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 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 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.[11,12] Moreover, the uniqueness of water as solvent has been questioned 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 solvents based on their dielectric constant, organic group type, acid-base properties or association through hydrogen-bonding[10], donor-acceptor properties[13], hard and soft acid-base principles[14] 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 non-electrolytes 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 physico-chemical 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 interaction can be studied spectroscopically where spectral 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. Sometimes, higher derivatives of these properties (e.g., partial molal volume, compressibility etc.) have been interpreted more effectively in terms of molecular interactions.

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, conductances, apparent molal volumes and adiabatic compressibilities of different tetraalkylammonium and alkali metal salts in the 'quasi-aprotic' solvent, 2-methoxyethanol (ME) and its binary aqueous mixtures.

Viscosity

Viscosity is one of the most important transport properties used for the determination of ion-solvent interactions and it has been studied extensively[15,16]. Viscosity is not a thermodynamic quantity, but viscosity of an electrolytic solution together with the thermodynamic property, $\bar{V}_2$, the 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 solvent, and the separation of these forces is not really possible. But from careful analysis, valid conclusion can be drawn regarding 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 was attempted by Grüneisen[17] in 1905. He noted non-linearity and 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 (η_r) of the electrolytes with molar concentration, c :

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

The equation reduces to

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

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 $Ac^{\frac{1}{2}}$, originally ascribed to Grüneisen effect, arose from the long range coulombic forces between the ions. The significance of the term had since then been realized due to the development of Debye-Hückel theory[19] of interionic 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 the solvent and solution using the Falkenhagen-Vernon[22] equation

$$A_{theo} = \frac{0.2577\,\Lambda^{o}}{\eta_{o}\,(\epsilon T)^{1/2}\,\lambda^{o}_{+}\lambda^{o}_{-}}\left[1 - 0.6863\left(\frac{\lambda^{o}_{+}-\lambda^{o}_{-}}{\Lambda^{o}}\right)^{2}\right] \qquad (3)$$

where Λ^o, λ^o_+ and λ^o_- are the limiting conductances of the electrolyte, cation and anion respectively at temperature T. ϵ and η_o are the dielectric constant and viscosity of the solvent respectively. 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].

$$\eta_r = 1 + Ac^{\frac{1}{2}} + Bc + Dc^2 \qquad (4)$$

The constant D can not 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 $(\eta_r - 1)/c^{\frac{1}{2}}$ 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 or deviation from linearity occur[24,28,29]. 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).

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[30,31].

(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 depolymerization effect) decreases η -values.

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

(4) Reduced B-values are obtained when the primary 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[32]

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

Several alternative formulations have been proposed for representing the 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

$$1/\eta = A \exp\left[-K'/(N_o-N)\right] \tag{6}$$

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_o is the hypothetical concentration at which the system becomes glass. The equation was recast by Majumdar <u>et al</u>[41-43] introducing the limiting condition that as $N \rightarrow 0$, $\eta \rightarrow \eta_o$, the viscosity of the pure solvent. Thus we have

$$\ln \frac{\eta}{\eta_o} = \ln \eta_{rel} = \frac{K'N}{N_o(N_o-N)} \tag{7}$$

Equation (7) predicts a straight line passing through the origin for the plot of $\ln \eta_{rel}$ vs. $N/(N_o-N)$, if a suitable choice for N_o is made. This equation has been tested by Majumdar <u>et al</u> 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 produces minimum deviation between η_{rel}(expt) and η_{rel}(theo) was accepted.

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

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

which is nothing but the Jones-Dole equation with the ion-ion interaction term represented as $B = K'/N_o^2$. 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, the equation (7) written in the form

$$\frac{N}{\ln \eta_{rel}} = \frac{N_o^2}{K'} - \frac{N_o}{K'} N \tag{9}$$

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

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

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 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[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 again proportional to the third power of the ionic mobilities. The method of Gurney[76] and also of Kaminsky[25] is based on

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

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°C. The assignment is supported from other thermodynamic properties[15]. Nightingale[77], however, preferred RbCl or CsCl rather than KCl from mobility considerations.

(2) The method suggested by Desnoyers and Perron[26] 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[78]:

$$B = 0.0025\ \bar{V}^{\circ} \qquad (12)$$

and by having an accurate value of the partial molal volume of the ion $\bar{V}^{\circ}$, it is possible to calculate the value of 0.359 for $B_{Et_4N^+}$ in water at 25°C.

Recently, Sacco et al[69] proposed the widely used "reference electrolyte" method. Thus for tetraphenylphosphonium tetraphenyl borate in water, we have

$$B_{BPh_4^-} = B_{PPh_4^+} = B_{BPh_4PPh_4}/2 \qquad (13)$$

$B_{BPh_4PPh_4}$ (since BPh_4PPh_4 is scarcely soluble in water) has been obtained from

$$B_{NaBPh_4} + B_{PPh_4Br} - B_{NaBr} = B_{BPh_4PPh_4} \qquad (14)$$

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 dilution. 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

$$B_{Bu_4N^+} = B_{Ph_4B^-} \tag{15}$$

since they thought that these ions have similar mobilities. However, according to Springer et al[81], $\lambda^{\circ}_{25}(Bu_4N^+) = 61.4$ and $\lambda^{\circ}_{25}(Ph_4B^-) = 58.3$ in acetonitrile.

(c) Gopal and Rastogi[45] 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[28] assuming

$$B\left[(i\text{-}Pe)_3BuN^+\right] = B\left[Ph_4B^-\right] = \tfrac{1}{2}B\left[(i\text{-}Pe)_3BuNPh_4B\right] \tag{17}$$

at all temperatures. 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 conductance for certain ion 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 and 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 $(i\text{-}Pe)_3BuN^{+}$ or $(i\text{-}Am)_3BuN^{+}$ 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[83,84] has recently proposed a method for the resolution of B-coefficients. The method is based on the fact that the large tetraalkylammonium ions are not solvated[85,86] in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic B-values for large R_4N^{+} ions (where $R > Bu$) in organic solvents are proportional to their ionic dimensions. Thus we have

$$B_{R_4NX} = a + b r^{3}_{R_4N^{+}} \tag{18}$$

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 $r^3_{R_4N^+}$ to zero cation dimension gives 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

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \tag{19}$$

and

$$\frac{B_{R_4N^+}}{B_{R'_4N^+}} = \frac{r^3_{R_4N^+}}{r^3_{R'_4N^+}} \tag{20}$$

The radii of the tetraalkylammonium ions 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 of Ph_4B^- (5.35 Å) 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

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

and

$$B_{Bu_4NBPh_4} = B_{Bu_4N^+} + B_{Ph_4B^-} \tag{22}$$

The method requires only the B-values of 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 in different organic solvents using the assumption :

$$B_{i-Am_3BuN^+} = B_{Ph_4B^-} = B_{i-Am_3BuNBPh_4}/2 \tag{23}$$

Recently Lawrence and Sacco[71,72a] used Bu_4NBBu_4 (tetrabutylammonium tetrabutyl borate) and Ph_4PBPh_4 (tetraphenyl phosphonium tetraphenyl borate) 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,

$$\frac{B(Bu_4N^+)}{B(Bu_4B^-)} = \frac{V_W(Bu_4N^+)}{V_W(Bu_4B^-)} \tag{24}$$

or,

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

A similar division can be made for the Ph_4PBPh_4 system.

Recently, Lawrence <u>et al</u>[72b] 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_4NBu_4B 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 <u>et al</u>[72c,d].

Jenkins and Pritcheit[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 halides by employing Fajans' competition principle[89] and 'volcano plots' of Morris[90]. 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[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 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[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 summarized as follows:

(i) A and $dA/dT > 0$ (26)

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

are characteristic of structure breaking ions, and

(iii) $B_{ion} > 0$ and $dB_{ion}/dT < 0$ (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[91], A, B, C zone 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_o) plus the viscosity changes resulting from competition between various effects occurring in the ionic neighbourhood. Thus,

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

(Jones-Dole equation)

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

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

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

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

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

whereas according to Lawrence and Sacco[71],

$$B_{ion} + B_W + B_{Solv} + B_{Shape} + B_{Ord} + B_{Disord} \quad (32)$$

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 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_{ion}^{Reinf} is the positive increment conditioned by the effect of 'reinforcement of the water structure' by large tetraalkylammonium ions due to hydrophobic hydration. The phenomenon is inherent in the intrinsic water structure and absent in organic solvents. B_W and B_{Solv} account for viscosity increases 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} 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} (A), B_{ion}^{Str} (D) is small for the ions. Thus B_{ion} will be larger and positive as $B_{ion}^{Einst} + B_{ion}^{Orient} \quad B_{ion}^{Str}$. However, B_{ion}^{Einst} and B_{ion}^{Orient} 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_{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 $B_{ion}^{Einst} + B_{ion}^{Orient} \quad B_{ion}^{Str}$ 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., $B_{ion}^{Einst} + B_{ion}^{Orient} = B_{ion}^{Str}$ so that B is close to zero.

Large molecular ions like tetraalkylammonium ions have large B_{ion}^{Einst} because of large size but B_{ion}^{Orient} and B_{ion}^{Str} would be small i.e. $B_{ion}^{Einst} + B_{ion}^{Orient} \quad B_{ion}^{Str}$ and B would be positive and large. The values 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}^{Eints} but the orientation of solvent molecules in the secondary layer will be decreased due to increasing thermal motion leading to decrease in B_{ion}^{Str} . B_{ion}^{Orient} 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_{ion}^{Orient} and B_{ion}^{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 ions 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[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-coefficients of salts. The ionic B-values show a linear relationship with the partial molar ionic entropies of hydration $\bar{S}^o_h$

$$\bar{S}^o_h = \bar{S}^o_{aq} - \bar{S}^o_g \qquad (33)$$

where $\bar{S}^o_{aq} = \bar{S}^o_{ref} + \Delta S^o$, $\bar{S}^o_g$ 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 ($\bar{S}^o_{H^+}$) 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 monatomic and polyatomic ions.

The correlation was utilised by Abraham <u>et al</u>[94] to assign single-ion B-coefficients so that a plot of ΔS^o_e [95,96], the electrostatic entropy of solvation or $\Delta S^o_{I,II}$ [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^o_e and ΔS^o_I, and the single-ion B-coefficients. Both entropy criteria (ΔS^o_e and $\Delta S^o_{I,II}$) 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-methyl formamide, dimethyl formamide, dimethyl sulfoxide, 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].

Thermodynamics of viscous flow

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

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

where E_{Vis} is the experimental energy of activation which is determined from the plot of log η 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[98] 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 $Ac^{\frac{1}{2}}$. Thus,

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

$$\Delta E^{\neq}_{\eta\,(soln)} = \Delta E^{\neq}_{\eta_0\,(solv)} + \Delta E^{\neq}_{V} \qquad (36)$$

$\Delta E_V^{\neq}$ 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 ions upon the viscous flow of the solvent molecules.

Feakins __et__ __al__[99] have suggested an alternative formulation based on the transition state treatment of the relative viscosity of the electrolytic solutions. They suggested the following expression

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000}\cdot\frac{(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})}{RT} \qquad (37)$$

where $\bar{V}_1^0$ and $\bar{V}_2^0$ are the partial molal 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[97]

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

and $\Delta\mu_2^{\ominus\neq}$ 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 and solutions (subscripts 1 and 2 respectively) can be calculated using the following equations

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

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

The separation of the thermodynamic parameters are based on the equality of effects for K^+ and Cl^- or BPh_4^- and $(i\text{-}Pe)_3$, BuN^+ ions. In aqueous solution, both $T\Delta S_2^{\ominus\neq}$ and $\Delta H_2^{\ominus\neq}$ 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^+, $\Delta H_2^{\ominus\neq}$ and $T\Delta S_2^{\ominus\neq}$ 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[15]. The ions in solution can be regarded as rigid spheres suspended in continuum. The hydrodynamic treatment presented by Einstein[78] leads to the equation

$$\eta/\eta_o = 1 + 2.5\phi \qquad (41)$$

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 monatomic cations). Thus, we have from (1) and (41)

$$2.5\,\phi = A\sqrt{c} + Bc \qquad (42)$$

Since the term A c can be neglected in comparison with Bc and $\phi = cV_i$ where V_i is the partial molal volume of the solute, we get

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

In the ideal case, the B-coefficient is a linear function of the solute partial molal volume (V_i) with slope equal to 2.5.

$B_{\pm}$ can be equated to

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

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 Stoke's 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]

$$B_{\pm} = \frac{2.5}{1000} (V_i + nV_s) \tag{45}$$

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.

Viscosity measurements in mixed solvents are very few[53,61-67]. 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 is water, such study can provide useful information on the effects induced by the cosolvent on the water structure.

Conductance

Conductance measurement is one of the most accurate and widely used physical methods for investigation of electrolytic 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 interaction theories are not applicable. Fortunately for us, accurate theories of electrolytic conductance are available to explain the results even upto a concentration limit of κd (κ = Debye-Huckel length, d = distance of closest approach of free ions). Recent development of experimental tehcniques 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.

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. 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 equations 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[102-115].

The studies on electrical conductances 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 conductances of ionophores (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 give the equivalent conductances at infinite dilution, the dissociation constants of ionogens, the association constants of ionophores and information about the structure of solutions in the vicinity of the ion[109].

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

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

where

$$S = \alpha\Lambda^{o} + \beta \qquad (47)$$

$$\alpha = \frac{(Ze)^2 \kappa}{3(2+\sqrt{2})\,\epsilon_r kT c^{1/2}} = 82.046 \times 10^4 \frac{Z^3}{(\epsilon_r T)^{3/2}} \Big/ \mathrm{mol}^{-1/2}\, \ell^{1/2} \quad (48)$$

and $$\beta = \frac{Z^2 e F \kappa}{3\pi\eta c^{1/2}} = 82.487 \frac{Z^3}{\eta(\epsilon_r T)^{1/2}} \Big/ \mathrm{S\,cm^2\,mol}^{-3/2}\, \ell^{1/2} \quad (49)$$

η = viscosity in poise.

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[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^o values obtained for the equivalent conductances at infinite dilution using Fuoss-Onsager theory differed considerably[117] from those obtained using Pitts 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]

$$\Lambda = \Lambda^{0} - \frac{\alpha \Lambda^{0} \sqrt{c}}{(1+\kappa a)(1+\kappa a/\sqrt{2})} - \frac{\beta \sqrt{c}}{1+\kappa a} + G(\kappa a) \qquad (50)$$

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

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

is generally employed in the analysis of experimental results.

However, it has been found that these equations have certain limitations and in some cases fail to fit the experimental data. Some of these results have been discussed elaborately by Fernandez-Prini[103,123,124]. Further correction of equation (51) was made by Fuoss and Accascina[107]. They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation is

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

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 Pitt's equation gives better fit to the experimental data in aqueous solutions[125].

Ion-association

The equation (52) given above successfully represents the behaviour of completely dissociated electrolytes. The plot of against c (limiting Onsager equation) is 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[126].

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

$$M^{z+} + A^{z-} \rightleftharpoons MA \qquad (53)$$

where

$$K_A = \frac{1-\alpha}{\alpha^2 c^2 \gamma_\pm^2} \qquad (54)$$

and

$$\alpha = 1 - \alpha^2 c K_A \gamma_\pm^2 \qquad (55)$$

For strongly associated electrolytes, K_A and Λ° have been determined using Fuoss-Kraus equation[127] or Shedlovsky's equation[128]

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

where $T(z) = F(z)$ (Fuoss-Kraus) and

$1/T(z) = S(z)$ (Shedlovsky)

$$F(z) = 1 - z\left(1 - z\left(1 - z\left(1 - \cdots\right)^{-1/2}\right)^{-1/2}\right)^{-1/2} \tag{57}$$

and $$S(z) = 1 + z + z^2/2 + z^3/8 + \cdots \tag{58}$$

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

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

This equation was modified by Justice[129]. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations

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

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

$$\ln \gamma_\pm = -K q^{1/2} / (1 + k_R \sqrt{\alpha c}) \tag{62}$$

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

$$R = q = e^2/2\epsilon kT \tag{63}$$

(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^o of two free ions to form an ion-pair. The following equation has been proposed by Fuoss[130]

$$K_A = (4\pi N a^3/3000) \exp(e^2/a\epsilon kT) \tag{64}$$

In some cases, the magnitude of K_A was too small to permit a calculation of a°. The distance parameter was finally determined from the more general equation due to Bjerrum[131]

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

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 utilised by Douhéret[132].

Ion-size parameter and ionic association

The equation (52) can be written as

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

(with J_2 term omitted)

Thus, a plot of Λ' vs. c gives a straight line with Λ° as intercept and J' or $(J-B\Lambda^\circ)$ as slope. Assuming $B\Lambda^\circ$ to be negligible, a° values can be calculated from J'. The a° values obtained by this method in DMSO were much smaller[126] 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° 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 $B\Lambda^{\circ}c$) leads to a larger value of a°[133], still the agreement is poor. However, little of real physical significance may be attached to the distance of closest approach derived from J[134].

Fuoss[135] in 1975 proposed a new conductance equation. He[135] subsequently put forward another conductance equation in 1978 which replaced the old one. He classified the ions 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 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 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:

$$A^+ + B^- \rightleftharpoons (A^+ \cdots\cdots B^-) \rightleftharpoons A^+ \quad B^- \rightleftharpoons AB \qquad (67)$$

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 ($r \leq R$), the concentration of solvent-separated pair is $c(1-\gamma)(1-\alpha)$ and that of contact pair is $\alpha c(1-\alpha)$.

The equilibrium constants for (67) are

$$K_R = (1-\alpha)(1-\gamma)/c\gamma^2 f^2 \qquad (68)$$

$$K_S = \alpha/(1-\alpha) = \exp(-E_S/kT) = e^{-\epsilon} \qquad (69)$$

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

$$1-\alpha = 1/(1 + K_S) \qquad (70)$$

Substitution in (68) gives the conductometric pairing constant

$$K_\Lambda = (1-\gamma)c\gamma^2 f^2 = K_R/(1-\alpha) = K_R(1+K_S) \qquad (71)$$

which determines the concentration $c\gamma$ of active ions, 'active' in the sense that they produce the long-range interionic effects. The 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 $\Delta\Lambda_e < 0$, the electrophoretic countercurrent). The various patterns can be reproduced by theoretical functions of the form

$$\Lambda = p[\Lambda^0(1 + \Delta X/X) + \Delta\Lambda_e] \qquad (72)$$

$$= p[\Lambda^0(1 + R_X) + E_L] \qquad (73)$$

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

$$p = 1 - \alpha(1 - \gamma) \qquad (74)$$

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

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

The quilibrium constant for the effective reaction

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

$$K_A = (1-\gamma)/\, c\gamma^2 f^2 \approx K_R K_S \qquad 976)$$

because $K_S \gg 1$.

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

$$\gamma = 1 - K\, c\gamma^2 f^2 \tag{77}$$

$$-\ln f = \beta\kappa/2(1+\kappa R), \quad \beta = e^2/\epsilon kT \tag{78}$$

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

The details of the calculations are presented in the 1978 paper[135]. The short comings 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 (0.1 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 dilution, the motion of an ion is limited solely by the interactions 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

$$\Lambda^{o} = \lambda^{o}_{+} + \lambda^{o}_{-} \qquad (80)$$

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.,

$$\lambda^{o}_{+} = t_{+}\Lambda^{o} \quad \text{and} \quad \lambda^{o}_{-} = t_{-}\Lambda^{o} \qquad (81)$$

Thus from the accurate values of λ^{o} of ions, it is possible to separate the contributions due to cations and anions in the solute-solvent interactions[136]. However, accurate transference number determinations are limited to few solvents only. Spiro[137] and more recently Krumgalz[138 (a)] 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[138a)] and some important points are mentioned below:

(i) Walden equation[139]

$$(\lambda^{\circ}_{\pm})^{25}_{\text{acetone}}\ \eta_{o\,\text{acetone}} = (\lambda^{\circ}_{\pm})^{25}_{\text{water}}\ \eta_{o\,\text{water}} \qquad (82)$$

$$\left.\begin{aligned} \text{(ii)}\ \lambda^{\circ}_{Pic}\cdot\eta_{o} &= 0.267^{139,140} \\ \lambda^{\circ}_{Et_4N^+}\,\eta_{o} &= 0.296 \end{aligned}\right\} \quad \text{based on } \Lambda^{\circ}_{Et_4NPic} = 0.563 \qquad (83)$$

Walden considered the products to be independent of temperature and solvent. However, the $_{Et_4NPic}$ 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.

$$\text{(iii)}\ \lambda^{\circ}_{25}(Bu_4N^+) = \lambda^{\circ}_{25}(Ph_4B^-)^{141} \qquad (84)$$

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

$$\text{(iv)}\ \lambda^{\circ}_{25}(Bu_4N^+) = \lambda^{\circ}_{25}(Bu_4B^-)^{142} \qquad (85)$$

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.

$$\text{(v)}\ \lambda^o_{25}(R_4N^+) = zF^2/6\pi N\eta_o[r_i - (0.0103\epsilon_o + r_y)]^{143} \tag{86}$$

where z and r_i are the charge and crystallographic radius of the proper ion; η_o and ϵ_o are the viscosity and dielectric constant of the medium; r_y is an adjustable parameter taken equal to 0.85Å for dipolar non-associated solvents and 1.13Å for hydrogen-bonded and other associated solvents.

However, large discrepancies were observed between the experimental and calculated values[138(a)]. In a recent paper[138(b)] Krumgalz examined Gill's approach more critically using conductance values in many solvents and found the method to be reliable in three solvents e.g., 1-butanol, acetonitrile and nitromethane.

$$\text{(vi)}\ \lambda^o_{25}(i\text{-}Am_3BuN^+) = \lambda^o_{25}(Ph_4B^-)^{144} \tag{87}$$

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

$$\text{(vii)}\ \lambda^o_{25}(Ph_4B^-) = 1.01\ \lambda^o_{25}(i\text{-}Am_4B^-)^{145} \tag{88}$$

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

Krumgalz[138(a)] suggested a method for determining the limiting ion conductances in organic solvents or organic mixtures. 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 utilised as a suitable model for apportioning Λ^o values into ionic components for non-aqueous electrolytic solution

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

$$r_S = \frac{|z|F^2}{A\pi N \eta_o \lambda^o_\pm} \qquad (89)$$

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

$$\lambda^o_\pm \eta_o = \text{constant} \qquad (90)$$

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

We have used Bu_4NBPh_4 as the 'reference electrolyte', but instead of equal division, we divided the Λ^o values using the method similar to that proposed by Krumgalz[83] for division of B-values

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

The r-values have been taken from the works Gill et al[146,147].

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 value of the ratio $\lambda^o(BPh_4^-)/\lambda^o(Bu_4N^+)$ becomes 1.06 if we choose $r(Bu_4N^+) = 3.85$ Å and $r(BPh_4^-) = 4.08$ Å as suggested by Krumgalz[83,148].

Fuoss et al[149-152] assumed, from extensive measurements of 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 ± 1%). This gives 1.079 for $\lambda^o(Bu_4N^+)/\lambda^o(Ph_4B^-)$ which is close to 1.07.

D'Aprano and Fuoss[152] used Bu_4NBPh_4 to calculate single-ion conductance in mixed organic solvents applying the relations

$\lambda^{o}(Bu_4N^+) = 0.213/\eta_o$ and $\lambda^{o}(Ph_4B^-) = 0.201/\eta_o$ which means $\lambda^{o}(Bu_4N^+)/\lambda^{o}(Ph_4B^-) = 1.06$.

Moreover, since the charge is equal to the number of ions, the equivalent conductances of these ions depend on their mobilities, the divisions may be in terms of the reciprocal of their van der Waals' volume i.e.,

$$\frac{\lambda^{o}(Bu_4N^+)}{\lambda^{o}(Ph_4B^-)} = \frac{186.8}{179.1} = 1.04 \qquad (92)$$

The van der Waals' volumes have been taken from the works of Lawrence and Sacco[71]. 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 <u>et al</u>[153] proposed the following equation

$$\frac{\lambda^{o}(Bu_4N^+)}{\lambda^{o}(Ph_4B^-)} = \frac{5.35 - (0.0103\epsilon_o + r_y)}{5.00 - (0.0103\epsilon_o + r_y)} \qquad (93)$$

and the ratio is close to 1.07 as used by us.

Solvation number[136]

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 shall V_s can be written as

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

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

$$n_s = V_s^s / \bar{V}_o \tag{95}$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects[154], from

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

when V_s^o 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[22,27,108] and theoretical corrections[155-158] have been suggested in order to apply it to most of the ions.

Stokes' law and Walden's rule

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

$$\lambda_i^o = \frac{0.819\,|z_i|}{\eta_o R_i} \tag{97}$$

where η_o, 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

$$\lambda_i^o \eta_o = \frac{0.819\ Z_i}{R_i} = \text{constant} \tag{98}$$

This is known as Walden rule[159]. The effective radii obtained using this equation can be used to estimate the solvation numbers. The failure of the Stokes' radii to give the effective size of the solvated ions for small ions is often attributed to the inapplicability of Stokes' law to molecular motion.

Robinson and Stokes[108], Nightingale[77] and others[160-162] 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[126] 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[163] was invoked without much success[164,165] but it has been found that

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

where p is usually 0.7 for alkali metal or halide ions and p = 1 for the large ions[166,167].

Attempts to explain the change in the Stokes' radius R_i have been made. The apparent increase in the real radius r has been attributed to ion-dipole polarisation and the effect of dielectric saturation on R. Fuoss noticed[168] the dependence of the Walden product, $\Lambda^o\eta_o$, on the dielectric constant 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

$$\lambda_{i,o}^o = \frac{Fe|z_i|}{6\pi R_\infty (1 + A/\epsilon R_\infty^2)} \tag{100}$$

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

$$R_i = R_\infty + A/\epsilon \tag{101}$$

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

In 1961, Boyd[156] gave the expression

$$\lambda_i^o = \frac{F e |Z_i|}{6 \pi \eta_o r_i} \left[1 + \frac{2}{27} \frac{1}{\pi \eta_o} \frac{Z_i^2 e^2 \tau}{r_i^4 \epsilon_o} \right] \tag{102}$$

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

Zwanzig[157] 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

$$\lambda_i^o = \frac{Z_i e F}{A_v \pi \eta_o r_i + A_D [Z_i^2 e^2 (\epsilon_r^o - \epsilon_r^\infty) \tau / \epsilon_r^o (2\epsilon_r^o + 1) r_i^3} \tag{103}$$

where $\epsilon_r^o, \epsilon_r^\infty$ 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

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

The theory predicts[169] that λ°_{i} passes through a maximum of $27^{1/4}/4B^{1/4}$ 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 the results in different solvents, equation (103) can be rearranged as[170]

$$\frac{Z_i^2 eF}{\lambda_i^{\circ}\eta_o} = A_V \pi r_i + \frac{A_D Z_i^2}{r_i^3} \frac{e^2(\epsilon_r^{\circ} - \epsilon_r^{\infty})}{\epsilon_r^{\circ}(2\epsilon_r^{\circ}+1)} \frac{\tau}{\eta_o} \tag{105}$$

or $$L^{*} = A_V \pi r_i + (A_D Z_i^2 / r_i^3)\, \rho^{*} \tag{106}$$

In order to test Zwanzig's theory, the equation (106) was applied to methanol, ethanol, acetonitrile, butanol and pentanol solutions where accurate conductance and transference data are available[169-174]. 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 solvent, dipole moment and free electron pairs were considered the predominant factors in the deviation from Stokes' law[136].

It is noted that the Zwanzig theory is successful for large organic cations in aprotic media where solvation is likely to be minima 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 theory has the inherent weakness of its ability to account for the structural features[175] 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[176].

(2) The theory does not distinguish between positively and negatively charged ions and therefore can not explain why certain anions in dipolar aprotic media possess considerably higher molar conductances than the fastest cations[175].

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 and DMA-H_2O mixtures[177-179] and other aqueous binary mixtures[180-183]. To derive expressions for the variation of the Walden products with the composition of mixed polar solvents, various attempts have been made[156,157,184] 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;

(2) it is not possible to account for some specific properties of different kinds of ions and solvent molecules[177]. Ions moving in a dielectric medium experience a frictional force due to dielectric loss arising from ion-solvent interactions with the hydrodynamic force. Zwanzig's expression though accounts for a change in Walden product with solvent composition does not account for the maxima. Hemmes[185] 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 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 by experimental observations. Hubbard and Onsager[186] 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.

However, quantitative expression is still awaited. Further improvements[187,188] naturally must be in terms of (1) sophisticated treatment of dielectric saturation, and (2) specific structural effects involving ion-solvent interactions.

Apparent and partial molal volumes and apparent molal adiabatic compressibility

One of the well recognised approaches to the study of molecular interactions in fluids is the use of thermodynamic methods. Thermodynamic properties are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in the solution phase. Fundamental properties such as enthalpy, entropy and Gibbs energy represent the macroscopic state of the system as an average of numerous microscopic states at a given temperature and pressure. An interpretation of these macroscopic properties in terms of molecular phenomena is generally difficult. Sometimes, higher derivatives of these properties can be interpreted more effectively in terms of molecular interactions. For example, the partial molal volume, the pressure derivative of partial molal Gibbs energy, is a useful parameter for interpreting solute-solvent interactions. Various concepts regarding molecular processes in solutions, electrostriction[189], hydrophobic hydration[190], micellization[191] and cosphere overlap during solute-solute interactions[76,192], to a large extent have been derived and interpreted from the partial molal volume data of many compounds. The compressibility property, which is the second derivative of the Gibbs energy, also is a sensitive indicator of molecular interactions and can provide useful information about these phenomena, particularly in cases where partial molal volume data alone fail to provide an unequivocal interpretation of the interactions.

Apparent and partial molal volumes

The apparent molal volumes, ϕ_V, of the solutes can be calculated by using the following relation

$$\phi_V = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \qquad (107)$$

where M is the molecular weight of the solute, ρ_o and ρ are the densities of solvent and solution respectively and c is the molarity of the solution.

The partial molal volumes, $\bar{V}_2$, can be obrained from from the equation

$$\bar{V}_2 = \phi_V + \frac{1000 - c\phi_V}{2000 + c^{1.5}\, d\phi_V/d\sqrt{c}}\, c^{1/2}\, \frac{d\phi_V}{d\sqrt{c}} \tag{108}$$

The extrapolation of the apparent molal volume of electrolytes to infinite dilution and the expression of the concentration dependence of the apparent molal volume have been made by four major equations over the period of years — the Masson equation[193], the Redlich-Meyer equation[194], the Owen-Brinkley equation[195] and the Pitzer equation[196]. Masson[193] found that the apparent molal volumes of electrolytes, ϕ_V , vary with the square root of the molar concentration by the linear equation

$$\phi_V = \phi_V^o + S_V^* \sqrt{c} \tag{109}$$

where ϕ_V^o is the apparent molal volume at infinite dilution (equal to the partial molal volume at infinite dilution, $\bar{V}_2^o$) and S_V^* is the experimental slope . The majority of ϕ_V data in water[197] and nearly all data in non-aqueous solvents[198-202] have been extrapolated to infinite dilution through the use of equation (109). However, Redlich and Meyer[194] have shown that an equation of the form of (109) can not be any more than a limiting law, where for a given solvent and temperature the slope, S_V^*, should depend only upon the valence type. The suggest representing by

$$\phi_V = \phi_V^o + S_V \sqrt{c} + b_V c \tag{110}$$

where

$$S_V = Kw^{3/2} \tag{111}$$

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

$$w = 0.5 \sum_i \nu_i Z_i^2 \tag{112}$$

and

$$K = N^2 e^3 \left(\frac{8\pi}{1000\, \epsilon^3 RT}\right)^{0.5} \left[\left(\frac{\partial \ln \epsilon}{\partial P}\right)_T - \frac{\beta}{3} \right] \tag{113}$$

where β is the compressibility of the solvent. Until recently, the variation of dielectric constant with pressure was not known accurately enough, even in water, to calculate accurate values of the theoretical limiting slope and in organic solvents accurate data of this type are almost totally lacking.

The Redlich-Meyer[194] extrapolation equation adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies[203-205] on some

2:1, 3:1 and 4:1 electrolytes show deviations from this equation. Thus, for polyvalent electrolytes, the more complete Owen-Brinkley equation[195] can be used to aid in the extrapolation to infinite dilution and to adequately represent the concentration dependency of ϕ_V.

The Owen-Brinkley equation[195], derived by including the ion-size parameter, a (in cm), is given by

$$\phi_V = \phi_V^o + S_V \tau(\kappa a)\sqrt{c} + 0.5 W_V \theta(\kappa a) c + 0.5 K_V c \qquad (114)$$

where the symbols have their usual significance. However, equation (114) has not been widely employed for the treatment of results for non aqueous solutions.

Recently, the Pitzer formalism has been used by Pogue and Atkinson[206] to fit the apparent molal volume data. The Pitzer equation for the apparent molal volume of a single salt $M_{\nu_M} X_{\nu_X}$ is

$$\phi_V = \phi_V^o + \phi_V^o + \nu|Z_M Z_X| A_v / 2b \ln(1 + bI^{0.5}) + \qquad (115)$$
$$2\nu_M \nu_X RT[m B_{MX}^V + m^2(\nu_M \nu_X)^{0.5} C_{MX}^V]$$

where the symbols have their usual significance.

Thorough tests of equations (109), (110), (114) and (115), however, will require more accurate data on densities and also on the pressure dependence of the dielectric constant of pure solvent.

Ionic limiting partial molal volumes

The calculation of the ionic limiting partial molal volumes in organic solvents is a very difficult task. At present, however, most of the existing ionic limiting partial molal volumes in organic solvents were obtained by the application of methods developed for aqueous solutions[207] to non-aqueous electrolyte solutions. In the last few years, the method suggested by Conway et al[207], has been used more frequently. These authors used the method to determine the limiting partial molal volumes of the anion for a series of homologous tetraalkylammonium chlorides, bromides and iodides in aqueous solution. They plotted the limiting partial molal volume, $\bar{V}^{o}_{R_4NX}$, for a series of these salts with a halide ion in common as a function of the formula weight of the cation, $M_{R_4N^+}$, and obtained straight-line graphs for each series. They suggested, therefore, that their results fitted the equation

$$\bar{V}^{o}_{R_4NX} = \bar{V}^{o}_{X^-} + bM_{R_4N^+} \tag{116}$$

and that extrapolation to zero cationic formula weight gave the limiting partial molal volumes of the halide ions, $\bar{V}^{o}_{X^-}$. Uosaki et al[208] have used this method for the separation of some literature values and of their own $\bar{V}^{o}_{R_4NX}$ values into ionic contributions in organic electrolyte solutions. Krumgalz[209] applied the same method to a large number of partial molal volume data for non-aqueous electrolyte solutions in a wide temperature range. Recently, we have also used this method for the division of partial molal volumes into the ionic components in 2-methoxyethanol[202].

Apparent molal adiabatic compressibility

Although for a long time attention has been paid to the apparent molal adiabatic compressibility for electrolytes and other compounds in aqueous solutions[210-214], measurements in non-aqueous solvents are still scarce. It has been emphasized by many authors[211,212] that the apparent molal adiabatic compressibility data can be used as a useful parameter in elucidating the solute-solvent and solute-solute interactions.

The values of the adiabatic compressibility coefficient (β) were calculated by using the Laplace equation

$$\beta = 1/u^2\rho \qquad (117)$$

where ρ is the solution density and u is the sound velocity in solution. The apparent molal adiabatic compressibility (ϕ_K) of liquid solution was calculated from the relation:

$$\phi_K = \frac{1000}{m\rho\rho_o} (\beta\rho - \beta^o\rho) + \beta\frac{M}{\rho_o} \tag{118}$$

where m is the molality of the solution; β^o and β are the compressibility coefficients of the solvent and solution respectively.

Plotting of apparent molal adiabatic compressibility (ϕ_K) against the square root of the molal concentration of the solutes and extrapolation to zero molal concentration gives the limiting apparent molal adiabatic compressibility (ϕ_K^o) according to equation[211,214]:

$$\phi_K = \phi_K^o + S_K\sqrt{m} \tag{119}$$

where S_K is the experimental slope.

The limiting apparent molal adiabatic compressibility (ϕ_K^o) and the experimental slope (S_K) can be interpreted in terms of solute-solvent and solute-solute interactions, respectively. It is well established that the solutes causing electrostriction lead to decrease the compressibility of the solution[215,216]. This is reflected by the negative values of ϕ^o_K of electrolyte solutions. Hydrophobic solutes often show negative compressibilities due to the ordering that is induced by them in the water structure[191,215]. The compresseibility of hydrogen bonded structure, however, varies depending on the nature of H-bonds involved[215]. On the other hand, the poor fit of the solute molecules[217,218] as well as the possibility of flexible H-bond formation appear to be responsible for causing a more compressible environment (and hence a positive ϕ^{o}_{K} value) in the aqueous medium. The positive ϕ^{o}_{K} values have been reported in aqueous non electrolyte[219] and non electrolyte-non electrolyte[220] solutions.

From the discussion it is apparent that the problem of ion-solvent interactions is intriguing as well as interesting. It is desirable to attack this problem using different experimental techniques. We have, therefore, utilized five important methods viz., viscometry, conductometry, densimetry, ultrasonic interferometry and spectrophotometry to study the problem of ion-solvent interactions of some tetraalkylammonium and alkali metal salts in 2-methoxyethanol and its aqueous binary mixtures.

2-Methoxyethanol (ME)

2-Methoxyethanol is a monomethyl ether of ethylene glycol (EG). Hence, it is very likely to show physico-chemical characteristics midway between protic and dipolar aprotic solvents. Therefore, it is of much interest to study the behaviour of electrolytes in such solvent media.

IR studies[221] indicate that the predominant configuration of ME molecules is the gauche form to facilitate intramolecular hydrogen bonding as shown in structure I.

Simple consideration of molecular structure indicates that due to the presence of electron repelling CH_3 group, ME is more basic than ethylene glycol and water. Also, the restricted availability of the acidic H atom of OH groupmakes ME molecules less acidic than ethylene glycol and water, thus imparting a 'quasi-aprotic' character to it.

Moreover, the basicity and proticity are likely to be relayed through co-operative structure of H-bonding[222] between the cosolvent and water molecules in aqueous solutions. Thus in ME + H_2O system, the possible hydrogen bonded cosolvent-water complex of the type II is also more basic and less acidic than water and EG-water mixtures.

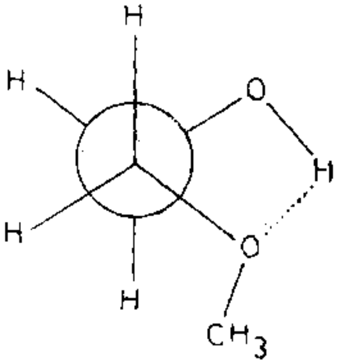
Studies on fundamental physico-chemical properties like density and dielectric constant for ME-water mixtures have been reported at different temperatures in the water rich region[223]. Recently, Douhéret and his coworker[224] studied these properties for ME-water mixtures at 25°C over the entire composition range. Dielectric constant is found to decrease monotonically with increasing ME content whereas the density goes through a maximum. Desnoyers et al[225] have reported apparent molal volume and heat capacity of aqueous ME at 25°C and showed that ME behaves as a fairly typical polar non electrolyte in water. Heat capacity and heat of solution of ME[226] have been reported by a number of workers. Partial molal volumes of ME have been studied with water[227]. The change in free energy, entropy and enthalpy associated with the transfer of ME from ideal gas phase to dilute aqueous solution at 25°C has also been reported[228].

Notably enough, relatively few studies have been reported with aqueous 2-methoxyethanol as solvent medium. Conductance behaviour of ion-pair formation of tetrabutylammonium bromide in aquo-ME[229] at 25°C was interpreted on the basis of the modification of water structure, depending on the nature of the solvent. Saits[230] studied the relation between the structure of water mixtures of organic solvents, their solvation and cation exchange selectivity of metal ions in aqueous ME. Morel and coworkers[231] also predicted the relation between the free energy of transfer and selectivity of an ion exchanger. Activity coefficients of NaCl in water mixtures of ME at 25°C were studied by Richard *et al*[232].

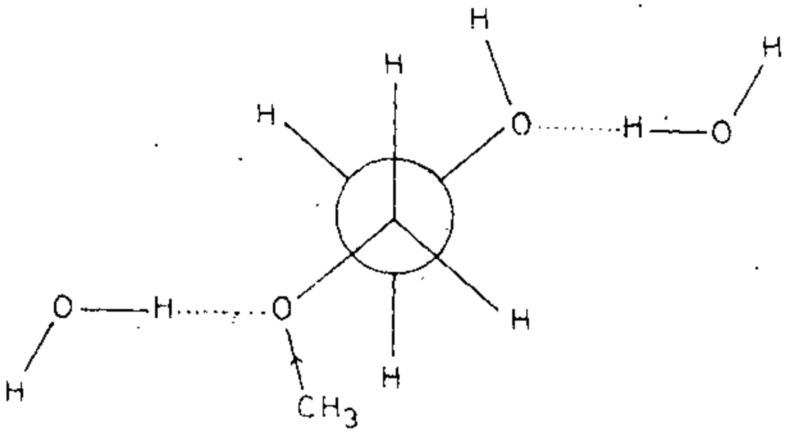
Works involving pure ME are comparatively large in number. Of these, studies on dielectric properties at various temperatures (-20°C to 50°C) of ME[233], solubility studies on alkali metal chlorides, temperature dependence of electrolytic conductance of salts in ME[234], dissociation constant studies of pure ME[235] and various thermodynamic studies, density, dielectric properties, viscosity etc. are noteworthy.

Again ME is commercially known as 'cellosolve' being used extensively as a solvating agent for cellulose. It finds its use in various chemical reactions and in analytical practice[236], in acid base conductometric titrations[237], and also as a solvent for electrolytes in high voltage capacitors and anti-icing additive for air-craft fuels. Consequently, the knowledge of ion-solvent interactions of different solutes in this solvent is capable of indicating the potential usefulness of ME in various technologies, e.g., high energy non-aqueous batteries, ion-exchangers etc. Transport parameters of electrolytic 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. Information on these interactions can also be had from such thermodynamic properties as apparent molal volumes and adiabatic compressibilities.

We have, therefore, devoted our attention to the study of the transport and thermodynamic properties of some electrolytes in ME and its aqueous binary mixtures.



I



II Hydrogen bonded ME-H_2O complex

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, Thermodynamics and Transport Processes, Ed. R.A. Horne, Wiley-Interscience, New York, 1972, Chapters 9 and 10.
3. J.S. Muishead-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 Solutions, Ed. J.E. Gordon, Wiley-Interscience, New York, 1975.
8. H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold Publishing Corporation, New York, 3rd Ed, 1958.
9. Chemical Physics of Ionic Solutions, Eds. B.E. Conway and R.G. Barradas, Wiley, New York, 1966.
10. Physical Chemistry of Organic Solvent Systems, Eds. A.K. Covington and T. Dickinson, Plenum Press, New York, 1973.
11. F. Franks, in Water - A Comprehensive Treatise, Ed. F. Franks, Vol. 1, Plenum Press, New York, 1973.
12. F. Franks, in Physico-Chemical Processes in Mixed Aqueous Solvents, Ed. F. Franks, Heinmann Educational Books Ltd., 1967, pp 141-157.

13. a) V. Gutmann, Electrochim. Acta, 21, 661, 1976.
b) U. Meyer and V. Gutmann, Adv. Inorg. Chem. Radiochem., 17, 189, 1975.

14. R.G. Pearson, 'Hard and Soft Acids and Bases' Dowdon, Hutchinson and Ross, Stroudsburgh, 1973.

15. R.H. Stokes and R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon Press Ltd., 1965.

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

17. Grúneisen, Wiss. Abhandl. Phsik-tech. Reichanstatt, 4, 239, 1905.

18. G. Jones and M. Dole, J. Am. Chem. Soc., 51, 2950, 1929.
19. P. Debye and E. Huckel, Z. Phys., 24, 185, 1923.
20. H. Falkenhagen and M. Dole, Z. Phys., 30, 611, 1929.
21. H. Falkenhagen, Z. Phys., 32, 745, 1931.
22. H. Falkenhagen and E.L. Vernon, Phil. Mag. 14, 537, 1932.
23. L. Onsager and R.M. Fuoss, J. Phys. Chem., 36, 2689, 1932.
24. Ref. 8, p. 240.
25. M. Kaminsky, Z. Phys. Chem. (Frankfurt), 12, 206, 1957.
26. J. Desnoyers and G. Perron, J. Soln. Chem., 1, 199, 1972.
27. R.T.M. Bicknell, K.G. Lawrence and D. Feakins, J. Chem. Soc., Faraday Trans. 1, 76, 637, 1980.

28. N.P. Yao and D.N. Bennion, J. Phys. Chem., 75, 1727, 1971.
29. R.L. Kay, T. Vituccio, C. Zawosky and D.F. Evans, J. Phys. Chem., 70, 2336, 1966.

30. M. Kaminsky, Discuss. Faraday Soc., 24, 171, 1957.
31. D. Feakins and K.G. Lawrence, J. Chem. Soc. A, 212, 1966.
32. Andrade, Phil. Mag., 17, 698, 1934.
33. D.E. Goldsack and R.C. Franchetto, Can. J. Chem., 55, 1062, 1977.

34. D.E. Goldsack and R.C. Franchetto, Can. J. Chem., 56, 1442, 1978.

35. D. England and G. Pilling, J. Phys. Chem., 76, 1902, 1972.

36. J. Vand, J. Phys. Chem., 52, 277, 1948.

37. S.P. Moulik, J. Ind. Chem. Soc., 49, 483, 1972.

38. D.G. Thomas, J. Colloid Sci., 20, 267, 1965.

39. C.A. Angell, J. Phys. Chem., 70, 2793, 1966.

40. C.A. Angell, J. Chem. Phys., 46, 4673, 1967.

41. K. Roy Choudhury and D.K. Majumdar, Electrochim. Acta, 28, 23, 1983.

42. K. Roy Choudhury and D.K. Majumdar, Electrochim. Acta, 28, 597, 1983.

43. K. Roy Choudhury and D.K. Majumdar, Electrochim. Acta, 29, 1371, 1984.

44. P.P. Rastogi, Bull. Chem. Soc. Japan, 43, 2442, 1970.

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

46. K. Tamaki, Y. Ohara and Y. Isomura, Bull. Chem. Soc. Japan, 46, 1551, 1973.

47. C.M. Criss and M.J. Mastroianni, J. Phys. Chem., 75, 2532, 1971.

48. K. Miyajima, M. Sawada and M. Nakagaki, Bull. Chem. Soc. Jpn., 56, 827, 1983.

49. J.I. Kim, J. Phys. Chem., 82, 191, 1978.

50. P.K. Mandal, B.K. Seal and A.S. Basu, Z. Physik. Chem. (Leipzig), 258, 809, 1977.

51. B.K. Seal, D.K. Chatterjee and P.K. Mandal, Ind. J. Chem., 21, 509, 1982.

52. A. Sacco, G. Petrella and M.D. Monica, J. Chem. Soc., Faraday Trans. 1, 75, 2325, 1979.

53. A. Sacco, G. Petrella, A.D'Atti and A.D. Giglio, J. Chem. Soc., Faraday Trans. 1, 78, 1507, 1982.

54. P.P. Deluca and T.V. Rebagay, J. Phys. Chem., 79, 2493, 1975.

55. A. Sacco, G. Petrella and M. Castagnolo, J. Phys. Chem., 80, 749, 1976.

56. R.L. Blokhra and Y.P. Segal, Ind. J. Chem., 15A, 36, 1977.

57. S.K. Vijaylakshamma, Ind. J. Chem., 17A, 511, 1979.

58. K. Kurotaki and S. Kawamura, J. Chem. Soc., Faraday Trans. 1, 77, 217, 1981.

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

60. N. Martinus and C.A. Vincent, J. Chem. Soc., Faraday Trans. 1, 77, 141, 1981.

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

62. C. Quintana, M.L. Llorente, M. Sanchez and A. Vivo, J. Chem. Soc., Faraday Trans. 1, 82, 3307, 1986.

63. 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.

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

65. S. Das, D.K. Hazra and S.C. Lahiri, Ind. J. Chem., 28A, 854, 1989.

66. S. Taniewska-Osinska and M. Jozwiak, J. Chem. Soc., Faraday Trans. 1, 85, 2141, 1989.

67. A. Kacperska, S. Taniewska-Osinska, A. Bald and A. Szejgis, J. Chem. Soc., Faraday Trans., 86, 2225, 1990.

68. a) R.T.M. Bicknell, K.G. Lawrence, M.A. Scelay, D. Feakins and L. Werblan, J. Chem. Soc., Faraday Trans. 1, 72, 307, 1976.
    b) D. Feakins, W.E. Waghorne and K.G. Lawrence, J. Chem. Soc., Faraday Trans. 1, 82, 563, 1986.

69. A. Sacco, A.D. Giglio, A.D. Atti, J. Chem. Soc., Faraday Trans. 1, 77, 2693, 1981.

70. D.S. Gill and A.N. Sharma, J. Chem. Soc., Faraday Trans. 1, 78, 475, 1982.

71. K.G. Lawrence and A. Sacco, J. Chem. Soc., Faraday Trans. 1, 79, 615, 1983.

72. a) A. Sacco, M.D. Monica, A.D. Giglio and K.G. Lawrence, J. Chem. Soc., Faraday Trans. 1, 79.

b) K.G. Lawrence, T.N. Bicknell, A. Sacco and A. Dell'Atti, J. Chem. Soc., Faraday Trans. 1, 81, 1133, 1985.

c) P.T. Thomson, M. Durbana, J.L. Turner and R.H. Wood, J. Soln. Chem., 9, 955, 1980.

d) P.T. Thomson, B. Fischer and R.H. Wood, J. Soln. Chem. II, 1, 1982.

73. D. Dasgupta, S. Das and D.K. Hazra, Bull. Chem. Soc. Jpn., 62, 1246, 1989.

74. D. Nandi and D.K. Hazra, J. Chem. Soc., Faraday Trans. 1, 85, 4227, 1989.

75. W.M. Cox and J.H. Wolfenden, Proc. Roy. Soc. London, 145A, 475, 1934.

76. R.W. Gurney, Ionic Processes in Solution, McGraw Hill, New York, 1954.

77. E.R. Nightingale, J. Phys. Chem., 63, 1381, 1959.

78. A. Einstein, Ann. Phys., 19, 289, 1906.

79. G.S. Benson and A.R. Gordon, J. Chem. Phys., 13, 473, 1945.

80. D.F. Tuan and R.M. Fuoss, J. Phys. Chem., 67, 1343, 1963.

81. C.H. Springer, J.F. Coetzee and R.L. Kay, J. Phys. Chem., 78, 471, 1969.

82. G. Petrella and A. Sacco, J. Chem. Soc., Faraday Trans. 1, 1, 74, 2070, 1978.

83. B.S. Krumgalz, J. Chem. Soc., Faraday Trans. 1, 76, 1275, 1980.

84. B.S. Krumgalz, Russ. J. Phys. Chem., 46, 858, 1972; 47, 528, 1973.

85. B.S. Krumgalz, Russ. J. Phys. Chem., 47, 956, 1973.

86. B.S. Krumgalz, Russ. J. Phys. Chem., 48, 1163, 1974.

87. B.S. Krumgalz, Russ. J. Phys. Chem., 45, 1448, 1971.

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

89. K. Fajans, Naturwissenschaften, 9, 729, 1921.

90. D.F.C. Morris, Struct. Bonding, 6, 157, 1969.

91. R.W. Gurney, Ionic Processes in Solutions, Dover, New York, 1962.

92. H.S. Frank and W.Y. Wen, Discussions Faraday Soc., 24, 133, 1957.

93. Asmus, Z. Naturforsch, 4A, 589, 1949.

94. M.H. Abraham, J. Liszi and E. Papp, J. Chem. Soc., Faraday Trans. 1, 78, 197, 1982.

95. M.H. Abraham, J. Liszi and L. Meszaros, J. Chem. Phys., 70, 249, 1979.

96. M.H. Abraham and J. Liszi, J. Chem. Soc., Faraday Trans. 1, 76, 1219, 1980.

97. S. Glasstone, K.J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw Hill, New York, 1941, p. 477.

98. E.R. Nightingale and R.F. Benck, J. Phys. Chem., 63, 1777, 1959.

99. D. Feakins, D.J. Freemantle and K.G. Lawrence, J. Chem. Soc., Faraday Trans. 1, 70, 795, 1974.

100. Sinha, J. Phys. Chem., 44, 25, 1940.

101. D. Feakins and K.G. Lawrence, J. Chem. Soc. A, 212, 1966.

102. D.F. Evans and S.M.A. Matesich in Electrochemistry, Vol. w, Eds. E. Yeager and A.J. Salkind, John Wiley and Sons Inc., 1973, Chapter 1.

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

104. D.A. McInnes, The Principles of Electrochemistry, Reinhold Publishing Corporation, 1961.

105. S. Glasstone, An Introduction to Electrochemistry, Van Nostrand, New York, 1942.

106. T. Shedlovsky, in Techniques of Organic Chemistry, Vol. 1, Part 4, Ed. A. Weissberger, 3rd Ed., Wiley, New York, 1959, pp. 3011-48.

107. R.M. Fuoss and F. Accascina, Electrolytic Conductance, Interscience, New York, 1959.

108. R.A. Robinson and R.H. Stokes, Electrolyte Solutions, 2nd Ed., Butterworths, London, 1959.

109. J. Barthel, Angew. Chem. Internat. Edit., 7, 260, 1968.

110. J. Barthel and G.D. Robbins, J. Chem. Educ., 48, 53, 1971.
111. E.J. King, Acid-base Equilibria, Pergamon Press, 1965.
112. G. Jones and R.C. Joseph, J. Am. Chem. Soc., 50, 1049,1928.
113. G. Jones and B.C. Bradshaw, J. Am. Chem. Soc., 55, 1780, 1933.

114. C.W. Davies, Ion Association, Butterworths, London, 1962.
115. R.M. Fuoss, J. Chem. Educ., 32, 527, 1955.
116. L. Onsager, Z. Phys., 28, 277, 1927.
117. R.M. Fuoss, Rev. Pure Appl. Chem., 18, 125, 1968.
118. E. Pitts, Proc. Roy. Soc., 217A, 43, 1953.
119. R.M. Fuoss and L. Onsager, J. Phys. Chem., 61, 668, 1957.
120. R.M. Fuoss, in Chemical Physics of Ionic Solutions, Eds. B.E. Conway and R.G. Barradas, Wiley, New York, 1966, p. 462.

121. E. Pitts, R.E. Tabor and J. Daly, Trans. Faraday Soc., 65, 849, 1969.

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

123. R. Fernandez-Prini, Trans. Faraday Soc., 65, 3311, 1969.

124. R. Fernandez-Prini and J.E. Prue, Z. Phys. Chem. (Leipzig), 288, 373, 1965.

125. D.F. Evans and R.L. Kay, J. Phys. Chem., 70, 366, 1966.

126. D.E. Arrington and E. Grinswold, J. Phys. Chem., 74, 123, 1970.

127. R.M. Fuoss and C.A. Kraus, J. Am. Chem. Soc., 55, 476, 1933.

128. T. Shedlovsky, J. Franklin. Instt., 225, 739, 1938.

129. a) J-C. Justice, J. Chim. Phys., 65, 353, 1968.
   b) J-C. Justice, R. Bury and C. Treiner, J. Chim. Phys., 65, 1707, 1968.

130. Ref. 107, p. 207.

131. N. Bjerrum, K. Dan. Vidensk. Selek, 7, No. 9, 1926.

132. M. Tissier and G. Douhéret, J. Soln. Chem., 7, 87, 1978.

133. R. Fernandez-Prini and J. Prue, Trans. Faraday Soc., 62, 1257, 1966.

134. R.M. Fuoss and L. Onsager, J. Phys. Chem., 66, 1722, 1962; 67, 621, 1963.

135. R.M. Fuoss, J. Phys. Chem., 49, 525, 1975; 82, 2427, 1978; Proc. Natl. Acad. Sci., USA, 75, 16, 1978.

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

137. 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.

138. 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.

139. P. Walden, H. Ulich and G. Busch, Z. Phys. Chem., 123, 429, 1926.

140. P. Walden and E.J. Birr, Z. Phys. Chem., Teil A, 144, 269, 1929.

141. R.M. Fuoss and E. Hirsch, J. Am. Chem. Soc., 82, 1013, 1960.

142. S. Takezawa, Y. Kondo and N. Tokura, J. Phys. Chem., 77, 2133, 1973.

143. D.S. Gill, J. Chem. Soc., Faraday Trans. 1, 77, 751, 1981.

144. M.A. Coplan and R.M. Fuoss, J. Phys. Chem., 68, 1177, 1964.

145. J.F. Coetzee and G.P. Cunningham, J. Am. Chem. Soc., 87, 2529, 1965.

146. D.S. Gill, Electrochim. Acta, 24, 701, 1979.

147. D.S. Gill and M.B. Sekhri, J. Chem. Soc., Faraday Trans. 1, 78, 119, 1982.

148. B.S. Krumgalz, Faraday Discuss. Chem. Soc., 64, 336, 1977.

149. D.S. Berns and R.M. Fuoss, J. Am. Chem. Soc., 82, 5565, 1960.

150. C.J. Jannes and R.M. Fuoss, J. Soln. Chem., 4, 91, 1975.

151. A. D'Aprano and R.M. Fuoss, J. Soln. Chem., 3, 45, 1974.

152. A.D'Aprano and R.M. Fuoss, J. Soln. Chem., 4, 175, 1975.

153. D.S. Gill, N. Kumari and M.S. Chauhan, J. Chem. Soc., Faraday Trans. 1, 81, 687, 1985.

154. R.H. Stokes and R.A. Robinson, Trans. Faraday Soc., 53, 301, 1957.

155. M. Born, Z. Physik, 1, 221, 1920.

156. R.H. Boyd, J. Chem. Phys., 35, 1281, 1961.

157. R. Zwanzig, J. Chem. Phys., 38, 1603& 1605, 1963.

158. E.J. Passeron, J. Phys. Chem., 68, 2728, 1964.

159. P. Walden, Z. Phys. Chem., 55, 207, 1906; 78, 257, 1912.

160. R. Gopal and M.M. Hussain, J. Ind. Chem. Soc., 40, 981, 1963.

161. L.G. Longsworth, J. Phys. Chem., 67, 689, 1963.

162. M. Della Monica, U. Lamanna and L. Senatore, J. Phys. Chem., 72, 2124, 1968.

163. S. Broers, J. Chem. Phys., 28, 1158, 1958.

164. D.G. Miller, J. Phys. Chem., 64, 1598, 1960.

165. G.J. Hills, in Chemical Physics of Ionic Solutions, Eds. B.E. Conway and R.G. Barradas, John Wiley and Sons Inc., New York, 1966, pp. 571-72.

166. R.H. Stokes and I.A. Weeks, Aust. J. Chem., 17, 304, 1964.

167. R.H. Stokes, in the Structure of Electrolytic Solutions, Ed. W.J. Hamer, Wiley, New York, 1959.

168. R.M. Fuoss, Proc. Natl. Acad. Sci. (U.S.A.), 45, 807, 1959.

169. H.S. Franks, in Chemical Physics of Ionic Solutions, Eds. B.E. Conway and R.G. Barradas, John Wiley and Sons Inc., New York, 1966, Chapter 4.

170. G. Atkinson and S.K. Koz, J. Phys. Chem., 69, 128, 1965.

171. 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.

172. R.L. Kay, B.J. Hales and G.P. Cunningham, J. Phys. Chem., 71, 3925, 1967.

173. R.L. Kay, C. Zawoyski and D.F. Evans, J. Phys. Chem., 69, 4208, 1965.

174. D.F. Evans and J.L. Broadwater, J. Phys. Chem., 72, 1037, 1968.

175. M. Spiro, in Physical Chemistry of Organic Solvent Systems, Eds. A.K. Covington and T. Dickinson, Plenum Press, New York, 1973, Chapter 5, Part 3.

176. R. Fernandez-Prini and G. Atkinson, J. Phys. Chem., 75, 239, 1971.

177. L. Bahadur and M.V. Ramanamurti, J. Chem. Soc., Faraday Trans. 1, 76, 1409, 1980.

178. L. Bahadur and M.V. Ramanamurti, J. Electrochem. Soc., 128, 339, 1981.

179. L. Bahadur and M.V. Ramanamurti, Can. J. Chem., 62, 1051, 1984.

180. J.L. Broadwater and R.L. Kay, J. Phys. Chem., 74, 3803, 1970.

181. S. Das and D.K. Hazra, Ind. J. Chem., 27A, 1073, 1988.

182. S. Das and D.K. Hazra, J. Ind. Chem. Soc., LXV, 100, 1988.

183. R.L. Kay and J.L. Broadwater, Electrochim. Acta, 16, 667, 1971; J. Soln. Chem., 5, 57, 1976.

184. A.D. Aprano and R.M. Fuoss, J. Phys. Chem., 1704 & 1722, 1963.

185. P. Hemmes, J. Phys. Chem., 78, 907, 1974.

186. J. Hubbard and L. Onsager, J. Chem. Phys., 67, 4850, 1977.

187. N. Islam, M.R. Islam and M. Ahmad, Z. Phys. Chem. (Leipzig), 262, 129, 1981.

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

189. H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolyte Solutions, Reinhold, New York, 1943, Chapter 8.

190. C. Tanford, Hydrophobic Effect : Formation of Micelles and Biological Membranes, 2nd ed., Wiley-Interscience, New York, 1980.

191. E. Vikingstad, Aggregation Process in Solutions, Eds. E. Wyn-Jones and J. Gormally, Elsevier, Amsterdam, 1983, pp. 100-117.

192. J.E. Desnoyers, M. Arel, G. Perron and C. Jolicoeur, J. Phys. Chem., 73, 3347, 1969.

193. D.O. Masson, Phil. Mag., 8, 218, 1929.

194. O. Redlich and D.M. Meyer, Chem. Rev., 64, 221, 1964.

195. B.B. Owen and S.R. Brinkley, Jr., Ann. N.Y. Acad. Sci., 51, 753, 1949.

196. K.S. Pitzer and G. Mayorga, J. Phys. Chem., 77, 2300, 1973.

197. F.J. Millero, in Water and Aqueous Solutions : Structure, Thermodynamics and Transport Processes, Ed. R.A. Horne, Wiley-Interscience, New York, 1972.

198. R. Gopal and M.A. Siddiqi, J. Phys. Chem., 73, 3390, 1969.
199. J. Padova and I. Abrahamer, J. Phys. Chem., 71, 2112, 1967.
200. R. Gopal, D.K. Agarwal and R. Kumar, Bull. Chem. Soc. Jpn., 46, 1973, 1973.
201. R. Gopal and P.P. Rastogi, Z. Phys. Chem. (N.F.), 69, 1, 1970.
202. B. Das, and D.K. Hazra, J. Chem. Eng. Data, 36, 403, 1991.
203. L.G. Hepler, J.M. Stokes and R.H. Stokes, Trans. Faraday Soc., 61, 20, 1965.
204. F.H. Spedding, M.J. Pikal and B.O. Ayres, J. Phys. Chem., 70, 2440, 1966.
205. L.A. Dunn, Trans. Faraday Soc., 64, 2951, 1968.
206. R. Pgue and G. Atkinson, J. Chem. Eng. Data, 33, 1988, 370.
207. B.E. Conway, R.E. Verral and J.E. Desnoyers, Trans. Faraday Soc., 62, 2738, 1966.
208. K. Uosaki, Y. Kondo and N. Tokura, Bull. Chem. Soc. Jpn., 45, 871, 1972.
209. B.S. Krumgalz, J. Chem. Soc., Faraday Trans. 1, 76, 1887, 1980.
210. J.G. Mathieson and B.E. Conway, J. Soln. Chem., 3, 455, 1974.
211. S. Bhowmik and R.K. Mohanty, Ind. J. Chem., 25A, 416, 1986.
212. M.V. Kaulgud and K.S. Mohan Rao, Ind. J. Chem., 27A, 12, 1988.
213. K.J. Patil, A.B. Wazalwar and G.R. Mehta, Ind. J. Chem., 27A, 799, 1988.
214. M. Iqbal and R.E. Verral, Can. J. Chem., 67, 727, 1989.
215. B.E. Conway and R.E. Verral, J. Phys. Chem., 70, 3952, 1966.
216. K. Gekko and H. Noguchi, J. Phys. Chem., 83, 2706, 1979.

217. W.L. Masterson, J. Chem. Phys., 22, 1830, 1954.

218. L.G. Hepler, Can. J. Chem., 47, 4613, 1969.

219. M.V. Kaulgud and K.J. Patil, J. Phys. Chem., 80, 138, 1976.

220. K.J. Patil, G.R. Mehta and R.K. Chandewar, Ind. J. Chem., 25A, 1147, 1986.

221. a) R. Iwamoto, Spectrochim. Acta Part A, 27, 2385, 1971.
b) L.P. Kuhn and R.A. Wires, J. Am. Chem. Soc., 86, 2161, 1964.

222. a) K.K. Kundu, A.K. Rakshit and M.N. Das, Electrochim. Acta, 17, 1921, 1972.
b) D. Feakins, in Physico-Chemical Processes in Mixed Aqueous Solvents, Ed. F. Franks, Hinemann, London, 1976, p. 71.
c) K.H. Khoo, J. Chem. Soc. (B), 2932, 1971.

223. H. Sadek, Th. F. Tadros and A.A. El-Harakany, Electrochim. Acta, 16, 339, 1971.

224. G. Douhéret and A. Pal, J. Chem. Eng. Data, 33, 40, 1988.

225. a) J.E. Desnoyers, Can. J. Chem., 56, 2808, 1978.
b) G. Roux, G. Perron and J.E. Desnoyers, J. Soln. Chem., 7, 639, 1978.

226. a) Kusano J. Suurkuusk and J. Wadso, J. Chem. Thermodynamics, 5, 757, 1973.
b) J. Peter Onthrie, Can. J. Chem., 55, 3700, 1977.
c) B.M. Arnett, E.J. Mitchell and T.S.S.R. Murthy, J. Am. Chem. Soc., 95, 3876, 1974.

227. a) S. Terasawa, R. Itsuki and S. Arakawa, J. Phys. Chem., 79, 2345, 1975.
b) J.T. Edward, P.G. Farrel and F. Sahidi, J. Chem. Soc., Faraday Trans. 1, 73, 705, 1977.

228. S. Cabani and V. Mollica, J. Chem. Soc., Faraday Trans. 1, 74, 2667, 1978.

229. S. Schiavo and B. Scrasati, Z. Phys. Chem., 102, 9, 1976.

230. R. Saits, Verh. K. Acad. West. Lett. Schone. Kunsten. Belg. Klwel., 40, 136, 1978.

231. J.P. Morel, J. Juillard, D.L. Massart and R. Smits, Anal. Chem., 48, 458, 1976.

232. J. Richard, Radidon, A. Kurt, Kraus,
(a) J. Chem. Eng. Data, 16, 241, 1971;
(b) U.S. Office Saline Water Res. Develop. Progr. Rep. 52-4, No. 685, 1971.

233. V. Viti and P. Zampetti, Chem. Phys., 2, 233, 1973.

234. A.D. Pethybridge, M.J. Blandamer and J. Barthel, Proc. 7th Int. Conf. on Non-aq. Solns. I.U.P.A.C. Resenberg, 11-15 Aug. 1980, p. D-20.

235. A.P. Kreshkov, N.T. Smolova, A. Ya. Veveris and B.A. Spintse, Zh. Fiz. Khim., 51, 1827, 1977 [Russ. J. Phys. Chem., 7, 1072, 1977 Eng.]

236. A.P. Kreshkov, in Osnovy Analiticheskoi Khimi (Fundamentals of Analytical Chemistry), Izd. Khimiya, Moscow, 1970, Vol. 5.

237. A.G. Schwartz and J.B. Barkar, Talenta, 22, 773, 1975.