolytes and Related Properaties*, Pergamon Press, 1965

19. F. Vaslow, in *Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes*, Ed. R. A. Horne, Wiley-Interscience, 1972, Chapter 12.

20. V. N. Afnasyev and I. E. Korolev, *Thermodynamics of Electrolyte Solutions*, Institute of Nonaqueous Solution Chemistry, Ivarovo, Russia, 1992.

21. H. D. B. Jenkins and Y. Marcus, *Chem. Rev.*, **95**, 2695 (1995).

22. Gruneisen, Wiss, Abhandl. *Phsik-Tech. Reichanstatt*, **4**, 239 (1905).

23. G. Jones and M. Dole, J. *Am. Chem. Soc.*, **51**, 2950 (1929).

24. P. Debye and E. Huckle, Z. Phys., **30**, 661 (1929).

25. H. Falkenhagen and M. Dole, *Z. Phys.*, **30**, 185 (1923).

26. H. Falkenhagen, *Z. Phys.*, **32**, 745 (1931).

27. H. Falkenhagen and E. L. Vernon, *Phil. Mag.* **14**, 537 (1932).

28. L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

29. Ref. 8, P. 240.

30. M. Kaminsky, *Z. Phys. Chem. (Frankfurt)*, **12**, 206 (1957).

31. J. Desnoyers and G. Perron, J. *Soln. Chem.*, **1**, 199 (1972).

32. R. T. M. Bicknell, K. G. Lawrence and D. Feakins, *J. Chem. Soc., Faraday Trans.* 1, **76**, 637 (1980).

33. N. P. Yao and D. N. Bennion, *J. Phys. Chem.*, **75**, 1727 (1971).

34. R. L. Kay, T. Vituccio, C. Zawoyski and D. F. Evans, *J. Phys. Chem.*, **70**, 2336 (1966).

35. M. Kaminsky, Discuss, *Faraday Soc.*, **24**. 171 (1957).

36. D. Feakins and K. G. Lawrence, *J. Chem. Soc.* A, **212** (1966).

37. Andrade, *Phil. Mag.*, **17**, 698, (1934).

38. D. E. Goldsack and R. C. Franchetto, *Can. J. Chem.*, **55**, 1062 (1977).

39. D. E. Goldsack and R. C. Franchetto, *Can. J. Chem.*, **56**, 1442 (1978).

40. D. England and G. Oiling, *J. Phys. Chem.*, **76**, 1902 (1972).

41. J. Vand, J. Phys. *Chem.*, **52**, 227 (1948).

42. S. P. Moulik, *J. Ind. Chem. Soc.*, **49**, 483 (1972).

43. D. G. Thomas, *J. Phys. Chem.*, **70**, 267 (1965).

44. C. A. Angel, *J. Phys. Chem.*, **70**, 2793 (1966).

45. C. A. Angel, *J. Chem. Phys.*, **46**, 4673 (1967).

46. K. Roy Choudhury and D. K. Majumder, *Electrochim. Acta,* **28**, 23 (1983).

47. K. Roy Choudhury and D. K. Majumder, *Electrochim. Acta*, **28**, 597 (1983).

48. K. Roy Choudhury and D. K. Majumder, *Electrochim. Acta,* **29**, 1371 (1984).

49. P. P. Rastogi, *Bull. Chem. Soc. Japan*, **43**, 2442 (1970).

50. R. Gopal and P. P. Rastogi, *Z. Physik. Chem.* (N. F.), **69**, 1 (1970).

51. K. Tamaki, Y. Ohara and Y. Isomura, *Bull. Chem. Soc. Japan*. **46**, 1551 (1973).

52. C. M. Criss and M. J. Mastroianni, *J. Phys. Chem.*, **75**, 2532, (1971).

53. K. Miyajima, M. Sawadas and M. Nakagaki, *Bull. Chem. Soc Jpn.*, **56**, 827 (1983).

54. J. I. Kim, J. Phys. *Chem.*, **82**, 191 (1978).

55. P. K. Mandal, B. K. Seal and A. S. Basu, *Z. Physic. Chem.* (Leipzig), **258**, 809 (1977).

56. B. K. Seal, D. K. Chatterjee and P. K. Mandal, *Ind. J. Chem.*, **21**, 509 (1982).

57. A. Sacco, G. Petrella, and M. D. Monica, *J. Chem. Soc., Faraday Trans.* 1, **75**, 2325 (1979).

58. A. Sacco, G. Petrella, A. D' Atti and A. D. Giglo, *J. Chem. Soc., Faraday Trans.* 1, **78**, 1507 (1982).

59. P. P. Deluca and T. V. Rebagy, *J. Phys. Chem.*, **79**, 2493 (1975).

60. A. Sacco, G. Petrella and M. Castagnoio, *J. Phys. Chem.*, **80**, 749 (1975).

61. R. L. Blokhar and Y. P. Segal, *Ind. J. Chem.*, **15A**, 36 (1977).

62. S. K. Vijaylakshaman, *Ind. J. Chem.*, **17A**, 551 (1979).

63. K. Kurotaki and S. Kawamura, *J. Chem. Soc., Faraday Trans.* 1. **77**, 217 (1981).

64. A. Sacco, G. Petrella, M. Della Monica and M. Castagnolo. *J. Chem. Soc., Faraday Trans.* 1, **73**, 1936 (1977).

65. N. Martinus and C. A. Vincent. *J. Chem Soc., Faraday Trans.* 1, **77**, 141 (1981).

66. A. Sacco, A. De Giglio, A. Dell' Atti and M. Castagnolo, *J. Chem. Soc., Faraday Trans.* 1, **79**, 431 (1983).

67. C. Quintana, M. L. Llornete, M. Sanchez and A. Vivo, *J. Chem. Soc., Faraday Trans.* 1, **82**, 3307 (1986).

68. J. Crudden, G. M. Delaney, D. Feakins, P. J. O'Reilly, W. E. Waghorne and K. G. Lawrence, *J. Chem. Soc., Faraday Trans.*1, **82**, 2195 (1986).

69. G. Kumar, N. C. Dey, B. K. Saikia and I. Haque, *Bull. Chem. Soc. Jpn.*, **59**, 1555 (1986).

70. S. Das, D. K. Hazra and S. C. Lahiri, Ind. *J. Chem.*, **28A**, 854 (1989).

71. S. Taniewska-Osinska and M. Jozwiak, *J. Chem. Soc., Faraday Trans.* 1, **85**, 2141 (1989).

72. A. Kacperska, S. Taniewska- Osniska, A. Bald and A. Szejgis, *J. Chem. Soc., Faraday Trans .*, **86**, 2225 (1990).

73. R. T. M. Bicknell, K. G. Lawrence, M. A. Seclay, D. Feakins and L. Werblan, *J. Chem. Soc., Faraday Trans.* 1, **72**, 307, 1976.

74. D. Feakins, W. E. Waghorne and R. G. Lawrence, *J. Chem. Soc., Faraday Trans.* 1, **82**, 563 (1986).

75. A. Sacco, A. D. Giglo, A. D. Atti, *J. Chem. Soc., Faraday Trans.* 1, **77**, 2693 (1981).

76. D. S. Gill and A. N. Sharma, *J. Chem. Soc., Faraday Trans.* 1, **78**, 475 (1982).

77. K. G. Lawrence and A. Sacco, *J. Chem. Soc., Faraday Trans.* 1, **79**, 675 (1983).

78. A. Sacco, M. D. Monica, A. D. Giglio and K. G. Lawrence, *J. Chem. Soc., Faraday Trans.* 1, 79, 2631 (1983).

79. K. G. Lawrence, T. M. Bicknell, A. Sacco and A. Dell' Atti, *J. Chem. Soc., Faraday Trans.* 1, **81**, 1133 (1985).

80. P. T. Thomson, M. Durbana, J. L. Turner and R. H. Wood, *J. Soln. Chem.*, **9**, 995 (1980).

81. P. T. Thomson, B. Fischer and R. H. Wood, *J. Soln. Chem.* **11**, 1 (1982).

82. D. Dasgupta, S. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **62**, 1246 (1989).

83. D. Nandi and D. K. Hazra, *J. Chem. Soc., Faraday Trans.* 1, **85**, 4227 (1989).

84. K. Ibuki and M. Nakahara, *J. Phys. Chem.* **94**, 8370 (1990).

85. L. M. Mukhujee and D. P. Boden, *J. Phys. Chem.* **73**, 3965 (1965).

86. P. K. Muhuri and D. K. Hazra, *Z. Naturforsch*, **48a**, 523 (1993).

87. A. Sacco, G. Petrella and M. Castagnolo, *J. Phys. Chem.* **80**, 799 (1976).

88. R. H. Stokes and R. Mills, *Viscosity of Electrolytes and Related properties*, Pergamon Press, Oxford, p-31, 1965.

89. S. Das, D. K. Hazra and S. C. Lahiri, *Z. Phys. Chem. (NF)*, **138**, 185 (1983).

90. D. Feakins, D. J. Freemantle and K. G. Lawrence, *J. Chem. Soc. Faraday Trans*, 1, **70**, 795 (1974).

91. D. S. Gill and B. Sing, *J. Chem. Soc. Faraday Trans* 1., **84**, 4417 (1988).

92. P. K. Muhuri, S. K. Ghosh and D. K. Hazra, *J. Chem. Eng. Data*, **38**, 242 (1993).

93. M. Kaminsky, *Z. Phys. Chem (Frankfurt)*, **5**, 154 (1955).

94. B. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **65**, 3407 (1992).

95. M. H. Abraham, *J. Chem. Soc. Faraday Trans.* 1, **69**, 1375 (1973).

96. D. S. Gill, P. Singh and J. Sing, *J. Chem. Soc. Faraday Trans.* 1, **91**, 2789 (1995).

97. R. Zana, G. Perron, and J. E. Desnoyers, *J. Solution Chem.*, **8**, 10, (1979).

98. W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc. London*, **145 A**, 475, (1934).

99. R. W. Gurney, *Ionic Processes in Solution*, McGraw Hill, New York (1954).

100. E. R. Nightingale, *J. Phys. Chem.*, **63**, 1381 (1959).

101. A. Einstein, *Ann, Phys.*, **19**, 289 (1906).

102. G. S. Benson and A. R. Gordon. *J. Chem. Phys.*, **13**, 473 (1945).

103. D. F. Tuan and R. M. Fuoss, *J. Phys. Chem.*, **67**, 1343 (1963).

104. C. H. Springer, J. F. Coetzee and R. L. Kay, *J. Phys. Chem.*,**78**, 471 (1969).

105. G. Petrella and A. Sacco, *J. Chem. Soc., Faraday Trans.* 1, **74**, 2070 (1978).

106. B. S. Krumgalz, *J. Chem. Soc., Faraday Trans.* 1, **76**, 1275 (1980).

107. B. S. Krumgalz, *Russ. J. Phys. Chem.*, **46**, 858 (1972)& **47**, 528 (1973).

108. B. S. Krumgalz, *Russ. J. Phys. Chem.*, **47**, 956 (1973).

109. B. S. Krumgalz, *Russ. J. Phys. Chem.*, **48**, 1163 (1974).

110. B. S. Krumgalz, *Russ. J. Phys. Chem.*, **45**, 1448 (1971).

111. H. D. B. Jenkins and M. S. F. Pritcheit, *J. Chem. Soc., Faraday Trans.* 1, **80**, 721,(1984).

112. K. Fajans, *Naturwissenschaften*, **9**, 729 (1921).

113. D. F. C. Morris, *Struct. Bonding*, **6**, 157 (1969).

114. R. W. Gurney, *Ionic Process in Solutions*, Dover, New York, 1962.

115. H. S. Frank and W. Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).

116. E. Asmus, *Z. Naturforsch*, **4A**, 589 (1949).

117. M. H. Abraham, J. Liszi and E. Papp, *J. Chem. Soc., Faraday Trans.* 1, **78**, 197 (1982).

118. M. H. Abraham, J. Liszi and E. Papp, *J. Chem. Phys.*, **70**, 249 (1979).

119. M. H. Abraham, J. Liszi, *J. Chem. Soc. Faraday Trans.* 1, **76**, 1219 (1980).

120. S. Glasstone, K. J. Laidler and H. Eyring, *The Theory of Rate Processes*, Mcgraw Hill, New York, 1941, P. 447.

121. E. R. Nightingale and R. F. Benck, *J. Phys. Chem.*, **63**, 1777 (1959).

122. D. Feakins, D. J. Freemantle and K. G. Lawrence, *J. Chem. Soc., Faraday Trans.* 1, **70**, 795 (1974).

123. R. Sinha, *J. Phys. Chem.*, **44**, 25 (1940).

124. D. Feakins and K. G. Lawrence, *J. Chem. Soc.* A, **212** (1966).

125. D. F. Evans and S. M. A. Matesich in *Electrochemistry*, Vol.2, Eds. E. Yeager and A. J. Salklnd, John Wiley and Sons., 1973, Chapter 1.

126. R. Fernandez-Prini, in *Physical Chemistry of Organic Solvent Systems*, Eds. A. K. Covington and T. Dickinson, Plenum Press, 1973, Chapter 5.

127. M. S. Gruskiaewicz and R. Wood, *J. Phys. Chem.*, **101**, 6549 (1997).

128. G. Zimmerman, N. S. Gruskiaewicz and R. Wood, *J. Phys. Chem.*, **99**, 11612 (1995).

129. P. Ho and D. Palmer, *Geochim. Cosmochin. Acta*, **61**, 3027 (1997).

130. D. A. McInnes, *The Principles of Electrochemistry*, Reinhold Publishing Corporation (1961).

131. S. Glasstone, *An introduction To Electrochemistry*, Van Nostrand, New York, 1942.

132. T. Shedlovsky, in *Techniques of Organic Chemistry*, Vol. 1, Part 4, Ed. A. Weiaaberger, 3rded., Wiley, New York, 1959. Pp. 3011-48.

133. R. M. Fuoss and F. Accascina, *Electrolytic Conductance, Interscience*, New York (1959).

134. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd E.D., Butterworths,London, (1959).

135. J. Barthel, *Angew. Chem. internat. Edit.*, **7**, 260 (1968).

136. J. Barthel and G. D. Ribbins, *J. Chem. Educ.*, **48**, 53 (1971).

137. E. J. King, *Acid-Base Equibilibria*, Pergamon Press (1965).

138. G. Jones and R. C. Joseph, *J. Am. Chem. Soc.*, **50**, 1049 (1928).

139. G. Jones and B. C. Bradshaw, *J. Am. Chem. Soc.*, **55**, 1760 (1933).

140. C. W. Davies, *Ion Association*, Butterworths, London 1962.

141. R. M. Fuoss, *J. Chem. Educ.*, **32**, 527 (1955).

142. J. Barthel and H. J. Gores, *in Chemistry of Nonaqueous Solutions*, Eds. G. Mamantov and A. I. Popov, VCH, New York 1994.

143. Yu. P. Syrrikov, in *Solutions-Electrolyte Systems (Russ.)*, Ivanovo, 1988.

144. L. Onsager, *Z. Phys.*, **28**, 277 (1927).

145. R. M. Fuoss, *Rev. Pure Appl. Chem.*, **18**,125 (1968).

146. E. Pitts, *Proc. Roy Soc.*, **217 A**, 43 (1953).

147. R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957).

148. R. M. Fuoss, in *Chemical Physics of Ionic Solutions*, Eds. B. E. Conway and R. G. Barraddas, Wiley, New York, 1966, P. 462.

149. E. Pitts, R.E. Tabor and J. Dely, *Trans. Faraday* Soc., **65**, 849 (1969).

150. R. M. Fuoss and K. L. Hsia, Proc. *Natl. Acad. Sci.*, **59**, 1550 (1967); *J. Am. Chem. Soc.*, **90**, 3055 (1968).

151. R. Fernandez-Prini, *Trans. Faraday. Soc.*, **65**, 3311,(1969).

152. R. Fernandez-Prini and J. E. Pure, *Z. Phys. Chem.* (Leipzig), **288**, 373 (1965).

153. D. F. Evans and R. L. Kay, *J. Phys. Chem.*, **70**, 366 (1966).

154. D. E. Arrington and E. Grinswold, *J. Phys. Chem.*, **74**, 130 (1970).

155. R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 476 (1933).

156. T. Shedlovsky, J. Franklin. *instt.*, **225**, 739 (1938).

157. a) J-C. Justice, *J. Chem Phys.*, **65**, 353 (1968).
   b) J-C. Justice, R. Bury and C. Treiner, *J. Chem. Phys.*, **65**, 1707 (1968).

158. *Ref.* 133, p. 207.

159. N. Bjerrum and K. Dan. *Vidensk. Selek*, **7**, No. 9 1926.

160. M. Tissier and G. Douhert, *J. Soln. Chem.*, **7**, 87 (1978).

161. R. Fernandez-Prini and J. Prue, *Trans. Faraday Soc.*, **62**, 1257 (1966).

162. R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **66**, 1722, (1962) and **67**, 621 (1963).

163. R. M. Fuoss, *J. Phys. Chem.*, **49**, 525, (1975) and **82**, 2427, (1978) *Proc. Natl. Acad. Sci.*, USA, **75**, 16 (1978).

164. O. Bernard, W. Kunz, P. Turq and L. Blum, *J. Phys. Chem.*, **96**, 3833 (1992).

165. P. Turq, L. Blum, O. Bernard and W. Kunz, *J. Phys. Chem.*, **99**, 822 (1995).

166. S. Durand-Vidal, P. Turq and O. Bernard, *J. Phys. Chem.*, **100**, 17345 (1996).

167. H. L. Bianchi, I. Dujove and R. Fernandez- Prini, *J. Soln. Chem.*, **29**, 237 (2000).

168. J. Padova, in *Strecture and Transport Process in Water and Aqueous Solutions*, Ed. R. A. Horne, John Wiley, New York, 1972, Chapter 4.

169. M. Spiro, in *Physical Chemistry of Organic Solvent Systems*, Eds. A. K. Covington and T. Dickinson, Plenum Press, New York, 1973, Chapter 5, Part 2.

170. a) B. S. Krumgalz, *J. Chem. Soc., Faraday Trans.* 1, **79**, 571 (1983).
     b) B. S. Krumgalz, *J. Chem. Soc., Faraday Trans.* 1, **81**, 241 (1985).

171. P. Walden. H. Ulich and G. Busch, Z. *Phys. Chem*., **123**.

172. P. Walden and E. J. Birr, Z. *Phys. Chem., Teli* A, **144**, 269 (1929).

173. R. M. Fuoss and E. Hirsch, *J. Am. Chem. Soc.*, **82**, 1013 (1960).

174. S. Takezawa, Y. Kondo and N. Tokura, *J. Phys. Chem*., **77**, 2133 (1973).

175. D. S. Gill, *J. Chem. Soc., Faraday Trans*. 1, **77**, 751 (1981).

176. M. A. Coplan and R. M. Fuoss, *J. Phys. Chem*., **68**, 1177 (1964).

177. J. F. Coetzee and G. P. Cunninggham, *J. Am. Chem., Soc*., **87**. 2529 (1965).

178. D. S. Gill, Electrochim. *Acta,* **24**, 701 (1979).

179. D. S. Gill and M. B. Sekhri, *J. Chem. Soc., Faraday Trans*. 1, **78**, 119 (1982).

180. B. S. Krumgalz, *Faraday Discuss. Chem. Soc*., **64**, 336 (1977).

181. D. S. Berns and R. M. Fuoss. *J. Am. Chem. Soc.,* **82**, 5565 (1960).

182. C. J. Jannes and R. M. Fuoss, *J. Soln. Chem*., **4**, 91 (1975).

183. A. D'Aprano and R. M. Fuoss. *J. Soln. Chem*., **3**, 45 (1974).

184. A. D'Aprano and R. M. Fuoss. *J. Soln. Chem*., **4**, 175 (1975).

185. D. S. Gill, N. Kumari and M. S. Chauhan, *J. Chem. Soc., Faraday Trans*. 1, **81**, 687 (1985).

186. R. H. Stokes and R. A. Robinson, *Trans. Faraday Soc*., **53**, 301 (1957).

187. M. Born, Z. *Physik*, **1**, 221 (1920).

188. R. H. Boyd, *J. Chem. Phys*., **35**, 1281 (1961).

189. R. Zwanzig, *J. Chem. Phys*., **38**, 1603 (1963).

190. E. J. Passerson, *J. Phys. Chem*., **68**, 2728 (1964).

191. P. Walden, Z. *Phys. Chem*., **55**, 207 (1906) and 78, 257 (1912).

192. R. Gopal and M. M. Hussain, *J. Ind. Chem. Soc*., **40**, 981 (1963).

193. L. G. Longsworth, *J. Phys. Chem.*, **67**, 689 (1963).
194. M. Della Monica, U. Lamanna and L. Senatore, *J. Phys. Chem.*, **72**, 2124 (1968).
195. S. Broers, *J. Chem. Phys.*, **28**, 1158 (1958).
196. D. G. Miller, *J. Phys. Chem.*, **64**, 1958 (1960).
197. G. J. Hills, in *Chemical Physics of Ionic Solutions*, Eds. B. E. Conway and R. G. Barradas, John Wiley and Sons., New York, 1966, pp. 571-72.
198. R. H. Stokes and I. A. Weeks, *Aust. J. Chem.*, **17**, 304 (1964).
199. R. H. Stokes, in The *Structure of Electrolytic Solutions*, Ed. W. J. Hamer, Wiley, New York 1959.
200. R. M. Fuoss, *Proc. Natl. Acad. Sci. (USA)* **45**, 807 (1959).
201. H. S. Franks, in *Chemical Physics of Ionic Solutions*, Eds B. E. Conway and R. G. Barradas, John Wiley and Sons., New York, 1966, Chapter 4.
202. G. Atkinson and S. K. Koz, *J. Phys. Chem.*, **69**,128 (1965).
203. R. L. Kay, G. P. Cunningham and D. F. Evans, in *Hydrogen Bonded Solvent Systems*, Eds. A. K. Covington, P. Jones Taylor and Francis, London, 1968, P. 249.
204. R. L. Kay, B. J. Hales and G. P. Cunningham, *J. Phys. Chem.*, **71**, 3925 (1967).
205. R. L. Kay, C. Zawoyski and D. F. Evans, *J. Phys. Chem.*, **69**, 4208 (1965).
206. D. F. Evans and J. L. Broadwater, *J. Phys. Chem.*, **72**, 1037 (1968).
207. M. Spiro, in *Physical Chemistry of Organic Solvent Systems*, Eds. A. K. Convington and T. Dickinson, Plenum Press, New York, 1973, Chapter 5, Part 3.
208. R. Fernandez-Prini and G. Atkinson, *J. Phys. Chem.*, **75**, 239 (1971).
209. L. Bahadur and M. V. Ramanamurti, *J. Chem. Soc., Faraday Trans.* **1**, **76**, 1409 (1980).
210. L. Bahadur and M. V Ramanamurti, *J. Electrochem. Soc.*, **128**, 339 (1981).
211. L. Bahadur and M. V Ramanamurti, *Can. J. Chem.*, **62**, 1051 (1984).
212. A. Szejgis, A. Bald and J. Gregorowich, *J. Mol. Liq.*, **75**, 237 (1998).

213. J. L. Broadwater and R. L. Kay, *J. Phys. Chem.*, **74**, 3808 (1970).

214. S. Das and D. K. Hazra, *Ind. J. Chem.*, **27 A,** 1073 (1988).

215. S. Das and D. K. Hazra, *J. Ind. Chem., Soc.*, **LXV**, 100 (1988).

216. R. L. Kay and J. L. Broadwater, Ellectrochim. *Acta*, **16**, 667 (1971), *J. Soln. Chem.*, **5**, 57 (1976).

217. B. Das and D. K. Hazra, *J. Chem. Eng. Data*, **41**, 1470 (1996).

218. B. Das and D. K. Hazra, *J. Soln. Chem.*, **27**, 107, 1021 (1998).

219. A. D'Aprano and R. M. Fuoss, *J. Soln. Chem.*, 1704 & 1722 (1963).

220. P. Hemmes, *J. Phys. Chem.*, **78**, 907 (1974).

221. J. Hubbard and L. Onsager, *J. Chem. Phys.*, **67**. 4850 (1937).

222. N. Islam, M. R. Islam and M. Ahmad, *Z. Phys. Chem. (Leipzig)*, **622**, 129 (1981).

223. D. S. Gill, A. N. Sharma and H. Schneider, *J. Chem. Soc., Faraday Trans.* 1, **78**, 465 (1982).