Ion-Ion and Ion-Solvent Interactions for Some 1:1 Electrolytes in 2-Ethoxyethanol and its Binary Mixtures with Water

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By

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PREFACE

Scope and object of the work

The solution properties have always been of interest to physical chemists but in recent years there has been an unprecedented interest in solution chemistry by physical organic chemists, inorganic chemists, electrochemists and most notably by biochemists. The interest stems from the fact that the majority of reactions that are of chemical, electrochemical and biological importance occur in solution. It was previously believed that the solvent merely provides an inert medium for chemical reactions. The significance of solute-solvent interactions was realized only recently as a result of extensive studies in aqueous, non-aqueous and mixed solvents. While proton transfer reactions are particularly sensitive to the nature of the solvent, it has become increasingly clear that the majority of the solutes are significantly modified by all solvents. Conversely, the nature of strongly structured solvents, such as water, is substantially modified by the presence of solutes. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute, solute-solvent and solvent-solvent interactions are elucidated[1].

In spite of vast collections of data on the different electrolytic and non-electrolytic solutions in water, the structure of water and the different types of interactions that water undergoes with electrolytes are yet to be properly understood. However, the studies on the properties of aqueous solutions have provided sufficient information on the thermodynamic properties of different electrolytes and non-electrolytes, the effects of variation in ionic-structure, ionic mobility and common ions on the properties of aqueous solutions and a host of other properties[2,3]. Nevertheless, during recent years there has been an increasing interest in the behaviors of electrolytes in non-aqueous and mixed solvents with a view to investigate ion-ion and ion-solvent interactions under varied conditions. However, different sequence of solubility, differences in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have opened new vistas for physical chemists, and interest in these organic solvents transcends the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry[4].

We have been mainly interested in the studies of the ion-solvent interactions as they are the controlling forces in dilute solutions where ion-ion interactions are absent. Influence of these ion-solvent interactions on transfer of electrolytes between solvents is small, but sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in such diverse areas as organic and inorganic syntheses, studies of reaction mechanisms, non-aqueous battery technology and extraction[5]. The importance of ionic hydration in biochemistry and biophysics has been stressed[6].

The applications and implications of the studies of reactions in non-aqueous and mixed solvents have been summarized by Meck[7], Franks[8,9], Popovych[10], Bates[11,12], Parker[13,14], Criss and Solomon[15], Marcus[16] and others [17-23]. The ion-ion and ion-solvent interactions have been the subject of wide interest as apparent from the discussions of Faraday Transactions of the Chemical Society[24].

The proper understanding of the ion-solvent interactions would from the basis of explaining quantitatively the influence of the solvent and the extent of interactions of ions in solvents and thus have the way for the real understanding of the different phenomena associated with solution chemistry. Estimates of ion-solvent interactions can be obtained thermodynamically and also from the measurements of viscosity *B*-coefficients, limiting ionic conductivities etc.

However, single-ion values cannot be obtained thermodynamically. Therefore, various theoretical and semi-empirical extra-thermodynamic assumptions have been made to estimate these values.

It is thus apparent that the real understanding of the ion-solvent interactions is a difficult task. The aspect embraces a wide range of topics but we concentrated only on the measurements of two important transport properties e.g., viscosity and conductivity of electrolyte solutions.

Attempts have been made to determine the single-ion values by the use of available methods and to elucidate the various aspects of ion-solvent interactions.

These are described in the subsequent chapters.

Summary of the works done

2-Ethoxyethanol (EE) and its binary aqueous mixtures have been chosen as the solvent system in the present study.

The present dissertation addresses the problem of solute-solvent and solute-solute interactions for some selected electrolytes in 2-ethoxyethanol and its mixtures with water using two well-established experimental techniques and has been divided into six chapters.

Chapter I forms the background of the present work. After presenting a brief review of the notable works in the field of ion-solvent interactions, conductivity and viscosity of electrolyte solutions have been discussed in details. The importance and utility of these methods for the determination of ion-solvent interactions are stressed. Critical evaluations of the different methods of obtaining the single-ion values and their implications have been made. The solvent properties are then discussed, stressing the importance of such work.

In Chapter II the different experimental techniques for obtaining the results presented in the dissertation have been described.

Chapter III entails a study on the electrical conductances of some symmetrical tetraalkylammonium and alkali metal salts (tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), tetrapentylammonium bromide (Pen_4NBr), tetraheptylammonium bromide (Hep_4NBr), sodium bromide (NaBr) and sodium tetraphenylborate ($NaBPh_4$) in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K. The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation in terms of the limiting molar conductance (Λ^0), the association constant (K_A) and the association diameter (R). The ionic contributions to the limiting molar conductance have been estimated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as the "reference electrolyte".

The analysis of the results provided important information on the ion-association and solvation behaviour of these electrolytes in 2-ethoxyethanol.

In Chapter IV the viscosity of solutions of some tetraalkylammonium bromide salts (Et_4NBr, Pr_4NBr, Bu_4NBr, Pen_4NBr and Hep_4NBr) have been measured in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K. The viscosity data have been analyzed by the Jones-Dole equation for the associated electrolytes to evaluate the viscosity B-coefficients of the electrolytes. The resulting B-coefficients along with their ionic contributions and their temperature dependences provide useful information regarding ion-ion and ion-solvent interactions in 2-ethoxyethanol.

Chapter V describes the studies on the conductances of solutions Et_4NBr, Pr_4NBr, Bu_4NBr, Pen_4NBr, NaBr and $NaBPh_4$ in EE-water mixtures containing 0.25, 0.50 and 0.75 mass fractions (w_1 = 0.25, 0.50 and 0.75) of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K. The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation in terms of the limiting molar conductance (Λ^0), the association constant (K_A) and the association diameter (R). The ionic contributions to the limiting molar conductance have been estimated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as the "reference electrolyte". The ionic Walden products have been determined and their variations with solvent composition discussed.

In Chapter VI, the viscosities of solutions Et_4NBr, Pr_4NBr, Bu_4NBr, NaBr and $NaBPh_4$ in 2-ethoxyethanol-water mixtures containing 0.25, 0.50 and 0.75 mass fractions (w_1 = 0.25, 0.50 and 0.75) of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K have been reported. The experimental results have been analyses by the Jones-Dole[25] and Feakins *et.* al[26]. The thermodynamic parameters of these electeolytes have been determined using the transition-state treatment of the relative viscosity[26]. The ionic B-coefficients and other single-ion parameters have been determined by appropriate division of those for the "reference electrolyte" Bu_4NBPh_4. The results were discussed in terms of structural changes of the solvent mixtures.

The dissertation ends with some concluding remarks in Chapter VII.

The solvent 2-ethoxyethanol (EE) and its importance

2-Ethoxyethanol belongs to a class of compounds commercially known as cellosolves. It is, in fact, the monoethyl ether of ethylene glycol. 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 medium.

Simple consideration of molecular structures indicates that, due to the presence of electron repelling CH_3CH_2- group, 2-ethoxyethanol is more basic than ethylene glycol and water. Also, the restricted availability of the acidic H atom of OH group makes 2-ethoxyethanol molecules less acidic than ethylene glycol and water, thus imparting a "quasi-aprotic" character to it. That is, it behaves as an amphiprotic dipolar solvent with low relative permittivity (ε =13.38 at 298.15 K)[27]. Moreover, it is completely miscible in water.

Studies on fundamental physico-chemical properties like density and dielectric constant alongwith isentropic compressibilities and heat capacities have been reported for 2-ethoxyethanol[28,29,30,31]. Density measurements on the 2-ethoxyethanol-water mixtures have been performed at 298.15 K by McKinley and Nibarger[32]. Later the Douheret[27, 31] group reported densities, dielectric constants and isentropic compressibilities for this mixed solvent media at 298.15 K. Excess apparent molal heat capacities and volumes of 2-ethoxyethanol in the water-rich region at different temperatures have been reported by Roux *et. al.*[29] and it has been shown that 2-ethoxyethanol behaves as a fairly typical polar nonelectrolyte in water.

In spite of the extensive use of cellosolves as solvents and solubilizing agents in many industries with interests ranging from pharmaceutical to plastic products[33, 34], the studies on the transport properties of electrolytes in these media and their mixtures with water have not stimulated much interest so far. However, the knowledge of transport properties of different electrolytes in these solvents is capable of indicating the potential usefulness of cellosolves in various technologies, *e.g.*, high-energy nonaqueous batteries, ion exchangers etc. The situation is somewhat better with the first homologue of this class, namely, 2-methoxyethanol. Extensive studies on the transport properties of various electrolytes have already been reported in pure 2-methoxyethanol as well as in its binary mixtures with water[35-44]. Unfortunately, such investigations in 2-ethoxyethanol and its aqueous mixtures are practically absent.

We have, therefore, devoted our attention to the study of the transport properties of some electrolytes in 2-ethoxyethanol and its aqueous binary mixtures.

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CHAPTER I

Introduction

The majority of reactions that are of chemical or biological interest occur in solution. It was previously believed that solvent merely provides an inert medium for chemical reactions. The significance of solute-solvent interactions was realized only recently as a result of extensive studies in aqueous, non-aqueous and mixed solvents[1-13].

Water is the most abundant solvent in nature. In view of its extreme importance in chemistry, biology, agriculture, geology etc. water has been extensively used in kinetic and equilibrium studies. In spite of such extensive studies, our knowledge of molecular interactions in water is extremely limited. Moreover the uniqueness of water as solvent has been questioned[14,15] in recent years and it has been realized that the studies in other solvent media (non-aqueous and mixed solvents) would be of great help in understanding different molecular interactions and a host of complicated phenomena[1-13].

Extensive studies on the physical properties of different solvent systems have been made but a lamentable gap still exists. Several classifications of organic solvents based on their dielectric constant, organic group type, acid-base properties or association through hydrogen-bonding[10], donor-acceptor properties[16], hard and soft acid-base principles[17] etc. have been made; the properties of different solvent systems show a wide divergence of properties which would naturally be reflected on the thermodynamic and transport properties of electrolytes and nonelectrolytes in these solvents. The determination of thermodynamic and transport properties of different electrolytes in various solvents would thus provide an important step in this direction. Naturally, in the development of theories dealing with electrolyte solutions, much attention has been devoted to ion-solvent interactions which are the "controlling forces" in infinitely dilute solutions where ion-ion interactions are absent. Ion-solvent (or broadly speaking solute-solvent) interactions manifest themselves in all thermodynamic and transport properties of electrolytes generally obtained by extrapolation to infinite dilution. By separating these functions into ionic contributions, it is possible to determine the contributions due to cations and anions in the solute-solvent interactions. Thus ion-solvent (or solute-solvent) interactions play very important role in understanding the physicochemical properties of solutions.

One of the reasons for the intricacies in solution chemistry is that the structure of the solvent molecule is not known with certainty. The introduction of an ion or solute modifies the solvent structure to an uncertain magnitude whereas the solute molecules are also modified and the interplay of forces like solute-solute, solute-solvent and solvent-solvent interactions becomes predominant though the isolated picture of any of them is still not known completely to the solution chemists.

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

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

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

Similarly, the ion-solvent interactions can be studied using solvational approaches involving the studies of different properties e.g., viscosity, conductance etc. of electrolytes and hence to derive the various factors associated with ionic solvation.

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

Viscosity

Viscosity is one of the most important transport properties used for the determination of ion-solvent interactions and it has been studied extensively[18-21]. Viscosity is not a thermodynamic quantity, but viscosity of an electrolytic solution together with the thermodynamic property, $\bar{V}_2$, the partial molar volume gives much information and insight regarding ion-solvent interactions and the structures of the electrolytic solutions. The viscosity relationships of electrolytic solutions are highly complicated. There are strong electrical forces between the ions and solvent, and the separation of these forces is not really possible. But from careful analysis, valid conclusion can be drawn as to the structure and the nature of solvation.

Viscosity is a measure of the friction between adjacent, relatively moving, parallel planes of the liquid. Anything that increases or decreases the interaction between the planes will raise or lower the friction and therefore increase or decrease the viscosity.

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

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

The equation reduces to

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

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 $Ac^{1/2}$ originally ascribed to Gruneisen effect arose, from the long range Coulombic forces between the ions. The significance of the term had since then been realized due to the development of Debye Huckel theory[24] of interionic attractions (1923), Falkenhagen's[25-27] theoretical calculation of the constant A, using the equilibrium theory and the theory of irreversible process in electrolytes developed by Onsager and Fuoss[28]. The A-coefficient depends on the ion-ion interactions and can be calculated from the physical properties of the solvent and solution using the Falkenhagen-Vernon[27] equation.

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

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

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

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

The plots of $(\eta_r - 1)/c^{1/2}$ against $c^{1/2}$ 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[29,33,34]. Thus, instead of determining the A-values from the plots or by least squares method, the *A* values are generally calculated using the Falkenhagen-Vernon equation (3).

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

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

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

The *B*-coefficient may be either positive or negative and it is actually the ion-solvent interaction parameter. It is conditioned by the ion-size and the solvent and cannot be calculated a priori. The *B*-coefficients are obtained as slopes of the straight lines using the least squares method and the intercepts being equal to the A-values. The factors which influence *B*-values are[35,36].

(1) The effect of ionic solvation and the action of the field of the ion in producing long range order in solvent increase η or *B*-values.
(2) The destruction of the three dimensional structure of solvent molecules (i.e., structure breaking effect or depolymerisation effect) decreases η-values.
(3) High molal volume and low relative permittivity, which yield high *B*-values for similar solvents.
(4) Reduced *B*-values are obtained when the primary solvation of ions is sterically hindered in high molal volume solvents or if either ion of a binary electrolyte cannot be specifically solvated.

Viscosities at higher concentrations

It had been found that the viscosity values at high concentrations (1M to saturation) can be represented by the empirical formula suggested by Andrade[37].

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

Several alternative formulations have been proposed for representing the result of viscosity measurements in the high concentration range[38-43] and the equation suggested by Angell[44,45] based on an extension of the free volume theory of transport phenomena in liquids and fused salts to ionic solutions is particularly noteworthy. The equation is

$$1/\eta = A\exp[-K'/(N_0 - N)] \tag{6}$$

where N represents the concentration of the salt in eqv.litre^{-1}, A and K' are constants supposed to be independent of the salt composition and N_0 is the hypothetical concentration at which the system becomes glass. The equation was recast by Majumdar *et.* a*l.*[46-48], introducing the limiting condition that as $N \to 0, \eta \to \eta_0$, the viscosity of the pure solvent. Thus we have

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

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

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

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

Further, equation (7) written in the form

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

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

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

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

Division of *B*-coefficient into ionic values

The viscosity B coefficients have been determined by a large number of workers in aqueous, mixed and non-aqueous solvents[24, 34, 49-97]. However, the B-coefficients as determined experimentally using Jones-Dole equation, do not give any impression regarding ion-solvent interactions unless there is some way to identify the separate contributions of cations and anions in the total solute-solvent interactions. The division of B-values into ionic components is quite arbitrarily based on some approximation or assumptions, the validity of which may be questioned.

The following methods have been used for the division of B-values into ionic components:

(1) Cox and Wolfenden[98] carried out the division on the assumption that B_{ion} values of Li^+ and IO_3^- in $LiIO_3$ are proportional to the ionic volumes which are

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

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

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

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

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

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

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

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

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

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

The ionic *B*-values obtained by these methods are in good agreement with those obtained by other methods.

The criteria adopted for the separation of *B*-coefficients in non-aqueous solvents differ from those generally used in water. However, the methods are based on the equality of equivalent conductances of counter ions at infinite dilution. Thus

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

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

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

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

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

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

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

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

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

The methods, however, have been strongly criticized by Krumgalz[106]. According to him, any method of resolution based on the equality of limiting equivalent conductance for certain ion suffers from the drawback that it is impossible to select any two ions for which $\lambda_{+}^{0} = \lambda_{-}^{0}$ in all solvents at proper temperatures. Thus, though $\lambda^{0}(K^{+}) = \lambda^{0}(Cl^{-})$ at 298.15 K in methanol, but not in ethanol and in other solvents. In addition, if the mobilities of some ions are even equal at infinite dilution, it is not necessarily true at moderate concentrations for which *B*-coefficient values are calculated. Further, according to him, equality of dimensions of (i-Pe)$_3$ BuN$^+$or (i-Am)$_3$ BuN$^+$ and Ph$_4$B$^-$ does not necessarily imply equality of *B*-coefficients of these ions and they are likely to be solvent and ion-structure dependent.

Krumgalz[106,107] later on proposed a method for the resolution of *B*-coefficients. The method is based on the fact that the large tetraalkylammonium ions are not solvated[108,109] in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic *B*-values for large R$_4$N$^+$ ions (R $\geq$Bu) in organic solvents are proportional to their ionic dimensions. Thus we have

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

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

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

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

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

and

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

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

Gill and Sharma[76] used Bu_4NBPh_4 as a reference electrolyte. The method of resolution of *B* is based on the assumption, like Krumgalz, that Bu_4N^+ and Ph_4B^- ions with large R-groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constant. The ionic radii of Bu_4N^+(5.00Å) and of Ph_4B^-(5.35Å) have been, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers. They proposed the equation

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

and

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

The method requires only the *B*-values of *B(Bu₄NBPh₄)* and is equally applicable to mixed non-aqueous solvents. The ionic *B*-values obtained by this method agree well with those reported by Sacco *et.al.*[75] in different organic solvents using the assumption

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

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

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

or,

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

A similar division can be made for the Ph_4PBPh_4 system.

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

Jenkins and Pritcheit[111] suggested a least square analytical technique to examine additivity relationship for combined ion thermodynamics data, to effect apportioning into single-ion components for alkali halides by employing Fajans' competition principle[112] and 'volcano plots' of Morris[113]. The principle was extended to derive absolute single ion *B*-values for alkali metals and halides in water. They also observed that $B(Cs^+)=B(I^-)$ suggested by Krumgalz[108] to be more reliable than $B(K^+)= B(Cl^-)$ in aqueous solutions. However, we require more data to test the validity of this method.

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

Temperature dependence of B_{ion}- values

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

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

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

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

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

are characteristic of structure breaking ion, and

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

are characteristic of structure making ions.

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

Stokes and Mills[18] gave an analysis of viscosity incorporating the basic ideas presented before. The viscosity of a dilute electrolyte solution has been equated to the viscosity of the solvent (η_0) plus the viscosity changes resulting from competition between various effect occurring in the ionic neighborhood.Thu

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

(Jones-Dole equation)

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

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

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

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

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

whereas according to Lawrence and Sacco[77],

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

B_{ion}^{Einst} is defined as the positive increment arising from the obstruction to the viscous flow of the solvent caused by the shape and size of the ions (the term corresponds to η^E *or* B_{shape}), B_{orient} is the positive increment arising from the alignment or structure-making action of the electric field of the ion on the dipoles of the solvent molecules (the term corresponds to η^A *or* B_{ord}). B_{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} from a firmly attached primary solvation sheath around these ions (B_{ion}^{Einst} or η^E positive).

At ordinary temperatures, alignment of the solvent molecules around the inner layer also causes increase in B_{ion}^{orient} (η^A), $B_{ion}^{str}(\eta)$ is small for the ions. Thus B_{ion} will be larger and positive as $B_{ion}^{Einst} + B_{ion}^{orient} > B_{ion}^{str}$. However, B_{ion}^{Einst} and B_{ion}^{orient} would be small for ions of 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 neighborhood of the ion due to competition between the ionic field and the bulk $B_{ion}^{orien} <$ structure. Thus $B_{ion}^{einst} + B_{iion}^{orient} = B_{ion}^{str}$ 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., $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{orient}} = B_{\text{ion}}^{\text{str}}$ so that B is close to zero.

Large molecular ions like tetraalkylammonium ions have large B_{ion}^{Einst} because of large size but B_{ion}^{orient} and $B_{\text{ion}}^{\text{str}}$ would be small i.e., $B_{\text{ion}}^{\text{Einst}} + B_{\text{ion}}^{\text{orient}}$

$>> B_{\text{ion}}^{\text{str}}$ and B-would be positive and large. The values would be further reinforced in water arising from $B_{\text{ion}}^{\text{Reinf}}$ due to hydrophobic hydrations.

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

It is clear that in case of structure-making ions, the ions are firmly surrounded by a solvation sheath and the secondary solvation zone will be considerably ordered leading to an increase in B_{ion} and concomitant decrease in entropy of solvation and the mobility of ions. Structure-breaking ions, on the other hand, are not solvated to a great extent and the secondary solvation zone will be disordered leading to a decrease in B_{ion} values and increase in entropy of solvation and the mobility of ions. Moreover, the temperature-induced change in viscosity of ions (or entropy of solvation or mobility of ions) would be more pronounced in case of smaller ion than in case of larger ions. So there is a clear correlation between the viscosity, entropy of solvation and the mobility of ions. Thus the ionic B-coefficients and entropy of solvation of ions have rightly been used as probes of ion-solvent interactions and as a direct indication of structure-making and structure-breaking characters of ions.

The linear plot of ionic *B*-coefficients against the ratios of mobility-viscosity products at two temperatures (a more sensitive variable than ionic mobility) by Gurney[99,114] clearly demonstrates a close relation between ionic *B*-coefficients and ionic mobilities.

Gurney also demonstrated a clear correlation between the molar entropy of solution values with *B*-coefficients of salts. The ionic B-values show a linear relationship with the partial molar ionic entropies of hydration $\overline{S_h^0}$

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

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

The correlation was utilized by Abraham *et. al.*[117] to assign single-ion B-coefficients so that a plot of ΔS_e^0[118,119], the electrostatic entropy of solvation or $\Delta S_{i,ii}^0$[118,119], the entropic contributions of the first and second solvation layers of ions against *B*-points (taken from the works of Nightingale) for both cations and anions lie on the same curve of the line. There are excellent linear correlations between ΔS_e^0 and ΔS_1^0, and the single-ion *B*-coefficients. Both entropy criteria (ΔS_e^0 and $\Delta S_{i,ii}^0$) and B_{ion} values indicate that in water the ions Li^+, Na^+, Ag^+ and F^- are net structure-makers, the ions Rb^+, Cs^+, Cl^-, Br^-, I^- and ClO_4^- are structure breakers and K^+ is a border line case [in non- aqueous solvents e.g., formamide, methanol, N-methylformamide, dimethylformamide, dimethylsulfoxide, acetonitrile, all the above ions are structure-makers with the exception of weakly structure-breaking ion ClO_4^- in formamide and the border line cases of ClO_4^- in methanol and I^- in formamide].

Themodynamics of viscous flow

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

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

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

The problem was dealt in a different way by Nightingale and Benck[121] who studied the thermodynamics of viscous flow of salts and ions in aqueous solution. E_{vis} value can be determined using the Jones-Dole equation neglecting the term $Ac^{1/2}$. Thus,

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

$$\Delta E^{\neq 0}_{\eta\ (soln)} = \Delta E^{\neq 0}_{\eta\ (solv)} = \Delta E^*_v \quad (36)$$

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

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

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

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

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

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

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

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

$$\Delta H_2^{o\neq} = \Delta\mu_2^{\emptyset \neq} + T\Delta S_2^{\emptyset \neq} \text{ and } \Delta H_1^{\emptyset \neq} = \Delta\mu_1^{\emptyset \neq} + T\Delta S_1^{\emptyset \neq} \qquad (40)$$

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 $T\Delta S_2^{\emptyset \neq}$ and $\Delta H_2^{\emptyset \neq}$ 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^+, $\Delta H_2^{\emptyset \neq}$ and $T\Delta S_2^{\emptyset \neq}$ are negative *i.e.*, the transition state is associated with bond-making and an increase in order.

Effects of shape and size

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

$$\eta/\eta_0 = 1 + 2.5\varphi \qquad (41)$$

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

Modifications of the equation have been proposed by (i) Sinha[123] on the basis of departures from spherical shape and (ii) Vand[41] on the basis of the dependence of the flow patterns around the neighbouring particles at higher concentrations. However, considering in different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monatomic cations. Thus, we have from (1) and (41)

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

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

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

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

$B_{\pm}$ can be equated to

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

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 Stokes radii if the ions are scarcely solvated and behave as spherical entities. But $R_\pm$ values of the ions, which are higher than the crystallographic radii indicate solvation.

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

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

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

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

Conductance

Electrolytic conductivity is a very useful classical experimental technique to determine transport as well as equilibrium properties of dilute electrolyte solution[125,126]. Because of its relative simplicity and versatility, the measurement of the conductivity of electrolyte solutions, which can be carried out to a very high precision, remains an important goal to obtain information about electrolytes in different solvents. Conductivity of aqueous systems has recently provided valuable information about the influence of the solvent's number-density in the low fluid-density regime and its effect on the ion pairing equilibrium[127-129]. Accurate theories of electrolytic conductance are available to explain the result even upto a concentration limit of *Kd* (*K*= Debye-Huckle length, *d* = distance of closest approach of free ions). Conductance measurements together with transference number determinations provide an unequivocal method of obtaining single-ion values. The chief limitation, however, is the colligative like nature of the information obtained.

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

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

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

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

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

$$\Lambda = \Lambda^{0} - S\sqrt{c} \tag{46}$$

where

$$S = \alpha\Lambda^{0} + \beta \tag{47}$$

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

and

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

$\eta =$ viscosity in poise and $Z =$ ionic valence.

The equation took no account for the short range interactions and shape or size of the ions in solution. The ions were regarded as rigid charged spheres in an electrostatic and hydrodynamic continuum i.e., the solvent[145]. In the subsequent years Pitts (1953)[146] and Fuoss and Onsager (1957)[133,147] independently worked out the solution of the problem of electrolytic conductance accounting for both long-range and short-range interactions.

However, the Λ^{0} values obtained for the equivalent conductances at infinite dilution using Fuoss-Onsager theory differed considerably[145] from those obtained using Pitts theory and the derivation of the Fuoss-Onsager equation was questioned[126,148,149]. The observation was confirmed by Fuoss-Hsia[150]. The original Fuoss-Onsager equation was modified by Fuoss and Hsia[150] who recalculated the relaxation field, retaining the terms had previously been neglected. The equation usually employed is of the form[126]

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

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

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

is generally employed in the analysis of experimental results.

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

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

In most cases, however, J_2 is made zero, but this leads to a systematic deviation of the experimental data from the theoretical equations.

It has been observed that Pitts equation gives better fit to the experimental data in aqueous solutions[153].

Ion-association

The equation (52) given above successfully represents the behaviour of completely dissociated electrolytes. The plot of Λ against $\sqrt{c}$ (limiting Onsager equation) is used to assign the dissociation or association of electrolytes. Thus, if Λ^0 (experimental) is greater than Λ^0 (theoretical) i.e., if positive deviations occur (ascribed to short range hard-core repulsive interactions between ions), the electrolyte may be regarded as completely dissociated but if negative deviations $(\Lambda^0_{\text{expt}} < \Lambda^0_{\text{theo}})$ or positive deviations from the Onsager limiting tangent, the electrolytes may be regarded to be associated. Here the electrostatic interactions are large so as to cause association between cations and anions. The difference in Λ^0_{expt} and Λ^0_{theo} would be considerable with increasing association[154].

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

(Bjerrum's critical distance)

According to Justice, the method of fixing the J coefficient by setting $R=q$ clearly permits a better-defined value of K_A to be obtained. Since the equation (60) is a series expansion truncated at the $c^{3/2}$ term, it would be preferable that the resulting errors be absorbed as much as possible by J_2 rather than by K_A, whose theoretical importance is greater as it contains the information concerning short-range cation-anion interaction.

From the experimental values of the association constant K_A, one can use two methods in order to determine the distance of closest approach a^0 of two free ions to from an ion-pair. The following equation has been proposed by Fuoss[158].

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

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

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

The equation neglects specific short-range interactions except for solvation in which the solvated ion can be approximated by a hard sphere model. The method has been successfully utilized by Douheret[160].

Ion-size parameter and ionic association

The equation (52) can be written as

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

(with J_2 term omitted)

Thus a plot of Λ' vs. c gives a straight line with Λ^0 as intercept and J' or (J - $B\Lambda^0$) as slope. Assuming $B\Lambda^0$ to be negligible, a^0 values can be calculated from J'. The a^0 values obtained by this method in dimethylsulfoxide were much smaller[154] than would be expected from the sums of the crystallographic radii of the ions. One of the reasons attributed to it is ion-solvent interactions which are not included in the continuum theory on which the conductance equations are based. The inclusion of dielectric saturation results in an increase in a^0 values (much in conformity with the crystallographic radii) of alkali metal salts (having ions of high surface charge density) in sulpholane. The viscosity correction (which should be $B\Lambda c$ rather than $B\Lambda^0 c$) leads to a larger value of a^0 [161], still the agreement is poor. However, little of real physical significance may be attached to the distance of closest approach derived from J[162].

Fuoss[163] in 1975 proposed a new conductance equation. He[163] subsequently put forward another conductance equation in 1978 which replaced the old one. He classified the ion of electrolytic solutions in one of the three categories:

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

(2) those with overlapping Gurney co-spheres (solvent separated pairs). For these $r_{ij} = a + ns$, where n is generally 1 but may be 2, 3 etc., 's' is the diameter of a sphere corresponding to the average volume (actual plus free) per solvent molecule, and contact pairs form by a sequence of ion-solvent site interchanges inside the *R*-spheres, until two ions of opposite charges become nearest neighbours.

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

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

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

(solvent-separated pair) contact pair neutral molecule

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

The equilibrium constants for (67) are

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

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

where K_R describes the formation and separation of solvent-separated pairs by diffusion in and out of spheres of diameter *R* around cations, and can be calculated by continuum theory, K_s is the constant describing the specific short-range ion-solvent and ion-ion interactions by which contact pairs form and dissociate, E_s is the difference in energy between a pair in the states ($r = R$) and ($r = a$), $\in$ is measured in units of kT. From (69)

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

Substitution in equation (68) gives the conductometric pairing constant

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

which determines the concentration $c\gamma$ of active ions, 'active' in the sense that they produce the long-range interionic effects. That contact pairs behave like electrical dipoles to an external field X, contributing only to charging current. Both contact pairs and solvent-separated pairs are left as virtual dipoles by unpaired ions, their interaction with unpaired ions is therefore neglected in calculating long-range effects $\Delta X/X < 0$, the relaxation field and $\Delta\Lambda_c < 0$, the electrophoretic countercurrent). The various patterns can be reproduced by theoretical functions of the form

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

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

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

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

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

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

The equilibrium constant for the effective reaction

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

is then

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

because $K_s >> 1$.

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

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

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

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

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

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

Limiting ionic equivalent conductances

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

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

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

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

Thus from the accurate values of λ^0 of ions, it is possible to separate the contribution due to cations and anions in the solute-solvent interactions[168]. However, accurate transference number determinations are limited to few solvents only. Spiro[169]and more recently Krumgalz[170a] have made extensive reviews on the subject.

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

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

(i) Walden equation[171]

$$\lambda_{\pm}^{0}.\eta_{0}(acetone) = \lambda_{\pm}^{0}.\eta_{0}(water) \tag{82}$$

at 298.15 K

(ii) $\lambda^{0}(Pic)\eta_{0} = 0.267$

$$\lambda^{0}(Et_4N^{+})\eta_{0} = 0.296 \text{ based on } \Lambda^{0}(Et_4NPic) = 0.563 \tag{83}$$ [171,172]

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

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

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

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

The method appears to be sound as the negative charge on boron in Bu_4B^- ion is completely shielded by four inert butyl groups as in the Bu_4N^+ ion while this phenomenon was not observed in case of Ph_4B^-. But the method could not be checked due to lack of accurate transference data.

(v) $$\lambda_{25}^{0}(R_4N^{+}) = ZF^{2}/\left[6\,\pi N\,\eta_{0}\left\{r_{1} - \left(0.0103\,\epsilon_{0} + r_{y}\right)\right\}\right] \tag{86}$$ [175]

where Z and r_1 are the charge and crystallographic radius of the relevant ion; η_0 and $\in_0$ are the viscosity and relative permittivity of the medium; r_y is an adjustable parameter taken to be equal to 0.85 for dipolar non-associated solvents and 1.13 for hydrogen-bonded and other associated solvent.

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

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

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

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

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

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

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

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

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

$$\lambda_{\pm}^0 \eta_0 = \text{constant} \tag{90}$$

This relation has been verified using $\lambda_{\pm}^0$ values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i-Am_4B^-, Ph_4As^+$ and Ph_4B^- ions and for tetraalkylammonium cations starting from Et_4N^+. The relationship can be well utilized to determine $\lambda_{\pm}^0$ values of ions in other organic solvents from the determined Λ^0 values.

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

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

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

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

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

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

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

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

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

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

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

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

and the ratio is to 1.07 as used by us.

Solvation number[168]

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

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

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

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

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

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

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

Stokes' law and Walden's rule

The limiting conductance λ_i^0 of a spherical ion of radius R_i moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

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

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

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

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

Robinson and Stokes[134], Nightingale[100] and others[192-194] have suggested a method of correcting the radii. The tetraalkylammonium ions were assumed to be not solvated and by plotting the Stokes' radii against the crystal radii of these large ions, a calibration curve was obtained for each solvent. This approach, however, suffers from one serious flaw. The basic assumption on which this approach rests is that the Walden product is invariant with temperature. Experimental results[154] indicate that his assumption is incorrect and that the resulting solvation numbers obtained from this type of correction to Stokes' law are meaningless. The idea of microscopic viscosity[195] was invoked without much success[196,197] but it has been found that

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

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

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

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

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

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

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

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

In 1961, Boyd[188] gave the expression

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

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

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

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

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

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

The theory predicts[201] that λ_i^0 passes through a maximum of (27/4)B at r_i= (3B). The phenomenon of maximum conductance is well known. The relationship holds good to a reasonable extent for cations in aprotic solvents but fails in case of anions. The conductance, however, fails off rather more rapidly than predicted with increasing radius.

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

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

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

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

It is noted that the Zwanzig's theory is successful for large organic cations in aprotic media where solvation is likely to be minimum and where viscous friction predominates over that caused by dielectric relaxation. The theory breaks down whenever the dielectric relaxation term becomes large *i.e.*, for solvent of high P^* and for ions of small r_i. Like any continuum theory, Zwanzig's theory has the inherent weakness of its ability to account for the structural features[207] e.g.,

(1) It does not allow for any correlation in the reorientation of the solvent molecules as the ion passes by and this may be the reason why the equation does not apply to hydrogen bonded solvents[208].

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

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

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

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

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

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CHAPTER II

Experimental Section

(Materials and Methods)

Chemicals

All salts were of Fluka's purum or puriss grade.

These are purified in the manner given in the literature[1-5]. Generally these salts were purified by recrystallisation. Higher tetraalkyl homologous were recrystallised second time to ensure the highest purity. The crystallized salts dried in vacuum and stored in glass bottles in darken dessicator over fused $CaCl_2$.

Tetraethylammonium bromide (Et_4NBr) was recrystallised from methanol and dried at 363 K for 24 hours.

Tetrapropylammonium bromide (Pr_4NBr) was taken in a minimum volume of methanol, reprecipitated from dry ether and dried at 363 K for 48 hours.

Tetrabutylammonium bromide (Bu_4NBr) was taken in a minimum volume of acetone. Ether was added to the solution till the commencement of precipitation. The solution was then cooled and the resulting crystals were filtered. After a preliminary drying, the salt was finally ground in a morter and dried at 333K for 48 hours.

Tetrapentylammonium bromide (Pen_4NBr) was recrystallised from acetone and ether mixtures and dried in vacuo at 333K for 48 hours.

Tetraheptylammonium bromide (Hep_4NBr) was washed with ether and dried in vacuo at room temperature for 48 hours.

Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) was prepared by dissolving sodium tetraphenylborate in distilled water (2% solution) and filtered to remove a small amount of insoluable impurities. To this an equivalent amount of tetrabutylammonium bromide in 2% aquous solution was slowly added. The bulky white precipitate thus obtained was washed five times by decantation. After preliminary drying the product was recrystallised four times from 1:3 water-acetone mixture and finally dried for several days at 313.15 K and 10^{-4} mm.Hg pressure (m.p.496.15-498.15 K).

Solvents

2-Ethoxyethanol (G. R. E. Merck) was dried with potassium carbonate and distilled twice in all glass distillation set immediately before use and the middle fraction was collected. The purified solution has a density (ρ_0) of 0.92497 g cm^{-3} and a coefficient of viscosity (η_0) of 1.8277 mPa s at 298.15 K; these values are found to be in good agreement with the literature values[9,10].

The mixed solvents containing 25%, 50%, 75% of 2-ethoxyethanol by weight were prepared accurately by mixing 2-ethoxyethanol with triple distilled water. Solvent properties of 2-ethoxyethanol + water mixtures at 308.15, 313.05, 318.15 and 323.15 K are given in Table-1.

Table 1. Properties of 2-ethxyethanol (1) + water (2) Mixtures with w_1 = 0.25, 0.50 and 0.75 at (308.15, 313.15, 318.15 and 323.15) K

T/K	ρ_0 /($g.cm^3$)	η_0/($mPa.s$)	ε
	w_1=0.25		
308.15	1.00354	1.8430	60.13
313.15	1.00021	1.5293	58.70
318.15	0.99751	1.2738	57.37
323.15	0.99582	1.0923	56.11
	w_1=0.50		
308.15	0.99361	1.9234	44.30
313.15	0.98514	1.7195	43.03
318.15	0.98004	1.4552	41.95
323.15	0.97610	1.2762	40.90
	w_1=0.75		
308.15	0.95451	1.7002	27.93
313.15	0.95147	1.5293	27.29
318.15	0.94873	1.3498	26.68
323.15	0.94625	1.1901	26.10

Preparation of experimental Solutions

A stock solution of each salt in pure as well as in different mixed solvents was prepared and the working solutions were obtained by mass dilution. The molar concentrations of the solutions were calculated from molality and density values.

Methods

(a) Density measurements

The densities were measured with an Ostwald-Sprengal type pycknometer having a bulb volume of 25 cm^3 and an internal diameter of the capacity of about 1 mm. The pycknometer was calibrated at 308.15, 313.15, 318.15 and 323.15 K with double distilled water. The precision of the density measurement was $\pm 3 \times 10^{-5}$ gcm^3. The measurements were made in a water bath maintained with an accuracy of ± 0.005 K of the desired temperature by means of a mercury-in-glass thermoregulator and the absolute temperature was determined by a platinum resistance thermometer and Muller bridge[6].

(b) Viscosity measurement

The kinematic viscosities were measured by means of a suspended-level Ubbelohde[6] viscometer with a flow time about 539s for distilled water at 298.15 K. The time of efflux was measured with a stop watch capable of recording ± 0.1 s. The viscometer was always kept in a vertical position in water thermostat. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations:

$$\nu = Ct - K/t \tag{1}$$

$$\eta = \nu\rho \tag{2}$$

where t is the efflux time, ρ is the density and C and K are the characteristic constants of the viscometer. The values of constants C and K , determined by using water, methanol, acetonitrile and 2-ethoxyethanol as the calibrating liquids at 308.15, 313.15, 318.15 and 323.15 K. were found to be 1.646 $\times 10^{-5}$ cm^2s^{-2} and – 0.02331647 cm^2 respectively. The precision of the viscosity measurements was ±0.02%. In all the cases the experiments were performed at least in five replicates and the results were averaged.

Relative viscosities (η_r) were obtained using the equation (3):

$$\eta_r = \eta/\eta_0 = \rho t/\rho_0 t_0 \qquad (3)$$

where η, η_0, ρ, ρ_0 and t, t_0 are the absolute viscosities, densities and flow times for the solution and solvent respectively.

The measurements were carried out in a thermostatic bath maintained with an accuracy of ±0.01 K of the desired temperature[7]. A 60 W heating element and a toluene-mercury thermoregulator were used to maintain the temperature of the experimental thermostat which was placed in a hot cum cold thermostat. The temperature of the hot-cum-cold thermostat was preset at the desired temperature using a contact thermometer and relay system. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.

(c) Conductance measurements

Conductance measurements were carried out on a Philips Pye-Unicam PW 9509 conductive meter with an accuracy of ±0.01%. A 2000 Hz cycle was used. The cell constant (0.751 cm^{-1}) of the dip type conductance cell was accurately determined using standard KCl solutions following the method of Lind and coworkers[8]. Conductivity cell was sealed to the side of 500cm^3 conical flask closed by a ground glass cap fitted with a side arm through which dry and pure nitrogen was passed to prevent the admission of air into the cell when solvent or solution were added. The measurements were made in an oil bath maintained at 298.15 ± 0.005 K as described earlier under density measurements. All data were corrected with the specific conductance of the solvent.

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CHAPTER III

Conductometric study of some tetraalkylammonium and alkali metal salts in 2-ethoxyethanol in the temperature range 308.15-323.15 K

Introduction

Studies on the transport properties of electrolytes in different solvent media are of great importance to obtain information as to the solvation and association behavior of ions in solutions. Earlier, these properties have been investigated[1-11] for a wide variety of electrolytes in different solvents from conductometry which is one of the most direct methods to study these behavior. Various concepts concerning ion-association have been derived from the conductivity data of electrolyte solutions. In the present study, an attempt has been made to unravel the nature of ion-ion and ion-solvent interactions for some tetralkylammonium bromide salts (R_4NBr) namely tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), tetrapentylammonium bromide (Pen_4NBr) and tetraheptylammonium bromide (Hep_4NBr) along with two alkali metal salts sodium tetraphenylborate ($NaBPh_4$) and sodium bromide (NaBr) in 2-ethoxyethanol by measuring their electrical conductances in the temperature range 308.15-323.15 K. The solvent 2-ethoxyethanol is an amphiprotic dipolar solvent with low relative permittivity (ε = 13.38 at 298.15 K)[12]. It has unique solvating properties associated with its "quasi-aprotic" character and is a good industrial solvent[13,14].

Experimental

2-Ethoxyethanol (G. R. E. Merck) was dried with potassium carbonate and distilled twice in an all glass distillation set immediately before use and the middle fraction was collected. The purified solvent had a density (ρ_0) of 0.92497 g cm^{-3} and a coefficient of viscosity (η_0) of 1.8277 mPa.s at 298.15 K; these values are found to be in good agreement with the literature values[12,14]. The densities, viscosities and the relative permittivities[11] of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K are reported in Table 1.

Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described in the literature[15]. These salts were purified by recrystallization and the higher homologues (tetrapentylammonium bromide and tetraheptylammonium bromide) were recrystallized twice to ensure maximum purity. The recrystallized salts were dried in vacuo at elevated temperatures for 12 h. Sodium tetraphenylborate ($NaBPh_4$) was recrystallised three times from acetone and then dried under vacuum at 353.15 K for 72 h. Sodium bromide (NaBr) was dried in vacuo for 72 h immediately prior to use and was used without further purification.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 1.15 cm^{-1} and having an accuracy of 0.1%. The measurements were made in a water bath maintained within ± 0.005 K of the desired temperature. The details of the experimental procedure have been described earlier[16,17]. Solutions were prepared by mass for the conduntance runs, the molalities being converted to molarities by the use of densities measured with an Ostwald-Sprengel type pycknometer of about 25 cm^3 capacity. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent.

In order to avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in five replicates for each solution and at each temperature, and the results were averaged.

Results and discussion

The measured molar conductances (Λ) of electrolyte solutions as functions of molar concentration (c) in 2- ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K are given in Table 2.

The conductance data have been analyzed by the 1978 Fuoss conduntance concentration equation [18, 19]. For a given set of conductivity values *(c)*, c_j, Λ_j ; *j=1, ..., n)*, three adjustable parameters -- the limiting molar conductivity (Λ^0), association constant (K_A), and the association diameter (R), are derived from the following set of equations:

$$\Lambda = p[\Lambda^0(1+RX)+EL] \tag{1}$$

$$p = 1-\alpha(1-\gamma) \tag{2}$$

$$\gamma = 1-K_A c\gamma^2 f^2 \tag{3}$$

$$-\ln f = \frac{\beta k}{2(1+kR)} \tag{4}$$

$$\beta = \frac{e^2}{\varepsilon k_B T} \tag{5}$$

$$K_A = K_R(1+K_s) \tag{6}$$

where RX is the relaxation field effect, *EL* is the electrophoretic countercurrent, γ is the fraction of unpaired ions, and α is the fraction of contact-pairs, K_A is the overall pairing constant evaluated from the association constant of contact-pairs, K_S, of solvent- separated pairs, K_R, ε is the relative permittivity of the solvent, *e* is the electronic charge, k_B is the Boltzmann constant, k^{-1} is the radius of the ion atmosphere, *c* is the molar concentration of the solution, *f* is the activity coefficient, *T* is the temperature in absolute scale, and β is twice the Bjerrum distance. The computations were performed on a computer using the program as suggested by Fuoss. The initial Λ^0 values for the iteration procedure were obtained from Shedlovsky extrapolation[20] of the data. Input for the program is the set (c_j, Λ_j; $j = 1,\ldots., n$), n, ε, η, *T*, initial value of Λ^0, and an instruction to cover a preselected range of *R* values.

In practice, calculations are performed by finding the values of Λ^0 and α which minimize the standard deviation, σ,

$$\sigma^2 = \sum[\Lambda_j(calcd)-\Lambda_j(obsd)]^2/(n-2) \tag{7}$$

for a sequence of R values and then plotting σ against R; the best-fit R corresponds to the minimum in $\sigma(\%)$ *vs.* R curve. However, for all of these electrolytes investigated, since a preliminary scan using a unit increment of R values from 4 to 20 produced no significant minima in the $\sigma(\%)$ *vs.* R curves, the R value was assumed to be $R = a + d$, where a is the sum of the ionic crystrallographic radii and d is given by[19]

$$d = 1.183(M/\rho_0)^{1/3} \tag{8}$$

where M is the molecular weight of the solvent and ρ_0 its density.

The values of Λ^0, K_A, and R obtained by this procedure are reported in Table 3.

In order to investigate the specific behavior of the individual ions comprising these electrolytes, it is necessary to split the limiting molar electrolyte conductances into their ionoic components.

In the absence of accurate transport number data *for the system in the* temperature range investigated here, we have used the "reference electrolyte" method for the division of Λ^0 into their ionic components. Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) has been used as the "reference electrolyte"[27]. This electrolyte was used as the "reference electrolyte" also by Fuoss and Hirsh[28] to evaluate the limiting ionic conductances in several organic solvents. We have divided the Λ^0 values of Bu_4NBPh_4 into ionic components using the following relationships[29].

$$\Lambda^0\,(Bu_4NBPh_4) = \lambda^0\left(Bu_4N^+\right) + \lambda^0\left(Ph_4B^-\right) \tag{9}$$

$$\frac{\lambda^0\left(Bu_4N^+\right)}{\lambda^0\left(Ph_4B^-\right)} = \frac{r\left(Ph_4B^-\right)}{r(Bu_4N^+)} = \frac{5.35}{5.00} \tag{10}$$

The ionic radii (r) values have been taken from the literature[30,31]. The limiting ion conductances calculated from the above equations are recorded in Table 4.

The limiting molar conductivity (Λ^0) of the "reference electrolyte" Bu_4NBPh_4 was obtained by considering the Kohlrausch rule which allows the calculation of Λ^0 value for a given electrolyte by the appropriate combination of others. The Λ^0 values of Bu_4NBPh_4, $NaBPh_4$ and NaBr obtained in this medium have been used to obtain the Λ^0 value of Bu_4NBPh_4 through the following equation:

$$\Lambda^0(Bu_4NBPh_4) = \Lambda^0(Bu_4NBr) + \Lambda^0(NaBPh_4) - \Lambda^0(NaBr) \qquad (11)$$

The standard Gibbs energy changes for the ion association processes, ΔG_T^0, have been calculated from the association constants using the equation:

$$\Delta G_T^0 = -RT \ln K_A(T) \qquad (12)$$

where T is the temperature in absolute scale and R is the universal gas constant.

In order to evaluate the standard enthalpy change, ΔH_T^0, and the standard entropy change, ΔS_T^0, the ΔG_T^0 values were fitted to an equation in T of the type:

$$\Delta G_T^0 = a_0 + a_1(308.15 - T) \qquad (13)$$

and the coefficients of the fits are compiled in Table 5, together with the σ% values of the fits.

The ΔH_T^0, and ΔS_T^0 values of the ion-association processes can then be evaluated from the temperature dependence of ΔG_T^0 values as follows:

$$\Delta H_T^0 = -T^2\left[\frac{d\left(\Delta G_T^0/T\right)}{dT}\right]_p \qquad (14)$$

$$\Delta S_T^0 = -\left(\frac{d\Delta G_T^0}{dT}\right)_p \qquad (15)$$

the standard values of the thermodynamic parameters at 308.15K can, therefore, be expressed as:

$$\Delta G_{308.15}^0 = a_0 \qquad (16)$$

$$\Delta S_{308.15}^0 = a_1 \qquad (17)$$

$$\Delta H_{308.15}^0 = a_0 + 308.15a_1 \qquad (18)$$

and can be found in Table 5.

Table 3 shows that for all salt the limiting molar conductances $\left(\Lambda^0\right)$ increase as the temperature increases. The Λ^0 values been fitted to the following equation in T:

$$\Lambda^0 = b_0 + b_1\left(308.15 - T\right) \qquad (19)$$

and the coefficients of these fits along with their standard percentage errors (σ%) are given in Table 6.

The single ion conductivities $\left(\lambda_\pm^0\right)$ at different temperatures were also fitted to the following equation:

$$\lambda_\pm^0 = c_0 + c_1\left(308.15 - T\right) \qquad (20)$$

and the coefficients of these fits are given in Table 7 together with the standard percentage errors (σ%).

The Walden product values ($\lambda_{\pm}^{0}\eta_0$) for the ions studied here in 2-ethoxyethanol solutions show pronounced variations with increasing temperature (Table 4).Therefore, the Stokes' law cannot be applied to the ion conductances in 2-ethoxyethanol since the $\lambda_{\pm}^{0}\eta_0$ values, according to this law, would be expected to be practically independent of temperature[32]. Since the ions are often far from being spherical and since they are of the same order of magnitude as the solvent molecules, it is questionable whether the retarding effect of the latter can be accurately described by the macroscopic viscosity as has been done in the derivation of the Stokes law. Hence, the Stokes law cannot be considered quantitatively reliable. Such failure of this law has also been reported recently in ethylene glycol solution of a variety of ions[33].

From Table 4, we see that the limiting ionic conductivity values of the tetraalkylammonium ions decrease in the order: $Et_4N^+ > Pr_4N^+ > Bu_4N^+ > Ph_4B^- > Pen_4N^+ > Hep_4N^+$. Now, a comparison of this trend in mobility with the crystallographic size of these ions, which is in the order[17] $Et_4N^+ < Pr_4N^+ < Bu_4N^+ < Ph_4B^- < Pen_4N^+ < Hep_4N^+$, shows that the larger the size of the bare ion, the smaller its ionic mobility. This indicates that the relative actual sizes of these ions as they exist in solutions follow the order: $Et_4N^+ < Pr_4N^+ < Bu_4N^+ < Ph_4B^- < Hep_4N^+$. This observation, thus, clearly demonstrates that these ions would remain unsolvated in 2-ethoxyethanol solutions which is quite expected because of their large crystallographic radii[17] and hence low surface charge density. Had these ions been solvated in this medium, their limiting ionic conductivity values should have been in the reverse order: $Et_4N^+ < Pr_4N^+ < Bu_4N^+ < Ph_4B^- < Pen_4N^+ < Hep_4N^+$, because smaller ions with greater surface charge densities are expected to be more solvated resulting in a bigger solvodynamic entity - which is obviously not the case here. The bromide ion is found to be solvated in 2-ethoxyethanol from our previous study[11].

The limiting ionic equivalent conductivity of Na^+ ion is found to be smaller than that of the Br^- ion in 2-ethoxyethanol (Table 4). Now, a comparison of this trend in mobility with the crystallographic size of ions, which is in the order[26] $Br^- > Na^+$, shows that the larger the size of the bare ion, the greater its ionic mobility; this is contrary to the expectation. However, it is well known that these ions do not exist as bare ions in a variety of solvents, but are solvated[26]. This trend of variation of ionic mobilities should, therefore, indicate the relative actual size of the ions as they exist in solutions concerned. In other words, the sizes of the ions as they exist in solutions follow the order: $Na^+ > Br^-$, which indicates that the extent of solvation also decreases in the same order. This can be attributed to the high charge density on these small ions which varies in the order $Na^+ > Br^-$ since their crystallographic sizes[27] vary in the reverse order. Thus, the ion with greater charge density (Na^+) is more solvated in 2-ethoxyethanol. Similar trend has also been reported in other solvents[26,34].

The association constants (K_A) listed in Table 3 indicate that all these salts are appreciably associated in the present medium over the entire temperature range investigated in this study. This is quite expected owing to the low relative permittivity of the solvent. The most outstanding feature of the association constants given in table 3 is the fact that the salts containing larger ions shows considerable amount of association. Furthermore, the process of ionic association in 2-ethoxyethanol does not exhibit the simple dependence upon ionic size predicted by electrostatic theory[21]. This type of behavior has also been reported for tetraalkylammonium salts in other solvents[15,22,23]. Moreover an increase in the temperature results in a lower level of ion-pairing for each of these salts (*cf.* Table 3).

It is observed from Table 5 that the $\Delta S^0_{308.15}$ values of ion association for the tetraalkylammonium salts are positive. These positive $\Delta S^0_{308.15}$ values may be attributed to the increasing number of degrees of freedom upon association mainly due to the release of solvent molecules for these systems as shown below:

$$M^+n(EE) + X^-m(EE) = MXz(EE) + (n+m-z)EE \qquad (21)$$

(for scarcely solvated R_4N^+ and ph_4B^- ions, $n = m = 0$)

In other words, the solvation of the bromide ion in (R_4NBr) solutions and that for sodium ion in $NaBPh_4$ solutions would be weakened as soon as the ion pairs are formed. A decrease in the entropy for NaBr solution, on the other hand, suggests that the ion pairs that are formed here organize the solvent molecules in their vicinity better than the ions do. Such loss of entropy has also been reported earlier in the solvent media[4,35].

It is especially noteworthy that the $\Delta H^0_{308.15}$ values for all of these electrolytes are negative (Table 5). The electrostatic theories of ionic association [21], however, never give negative values for $\Delta H^0_{308.15}$, because the theoretical equation for $\Delta H^0_{308.15}$ contains the $[1+(d\ln\varepsilon/d\ln T)_p]$ term. According to the experimental values of $(d\ln\varepsilon/d\ln T)_p$, there are few solvents[24,25] which make theoretical values of $\Delta H^0_{308.15}$ and/or $\Delta S^0_{308.15}$ negative. Though, for instance, $\Delta H^0_{308.15}$ is negative[24] when $(d\ln\varepsilon/d\ln T)_p > -1$, almost all of the solvents used for the investigation of the electrolyte solutions do not meet the requirement[26] – the $(d\ln\varepsilon/d\ln T)_p$ value for 2-ethoxyethanol is -1.39. Thus the experimental value of $(d\ln\varepsilon/d\ln T)_p$ makes the theoretical $\Delta H^0_{308.15}$ value positive for the present solvent system, contrary to the observation.

The negative values of $\Delta H^0_{308.15}$ can be interpreted by considering the participation of a specific covalent interaction in the ion-association reaction which somewhat works between the ions and hence, the binding enthalpy between the ions is sufficiently negative to compensate for the positive contribution from the weakening of ion solvation. In this case, $\Delta G^0_{308.15}$ of the ion association should have a large negative value (a large K_A value) and should depend on the kind of ions and this is found to be true here (*cf.* Table 3).

It may thus be concluded that the electrolyte investigated here, are highly associated and exist in the form of solvent-separated ion-pair in 2-ethoxyethanol. The sodium and bromide ions are found to be appreciably solvated where as the tetraalkylammonium and tetraphenyl borate ions are found to remain scarcely solvated in this solvent medium. The solvation of the bromide ions for tetraalkylammonium bromide solution and that for the sodium ions for sodium tetraphenylborate solutions are weakened as soon as these ion pairs are formed. For sodium bromide solution, on the other hand, the ion pairs that are formed are found to organize the solvent molecules in their vicinity better than the ions do.

It may thus be concluded that the electrolytes investigated here, are appreciably associated to form ion-pairs in 2-ethoxyethanol. Moreover, the tetraalkylammonioum ions are found to be scarcely solvated in present solvent medium. The solvation of the bromide ion in these trtralkylammonium bromide is found to be weakened as soon as the ion-pairs are formed. An increase in the temperature results in a lower level of ion-pairing for each of these salts.

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Table 1. Properties of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

T (K)	ρ_0 / gcm^3	η_0 / mPas	ε
308.15	0.91735	1.518	12.81
313.15	0.91370	1.359	12.52
318.15	0.90994	1.189	12.25
323.15	0.90602	1.089	11.99

Table 2. Equivalent conductances (Λ) and corresponding molarities (c) of five tetraakylammonium bromides and two alkali metal salts in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K.

10^4c/mol dm^3	Λ / Scm^{2}mol^{-1}	10^4c/mol dm^3	Λ / Scm^{2}mol^{-1}
	Et_4NBr		
T = 308.15 K		T = 313.15 K	
0.5353	34.93	0.5332	36.20
1.0706	33.26	1.0664	34.46
1.6060	32.08	1.5996	33.17
2.1413	30.96	2.1328	32.09
2.6766	30.03	2.6660	31.14
3.2119	29.20	3.1993	30.28
3.7472	28.42	3.7325	29.49
4.2826	27.71	4.2657	28.75
T = 318.15 K		T = 323.15 K	
0.5310	37.44	0.5287	38.92
1.0620	35.74	1.0575	37.09
1.5930	34.44	1.5862	35.77
2.1240	33.34	2.1149	34.67
2.6550	32.37	2.6436	33.69
3.1860	31.49	3.1724	32.81
3.7170	30.68	3.7011	32.00
4.2480	29.93	4.2298	31.20

Table 2(contd.)

Table 2(contd.)

10^4c/mol dm^3	Λ / Scm^{2}mol^{-1}	10^4c/mol dm^3	Λ / Scm^{2}mol^{-1}
	Pr_4NBr		
T = 308.15 K		T = 313.15 K	
0.4201	34.02	0.4184	35.08
0.8402	33.39	0.8368	34.40
1.2602	32.81	1.2552	33.82
1.6803	32.33	1.6736	33.33
2.1004	31.90	2.0921	32.90
2.5205	31.51	2.5105	32.51
2.9055	31.15	2.9289	32.15
3.3606	30.82	3.3473	31.82
T = 318.15 K		T = 323.15 K	
0.4167	36.29	0.4149	37.64
0.8334	35.46	0.8298	36.68
1.2451	34.89	1.2447	36.10
1.6668	34.39	1.6596	35.61
2.0835	33.96	2.0746	35.18
2.5002	33.57	2.4895	34.79
2.9169	33.21	2.9044	34.44
3.3336	32.88	3.3193	34.10

Table 2(contd.)

Table 2(contd.)

10^4c/mol dm^3	Λ / Scm^{2}mol^{-1}	10^4c/mol dm^3	Λ / Scm^{2}mol^{-1}
Bu_4NBr			
T = 308.15 K		T = 313.15 K	
0.4451	30.26	0.4433	31.18
0.8902	28.67	0.8866	29.55
1.3353	27.47	1.3299	28.35
1.7804	26.46	1.7733	27.29
2.2255	25.56	2.2166	26.39
2.6706	24.76	2.6599	25.60
3.1157	24.01	3.1032	24.91
3.5608	23.32	3.5465	24.19
T = 318.15 K		T = 323.15 K	
0.4415	32.08	0.4396	32.96
0.8831	30.37	0.8792	31.20
1.3246	29.16	1.3189	29.97
1.7661	28.15	1.7585	28.98
2.2077	27.26	2.1981	28.11
2.6492	26.45	2.6377	27.32
3.0907	25.71	3.0773	26.59
3.5323	25.02	3.5169	25.91

Table 2(contd.)

Table 2(contd.)

10^4c/mol dm^3	Λ/Scm^{2}mol^{-1}	10^4c/mol dm^3	Λ/Scm^{2}mol^{-1}
	Pen$_4$NBr		
T =308.15 K		T = 313.15 K	
0.4188	28.92	0.4171	29.78
0.8376	27.94	0.8342	28.77
1.2564	27.22	1.2513	27.97
1.6752	26.62	1.6884	27.39
2.0940	25.98	2.0855	26.85
2.5127	25.55	2.5027	26.33
2.9315	25.22	2.9198	25.89
3.3503	24.71	3.3369	25.50
T =318.15 K		T =323.15 K	
0.4154	30.57	0.4136	31.36
0.8309	29.61	0.8272	30.17
1.2463	28.89	1.2409	29.48
1.6617	28.22	1.6545	28.91
2.0771	27.68	2.0681	28.39
2.4926	27.20	2.4817	27.93
2.9078	26.69	2.8953	27.51
3.3234	26.30	3.3090	27.11

Table 2(contd.)

Table 2(contd.)

10^4c/mol dm^3	Λ/Scm^{2}mol^{-1}	10^4c/mol dm^3	Λ/Scm^{2}mol^{-1}
	Hep_4NBr		
T =308.15 K		T = 313.15 K	
0.4505	25.40	0.4487	25.78
0.9009	24.74	0.8973	25.36
1.3514	24.42	1.3460	24.9
1.8019	24.15	1.7946	24.68
2.2523	23.92	2.2433	24.40
2.7028	23.70	2.6919	24.15
3.1533	23.51	3.1406	23.92
3.6037	23.33	3.5892	23.71
T =318.15 K		T =323.15 K	
0.4468	26.70	0.4449	27.52
0.8937	26.09	0.8898	26.84
1.3405	25.73	1.3347	26.46
1.7873	25.41	1.7796	26.15
2.2342	25.13	2.2245	25.87
2.6810	24.88	2.6694	25.62
3.1278	24.65	3.1143	25.39
3.5746	24.44	3.5592	25.18

Table 2 (contd.)

Table 2 (contd.)

10^4c/mol dm^3	Λ/Scm^{2}mol^{-1}	10^4c/mol dm^3	Λ/Scm^{2}mol^{-1}
NaBPh$_4$			
T = 308.15 K		T = 313.15 K	
0.5969	25.48	0.5944	26.24
1.1922	24.14	1.1872	24.93
1.4902	23.60	1.4839	24.33
2.0863	22.67	2.0776	23.44
2.6824	21.87	2.6712	22.61
2.9805	21.50	2.9690	22.30
3.2785	21.15	3.2648	21.93
3.5765	20.81	3.5616	21.59
T = 318.15 K		T = 323.15 K	
0.5918	27.12	0.5892	27.92
1.1820	25.72	1.1769	26.51
1.4775	25.11	1.4711	25.90
2.0684	24.22	2.0595	25.01
2.6594	23.46	2.6479	24.28
2.9589	23.05	2.9462	23.90
3.2603	22.73	3.2462	23.50
3.5469	22.39	3.5306	23.20

Table 2 (contd.)

Table 2 (contd.)

10^4c/mol dm^3	Λ/Scm^{2}mol^{-1}	10^4c/mol dm^3	Λ/Scm^{2}mol^{-1}
NaBr			
T =308.15 K		T = 313.15 K	
0.5685	25.18	0.5663	25.99
1.1371	24.38	1.1326	25.21
1.7056	23.80	1.6989	24.65
2.2742	23.35	2.2651	24.18
2.8427	22.90	2.8314	23.76
3.4113	22.51	3.3977	23.39
3.9798	22.21	3.9482	23.05
4.5484	21.90	4.5303	22.72
T = 318.15 K		T = 323.15 K	
0.5640	26.77	0.5615	27.55
1.1279	25.98	1.1231	26.75
1.6919	25.42	1.6846	26.20
2.2558	25.00	2.2461	25.74
2.8198	24.58	2.8076	25.33
3.3837	24.20	3.3692	24.97
3.9477	23.84	3.9307	24.63
4.5116	23.49	4.4922	24.32

Table 3. Derived conductivity parameters of five tetraakylammonium bromides and two alkali metal salts in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K.

T/K	$\Lambda^0 / Scm^2mol^{-1}$	$K_\Lambda / \mathrm{dm^3mol^{-1}}$	$R / \overset{0}{A}$	σ%
		Et_4NBr		
308.15	38.43±0.14	1250±39	11.41	0.28
313.15	39.76±0.13	1215±36	11.41	0.26
318.15	41.11±0.15	1141±39	11.42	0.29
323.15	42.65±0.13	1095±33	11.43	0.25
		Pr_4NBr		
308.15	35.79±0.06	279±15	11.93	0.16
313.15	36.90±0.05	253±11	11.93	0.12
318.15	38.15±0.02	235± 5	11.94	0.06
323.15	39.52±0.04	217± 8	11.95	0.10
		Bu_4NBr		
308.15	33.53±0.17	1792±69	12.41	0.37
313.15	34.47±0.12	1700±47	12.41	0.26
318.15	35.38±0.11	1606±43	12.42	0.42
323.15	36.23±0.12	1497±31	12.43	0.18
		Pen_4NBr		
308.15	30.87±0.04	742±13	12.70	0.11
313.15	31.77±0.03	704± 8	12.70	0.07
318.15	32.68±0.05	646±15	12.71	0.13
323.15	33.32±0.07	560±21	12.72	0.19

Table 3(contd.)

Table 3(contd.)

T/K	$\Lambda^0 / Scm^2mol^{-1}$	K_A / dm^3mol^{-1}	$R / \overset{0}{A}$	σ%
		Hep_4NBr		
308.15	26.58±0.05	112±14	13.29	0.18
313.15	27.20±0.03	111±15	13.29	0.19
318.15	28.14±0.02	106 ± 7	13.31	0.09
323.15	29.00±0.03	90± 8	13.31	0.11
		$NaBPh_4$		
308.15	28.36±0.08	1276±34	11.76	0.21
313.15	29.36±0.05	1252±21	11.76	0.13
318.15	30.04±0.05	1103±20	11.76	0.13
323.15	30.86±0.06	1014±22	11.78	0.15
		NaBr		
308.15	26.90±0.03	300± 8	8.36	0.09
313.15	27.79±0.03	259± 9	8.36	0.11
318.15	28.64±0.64	202±15	8.37	0.19
323.15	29.46±0.03	156± 8	8.38	0.10

Table 4. Limiting ionic conductances in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K.

T/K	$\lambda^0_\pm$ /Scm^{2}mol^{-1}			
	Et_4N^+	Pr_4N^+	Bu_4N^+	Pen_4N^+
308.15	22.99	20.35	18.09	15.43
313.15	23.92	21.06	18.63	15.93
318.15	24.74	21.78	19.01	16.31
323.15	25.87	22.74	19.45	16.54

T/K	$\lambda^0_\pm$ /Scm^{2}mol^{-1}			
	Hep_4N^+	Na^+	Ph_4B^-	Br^-
308.15	11.14	11.46	16.90	15.44
313.15	11.36	11.95	17.41	15.84
318.15	24.74	12.27	17.77	16.37
323.15	12.22	12.68	18.17	16.78

Table 5. Coefficients of Eq. (13), and the thermodynamic standard data of ion association.

	a_0	a_1		$a_0 + 308.15\ a_1$
Electrolyte	$\Delta G^0_{308.15}/\mathrm{Jmol}^{-1}$	$\Delta S^0_{308.15}/\mathrm{JK}^{-1}\mathrm{mol}^{-1}$	σ^0	$\Delta H^0_{308.15}/Jmol^{-1}$
Et_4Nbr	-18286.5	34.60	0.05	-7624.5
Pr_4NBr	-14414.7	2.32	0.04	-13699.8
Bu_4NBr	-19204.6	30.23	0.04	-9899.2
Pen_4NBr	-16993.7	4.71	0.19	-15542.3

	a_0	a_1		$a_0 + 308.15\ a_1$
Electrolyte	$\Delta G^0_{308.15}/\mathrm{Jmol}^{-1}$	$\Delta S^0_{308.15}/\mathrm{JK}^{-1}\mathrm{mol}^{-1}$	σ^0	$\Delta H^0_{308.15}/Jmol^{-1}$
Hep_4NBr	-12181.2	1.53	0.44	-11709.7
$NaBPh_4$	-18387.0	15.69	0.17	-13552.1
NaBr	-14706.6	-71.26	0.21	-36665.4

Table 6. Coefficients of Eq. (19).

Electrolyte	b_0	b_1	σ %
Et_4NBr	38.39	-0.2802	0.03
Pr_4NBr	35.72	-0.2488	0.05
Bu_4NBr	33.55	-0.1802	0.03
Pen_4NBr	30.92	-0.1652	0.12
Hep_4NBr	26.50	-0.1652	0.12
$NaBPh_4$	28.43	-0.1636	0.12
NaBr	26.92	-0.1912	0.03

Table 7. Coefficients of the polynomial Eq. (20).

ion	C_0	C_1	σ %
Et_4N^+	22.96	-0.1892	0.11
Pr_4N^+	20.30	-0.1578	0.12
Bu_4N^+	18.13	-0.0892	0.09
Pen_4N^+	15.50	-0.0742	0.22
Hep_4N^+	11.08	-0.0730	0.23
Na^+	11.49	-0.0796	0.15
Ph_4B^-	16.94	-0.0834	0.10
Br^-	15.43	-0.0910	0.09

CHAPTER IV

Viscosities of some tetraalkylammonium bromides in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

Introduction

Recently, we have initiated a comprehensive program to study the solvation and association behaviour of several 1:1 electrolytes in different nonaqueous solvents from the measurements of various transports, thermodynamic and spectroscopic properties[1-5]. As a part of this series of investigations, we have, very recently, reported[6,7] the results of conductance measurements on a number of tetraalkylammonium salts *e.g.*, tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), tetrapentylammonium bromide (Pen_4NBr), and tetraheptylammonium bromide (Hep_4NBr) in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K. We have now extended this work to study the viscometric behavior of these electrolyte solutions since viscometry is well-suited to provide information concerning the solvation of the ions and their effects on the structure of the solvent in the near environment of the solute particles[8-10].

Experimental

2-Ethoxyethanol (G. R. E. Merck) was dried with potassium carbonate and distilled twice in an all glass distillation set immediately before use and the middle fraction was collected. The densities, and viscosities of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K are reported in Table 1. The physical properties of the purified solvent are found to be in good agreement with the literature values[11-15]. Also included in this table are the relative permittivities (ε) of 2-ethoxyethanol at different temperatures obtained from the literature[7,11].

Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described in the literature[16]. These salts were purified by recrystallization and the higher homologues (tetrapentylammonium bromide and tetraheptylammonium bromide) were recrystallized twice to ensure maximum purity. The recrystallized salts were dried *in vacuo* at elevated temperatures for 12h immediately prior to use.

The kinematic viscosities (ν) were measured by means of a suspended level Ubbelohde viscometer. The viscometer was kept in a vertical position in a water thermostat controlled to ± 0.01 K. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations:

$$\nu = Ct - K/t \qquad (1)$$

$$\eta = \nu\rho \qquad (2)$$

where t is the efflux time, ρ is the density, and C and K are the characteristic constants of the viscometer. The values of the constants C and K, determined by using the density and the viscosity values of water and 2-methoxyethanol[17], were found to be 1.646×10^{-5} $cm^2 . s^{-2}$ and -0.02331647 cm^2, respectively. The calibration constants were also checked with methanol[18]. The estimated error of the viscosity measurements was ± 0.05 %. The required densities (ρ) were measured with an Ostwald-Sprengel type pycknometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The relative viscosity (η_r) was obtained as the ratio of the absolute viscosity of the solution (η) to that of the pure solvent (η_0).

The solutions were prepared by mass for the viscosity runs, the molalities being converted to molarities by the use of densities. In order to avoid moisture pick-up, all solutions were prepared in a dehumidified room with utmost care. In all cases the experiments were performed at least in five replicates for each solution and the results were averaged. Several independent solutions were prepared and the runs were performed to ensure the reproducibility of the results.

Results and discussion

The measured relative viscosities (η_r) and densities (ρ) of electrolyte solutions as functions of molar concentrations (c) at 308.15, 313.15, 318.15 and 323.15 K are given in Table 2.

The relative viscosities of the electrolytes in solution are generally analyzed by the Jones-Dole equation[19]:

$$\eta_r = 1 + Ac^{1/2} + Bc \tag{3}$$

where A and B, the characteristic parameters for salt and solvent, depend on ion-ion and ion-solvent interactions, respectively.

As the electrolytes investigated here are found to be somewhat associated from our earlier conductivity measurements[6,7], the viscosity data have been analyzed by the following equation [19]:

$$\eta_r = 1 + A(\alpha c)^{1/2} + B\alpha c + B'(1-\alpha)c \tag{4}$$

Here A, B, and B' are the characteristic constants and α is the degree of dissociation of the ion pair.

Eq. (4) can be rearranged to give

$$[\eta_r - 1 - A(\alpha c)^{1/2}]/\alpha c = B + B'\left(\frac{1-\alpha}{\alpha}\right) \tag{5}$$

For the evaluation of B-coefficients from Eq. (5), plots of $[\eta_r - 1 - A(\alpha c)^{1/2}]/\alpha c$ against $(1-\alpha)/\alpha$ were constructed. These were found to be linear in all cases. A representative plot displays the variation of $[\eta_r - 1 - A(\alpha c)^{1/2}]/\alpha c$ against $(1-\alpha)/\alpha$ at 308.15 K (Fig.1). The values of α were calculated from the conductance data[6,7] using the equations described in the literature[9]. The A values were calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances using the Falkenhagen and Vernon equation [20]:

$$A = \frac{0.2577\Lambda^0}{\eta_0(\varepsilon T)^{1/2}\lambda_+^0\lambda_-^0}\left[1 - 0.6863\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0}\right)^2\right] \tag{6}$$

where η_0 is the coefficient of viscosity of the solvent, ε is its relative permittivity, T is the temperature in absolute scale, and Λ^0, λ_+^0, and λ_-^0 are the limiting equivalent conductivities of the electrolyte, cation, and anion respectively. The values of the A coefficients thus obtained are recorded in Table 3. These have been used for the analysis of the viscosity data. The viscosity B-coefficients have also been included in Table 3. The viscosity data have also been analyzed on the basis of the transition-state treatment of the relative viscosity of electrolyte solutions, as suggested by Feakins *et. al.*[21]:

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000}\left(\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT}\right) \tag{7}$$

In the above equation, $\bar{V}_1^0$ and $\bar{V}_2^0$ are the partial molar volumes of the solvent and solute, respectively. The contribution per mole of solute to the free energy of activation for viscous flow of the solution, $\Delta\mu_2^{0\neq}$, has been determined from the above relationship and is reported in Table 3. The free energy of activation per mole of the pure solvent, $\Delta\mu_1^{0\neq}$ is given by the equation:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln\left(\frac{\eta_0\bar{V}_1^0}{hN}\right) \tag{8}$$

where N is the Avogadro's number and the other symbols have their usual significance.

The action parameters for viscous flow for the electrolytes obtained from Eq. (7) are given in Table 3.

The viscosity *B*-coefficients shown in Table 3 are large and positive for all the electrolytes studied. The *B* values for the tetraalkylammonium bromides increase regularly as we go from tetraethylammonium bromide through tetraheptylammonium bromide. From this table we see that $\Delta\mu_2^{0\neq}$ values for all the electrolytes are also large and positive, and they follow the same pattern as the *B* values.

In order to investigate the specific behavior of the individual ions comprising these electrolytes, it is necessary to split the viscosity *B*-coefficients into their ionic components.

Krumgalz[22] proposed a method, to be applied for nonaqueous solvents, based on his contention that the larger tetraalkylammonium ions are essentially unsolvated in such solvents. Plots of the *B*-coefficients of iodides of these cations in several organic solvents against the cubes of the radii of the ions are indeed found to be linear for Bu_4N^+ and larger cations, values being known upto Hep_4N^+ [22]. The intercepts of the straight lines then give the *B*-coefficient of the counterion, iodide.

$$B(R_4N^+) = B(I^-) + br^3_{R_4N^+} \tag{9}$$

The slope depends on the solvent and the temperature. The *B*-coefficient of Pr_4NI may conform to the straight line obtained using the larger cations in some solvents and not in others, whereas the values for Et_4NI and Me_4NI generally fall below the line. Possibly the position of these tetraalkylammonium ions are caused by the shape of these ions during the viscous flow process in 2-ethoxyethanol making a relatively smaller contribution to *B*-values. This would result from a more compact arrangement of the alkyl groups around the central nitrogen.

Since, the tetraalkylammonium ions investigated in this work are found to be unsolvated in 2-ethoxyethanol from our earlier conductivity study[6,7], the method of Krumgalz[22] described above should, in principle, be applicable to the present viscosity data. In fact, we obtained very good straight lines (*cf.* Fig. 2) for tetraalkylammonium bromides with tetrapropylammonium and larger cations when B (R_4NBr) values are plotted against the cubes of the radii of the cations (r) obtained from the literature[23-25] at all temperatures investigated (Et_4NBr being an exception, B-coefficients of which always fall below the lines). The ionic viscosity B-coefficients obtained following the Krumgalz method[22] are given in Table 4.

The observed order of the viscosity B-values for the tetraalkylammonium ions (Table 3), $Hep_4N^+ > Pen_4N^+ > Bu_4N^+ > Pr_4N^+ > Et_4N^+$ (anion being common), shows that the obstruction of the solvent viscous flow increases with an increase in the size of these species in solution. This clearly indicates lack of solvation of these ions in 2-ethoxyethanol solutions. Had these ions been solvated in 2-ethoxyethanol, the smaller ions with greater charge density would have been more solvated and the order of the ionic viscosity B-coefficients would have been in the reverse order which is, obviously, not the case here.

Fig. 3 shows the temperature dependence of the viscosity B-coefficients of the bromide and tetraalkylammonium ions in 2-ethoxyethanol. For all the ions studied, the B-values are positive and their temperature coefficients are small; although positive coefficients are exhibited by the tetraalkylammonium ions, they are negligibly small. Bromide ion, however, shows a comparatively larger negative temperature coefficient. The temperature dependence of the B-coefficients for the tetraalkylammonium ions in methanol, *N*-methylformamide, *N*-methylpropionamide, and *N*-methylacetamide are also small[10,26,27], and we find the same behavior in the present solvent medium. This finding is in sharp contrast to the abnormally large temperature dependence of the B-coefficients in water[10], and the remarkable difference can be ascribed to the extensive-hydrogen-bonded structure of water. The negligibly small dB/dT values of the tetraalkylammonium ions indicate that they behave neither as structure breaker nor as structure maker in 2-ethoxyethanol whereas the negative dB/dT value for bromide ion in this medium demonstrates its structure-making behavior.

The ionic free energies of activation for viscous flow, $\Delta\mu_2^{0\neq}$(ion), based on a method similar to that used for the separation of the viscosity *B*-coefficients have been presented in Table 4. The $\Delta\mu_2^{0\neq}$ values of the tetraalkylammonium ions are always found to be positive thus indicating that the formation of the transition state is made less favorable in the presence of these ions. The ionic $\Delta\mu_2^{0\neq}$ values in the present series of tetraalkylammonium ions increase steadily with the formula weight of the cations (*cf.* Table 4); this behavior is reasonable when solvation effects are not over-riding.

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Table 1. Physicochemical properties of 2-ethoxyethanol at different temperatures.

T / K	ρ_0 / g cm^{-3}		η_0 / mPa. s		ε
	exptl.	lit.	exptl.	lit.	
298.15	0.92497	0.92502 (11) 0.9252 (12) 0.9258 (13)	1.8277	1.85 (12)	13.38
308.15	0.91735	0.91674 (14) 0.91671 (15) 0.9163 (13)	1.5179		12.81
313.15	0.91370		1.3594		12.52
318.15	0.90994		1.1893		12.25
323.15	0.90602		1.0871		11.99

Table 2. Molar concentrations, densities and relative viscosities of some tetraalkylammoniumbromides in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

c /mol dm^{-3}	ρ /g cm^{-3}	η_r	c /mol dm^{-3}	ρ /g cm^{-3}	η_r
308.15 K					
Et_4NBr			Pr_4NBr		
0.01015	0.91836	1.0080	0.01008	0.91838	1.0091
0.02031	0.91933	1.0160	0.02016	0.91935	1.0181
0.03046	0.92029	1.0237	0.03024	0.92032	1.0271
0.04062	0.92127	1.0314	0.04032	0.92130	1.0362
0.05077	0.92222	1.0397	0.05040	0.92226	1.0453
0.06092	0.92318	1.0477	0.06048	0.92323	1.0541
Bu_4NBr			Pen_4NBr		
0.00999	0.91842	1.0106	0.00996	0.91844	1.0111
0.0199	0.91939	1.0211	0.01992	0.91941	1.0214
0.02997	0.92037	1.0312	0.02988	0.92039	1.0317
0.03996	0.92136	1.0411	0.03984	0.92138	1.0418
0.04995	0.92233	1.0511	0.04980	0.92234	1.0518
0.05994	0.92331	1.0611	0.05976	0.92333	1.0621
Hep_4NBr					
0.01012	0.91847	1.0128			
0.02024	0.91944	1.0246			
0.03036	0.92043	1.0346			
0.04048	0.92142	1.0458			
0.05060	0.92238	1.0561			
0.06072	0.92336	1.0689			
313.15 K					
Et_4NBr			Pr_4NBr		
0.01011	0.91471	1.0081	0.01004	0.91473	1.0092
0.02023	0.91572	1.0162	0.02008	0.91575	1.0183
0.03034	0.91674	1.0239	0.03012	0.91675	1.0274

Table 2. Continued

Table 2. (Contd.)

c /mol dm^{-3}	ρ /g cm^{-3}	η_r	c /mol dm^{-3}	ρ /g cm^{-3}	η_r
0.04046	0.91774	1.0319	0.04016	0.91775	1.0365
0.05058	0.91876	1.0401	0.05021	0.91876	1.0457
0.06070	0.91975	1.0480	0.06025	0.91975	1.0545
Bu_4NBr			Pen_4NBr		
0.00995	0.91475	1.0107	0.00992	0.91476	1.0112
0.01990	0.91577	1.0212	0.01984	0.91576	1.0216
0.02985	0.91676	1.0314	0.02976	0.91677	1.0319
0.03980	0.91778	1.0412	0.03968	0.91779	1.0421
0.04976	0.91878	1.0512	0.04961	0.91879	1.0521
0.05971	0.91979	1.0612	0.05935	0.91982	1.0621
Hep_4NBr					
0.01008	0.91481	1.0129			
0.02016	0.91581	1.0249			
0.03024	0.91682	1.0368			
0.04032	0.91785	1.0462			
0.05038	0.91885	1.0566			
0.06049	0.91987	1.0695			
318.15 K					
Et_4NBr			Pr_4NBr		
0.01007	0.91095	1.0083	0.01000	0.91099	1.0094
0.02014	0.91196	1.0163	0.02000	0.91198	1.0185
0.03022	0.91297	1.0239	0.03000	0.91298	1.0277
0.04029	0.91396	1.0321	0.04000	0.91399	1.0368
0.05037	0.91498	1.0401	0.0500	0.91501	1.0461
0.06045	0.91601	1.0482	0.06000	0.91604	1.0549
Bu_4NBr			Pen_4NBr		
0.00991	0.91101	1.0109	0.00988	0.91103	1.0115
0.01982	0.91201	1.0213	0.01976	0.91202	1.0220
0.02973	0.91299	1.0315	0.02964	0.91300	1.0323

Table 2 (Contd.)

Table 2 (Contd.)

c /mol dm^{-3}	ρ /g cm^{-3}	η_r	c /mol dm^{-3}	ρ /g cm^{-3}	η_r
0.03964	0.91401	1.0413	0.03952	0.91403	1.0425
0.04956	0.91504	1.0515	0.04941	0.91505	1.0527
0.05947	0.91607	1.0613	0.05929	0.91608	1.0630
Hep$_4$NBr					
0.01004	0.91107	1.0133			
0.02008	0.91207	1.0253			
0.03012	0.91305	1.0373			
0.04016	0.91409	1.0468			
0.05020	0.91509	1.0571			
0.06024	0.91612	1.0699			
323.15 K					
Et$_4$NBr			Pr$_4$NBr		
0.01003	0.90703	1.0084	0.00996	0.90705	1.0095
0.02006	0.90802	1.0165	0.01991	0.90805	1.0187
0.03009	0.90905	1.0240	0.02987	0.90907	1.0280
0.04012	0.91004	1.0324	0.03983	0.91009	1.0371
0.05016	0.91107	1.0407	0.04980	0.91112	1.0465
0.06019	0.91208	1.0485	0.05975	0.91213	1.0554
Bu$_4$NBr			Pen$_4$NBr		
0.00987	0.90708	1.0110	0.00984	0.90709	1.0116
0.01978	0.90806	1.0215	0.01967	0.90807	1.0222
0.02960	0.90909	1.0316	0.02951	0.90911	1.0325
0.03947	0.91012	1.0413	0.03935	0.91014	1.0427
0.04934	0.91115	1.0515	0.04920	0.91116	1.0530
0.05921	0.91215	1.0614	0.05904	0.91216	1.0631
Hep$_4$NBr					
0.00999	0.90704	1.0135			
0.01999	0.90812	1.0257			
0.02999	0.90916	1.0378			
0.03999	0.91019	1.0474			
0.04999	0.91118	1.0577			
0.05999	0.91221	1.0706			

Table 3. Theoretical *A*-coefficients, the viscosity *B*-coefficients and the free energies of activation for viscous flow of electrolytes in 2-ethoxyethanol at 308.15, 313.15, 318.15, and 323.15 K.

Electrolyte	A /dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$	B /dm^3 mol^{-1}	$\Delta\mu_2^{\theta\neq}$ /kJ mol^{-1}
308.15 K			
Et_4NBr	0.0290	0.216 ± 0.001	21.52
Pr_4NBr	0.0309	0.444 ± 0.001	29.02
Bu_4NBr	0.0328	0.554 ± 0.005	33.44
Pen_4NBr	0.0356	0.649 ± 0.001	37.51
Hep_4NBr	0.0417	0.833 ± 0.002	45.55
313.15 K			
Et_4NBr	0.0316	0.196 ± 0.001	20.91
Pr_4NBr	0.0339	0.428 ± 0.001	28.65
Bu_4NBr	0.0361	0.534 ± 0.006	33.02
Pen_4NBr	0.0391	0.629 ± 0.001	37.13
Hep_4NBr	0.0460	0.820 ± 0.004	45.46
318.15 K			
Et_4NBr	0.0354	0.179 ± 0.001	20.41
Pr_4NBr	0.0378	0.411 ± 0.001	28.23
Bu_4NBr	0.0406	0.512 ± 0.004	32.54
Pen_4NBr	0.0444	0.603 ± 0.001	36.62
Hep_4NBr	0.0514	0.814 ± 0.004	45.57
323.15 K			
Et_4NBr	0.0377	0.168 ± 0.002	20.16
Pr_4NBr	0.0404	0.396 ± 0.001	27.95
Bu_4NBr	0.0444	0.493 ± 0.005	32.32
Pen_4NBr	0.0476	0.587 ± 0.001	36.40
Hep_4NBr	0.0551	0.800 ± 0.004	45.52

Table 4. Ionic viscositiy *B*-coefficients, and ionic free energies of activation for viscous flow in 2-ethoxyethanol at 308.15, 313.15, 318.15, and 323.15 K.

ion	308.15 K	313.15 K	318.15 K	323.15 K
$B_{\pm}$/dm^3 mol^{-1}				
Et_4N^+	0.099	0.102	0.117	0.125
Pr_4N^+	0.327	0.333	0.349	0.353
Bu_4N^+	0.437	0.439	0.450	0.450
Pen_4N^+	0.532	0.534	0.541	0.544
Hep_4N^+	0.716	0.725	0.752	0.757
Br^-	0.117	0.095	0.062	0.044
$\Delta\mu_2^{\theta\neq}$/kJ mol^{-1}				
Et_4N^+	6.56	6.65	7.19	7.43
Pr_4N^+	14.06	14.39	15.01	15.22
Bu_4N^+	18.48	18.76	19.32	19.59
Pen_4N^+	22.55	22.87	23.40	23.67
Hep_4N^+	30.59	31.20	32.35	32.79
Br^-	14.96	14.2	13.2	12.73

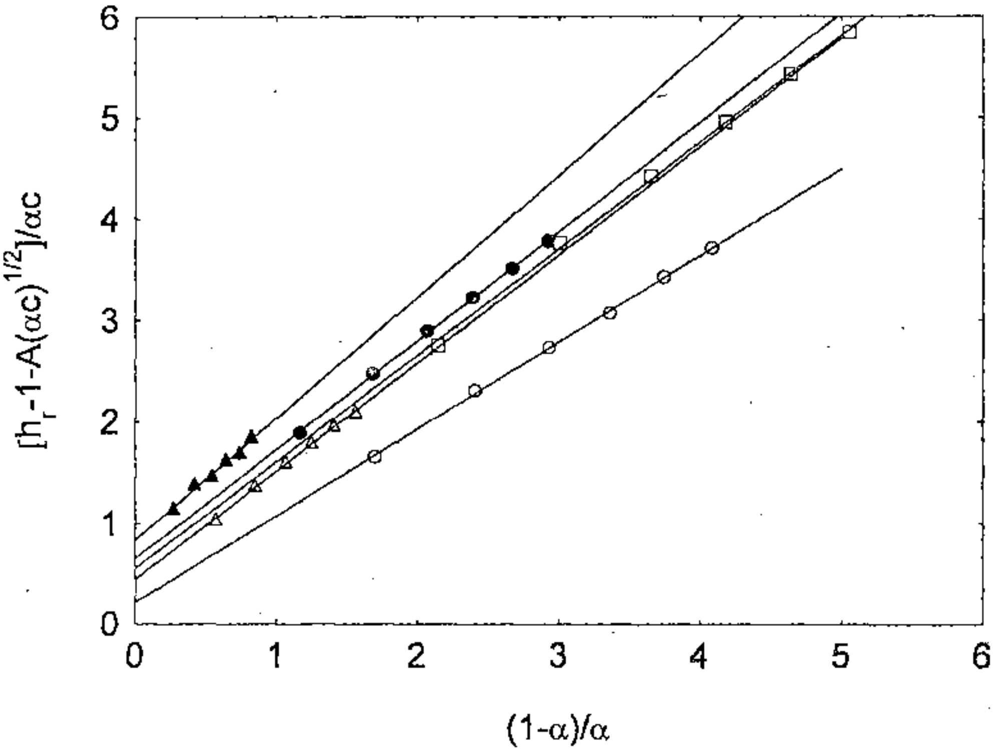

Fig. 1. Variation of $[\eta_r - 1 - A(\alpha c)^{1/2}]/\alpha c$ against $(1-\alpha)/\alpha$ at 308.15 K in 2-ethoxyethanol for Et_4NBr (○), Pr_4NBr (△), Bu_4NBr (□), Pen_4NBr (●) and Hep_4NBr (▲).

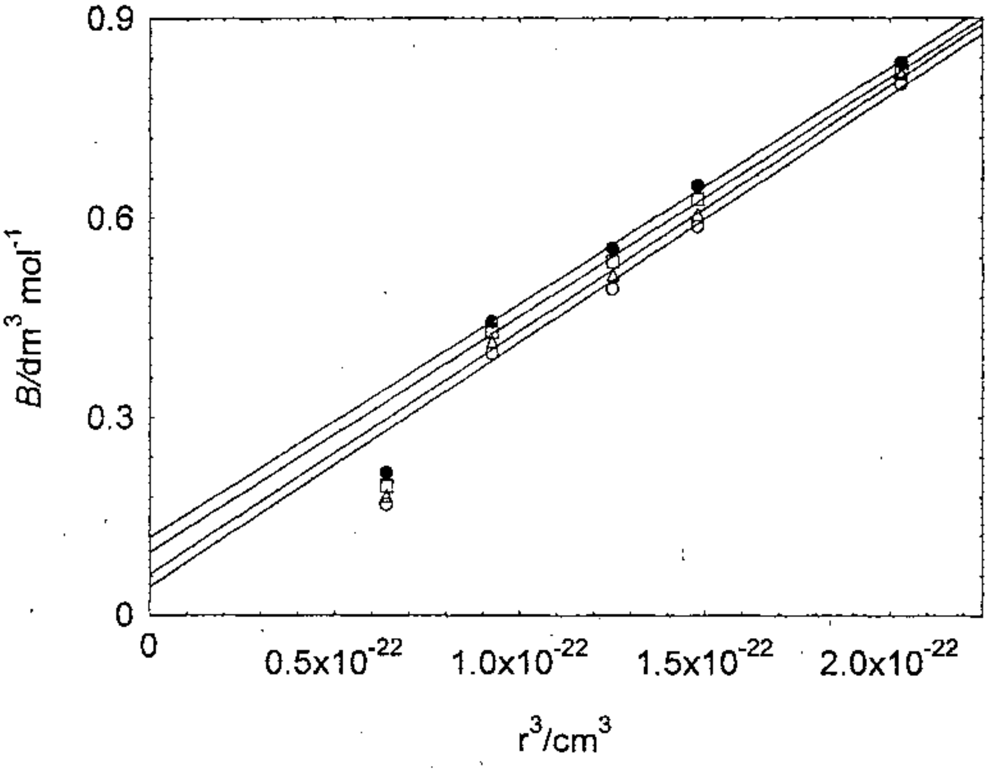

Fig. 2. Representative plot for the variation of the viscosity *B*-coefficient of the tetraalkylammonium bromides against the cube of cationic radius in 2-ethoxyethanol at 308.15 K (○), 313.15 K (△), 318.15 K (□) and 323.15 K (●).

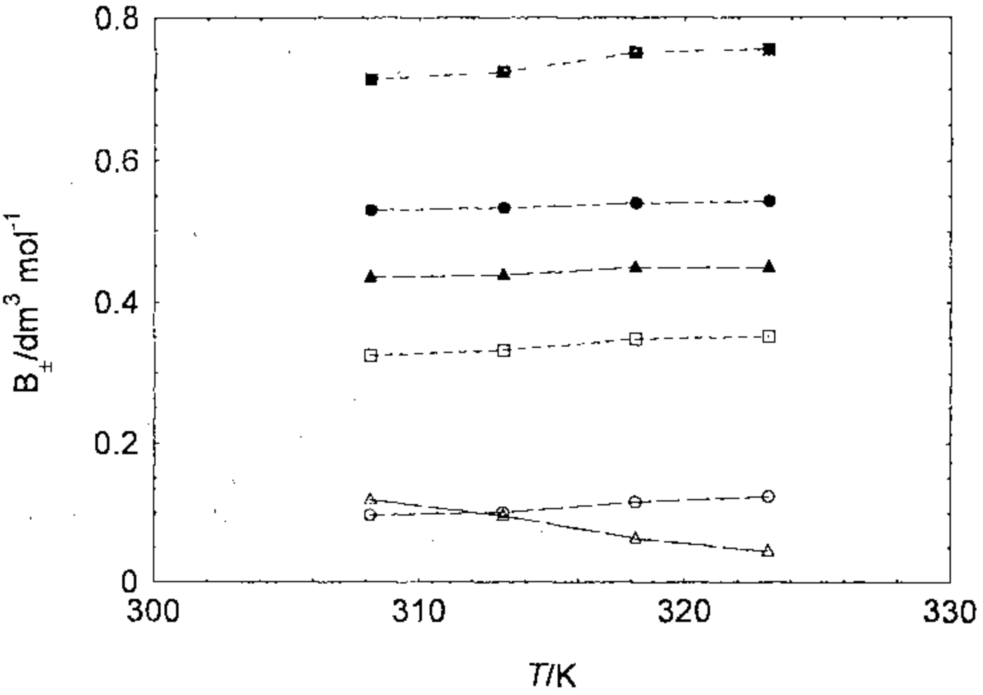

Fig. 3. Temperature dependence of the ionic viscosity B-coefficients in 2-ethoxyethanol for Br^-(△), Et_4N^+(○), Pr_4N^+(□), Bu_4N^+(▲), Pen_4N^+(●), Hep_4N^+(■).

CHAPTER V

Electrical conductances of some tetraalkylammonium and alkali metal salts in 2-ethoxyethanol + water mixtures at 308.15, 313.15, 318.15 and 323.15 K

Introduction

Studies on the transport properties of electrolytes in different solvent media are of great importance to obtain information as to the solvation and association behavior of ions in solutions. These properties have been investigated[1-8] for a wide variety of electrolytes in different solvents in great detail by one of us. The solvent properties like the viscosity and the relative permittivity have also been taken into account in determining the extent of ionic association and the solute-solvent interactions which enabled many to interpret the unique structure of the solvent. The present paper reports the molar conductivities of four tetraalkylammonium salts, namely tetraethylammonium bromide (Et_4NBr), and tetrapropylammonium bromide (Pr_4NBr), tetrabuylammonium bromide (Bu_4NBr), tetrapentylammonium bromide (Pen_4NBr) and two alkali metal salts *e.g.*, sodium bromide (NaBr) and sodium tetraphenylborate ($NaBPh_4$) in 2-ethoxyethanol-water mixtures at 308.15, 313.15, 318.15 and 323.15 K to investigate the ion-ion and ion-solvent interactions in these media.

Experimental

2-Ethoxyethanol (G. R. E. Merck) was dried with potassium carbonate and distilled twice in an all glass distillation set immediately before use and the middle fraction was collected. The purified solvent had a density (ρ_0) of 0.92497 g·cm^{-3} and a viscosity (η_0) of 1.8277 mPa·s at 298.15 K; these values are found to be in good agreement with the literature values.[9,10] Triply distilled water with a specific conductance of less than 10^{-6} S·cm^{-1} at 308.15 K was used for the preparation of the mixed solvents by mass. The physical properties of 2-ethoxyethanol-water mixed solvents used in this study at 308.15, 313.15, 318.15 and 323.15 K are reported in Table 1. The relative permittivities of 2-ethoxyethanol-water mixtures at the experimental temperatures were obtained with the equations as described in the literature[11] using the literature density and relative permittivity data of the pure solvents[7,12] and the densities of the mixed solvents given in Table 1.

Tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr) and tetrapentylammonium bromide (Pen_4NBr) were of Fluka purum grade and were purified by recrystallization from acetone and the recrystallized salts were dried *in vacuo* at 333.15 K for 48 h.

Sodium tetraphenylborate (Fluka, purissimum) was recrystallized from acetone and dried in vacuo at 353.15 K for 72 h. Sodium bromide (Fluka, purum) was dried in vacuo for 72 h and was used without further purification.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 1.15 cm^{-1} and having a precision of 0.10 %. The cell was calibrated by the method of Lind and co-workers[13] using aqueous potassium chloride solutions. The measurements were made in a water bath maintained within ± 0.005 K of the desired temperature. The details of the experimental procedure have been described earlier.[14,15] Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities measured with an Ostwald-Sprengel type pycnometer of about 25 cm^3 capacity. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium from those of the salt solutions.

The kinematic viscosities were measured using a suspended level Ubbelohde-type viscometer.

In order to avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in five replicates for each solution and at each temperature, and the results were averaged (repeatibilities were always within ± 0.10 $S\cdot cm^2\cdot mol^{-1}$).

Results and Discussion

The measured molar conductances (Λ) of electrolyte solutions as functions of molar concentration (c) in 2-ethoxyethanol-water mixtures with $w_1 = 0.25$, 0.50 and 0.75 at 308.15, 313.15, 318.15 and 323.15 K are given in Table 2.

The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation.[16,17] For a given set of conductivity values (c_j, Λ_j; $j = 1, \ldots, n$), three adjustable parameters - the limiting molar conductivity (Λ^0), association constant (K_A), and the association diameter (R), are derived from the following set of equations :

$$\Lambda = p[\Lambda^0(1 + RX + EL] \tag{1}$$

$$p = 1 - \alpha(1 - \gamma) \tag{2}$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \tag{3}$$

$$-\ln f = \frac{\beta k}{2(1 + kR)} \tag{4}$$

$$\beta = \frac{e^2}{\varepsilon k_B T} \tag{5}$$

$$K_A = K_R(1 + K_S) \tag{6}$$

where RX is the relaxation field effect, EL is the electrophoretic countercurrent, γ is the fraction of unpaired ions, and α is the fraction of contact-pairs, K_A is the overall pairing constant evaluated from the association constants of contact-pairs, K_S, of solvent-separated pairs, K_R, ε is the relative permittivity of the solvent, e is the electronic charge, k_B is the Boltzmann constant, k^{-1} is the radius of the ion atmosphere, c is the molarity of the solution, f is the activity coefficient, T is the temperature in absolute scale, and β is twice the Bjerrum distance. The computations were performed on a computer using the program as suggested by Fuoss. The initial Λ^0 values for the iteration procedure were obtained from Shedlovsky extrapolation[18] of the data. Input for the program is the set (c_j, Λ_j; $j = 1, \ldots, n$), n, ε, η, T, initial value of Λ^0, and an instruction to cover a preselected range of R values.

In practice, calculations are made by finding the values of Λ^0 and α which minimize the standard deviation, σ,

$$\sigma = \left[\sum [\Lambda_j(calcd)\text{-}\Lambda_j(obsd)]^2/(n-2)\right]^{1/2} \tag{7}$$

for a sequence of R values and then plotting σ against R; the best-fit R corresponds to the minimum in σ vs. R curve. However, for the electrolytes investigated here, since a preliminary scan using a unit increment of R values from 4 to 20 produced no significant minima in the σ *vs*. R curves, the R value was assumed to be $R = a + d$, where a is the sum of the ionic crystallographic radii and d is given by[17]

$$d = 1.183(M / \rho_0)^{1/3} \tag{8}$$

where M is the molecular weight of the solvent and ρ_0 its density.

The values of Λ^0, K_A, and R obtained by this procedure are reported in Table 3.

In order to investigate the specific behavior of the individual ions comprising these electrolytes, it is necessary to split the limiting molar electrolyte conductances into their ionic components.

The limiting ionic molar conductivities have been evaluated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as the "reference electrolyte" from the following equations[19,20]:

$$\Lambda^0(Bu_4NBPh_4) = \lambda^0(Bu_4N^+) + \lambda^0(Ph_4B^-) \tag{9}$$

$$\frac{\lambda^0(Bu_4N^+)}{\lambda^0(Ph_4B^-)} = \frac{r(Ph_4B^-)}{r(Bu_4N^+)} = \frac{5.35}{5.00} \tag{10}$$

The Λ^0 values of Bu_4NBPh_4 have been obtained by an appropriate combination of those of NaBr, $NaBPh_4$, Bu_4NBr using the Kohlrausch additivity rule:

$$\Lambda^0(Bu_4NBPh_4) = \Lambda^0(Bu_4NBr) + \Lambda^0(NaBPh_4) - \Lambda^0(NaBr) \tag{11}$$

The r-values for the Bu_4N^+ and Ph_4B^- ions were taken from the literature[21].

Table 3 and Figures 1-3 show that the equivalent conductivity values (Λ^0) of the electrolytes investigated increase as the temperature increases in all 2-ethoxyethanol-water mixtures. The Λ^0 values have been fitted to the following polynomial in T:

$$\Lambda^0/S \cdot cm^2 \cdot mol^{-1} = a_0 + a_1(308.15 - T/K) + a_2(308.15 - T/K)^2 \tag{12}$$

and the coefficients of these fits along with the standard deviations (σ) are given in Table 4.

The association constants (K_A) listed in Table 3 for the electrolytes investigated are practically negligible (*i.e.*, the K_A values are either very close to or less than 10 in the mixed solvent media with $w_1 = 0.25$, and 0.50 over the entire temperature range. So, the numerical values of K_A should not be taken seriously.[23] One can only conclude that these electrolytes exist essentially as free ions in both the solvent mixtures in the temperature range 308.15 to 323.15 K. This is expected because the relative permittivities of the solvent mixtures are fairly high ($40.96 \le \varepsilon \le 60.13$). For $NaBPh_4$, however, slight ionic association is noticed even in these solvent mixtures especially in the low temperature region. In the solvent mixture with $w_1 = 0.75$ with comparatively lower relative permittivity, all of these electrolytes are found to be somewhat more associated. Interestingly, the salt NaBr exist in the form of free ions over the entire composition range, irrespective of the temperature.

From Table 4, we see that the limiting ionic conductivity values of the tetraalkylammonium ions decrease in the order: $Et_4N^+ > Pr_4N^+ > Bu_4N^+ > Pen_4N^+$ in the present 2-ethoxyethanol-water mixtures over the entire temperature range. Now, a comparison of this trend in mobility with the crystallographic size of these ions, which is in the order[22] : $Et_4N^+ < Pr_4N^+ < Bu_4N^+ < Pen_4N^+$, shows that the larger the size of the bare ion, the smaller its ionic mobility. This indicates that the relative actual sizes of these ions as they exist in solutions follow the order: $Et_4N^+ < Pr_4N^+ < Bu_4N^+ < Pen_4N^+$. This observation, thus, clearly demonstrates that these ions would remain unsolvated in aqueous 2-ethoxyethanol solutions which is quite expected because of their large crystallographic radii[22] and hence low surface charge density. Had these ions been solvated in these media, their limiting ionic conductivity values should have been in the reverse order: $Et_4N^+ < Pr_4N^+ < Bu_4N^+ < Pen_4N^+$, because smaller ions with greater surface charge densities are expected to be more solvated resulting in a bigger solvodynamic entity – which is obviously not the case here. The bromide ion is found to be solvated in 2-ethoxyethanol from our previous study[7].

The limiting molar conductivity values (Λ^0) of sodium bromide are always found to be higher than those of sodium tetraphenylaborate. This means that the mobility of the bromide ion (Br^-) is greater than that of the tetraphenylborate ion (Ph_4B^-) (cation being common) in all of the mixed solvent media over the entire temperature range investigated. Now, a comparison of this trend in mobility with the crystallographic sizes of these ions, which is in the order[22] : $Br^- < Ph_4B^-$, shows that the larger the size of the bare ion, the smaller is its ionic mobility. This indicates that the relative actual sizes of these ions as they exist in solutions follow the order: $Br^- < Ph_4B^-$.

An important conclusion concerning ion solvation can be drawn if one compares the variation in the mobility difference between the bromide and tetraphenylborate ions, *i.e.*, $\lambda^0(Br^-) - \lambda^0(Ph_4B^-)$ with the composition of the mixed solvent media (*cf.* Table 4). In pure 2-ethoxyethanol (Chapter III), the mobility of the tetraphenylborate ion is always greater than that of the bromide ion thus indicating that the relative actual size of the tetraphenylborate ion is smaller than that of the bromide ion in this medium. That is, the bromide ions must remain significantly solvated in 2-ethoxyethanol thus making them bigger hydrodynamic entities as compared to the tetraphenylborate ions. But the situation is entirely different in 2-ethoxyethanol-water systems, where a reverse trend in the mobilities and hence in the actual sizes for these ions in solutions is observed. Furthermore, the richer the solvent medium in water, the greater is the difference in the mobilities of these ions. Now, since the tetraphenylborate ion is expected to remain unsolvated in solution because of its large size and hence very low surface charge density, the extent of solvation of the bromide ion must decrease monotonically with the addition of water to 2-ethoxyethanol. In other words, the solvation of the bromide ion gradually weakened as the 2-ethoxyethanol content of the medium increases.

A similar behavior of decreasing solvation with increasing amount of 2-ethoxyethanol in aqueous 2-ethoxyethanol mixtures is also exhibited by sodium ion. This can be easily ascertained by comparing the composition dependence of the mobility difference (Table 4) between the sodium ion with any of the tetraalkylammonium or the tetraphenylborate ion which is known to be unsolvated in pure 2-ethoxyethanol (Chapter III) as well as in its aqueous mixture (see above).

The Walden product values $(\Lambda^0\eta_0)$ for the electrolytes studied here show pronounced variations with increasing temperature (Table 3). Therefore, the

Stokes law cannot be applied in 2-ethoxyethanol-water because the $\Lambda^0\eta_0$ values, according to this law, would be expected to be independent of temperature.[23] Since the ions are often far from being spherical and since they are of the same order of magnitude as the solvent molecules, it is questionable whether the retarding effect of the later can be accurately described by the macroscopic viscosity as has been done in the derivation of the Stokes law. Hence, the Stokes law cannot be considered quantitatively reliable. Such failure of this law has also been observed earlier in other solvent media.[20,23]

Thus, it can be concluded that the tetraalkylammonium bromides investigated here exist essentially in the form of free ions aqueous 2-ethoxyethanol solutions with $w_1 = 0.25$ and 0.50 over the entire temperature range investigated (308.15 to 323.15) K. Slight ionic association was observed in the mixed solvent medium with $w_1 = 0.75$. For sodium tetraphenylborate, on the other hand, slight ionic association was always observed and the extent of ionic association is found to increase with increasing amount of 2-ethoxyethanol in the present mixed solvent media. The electrostatic ion-solvent interaction is found to be very weak for the tetraalkylammonium ions and the tetraphenylborate ion in the aqueous 2-ethoxyethanol mixtures investigated. The solvations of the bromide ion and of the sodium ion were found to be gradually weakened as the 2-ethoxyethanol content of the medium increases. Furthermore, the limiting equivalent conductivity values of the electrolytes increase monotonically as the temperature increases in all 2-ethoxyethanol-water mixtures which have been described by polynomial equations.

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Table 1. Properties of 2-ethoxyethanol + water mixtures with w_1 = 0.25, 0.50 and 0.75 at 308.15, 313.15, 318.15 and 323.15 K

T/ K	ρ_0 /(g·cm^3)	η_0 /(mPa·s)	ε
		$w_1 = 0.25$	
308.15	1.00354	1.8430	60.13
313.15	1.00021	1.5293	58.70
318.15	0.99781	1.2738	57.37
323.15	0.99582	1.0923	56.11
		$w_1 = 0.50$	
308.15	0.99361	1.9234	44.30
313.15	0.98514	1.7195	43.03
318.15	0.98004	1.4552	41.95
323.15	0.97610	1.2762	40.96
		$w_1 = 0.75$	
308.15	0.95451	1.7002	27.93
313.15	0.95147	1.5293	27.29
318.15	0.94873	1.3498	26.68
323.15	0.94625	1.1901	26.10

Table 2. Equivalent conductances and corresponding molarities of electrolytes in 2-ethoxyethanol + water mixtures with $w_1 = 0.25$, 0.50 and 0.75 at 308.15, 313.15, 318.15 and 323.15 K

$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
$c/(\mathrm{mol\cdot dm^{-3}})$	$\Lambda/(\mathrm{S\cdot cm^2\cdot mol^{-1}})$	$c/(\mathrm{mol\cdot dm^{-3}})$	$\Lambda/(\mathrm{S\cdot cm^2\cdot mol^{-1}})$	$c/(\mathrm{mol\cdot dm^{-3}})$	$\Lambda/(\mathrm{S\cdot cm^2\cdot mol^{-1}})$
		T = 308.15 K			
		Et_4NBr			
0.005122	66.77	0.002120	58.49	0.000501	49.08
0.007683	64.95	0.003181	57.55	0.000752	48.54
0.010244	63.64	0.004240	56.84	0.001002	48.18
0.012055	62.39	0.005300	56.23	0.001253	47.80
0.015367	61.24	0.006358	55.66	0.001504	47.55
0.017928	60.19	0.007420	55.12	0.001754	47.37
0.020489	59.30	0.008482	54.60	0.002005	47.08
0.025611	57.59	0.010600	53.77	0.002506	46.68
		Pr_4NBr			
0.007359	62.21	0.003045	55.17	0.000763	44.07
0.010052	60.78	0.004060	54.43	0.001017	43.44
0.012565	59.61	0.005075	53.79	0.001271	42.88
0.015078	58.50	0.006090	53.37	0.001525	42.38
0.017591	57.47	0.007105	52.78	0.001780	41.93
0.025130	54.75	0.010150	51.63	0.002542	40.94
		Bu_4NBr			
0.005012	61.25	0.002013	54.14	0.000503	43.37
0.007518	59.72	0.003020	53.31	0.000754	42.97
0.010024	58.26	0.004026	52.90	0.001005	42.57
0.012530	57.06	0.005033	52.45	0.001257	42.26
0.015036	55.93	0.006040	51.99	0.001508	41.98
0.017542	55.01	0.007046	51.66	0.001759	41.72
0.020048	54.12	0.008053	51.16	0.002010	41.43
0.025060	52.23	0.010066	50.57	0.002513	40.98

Table 2 (contd.)

Table 2 (contd.)

$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
c/(mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})	c/(mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})	c/(mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})
		Pen$_4$NBr			
0.005008	58.91	0.002103	50.89	0.000499	40.14
0.007312	57.35	0.003154	50.10	0.000748	39.57
0.010016	55.91	0.004205	49.46	0.000997	39.10
0.012520	54.87	0.005256	48.91	0.001247	38.66
0.015024	53.78	0.006308	48.35	0.001496	38.30
0.017528	52.77	0.007359	47.97	0.001745	37.93
0.020032	51.92	0.008410	47.44	0.001995	37.60
0.025040	50.20	0.010513	46.70	0.002493	37.06
		NaBr			
0.005006	79.50	0.001999	60.04	0.000526	43.50
0.007509	77.91	0.002998	59.37	0.000789	42.98
0.010012	76.61	0.003998	58.78	0.001052	42.69
0.012515	75.35	0.004997	58.23	0.001315	42.44
0.015018	74.31	0.005996	57.70	0.001578	42.22
0.017521	73.28	0.006996	57.32	0.001841	42.00
0.020024	72.36	0.007995	56.91	0.002103	41.74
0.025030	70.59	0.009994	56.03	0.002629	41.30
		NaBPh$_4$			
0.005112	49.29	0.002085	40.28	0.000501	32.70
0.007668	47.73	0.003128	39.32	0.000752	32.17
0.010224	46.36	0.004171	38.60	0.001003	31.71
0.012780	45.30	0.005213	38.17	0.001254	31.19
0.015337	44.27	0.006256	37.56	0.001504	30.78
0.017893	43.26	0.007299	37.13	0.001755	30.42
0.020449	42.50	0.008342	36.56	0.002006	30.06
0.025561	40.88	0.010427	35.77	0.002507	29.47

Table 2 (contd.)

Table 2 (contd.)

$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
$c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$	$c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$	$c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$
T = 313.15 K					
Et_4NBr					
0.005099	71.97	0.002110	63.03	0.000499	53.32
0.007649	70.34	0.003165	62.55	0.000748	52.92
0.010198	68.93	0.004220	61.61	0.000998	52.52
0.012748	67.70	0.005275	61.04	0.001247	52.12
0.015298	66.61	0.006330	60.34	0.001496	51.85
0.017848	65.50	0.007386	59.98	0.001746	51.49
0.020398	64.52	0.008441	59.47	0.001995	51.22
0.025498	62.87	0.010551	58.48	0.002494	50.71
Pr_4NBr					
0.005003	68.95	0.002020	60.88	0.000506	49.20
0.007505	67.15	0.003031	60.05	0.000759	48.34
0.010007	65.75	0.004041	59.39	0.001012	47.72
0.012509	64.75	0.005052	58.99	0.001265	47.11
0.015012	63.55	0.006062	58.40	0.001518	46.50
0.017514	62.52	0.007072	57.97	0.001771	46.01
0.020016	61.50	0.008083	57.53	0.002024	45.50
0.025021	59.71	0.010104	56.81	0.002530	44.92
Bu_4NBr					
0.004990	66.34	0.002004	58.89	0.000500	48.57
0.007484	64.67	0.003006	58.22	0.000750	48.11
0.009980	63.23	0.004008	57.64	0.001001	47.67
0.012475	61.96	0.005010	57.09	0.001251	47.33
0.014970	60.92	0.006012	56.55	0.001501	47.04
0.017466	59.83	0.007014	56.17	0.001751	46.77
0.019961	58.96	0.008016	55.76	0.002001	46.47
0.024953	57.19	0.010020	55.09	0.002501	46.01

Table 2 (contd.)

Table 2 (contd.)

$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
$c/(\text{mol}\cdot\text{dm}^{-3})$	$\Lambda/(\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1})$	$c/(\text{mol}\cdot\text{dm}^{-3})$	$\Lambda/(\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1})$	$c/(\text{mol}\cdot\text{dm}^{-3})$	$\Lambda/(\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1})$
Pen_4NBr					
0.004986	63.99	0.002093	55.91	0.000496	45.93
0.007478	62.31	0.003139	54.79	0.000745	45.26
0.009971	60.97	0.004186	54.23	0.000993	44.93
0.012464	59.77	0.005232	53.71	0.001241	44.57
0.014958	58.77	0.006279	53.20	0.001489	44.26
0.017451	57.76	0.007325	52.69	0.001737	43.98
0.019944	56.81	0.008372	52.32	0.001985	43.72
0.024932	55.15	0.010465	51.50	0.002482	43.19
NaBr					
0.004984	84.88	0.001989	64.84	0.000523	49.10
0.007475	83.21	0.002984	64.34	0.000785	48.66
0.009967	81.87	0.003979	63.83	0.001047	48.30
0.012459	80.74	0.004974	63.13	0.001308	47.95
0.014951	79.59	0.005968	62.66	0.001570	47.63
0.017442	78.48	0.006963	62.18	0.001832	47.32
0.019935	77.60	0.007958	61.82	0.002094	47.06
0.024920	75.76	0.009948	60.92	0.002617	46.58
NaBPh_4					
0.005089	53.84	0.002076	44.32	0.000499	38.07
0.007634	52.40	0.003114	43.68	0.000749	37.40
0.010179	51.09	0.004151	42.88	0.000998	36.97
0.012724	49.91	0.005189	42.39	0.001247	36.55
0.015269	48.86	0.006227	41.91	0.001497	36.13
0.017814	47.83	0.007265	41.92	0.001747	35.78
0.020360	47.20	0.008303	41.29	0.001996	35.41
0.025451	45.46	0.010379	40.95	0.002496	34.78

Table 2 (contd.)

Table 2 (contd.)

$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
c/(mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})	c/(mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})	c/(mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})
T = 318.15 K					
Et_4NBr					
0.005079	77.18	0.002099	68.60	0.000496	58.68
0.007619	75.47	0.003149	67.64	0.000744	57.94
0.010158	74.03	0.004198	66.69	0.000992	57.37
0.012698	72.77	0.005248	66.12	0.001240	56.86
0.015238	71.60	0.006298	65.58	0.001488	56.46
0.017778	70.65	0.007347	65.06	0.001736	56.11
0.020318	69.64	0.008397	64.55	0.001984	55.70
0.025398	67.80	0.010496	63.55	0.002480	55.01
Pr_4NBr					
0.004984	73.84	0.002010	65.67	0.000503	54.84
0.007476	72.37	0.003015	65.00	0.000755	53.91
0.009968	70.83	0.004020	64.42	0.001007	53.15
0.012461	69.58	0.005025	63.88	0.001258	52.54
0.014953	68.48	0.006031	63.34	0.001510	51.99
0.017446	67.41	0.007036	62.96	0.001762	51.38
0.019939	66.40	0.008041	62.43	0.002013	50.81
0.024925	64.63	0.010051	61.58	0.002516	49.91
Bu_4NBr					
0.004970	71.43	0.001993	63.71	0.000498	54.47
0.007455	69.75	0.002990	63.20	0.000746	54.00
0.009941	68.20	0.003987	62.45	0.000995	53.67
0.012426	67.04	0.004984	62.00	0.001244	53.31
0.014912	65.92	0.005981	61.53	0.001493	53.00
0.017398	64.84	0.006978	61.05	0.001741	52.72
0.019884	63.92	0.007975	60.57	0.001990	52.41
0.024857	62.12	0.009968	59.89	0.002488	52.02

Table 2 (contd.)

Table 2 (contd.)

$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
$c/(\mathrm{mol \cdot dm^{-3}})$	$\Lambda/(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$	$c/(\mathrm{mol \cdot dm^{-3}})$	$\Lambda/(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$	$c/(\mathrm{mol \cdot dm^{-3}})$	$\Lambda/(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$
		Pen_4NBr			
0.004966	69.07	0.002082	60.52	0.000494	51.26
0.007449	67.52	0.003123	59.88	0.000740	50.78
0.009932	66.15	0.004164	59.08	0.000987	50.34
0.012416	65.00	0.005205	58.60	0.001234	49.92
0.014900	63.89	0.006246	57.95	0.001481	49.57
0.017384	62.87	0.007287	57.50	0.001728	49.20
0.019868	61.96	0.008329	57.03	0.001974	48.87
0.024836	60.31	0.010411	56.19	0.002468	48.30
		NaBr			
0.004964	90.66	0.001979	71.24	0.000520	55.72
0.007446	89.04	0.002969	70.40	0.000781	55.20
0.009928	87.83	0.003958	69.73	0.001041	54.76
0.012410	86.62	0.004948	69.12	0.001301	54.41
0.014893	85.54	0.005938	68.55	0.001561	53.99
0.017375	84.54	0.006927	68.14	0.001822	53.69
0.019858	83.64	0.007917	67.70	0.002082	53.36
0.024824	81.74	0.009896	66.79	0.002602	52.87
		$NaBPh_4$			
0.005069	58.19	0.002064	49.40	0.000496	43.52
0.007604	56.68	0.003097	48.43	0.000744	42.98
0.010139	55.43	0.004130	47.94	0.000993	42.51
0.012675	54.20	0.005163	47.46	0.001241	42.15
0.015210	53.12	0.006195	46.65	0.001489	41.77
0.017746	52.18	0.007228	46.21	0.001737	41.50
0.020281	51.33	0.008261	45.76	0.001985	41.15
0.025354	49.62	0.010326	44.83	0.002482	40.62

Table 2 (contd.)

Table 2 (contd.)

$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
$c/(\mathrm{mol \cdot dm^{-3}})$	$\Lambda/(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$	$c/(\mathrm{mol \cdot dm^{-3}})$	$\Lambda/(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$	$c/(\mathrm{mol \cdot dm^{-3}})$	$\Lambda/(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$
		T = 323.15 K			
		Et_4NBr			
0.005060	83.00	0.002087	73.79	0.000494	64.23
0.007590	80.76	0.003130	72.83	0.000740	63.35
0.010120	79.24	0.004174	72.11	0.000987	62.74
0.012651	78.02	0.005217	71.49	0.001234	62.01
0.015181	76.80	0.006261	70.91	0.001481	61.53
0.017712	75.77	0.007305	70.37	0.001727	61.02
0.020243	74.69	0.008483	69.83	0.001974	60.54
0.025304	72.87	0.010436	68.99	0.002468	59.65
		Pr_4NBr			
0.004965	79.15	0.001998	71.06	0.000501	61.32
0.007448	77.47	0.002998	70.39	0.000751	60.39
0.009931	75.82	0.003997	69.80	0.001001	59.62
0.012414	74.67	0.004996	69.25	0.001252	58.76
0.014898	73.57	0.005996	68.72	0.001502	58.19
0.017382	72.49	0.006995	68.19	0.001752	57.61
0.019866	71.43	0.007994	67.80	0.002003	56.98
0.024834	69.70	0.009994	66.94	0.002503	55.77
		Bu_4NBr			
0.004951	76.14	0.001982	69.13	0.000495	60.12
0.007427	74.18	0.002973	68.29	0.000742	59.50
0.009904	72.60	0.003964	67.61	0.000990	59.11
0.012380	71.32	0.004955	67.20	0.001237	58.90
0.014857	70.07	0.005946	66.77	0.001485	58.47
0.017334	69.05	0.006937	66.16	0.001732	58.17
0.019812	67.89	0.007928	65.84	0.001980	57.90
0.024767	66.06	0.009911	64.98	0.002475	57.43

Table 2 (contd.)

Table 2 (contd.)

$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
c/(mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})	c/(mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})	c/(mol·dm^{-3})	Λ/(S·cm^2·mol^{-1})
		Pen$_4$NBr			
0.004947	74.58	0.002070	66.19	0.000491	57.23
0.007422	72.90	0.003105	65.38	0.000737	56.62
0.009896	71.44	0.004140	64.49	0.000982	56.21
0.012370	70.33	0.005175	63.96	0.001228	55.72
0.014845	69.25	0.006210	63.44	0.001473	55.39
0.017320	68.30	0.007245	63.07	0.001719	54.99
0.019795	67.34	0.008281	62.68	0.001964	54.65
0.024746	65.67	0.010351	61.92	0.002455	54.09
		NaBr			
0.004945	96.25	0.001968	77.25	0.000518	62.96
0.007418	94.63	0.002951	76.23	0.000777	62.32
0.009891	93.11	0.003935	75.72	0.001035	61.80
0.012365	91.87	0.004919	75.01	0.001294	61.42
0.014838	90.78	0.005903	74.53	0.001553	61.03
0.017312	89.76	0.006887	74.05	0.001812	60.70
0.019786	88.80	0.007871	73.43	0.002071	60.35
0.024734	86.84	0.009839	72.67	0.002589	59.79
		NaBPh$_4$			
0.005050	62.96	0.002053	54.29	0.000494	49.37
0.007576	61.38	0.003079	53.58	0.000741	48.74
0.010102	60.09	0.004106	52.85	0.000988	48.40
0.012628	58.92	0.005133	52.21	0.001234	48.04
0.015154	57.80	0.006159	51.63	0.001481	47.73
0.017681	56.84	0.007186	51.21	0.001728	47.45
0.020208	55.92	0.008213	50.65	0.001975	47.19
0.025262	54.66	0.010267	49.87	0.002469	46.70

Table 3. Derived conductivity parameters of electrolytes in 2-ethoxyethanol-water mixtures with w_1 = 0.25, 0.50, and 0.75 at 308.15, 313.15, 318.15 and 323.15 K

T/K	Λ^0/(S·cm^2·mol^{-1})	K_A / (dm^3·mol^{-1})	$\Lambda^0\eta_0$/(S·cm^2· mol^{-1}·Pa·s)	R / $\overset{0}{A}$	$100\sigma / \Lambda^0$
			w_1 = 0.25		
			Et$_4$NBr		
308.15	72.90 ± 0.06	11.77 ± 0.12	0.1343	9.29	0.07
313.15	78.45 ± 0.06	10.16 ± 0.09	0.1200	9.31	0.06
318.15	84.05 ± 0.0	9.10 ± 0.09	0.1071	9.31	0.06
323.15	90.28 ± 0.17	8.85 ± 0.24	0.0986	9.30	0.15
			Pr$_4$NBr		
308.15	69.93 ± 0.05	12.76 ± 0.11	0.1288	10.81	0.06
313.15	75.22 ± 0.13	11.12 ± 0.23	0.1150	10.83	0.14
318.15	80.64 ± 0.06	9.94 ± 0.14	0.1027	10.83	0.09
323.15	86.22 ± 0.08	8.94 ± 0.12	0.0942	10.82	0.08
			Bu$_4$NBr		
308.15	67.35 ± 0.11	13.31 ± 0.23	0.1241	10.29	0.12
313.15	72.67 ± 0.06	11.74 ± 0.11	0.1111	10.31	0.06
318.15	78.15 ± 0.06	10.46 ± 0.09	0.0996	10.31	0.06
323.15	83.52 ± 0.08	10.54 ± 0.13	0.0912	10.30	0.07
			Pen$_4$NBr		
308.15	64.80 ± 0.08	13.41 ± 0.18	0.1194	10.58	0.09
313.15	70.11 ± 0.05	11.72 ± 0.10	0.1072	10.60	0.16
318.15	75.55 ± 0.04	10.02 ± 0.07	0.0963	10.60	0.04
323.15	81.33 ± 0.05	8.73 ± 0.08	0.0888	10.59	0.05
			NaBr		
308.15	85.74 ± 0.07	8.29 ± 0.11	0.1580	6.24	0.07
313.15	91.53 ± 0.11	7.45 ± 0.15	0.1400	6.26	0.10
318.15	97.62 ± 0.15	6.03 ± 0.18	0.1243	6.26	0.13
323.15	103.83 ± 0.12	5.79 ± 0.14	0.1134	6.25	0.10
			NaBPh$_4$		
308.15	55.21 ± 0.08	16.52 ± 0.22	0.1018	9.64	0.10
313.15	60.00 ± 0.12	13.78 ± 0.30	0.0918	9.64	0.15

Table 3 (contd.)

Table 3 (contd.)

T/K	Λ^0/(S·cm^2·mol^{-1})	K_A/(dm^3·mol^{-1})	$\Lambda^0\eta_0$/(S·cm^2· mol^{-1}·Pa·s)	R/Å	$100\sigma/\Lambda^0$
$w_1 = 0.25$					
318.15	64.73 ± 0.10	12.11 ± 0.23	0.0825	9.66	0.12
323.15	69.63 ± 0.12	10.01 ± 0.23	0.0761	9.65	0.13
$w_1 = 0.50$					
Et_4NBr					
308.15	62.13 ± 0.03	11.39 ± 0.13	0.1195	9.63	0.04
313.15	67.06 ± 0.14	9.57 ± 0.57	0.1153	9.65	0.19
318.15	72.82 ± 0.08	9.01 ± 0.30	0.1060	9.65	0.10
323.15	78.26 ± 0.03	6.97 ± 0.11	0.0942	9.66	0.04
Pr_4NBr					
308.15	59.17 ± 0.11	10.41 ± 0.49	0.1138	10.15	0.16
313.15	64.35 ± 0.05	8.21 ± 0.22	0.1106	10.17	0.08
318.15	69.60 ± 0.10	6.83 ± 0.39	0.1013	10.17	0.14
323.15	75.30 ± 0.10	5.74 ± 0.35	0.0961	10.18	0.12
Bu_4NBr					
308.15	57.13 ± 0.07	7.96 ± 0.34	0.1099	10.63	0.12
313.15	62.31 ± 0.04	8.07 ± 0.17	0.1071	10.65	0.06
318.15	67.54 ± 0.10	6.79 ± 0.38	0.0983	10.65	0.13
323.15	73.14 ± 0.09	5.96 ± 0.11	0.0933	10.66	0.11
Pen_4NBr					
308.15	54.20 ± 0.04	11.83 ± 0.18	0.1042	10.92	0.06
313.15	59.29 ± 0.11	10.35 ± 0.49	0.1019	10.94	0.17
318.15	64.49 ± 0.08	9.04 ± 0.32	0.0938	10.94	0.11
323.15	70.21 ± 0.09	6.92 ± 0.33	0.0896	10.95	0.12
NaBr					
308.15	63.53 ± 0.08	6.83 ± 0.34	0.1222	6.58	0.11
313.15	68.69 ± 0.16	5.50 ± 0.62	0.1181	6.60	0.21
318.15	75.37 ± 0.06	5.21 ± 0.21	0.1097	6.60	0.07
323.15	81.70 ± 0.10	4.20 ± 0.34	0.1043	6.61	0.12
$NaBPh_4$					
308.15	43.57 ± 0.09	18.32 ± 0.62	0.0838	9.98	0.17

Table 3 (contd.)

Table 3 (contd.)

T/K	Λ^0/(S·cm^2·mol^{-1})	K_A/(dm^3·mol^{-1})	$\Lambda^0\eta_0$/(S·cm^2·mol^{-1}·Pa·s)	R/Å	$100\sigma/\Lambda^0$
313.15	47.84 ± 0.08	14.22 ± 0.51	0.0823	10.00	0.15
318.15	52.23 ± 0.13	12.59 ± 0.72	0.0760	10.00	0.22
323.15	58.42 ± 0.07	10.11 ± 0.32	0.0746	10.01	0.10
$w_1 = 0.75$					
Et_4NBr					
308.15	51.38 ± 0.04	11.52 ± 0.77	0.0874	10.23	0.07
313.15	56.02 ± 0.07	12.38 ± 1.29	0.0857	10.23	0.12
318.15	61.82 ± 0.04	23.72 ± 0.66	0.0834	10.23	0.06
323.15	68.00 ± 0.05	32.84 ± 0.88	0.0809	10.23	0.07
Pr_4NBr					
308.15	49.63 ± 0.11	49.58 ± 1.32	0.0894	10.75	0.10
313.15	52.44 ± 0.09	52.69 ± 1.94	0.0802	10.75	0.14
318.15	58.59 ± 0.05	53.17 ± 1.11	0.0791	10.75	0.08
323.15	65.56 ± 0.12	53.31 ± 2.15	0.0780	10.76	0.15
Bu_4NBr					
308.15	45.68 ± 0.04	17.85 ± 0.93	0.0777	11.23	0.08
313.15	51.09 ± 0.03	15.60 ± 0.58	0.0781	11.23	0.05
318.15	57.19 ± 0.09	8.82 ± 0.93	0.0772	11.23	0.09
323.15	63.07 ± 0.07	7.01 ± 1.16	0.0750	11.23	0.19
Pen_4NBr					
308.15	42.61 ± 0.03	38.73 ± 0.69	0.0894	11.52	0.05
313.15	48.35 ± 0.05	20.14 ± 1.10	0.0802	11.52	0.10
318.15	54.11 ± 0.06	19.94 ± 1021	0.0791	11.52	0.11
323.15	60.34 ± 0.05	16.96 ± 0.96	0.0780	11.53	0.08
NaBr					
308.15	45.70 ± 0.08	2.41 ± 1.40	0.0777	7.18	0.13
313.15	51.73 ± 0.06	5.40 ± 1.18	0.0791	7.18	0.11
318.15	58.69 ± 0.05	5.30 ± 0.96	0.0792	7.18	0.09
323.15	66.33 ± 0.05	5.01 ± 0.76	0.0789	7.19	0.07

Table 3 (contd.)

Table 3 (contd.)

T/K	Λ^0/(S·cm^2·mol^{-1})	K_A/(dm^3·mol^{-1})	$\Lambda^0\eta_0$/(S·cm^2·mol^{-1}·Pa·s)	$R/\overset{0}{A}$	$100\sigma/\Lambda^0$
		NaBPh$_4$			
308.15	35.27 ± 0.05	59.64 ± 1.76	0.0600	10.58	0.12
313.15	40.70 ± 0.05	43.46 ± 1.36	0.0622	10.58	0.10
318.15	46.20 ± 0.03	23.50 ± 0.79	0.0624	10.58	0.07
323.15	52.10 ± 0.04	10.27 ± 0.84	0.0620	10.59	0.08

Table 4. Coefficients of Eq. (12) and the standard deviations (σ)

w_1	Electrolyte	a_0 / ($\mathrm{S \cdot cm^2 \cdot mol^{-1}}$)	$-a_1$ / ($\mathrm{S \cdot cm^2 \cdot mol^{-1} \cdot K^{-1}}$)	a_2 / ($\mathrm{S \cdot cm^2 \cdot mol^{-1} \cdot K^{-2}}$)	σ / ($\mathrm{S \cdot cm^2 \cdot mol^{-1}}$)
0.25	Et_4NBr	72.93 ± 0.13	1.0528 ± 0.0406	0.0068 ± 0.0026	0.13
	Pr_4NBr	69.93 ± 0.01	1.0423 ± 0.0021	0.0029 ± 0.0001	0.01
	Bu_4NBr	72.93 ± 0.13	1.0528 ± 0.0406	0.0068 ± 0.0026	0.13
	Pen_4NBr	69.93 ± 0.01	1.0423 ± 0.0021	0.0029 ± 0.0001	0.01
	NaBr	85.73 ± 0.03	1.1442 ± 0.0089	0.0042 ± 0.0001	0.04
	$NaBPh_4$	55.22 ± 0.04	0.9433 ± 0.0114	0.0011 ± 0.0007	0.05
0.50	Et_4NBr	62.07 ± 0.25	1.0065 ± 0.0805	0.0051 ± 0.0041	0.26
	Pr_4NBr	59.19 ± 0.08	0.9948 ± 0.0266	0.0052 ± 0.0017	0.08
	Bu_4NBr	62.07 ± 0.25	1.0065 ± 0.0805	0.0051 ± 0.0041	0.26
	Pen_4NBr	59.19 ± 0.08	0.9948 ± 0.0266	0.0052 ± 0.0017	0.08
	NaBr	63.44 ± 0.29	1.0483 ± 0.0926	0.0117 ± 0.0059	0.42
	$NaBPh_4$	43.50 ± 0.26	0.8608 ± 0.0832	0.0092 ± 0.0053	0.30
0.75	Et_4NBr	51.34 ± 0.17	0.8822 ± 0.0546	0.0154 ± 0.0035	0.17
	Pr_4NBr	49.50 ± 0.55	0.4548 ± 0.1764	0.0416 ± 0.0113	0.56
	Bu_4NBr	51.34 ± 0.17	0.8822 ± 0.0546	0.0154 ± 0.0035	0.17
	Pen_4NBr	49.50 ± 0.55	0.4548 ± 0.1764	0.0416 ± 0.0113	0.56
	NaBr	45.68 ± 0.04	1.1445 ± 0.0014	0.0151 ± 0.0009	0.08
	$NaBPh_4$	35.29 ± 0.05	1.0457 ± 0.0163	0.0051 ± 0.0010	0.08

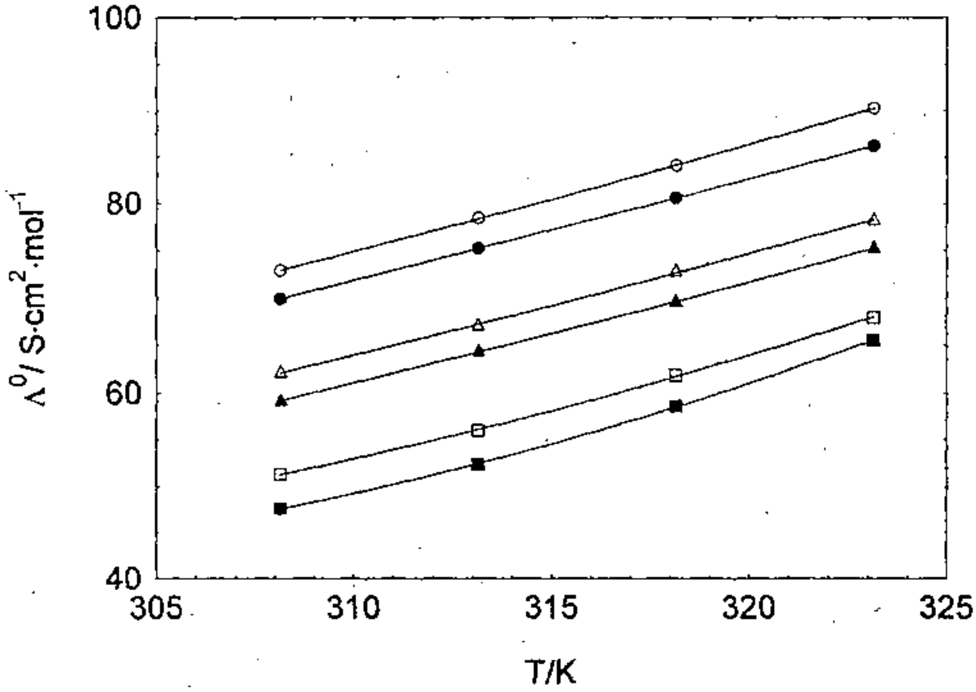

Figure 1. Temperature dependence of the limiting molar conductances of tetraethylammonium bromide (○, w_1 = 0.25; △, w_1 = 0.50; □, w_1 = 0.75) and tetrapropylammonium bromide (●, w_1 = 0.25; ▲, w_1 = 0.50; ■, w_1 = 0.75) in 2-ethoxyethanol- water mixtures.

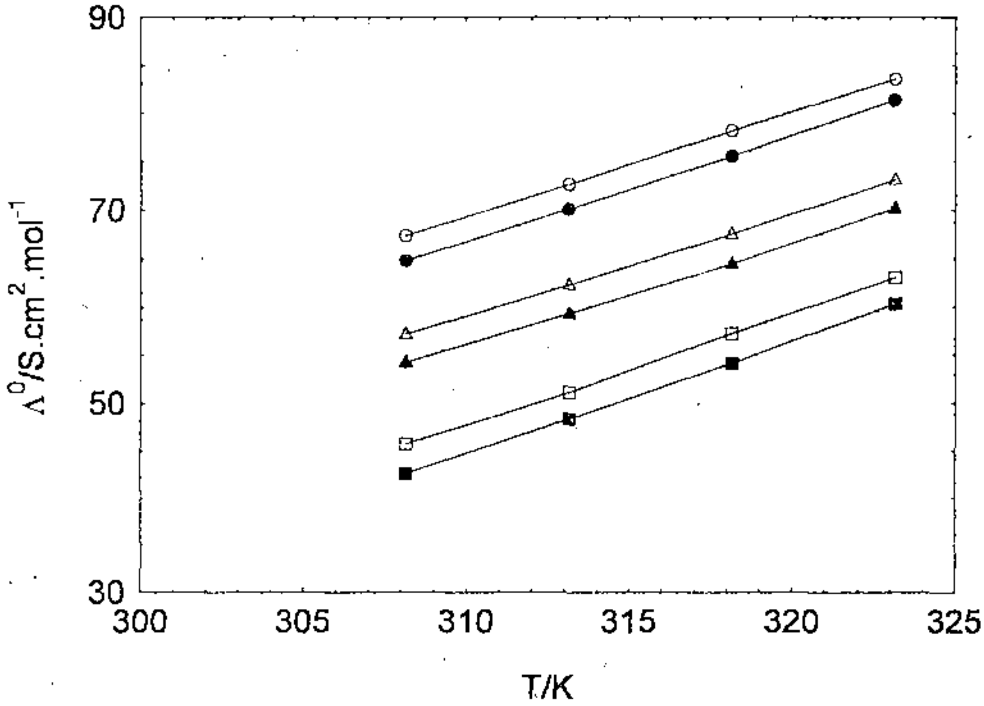

Figure 2. Temperature dependence of the limiting molar conductances of tetrabutylammonium bromide (○, w_1 = 0.25; △, w_1 = 0.50; □, w_1 = 0.75) and tetrapentylammonium bromide (●, w_1 = 0.25; ▲, w_1 = 0.50; ■, w_1 = 0.75) in 2-ethoxyethanol-water mixtures.

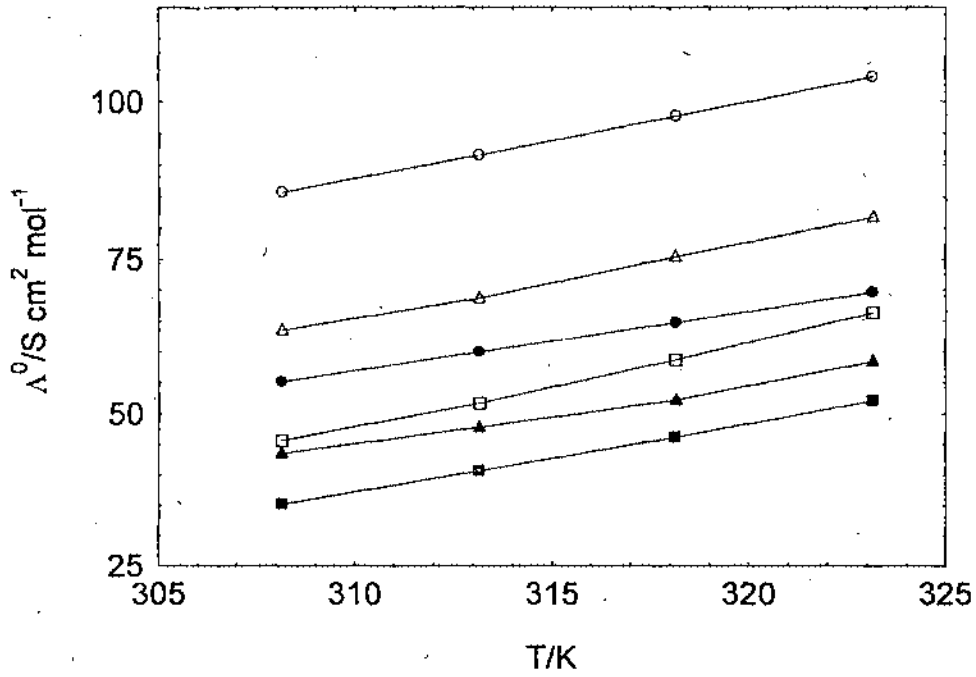

Figure 3. Temperature dependence of the limiting molar conductances of sodium bromide (○, $w_1 = 0.25$; △, $w_1 = 0.50$; □, $w_1 = 0.75$) and sodium tetraphenylborate (●, $w_1 = 0.25$; ▲, $w_1 = 0.50$; ■, $w_1 = 0.75$) in 2-ethoxyethanol-water mixtures.

CHAPTER VI

Viscosities of some tetraalkylammonium and alkali metal salts in 2-ethoxyethanol + water mixed solvent media at 308.15, 313.15, 318.15 and 323.15 K

Introduction

Recently, we have initiated a comprehensive program to study the solvation and association behaviour of several 1:1 electrolytes in different nonaqueous solvents from the measurements of various transport, thermodynamic and spectroscopic properties[1-5]. As a part of this series of investigations, we have, very recently, reported [6,7] the results of conductance measurements on a number of tetraalkylammonium salts *e.g.*, tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), tetrapentylammonium bromide (Pen_4NBr), and tetraheptylammonium bromide (Hep_4NBr) in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K. We have now extended this work to study the viscometric behavior of these electrolyte solutions since viscometry is well-suited to provide information concerning the solvation of the ions and their effects on the structure of the solvent in the near environment of the solute particles[8-10].

Experimental

2-Ethoxyethanol (G. R. E. Merck) was dried with potassium carbonate and distilled twice in an all glass distillation set immediately before use and the middle fraction was collected. The purified solvent had a density (ρ_0) of 0.92497 g·cm^{-3} and a viscosity (η_0) of 1.8277 mPa·s at 298.15 K; these values are found to be in good agreement with the literature values[11,12]. Triply distilled water with a specific conductance of less than 10^{-6} S·cm^{-1} at 308.15 K was used for the preparation of the mixed solvents by mass. The physical properties of 2-ethoxyethanol-water mixed solvents used in this study at 308.15, 313.15, 318.15, and 323.15 K are reported in Table 1. The relative permittivities of 2-ethoxyethanol-water mixtures at the experimental temperatures were obtained with the equations as described in the literature[13] using the literature density and relative permittivity data of the pure solvents[7,14] and the densities of the mixed solvents given in Table 1.

Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described in the literature[15]. These salts were purified by recrystallization. The recrystallized salts were dried *in vacuo* at elevated temperatures for 12 h immediately prior to use.

Sodium tetraphenylborate (Fluka, purissimum) was recrystallized from acetone and dried in vacuo at 353.15 K for 72 h. Sodium bromide (Fluka, purum) was dried in vacuo for 72 h and was used without further purification.

The kinematic viscosities (ν) were measured by means of a suspended level Ubbelohde viscometer. The viscometer was kept in a vertical position in a water thermostat controlled to ± 0.01 K. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations:

$$\nu = Ct - K/t \qquad (1)$$

$$\eta = \nu\rho \qquad (2)$$

where t is the efflux time, ρ is the density, and C and K are the characteristic constants of the viscometer. The values of the constants C and K, determined by using the density and the viscosity values of water and 2-methoxyethanol[16], were found to be 1.646×10^{-5} cm^2 s^{-2} and -0.02331647 cm^2, respectively. The calibration constants were also checked with methanol[17]. The estimated error of the viscosity measurements was ± 0.05 %. The required densities (ρ) were measured with an Ostwald-Sprengel type pycknometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The relative viscosity (η_r) was obtained as the ratio of the absolute viscosity of the solution (η) to that of the pure solvent (η_0).

The solutions were prepared by mass for the viscosity runs, the molalities being converted to molarities by the use of densities. In order to avoid moisture pick-up, all solutions were prepared in a dehumidified room with utmost care. In all cases the experiments were performed at least in several replicates for each solution and the results were averaged. Several independent solutions were prepared and the runs were performed to ensure the reproducibility of the results.

Results and discussion

The measured relative viscosities (η_r) and densities (ρ) of electrolyte solutions as functions of molar concentrations (c) at 308.15, 313.15, 318.15 and 323.15 K are given in Table 2.

The relative viscosities of the electrolytes in solution are generally analyzed by the Jones-Dole equation[18]:

$$\eta_r = 1 + Ac^{1/2} + Bc \qquad (3)$$

where A and B, the characteristic parameters for salt and solvent, depend on ion-ion and ion-solvent interactions, respectively.

As the electrolytes investigated here are found to be somewhat associated from our earlier conductivity measurements (Chapter V), the viscosity data have been analyzed by the following equation[9]:

$$\eta_r = 1 + A(\alpha c)^{1/2} + B\alpha c + B'(1-\alpha)c \qquad (4)$$

Here A, B, and B' are the characteristic constants and α is the degree of dissociation of the ion pair.

$$[\eta_r - 1 - A(\alpha c)^{1/2}]/\alpha c = B + B'\left(\frac{1-\alpha}{\alpha}\right) \qquad (5)$$

For the evaluation of *B*-coefficients from Eq. (5), plots of $[\eta_r - 1 - A(\alpha c)^{1/2}]/\alpha c$ against $(1-\alpha)/\alpha$ were constructed. These were found to be linear in all cases. The values of α were calculated from the conductance data (Chapter V) using the equations described in the literature[9]. The *A* values were calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances using the Falkenhagen and Vernon equation[19]:

$$A = \frac{0.2577\Lambda^0}{\eta_0(\varepsilon T)^{1/2}\lambda_+^0\lambda_-^0}\left[1 - 0.6863\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0}\right)^2\right] \qquad (6)$$

where η_0 is the coefficient of viscosity of the solvent, ε is its relative permittivity, T is the temperature in absolute scale, and Λ^0, λ_+^0, and λ_-^0 are the limiting equivalent conductivities of the electrolyte, cation, and anion respectively. The values of the *A* coefficients thus obtained are recorded in Table 3. These have been used for the analysis of the viscosity data. The viscosity *B*-coefficients have also been included in Table 3.

The viscosity data have also been analyzed on the basis of the transition-state treatment of the relative viscosity of electrolyte solutions, as suggested by Feakins *et. al.*[20]:

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000}\left(\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT}\right) \qquad (7)$$

In the above equation, $\bar{V}_1^0$ and $\bar{V}_2^0$ are the partial molar volumes of the solvent and solute, respectively. The contribution per mole of solute to the free energy of activation for viscous flow of the solution, $\Delta\mu_2^{0\neq}$, has been determined from the above relationship and is reported in Table 3. The free energy of activation per mole of the pure solvent, $\Delta\mu_1^{0\neq}$ is given by the equation:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln\left(\frac{\eta_0 \bar{V}_1^0}{hN}\right) \tag{8}$$

where N is the Avogadro's number and the other symbols have their usual significance.

The activation parameters for viscous flow for the electrolytes obtained from Eq. (7) are given in Table 3.

The viscosity *B*-coefficients shown in Table 3 are found to be large and positive in 2-ethoxyethanol-water mixtures for the electrolytes studied. The *B* values for the tetraalkylammonium bromides increase regularly as we go from tetraethylammonium bromide to tetrabutylammonium bromide. From this table we see that $\Delta\mu_2^{0\neq}$ values for all the electrolytes are also large and positive, and they follow the same pattern as the *B* values.

In order to investigate the specific behavior of the individual ions comprising these electrolytes, it is necessary to split the viscosity *B*-coefficients of the electrolytes into their ionic components. The ionic *B*-values were calculated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as the "reference electrolyte" from the following equations[21,22]:

$$B(Bu_4NBPh_4) = B(Bu_4N^+) + B(Ph_4B^-) \tag{9}$$

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \left(\frac{5.35}{5.00}\right)^3 \tag{10}$$

The *r*-values for the Bu_4N^+ and Ph_4B^- ions were taken from the literature [23,24].

The ionic *B*-coefficients obtained from the above relationships are given in Table 4. This table shows that in 2-ethoxyethanol-water mixed solvent media the viscosity *B*-coefficients for all cations and anions are positive and are also very high with the exception of sodium ion. The observed order of the ionic *B* values for the molecular ions, $Ph_4B^- > Bu_4N^+ > Pr_4N^+ > Et_4N^+$, shows that the obstruction of the solvent viscous flow increases with an increase of size of these species in solution. This clearly indicates lack of solvation of these ions in 2-ethoxyethanol-water mixed solvent media within the temperature range investigated. Had these ions been solvated in aqueous 2-ethoxyethanol solutions, the smaller ions with greater charge density would have been more solvated and the order of the ionic viscosity *B*-coefficients would have been in the reverse order which is, obviously, not the case here. In case of Na^+ ion, it might be that the viscosity of the solvent is very little modified by its presence in solution resulting in a very low viscosity *B* coefficient for this ion.

Figs. 1-3 shows the temperature dependence of the ionic viscosity *B*-coefficients in 2-ethoxyethanol-water mixtures. For all the ions studied, the *B*-values are positive (except sodium ion for which *B*-values are found to slightly negative at least for two temperatures investigated in 2-ethoxyethanol-water mixture containing 75 per cent of 2-ethoxyethanol) and their temperature coefficients (which are always positive) are negligibly small. The temperature dependence of the *B*-coefficients for the tetraalkylammonium ions in methanol, *N*-methylformamide, *N*-methylpropionamide, and *N*-methylacetamide are also small [10,25,26], and we find the same behavior in the present mixed solvent media. This finding is in sharp contrast to the abnormally large temperature dependence of the *B*-coefficients in water[10], and the remarkable difference can be ascribed to the extensive hydrogen-bonded structure of water. The negligibly small dB/dT values of the investigated ions indicate that they behave neither as structure breaker nor as structure maker in 2-ethoxyethanol-water mixtures.

The ionic free energies of activation for viscous flow, $\Delta\mu_2^{0\neq}$ (ion), based on a method similar to that used for the separation of the viscosity *B*-coefficients have been presented in Table 4. The $\Delta\mu_2^{0\neq}$ values of the ions investigated are always found to be positive thus indicating that the formation of the transition state is made less favorable in the presence of these ions in 2-ethoxyethanol-water mixed solvent media. The ionic $\Delta\mu_2^{0\neq}$ values for the tetraalkylammonium and tetraphenylborate ions increase monotonically with the formula weight of these ions (*cf.* Table 4) thus supporting their scarce solvation in the present mixed solvent media.

The composition dependence of the ionic viscosity *B*-coefficients in 2-ethoxyethanol-water mixtures are depicted in Figs. 4-7. The reason for the observed change in the viscosity *B*-coefficients of the ions (except the sodium ion) in the region of 70-80 weight per cent of 2-ethoxyethanol may be attributed to the structural changes and changed ion-solvent interactions in this region. Intermolecular hydrogen bonding gives water a distinct geometrical structure in the form of three dimensional arrays. Due to lack of non-chemical forces, water has an open and flexible structure [27]. The addition of 2-ethoxyethanol to water first strengthens the three dimensional structure of water. Further addition of 2-ethoxyethanol causes depolymerisation of water structure but interactions between 2-ethoxyethanol and water lead to the formation of 2-ethoxyethanol-water complexes, with a bigger solvodynamic entity. Viscosity thus increases upto approximately 40-50 weight per cent of 2-ethoxyethanol after which 2-ethoxyethanol-water structure breaks down leading to a decrease in the viscosity *B*-coefficients of the ions.

It may thus be concluded that the tetraalkylammonium, tetraphenylborate and bromide ions greatly modify the viscosity of the 2-ethoxyethanol-water mixed solvent media. In case of Na^+ ion, however, the viscosity of the solvent is very little modified by its presence in solution resulting in a very low viscosity *B*-coefficient for this ion. The tetraalkylammonium and tetraphenylborate ions are found to remain unsolvated in 2-ethoxyethanol-water mixed solvent media within the temperature range investigated. Moreover, the investigated ions behave neither as structure breaker nor as structure maker and the formation of the transition state is made less favorable in the presence of these ions in 2-ethoxyethanol-water mixed solvent media.

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Table 1. Properties of 2-ethoxyethanol + water mixtures with 0.25, 0.50, and 0.75 mass fractions (w_1) of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

T/K	ρ_0/g cm^{-3}	η_0/mPa s	ε
	$w_1 = 0.25$		
308.15	1.00354	1.8430	60.13
313.15	1.00021	1.5293	58.70
318.15	0.99781	1.2738	57.37
323.15	0.99582	1.0923	56.11
	$w_1 = 0.50$		
308.15	0.99361	1.9234	44.30
313.15	0.98514	1.7195	43.03
318.15	0.98004	1.4552	41.95
323.15	0.97610	1.2762	40.96
	$w_1 = 0.75$		
308.15	0.95451	1.7002	27.93
313.15	0.95147	1.5293	27.29
318.15	0.94873	1.3498	26.68
323.15	0.94625	1.1901	26.10

Table 2. Molar concentrations, densities and relative viscosities of some tetraalkylammonium and alkali metal salts in 2-ethoxyethanol + water mixtures with 0.25, 0.50 and 0.75 mass fractions (w_1) of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

c/mol.dm^{-3}	ρ/g.cm^{-3}	η_r	c/mol.dm^{-3}	ρ/g.cm^{-3}	η_r
			Et_4NBr		
	T = 308.15 K			T = 313.15 K	
0.00998	1.00479	1.0036	0.00995	1.00144	1.0038
0.01996	1.00606	1.0069	0.01989	1.00266	1.0074
0.02994	1.00725	1.0103	0.02984	1.00389	1.0109
0.03992	1.00854	1.0133	0.03979	1.00513	1.0146
0.04990	1.00982	1.0172	0.04973	1.00636	1.0182
0.05988	1.01104	1.0205	0.05968	1.00761	1.0219
	T = 308.15 K			T = 313.15 K	
0.00992	0.99902	1.0039	0.00990	0.99702	1.0041
0.01984	1.00023	1.0076	0.01980	0.99823	1.0078
0.02977	1.00144	1.0113	0.02971	0.99944	1.0110
0.03969	1.00266	1.0151	0.03961	1.00065	1.0147
0.04961	1.00388	1.0186	0.04951	1.00186	1.0181
0.05953	1.00510	1.0221	0.05941	1.00308	1.0216
			Pr_4NBr		
	T = 308.15 K			T = 313.15 K	
0.01016	1.00481	1.0039	0.01013	1.00148	1.0041
0.02032	1.00602	1.0075	0.02025	1.00275	1.0081
0.03048	1.00736	1.0111	0.03038	1.00403	1.0120
0.04064	1.00865	1.0147	0.04051	1.00531	1.0159
0.05080	1.00993	1.0183	0.05063	1.00660	1.0198
0.06096	1.01118	1.0219	0.06076	1.00789	1.0237

Table 2 (contd.)

Table 2 (contd.)

c/mol.dm^{-3}	ρ /g.cm^{-3}	η_r	c/mol.dm^{-3}	ρ /g.cm^{-3}	η_r
	T = 318.15 K			T = 323.15 K	
0.01010	0.99904	1.0042	0.01008	0.99705	1.0044
0.02020	1.00028	1.0082	0.02016	0.99828	1.0085
0.03030	1.00152	1.0123	0.03024	0.99951	1.0127
0.04040	1.00276	1.0159	0.04032	1.00075	1.0167
0.05050	1.00400	1.0199	0.05040	1.00199	1.0209
0.06060	1.00525	1.0239	0.06048	1.00324	1.0250
			Bu_4NBr		
	T = 308.15 K			T = 313.15 K	
0.01023	1.00482	1.0052	0.01020	1.00147	1.0053
0.02046	1.00615	1.0101	0.02039	1.00273	1.0103
0.03069	1.00739	1.0149	0.03059	1.00400	1.0151
0.04092	1.00867	1.0194	0.04078	1.00528	1.0196
0.05115	1.00995	1.0243	0.05098	1.00665	1.0246
0.06138	1.01123	1.0289	0.06117	1.00784	1.0294
	T = 318.15 K			T = 323.15 K	
0.01017	0.99905	1.0054	0.01015	0.99706	1.0055
0.02034	1.00030	1.0105	0.02030	0.99830	1.0106
0.03051	1.00155	1.0153	0.03045	0.99955	1.0155
0.04068	1.00281	1.0198	0.04060	1.00080	1.0202
0.05085	1.00407	1.0248	0.05075	1.00206	1.0254
0.06102	1.00534	1.0297	0.06090	1.00332	1.0302
			NaBr		
	T = 308.15 K			T = 313.15 K	
0.01023	1.00421	1.0025	0.01020	1.00086	1.0026
0.02046	1.00488	1.0049	0.02039	1.00151	1.0050
0.03069	1.00554	1.0072	0.03059	1.00216	1.0074
0.04092	1.00621	1.0096	0.04078	1.00281	1.0099
0.05115	1.00688	1.0118	0.05098	1.00347	1.0122
0.06138	1.00755	1.0141	0.06117	1.00412	1.0146

Table 2 (contd.)

Table 2 (contd.)

c/mol.dm^{-3}	ρ/g.cm^{-3}	η_r	c/mol.dm^{-3}	ρ/g.cm^{-3}	η_r
	$T = 318.15$ K			$T = 323.15$ K	
0.01017	0.99844	1.0027	0.01015	0.99643	1.0028
0.02034	0.99908	1.0051	0.02030	0.99704	1.0053
0.03051	0.99971	1.0075	0.03045	0.99766	1.0077
0.04068	1.00034	1.0102	0.04060	0.99829	1.0105
0.05085	1.00098	1.0126	0.05074	0.99889	1.0131
0.06102	1.00161	1.0151	0.06089	0.99950	1.0156
			$NaBPh_4$		
	$T = 308.15$ K			$T = 313.15$ K	
0.01012	1.00488	1.0058	0.01009	1.00152	1.0060
0.02024	1.00622	1.0113	0.02017	1.00284	1.0116
0.03036	1.00755	1.0169	0.03026	1.00417	1.0175
0.04048	1.00889	1.0223	0.04034	1.00550	1.0232
0.05060	1.01023	1.0278	0.05043	1.00684	1.0289
0.06072	1.01157	1.0332	0.06052	1.00818	1.0345
	$T = 318.15$ K			$T = 323.15$ K	
0.01006	0.99912	1.0062	0.01004	0.99711	1.0064
0.02012	1.00043	1.0121	0.02008	0.99841	1.0124
0.03018	1.00175	1.0178	0.03012	0.99972	1.0179
0.04025	1.00307	1.0235	0.04016	1.00103	1.0244
0.05031	1.00440	1.0295	0.05021	1.00235	1.0304
0.06037	1.00573	1.0352	0.06025	1.00367	1.0364
			$w_1 = 0.50$		
			Et_4NBr		
	$T = 308.15$ K			$T = 313.15$ K	
0.01003	0.99505	1.0055	0.00994	0.98657	1.0057
0.02006	0.99648	1.0108	0.01989	0.98800	1.0111
0.03009	0.99792	1.0161	0.02983	0.98943	1.0167
0.04012	0.99935	1.0213	0.03978	0.99086	1.0221
0.05015	1.00079	1.0264	0.04972	0.99229	1.0278
0.06018	1.00222	1.0321	0.05967	0.99373	1.0331

Table 2 (contd.)

Table 2 (contd.)

c/mol.dm^{-3}	ρ/g.cm^{-3}	η_r	c/mol.dm^{-3}	ρ/g.cm^{-3}	η_r
	T = 318.15 K			T = 323.15 K	
0.00989	0.98146	1.0058	0.00985	0.97751	1.0060
0.01979	0.98289	1.0114	0.01971	0.97893	1.0119
0.02968	0.98432	1.0171	0.02956	0.98035	1.0177
0.03957	0.98575	1.0236	0.03941	0.98177	1.0232
0.04947	0.98727	1.0282	0.04927	0.98319	1.0295
0.05936	0.98862	1.0337	0.05912	0.98462	1.0349
			Pr_4NBr		
	T = 308.15 K			T = 313.15 K	
0.00982	0.99502	1.0059	0.00974	0.98654	1.0061
0.01964	0.99638	1.0115	0.01947	0.98794	1.0121
0.02946	0.99783	1.0171	0.02921	0.98935	1.0179
0.03928	0.99926	1.0227	0.03895	0.99075	1.0238
0.04910	1.00064	1.0283	0.04868	0.99217	1.0297
0.05892	1.00208	1.0339	0.05842	0.99358	1.0357
	T = 318.15 K			T = 323.15 K	
0.00969	0.98144	1.0062	0.00964	0.97729	1.0064
0.01937	0.98284	1.0122	0.01929	0.97848	1.0123
0.02906	0.98424	1.0181	0.02892	0.97967	1.0182
0.03874	0.98564	1.0239	0.03856	0.98087	1.0244
0.04843	0.98705	1.0299	0.04819	0.98207	1.0303
0.05812	0.98847	1.0356	0.05781	0.98327	1.0363
			Bu_4NBr		
	T = 308.15 K			T = 313.15 K	
0.01009	0.99506	1.0071	0.01000	0.98658	1.0072
0.02018	0.99650	1.0138	0.02001	0.98802	1.0141
0.03027	0.99795	1.0205	0.03001	0.98947	1.0210
0.04036	0.99939	1.0271	0.04002	0.99092	1.0276
0.05045	1.00084	1.0338	0.05002	0.99238	1.0343
0.06054	1.00228	1.0404	0.06003	0.99385	1.0411

Table 2 (contd.)

Table 2 (contd.)

c/mol.dm^{-3}	ρ/g.cm^{-3}	η_r	c/mol.dm^{-3}	ρ/g.cm^{-3}	η_r
	T = 318.15 K			T = 323.15 K	
0.00995	0.98148	1.0074	0.00991	0.97732	1.0075
0.01990	0.98292	1.0143	0.01982	0.97855	1.0146
0.02986	0.98436	1.0210	0.02972	0.97978	1.0213
0.03981	0.98581	1.0278	0.03962	0.98102	1.0282
0.04977	0.98727	1.0346	0.04951	0.98226	1.0351
0.05972	0.98873	1.0414	0.05941	0.98350	1.0420
			NaBr		
	T = 308.15 K			T = 313.15 K	
0.01036	0.99442	1.0031	0.01027	0.98594	1.0033
0.02072	0.99523	1.0061	0.02054	0.98674	1.0064
0.03108	0.99604	1.0090	0.03081	0.98754	1.0096
0.04144	0.99685	1.0119	0.04109	0.98834	1.0124
0.05180	0.99766	1.0147	0.05136	0.98914	1.0157
0.06216	0.99847	1.0176	0.06163	0.98995	1.0188
	T = 318.15 K			T = 323.15 K	
0.01022	0.98082	1.0034	0.01018	0.97686	1.0036
0.02044	0.98161	1.0065	0.02035	0.97762	1.0068
0.03065	0.98239	1.0099	0.03053	0.97839	1.0102
0.04087	0.98317	1.0125	0.04070	0.97915	1.0128
0.05109	0.98396	1.0162	0.05088	0.97991	1.0166
0.06130	0.98474	1.0194	0.06105	0.98068	1.0199
			$NaBPh_4$		
	T = 308.15 K			T = 313.15 K	
0.01037	0.99523	1.0075	0.01028	0.98675	1.0077
0.02074	0.99685	1.0148	0.02056	0.98837	1.0151
0.03111	0.99847	1.0219	0.03085	0.99000	1.0226
0.04148	1.00009	1.0289	0.04113	0.99163	1.0299
0.05185	1.00171	1.0363	0.05141	0.99326	1.0373
0.06222	1.00333	1.0435	0.06170	0.99491	1.0447

Table 2 (contd.)

Table 2 (contd.)

c/mol.dm^{-3}	ρ /g.cm^{-3}	η_r	c/mol.dm^{-3}	ρ /g.cm^{-3}	η_r
	T = 318.15 K			T = 323.15 K	
0.01023	0.98164	1.0078	0.01018	0.97769	1.0080
0.02046	0.98325	1.0153	0.02037	0.97928	1.0153
0.03069	0.98486	1.0225	0.03056	0.98087	1.0228
0.04091	0.98648	1.0301	0.04075	0.98248	1.0304
0.05115	0.98810	1.0374	0.05094	0.98409	1.0379
0.06138	0.98973	1.0449	0.06113	0.98571	1.0453
		$w_1 = 0.75$			
		Et_4NBr			
	T = 308.15 K			T = 313.15 K	
0.01007	0.95571	1.0068	0.01004	0.95271	1.0071
0.02014	0.95682	1.0134	0.02008	0.95394	1.0139
0.03021	0.95821	1.0201	0.03012	0.95519	1.0208
0.04028	0.95931	1.0269	0.04016	0.95643	1.0272
0.05035	0.96053	1.0334	0.05020	0.95767	1.0347
0.06042	0.96172	1.0397	0.06024	0.95892	1.0415
	T = 318.15 K			T = 323.15 K	
0.01001	0.94995	1.0073	0.00998	0.94745	1.00735
0.02002	0.95117	1.0142	0.01997	0.94865	1.0147
0.03003	0.95239	1.0215	0.02995	0.94986	1.0220
0.04004	0.95361	1.0285	0.03993	0.95107	1.0292
0.05005	0.95484	1.0356	0.04992	0.95228	1.0365
0.06006	0.95607	1.0425	0.05990	0.95349	1.0438
		Pr_4NBr			
	T = 308.15 K			T = 313.15 K	
0.00993	0.95569	1.0076	0.00990	0.95269	1.0078
0.01986	0.95686	1.0149	0.01980	0.95391	1.0152
0.02979	0.95806	1.0222	0.02970	0.95514	1.0227
0.03972	0.95925	1.0295	0.03960	0.95637	1.0302
0.04965	0.96043	1.0368	0.04950	0.95761	1.0377
0.05958	0.96159	1.0441	0.05941	0.95885	1.0453

Table 2 (contd.)

Table 2 (contd.)

c/mol.dm^{-3}	ρ/g.cm^{-3}	η_r	c/mol.dm^{-3}	ρ/g.cm^{-3}	η_r
	T = 318.15 K			T = 323.15 K	
0.00987	0.94993	1.0079	0.00984	0.94744	1.0080
0.01974	0.95114	1.0154	0.01969	0.94862	1.0158
0.02961	0.95235	1.0231	0.02953	0.94982	1.0235
0.03948	0.95356	1.0307	0.03938	0.95101	1.0312
0.04936	0.95478	1.0383	0.04923	0.95221	1.0389
0.05923	0.95600	1.0460	0.05907	0.95342	1.0465
			Bu_4NBr		
	T = 308.15 K			T = 313.15 K	
0.00978	0.95568	1.0089	0.00975	0.95267	1.0091
0.01956	0.95684	1.0174	0.01950	0.95388	1.0179
0.02934	0.95801	1.0259	0.02925	0.95509	1.0264
0.03912	0.95917	1.0344	0.03900	0.95631	1.0346
0.04890	0.96034	1.0428	0.04876	0.95754	1.0433
0.05868	0.96150	1.0511	0.05851	0.95876	1.0520
	T = 318.15 K			T = 323.15 K	
0.00972	0.94991	1.0092	0.00970	0.94742	1.0094
0.01944	0.95110	1.0180	0.01939	0.94859	1.0181
0.02916	0.95230	1.0262	0.02909	0.94977	1.0268
0.03889	0.95350	1.0349	0.03878	0.95095	1.0354
0.04861	0.95470	1.0435	0.04848	0.95214	1.0442
0.05840	0.95591	1.0524	0.05818	0.95334	1.0531
			NaBr		
	T = 308.15 K			T = 313.15 K	
0.01047	0.95513	1.0037	0.01044	0.95210	1.0038
0.02094	0.95574	1.0073	0.02087	0.95273	1.0075
0.03141	0.95636	1.0108	0.03131	0.95336	1.0111
0.04188	0.95697	1.0143	0.04175	0.95399	1.0146
0.05235	0.95759	1.0179	0.05219	0.95462	1.0183
0.06282	0.95820	1.0214	0.06263	0.95525	1.0219

Table 2 (contd.)

Table 2 (contd.)

c/mol.dm^{-3}	ρ/g.cm^{-3}	η_r	c/mol.dm^{-3}	ρ/g.cm^{-3}	η_r
	T = 318.15 K			T = 323.15 K	
0.01041	0.94934	1.0040	0.01041	0.94932	1.0042
0.02081	0.94995	1.0076	0.02081	0.94991	1.0078
0.03122	0.95056	1.0112	0.03122	0.95050	1.0115
0.04163	0.95117	1.0147	0.04163	0.95109	1.0151
0.05203	0.95178	1.0185	0.05203	0.95168	1.0187
0.06244	0.95240	1.0223	0.06243	0.95227	1.0228
$NaBPh_4$					
	T = 308.15 K			T = 313.15 K	
0.01061	0.95582	1.0092	0.01058	0.95282	1.0093
0.02122	0.95713	1.0180	0.02116	0.95418	1.0183
0.03183	0.95844	1.0269	0.03173	0.95554	1.0272
0.04244	0.95975	1.0360	0.04231	0.95691	1.0362
0.05305	0.96106	1.0449	0.05290	0.95829	1.0453
0.06366	0.96236	1.0537	0.06348	0.95968	1.0542
	T = 318.15 K			T = 323.15 K	
0.01055	0.95007	1.0095	0.01052	0.94759	1.0096
0.02109	0.95141	1.0185	0.02104	0.94893	1.0188
0.03164	0.95277	1.0277	0.03156	0.95028	1.0279
0.04219	0.95412	1.0367	0.04208	0.95164	1.0372
0.05274	0.95549	1.0459	0.05260	0.95300	1.0463
0.06330	0.95686	1.0551	0.06313	0.95437	1.0556

Table 3. Theoretical *A*-coefficients, the viscosity *B*-coefficients and the free energies of activation for viscous flow of electrolytes in 2-ethoxyethanol + water mixtures with 0.25, 0.50, and 0.75 mass fractions (w_1) of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

Electrolyte	A /dm$^{3/2}$mol$^{-1/2}$	B /dm^3 mol^{-1}	$\Delta\mu_2^{0\neq}$ /kJ mol^{-1}
	$w_1 = 0.25$		
	T = 308.15 K		
Et_4NBr	0.0059	0.294	52.55
Pr_4NBr	0.0063	0.318	61.62
Bu_4NBr	0.0067	0.447	82.78
NaBr	0.0049	0.190	35.30
$NaBPh_4$	0.0116	0.447	84.26
	T = 313.15 K		
Et_4NBr	0.0067	0.307	54.51
Pr_4NBr	0.0071	0.330	63.39
Bu_4NBr	0.0075	0.450	83.93
NaBr	0.0056	0.193	35.85
$NaBPh_4$	0.0124	0.455	86.02
	T = 318.15 K		
Et_4NBr	0.0076	0.313	55.68
Pr_4NBr	0.0080	0.334	64.69
Bu_4NBr	0.0084	0.454	85.30
NaBr	0.0064	0.194	36.19
$NaBPh_4$	0.0133	0.474	89.06
	T = 323.15 K		
Et_4NBr	0.0083	0.334	58.60
Pr_4NBr	0.0088	0.342	66.20
Bu_4NBr	0.0092	0.455	86.28
NaBr	0.0071	0.196	36.76
$NaBPh_4$	0.0140	0.480	90.77

Table 3 (contd.)

Table 3 (contd.)

Electrolyte	A /dm$^{3/2}$mol$^{-1/2}$	B /dm^{3} mol^{-1}	$\Delta\mu_2^{\theta*}$ /kJ mol^{-1}
$w_1 = 0.50$			
T = 308.15 K			
Et_4NBr	0.0076	0.465	55.34
Pr_4NBr	0.0081	0.512	64.04
Bu_4NBr	0.0085	0.616	77.70
NaBr	0.0074	0.224	31.29
$NaBPh_4$	0.0108	0.608	77.61
T = 313.15 K			
Et_4NBr	0.0080	0.481	56.93
Pr_4NBr	0.0084	0.535	66.39
Bu_4NBr	0.0088	0.632	79.50
NaBr	0.0078	0.238	32.59
$NaBPh_4$	0.0112	0.624	79.41
T = 318.15 K			
Et_4NBr	0.0089	0.489	57.85
Pr_4NBr	0.0093	0.542	67.34
Bu_4NBr	0.0097	0.646	81.22
NaBr	0.0085	0.244	33.21
$NaBPh_4$	0.0120	0.634	80.84
T = 323.15 K			
Et_4NBr	0.0095	0.506	59.76
Pr_4NBr	0.0100	0.551	70.52
Bu_4NBr	0.0103	0.654	84.49
NaBr	0.0090	0.257	34.58
$NaBPh_4$	0.0126	0.645	82.58

Table 3 (contd.)

Table 3 (contd.)

Electrolyte	A /dm$^{3/2}$mol$^{-1/2}$	B /dm^3 mol^{-1}	$\Delta\mu_2^{\theta\neq}$ /kJ mol^{-1}
	$w_1 = 0.25$		
	T = 308.15 K		
Et_4NBr	0.0130	0.530	44.97
Pr_4NBr	0.0140	0.598	51.84
Bu_4NBr	0.0147	0.747	63.13
NaBr	0.0147	0.193	24.02
$NaBPh_4$	0.0188	0.634	57.88
	T = 313.15 K		
Et_4NBr	0.0134	0.553	46.35
Pr_4NBr	0.0144	0.610	52.72
Bu_4NBr	0.0148	0.778	65.18
NaBr	0.0146	0.206	24.72
$NaBPh_4$	0.0184	0.663	59.74
	T = 318.15 K		
Et_4NBr	0.0136	0.568	47.61
Pr_4NBr	0.0145	0.620	53.77
Bu_4NBr	0.0149	0.787	66.35
NaBr	0.0144	0.227	26.03
$NaBPh_4$	0.0182	0.693	61.98
	T = 323.15 K		
Et_4NBr	0.0145	0.578	48.58
Pr_4NBr	0.0151	0.634	55.08
Bu_4NBr	0.0158	0.796	67.45
NaBr	0.0149	0.242	23.49
$NaBPh_4$	0.0189	0.706	63.24

Table 4. Ionic viscosity *B*-coefficients in 2-ethoxyethanol-water mixtures at 308.15, 313.15, 318.15 and 323.15 K

Ion	$B_{\pm}$/dm^3 mol^{-1}			
	T = 308.15 K	T = 313.15 K	T = 318.15 K	T = 323.15 K
		$w_1 = 0.25$		
Et_4N^+	0.163	0.177	0.189	0.212
Pr_4N^+	0.187	0.200	0.210	0.220
Bu_4N^+	0.316	0.320	0.330	0.332
Na^+	0.059	0.063	0.070	0.073
Br^-	0.131	0.130	0.124	0.123
Ph_4B^-	0.388	0.392	0.404	0.407
		$w_1 = 0.50$		
Et_4N^+	0.298	0.307	0.308	0.320
Pr_4N^+	0.345	0.361	0.361	0.365
Bu_4N^+	0.449	0.458	0.466	0.468
Na^+	0.057	0.064	0.064	0.071
Br^-	0.167	0.174	0.181	0.186
Ph_4B^-	0.551	0.560	0.570	0.574
		$w_1 = 0.75$		
Et_4N^+	0.317	0.330	0.344	0.348
Pr_4N^+	0.385	0.387	0.396	0.404
Bu_4N^+	0.534	0.555	0.563	0.566
Na^+	-0.020	-0.017	0.003	0.012
Br^-	0.213	0.223	0.224	0.230
Ph_4B^-	0.654	0.380	0.690	0.694

Table 5. Ionic free energies of activation for viscous flow in 2-ethoxyethanol-water mixtures at 308.15, 313.15, 318.15 and 323.15 K

Ion	$\Delta\mu_{\pm}^{\theta*}$/kJ mol^{-1}			
	T = 308.15 K	T = 313.15 K	T = 318.15 K	T = 323.15 K
		$w_1 = 0.25$		
Et_4N^+	28.98	30.85	32.48	35.37
Pr_4N^+	38.05	39.73	41.49	42.97
Bu_4N^+	59.21	60.27	62.10	63.05
Na^+	11.73	12.19	12.99	13.53
Br^-	23.57	23.66	23.20	23.23
Ph_4B^-	72.53	73.83	76.07	77.24
		$w_1 = 0.50$		
Et_4N^+	33.38	34.20	34.50	34.82
Pr_4N^+	42.08	43.66	44.03	45.58
Bu_4N^+	55.74	56.77	59.91	59.55
Na^+	9.33	9.86	9.90	9.64
Br^-	21.96	22.73	23.31	29.94
Ph_4B^-	68.28	69.55	70.94	72.94
		$w_1 = 0.75$		
Et_4N^+	25.43	26.20	27.24	29.31
Pr_4N^+	32.30	32.57	33.40	35.81
Bu_4N^+	43.59	45.03	45.98	48.18
Na^+	4.48	4.57	5.66	4.22
Br^-	19.54	20.15	20.37	19.27
Ph_4B^-	53.40	55.17	56.32	59.02

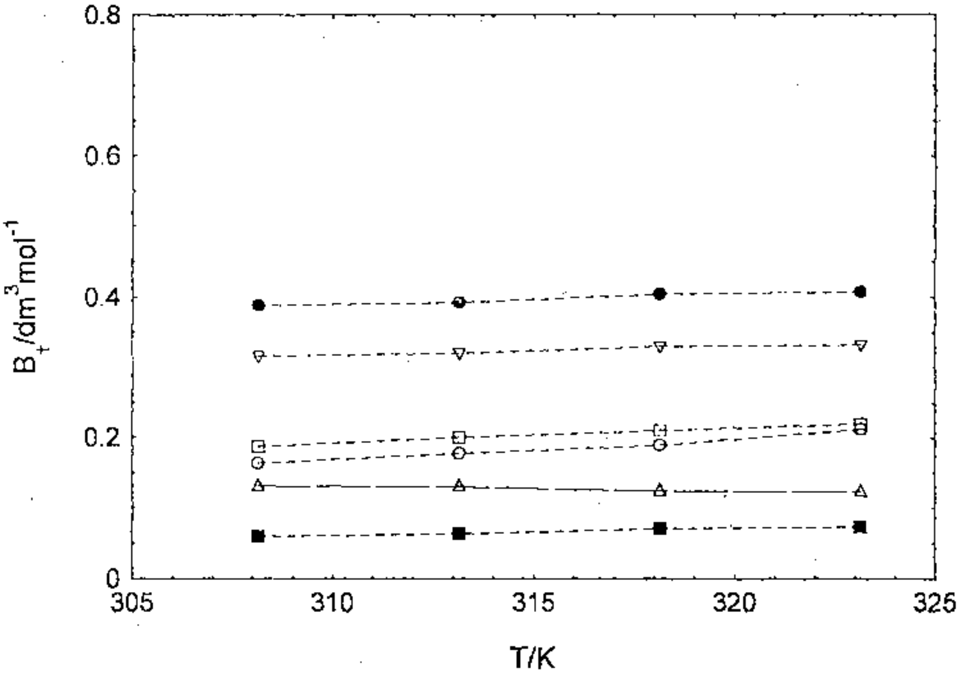

Fig. 1. Temperature dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures (w_1 = 0.25) for Na^+ (■), Br^-(Δ), Et_4N^+(○), Pr_4N^+(□), Bu_4N^+(∇), Ph_4B^-(●).

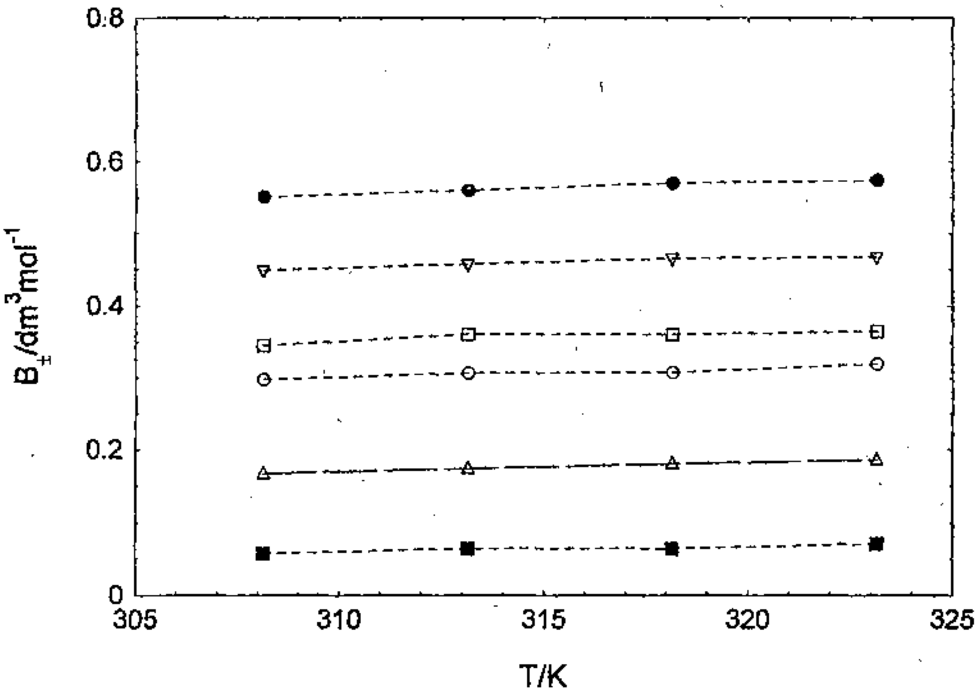

Fig. 2. Temperature dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures ($w_1 = 0.50$) for Na^+ (■), Br^-(Δ), Et_4N^+(○), Pr_4N^+(□), Bu_4N^+(∇), Ph_4B^-(●).

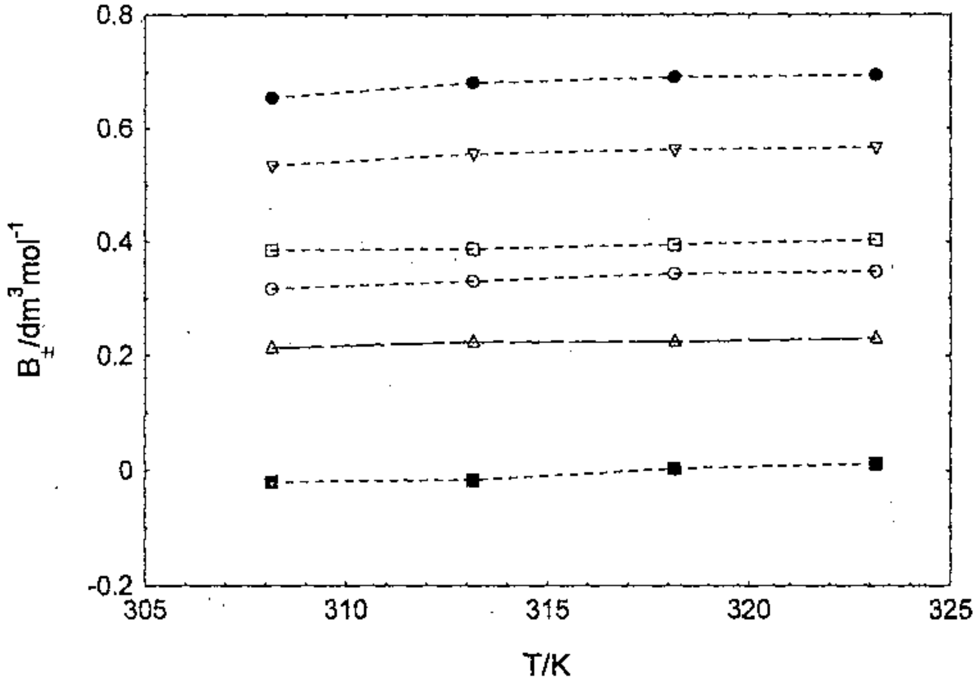

Fig. 3. Temperature dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures (w_1 = 0.75) for Na^+ (■), Br^-(Δ), Et_4N^+(○), Pr_4N^+(□), Bu_4N^+(∇), Ph_4B^-(●).

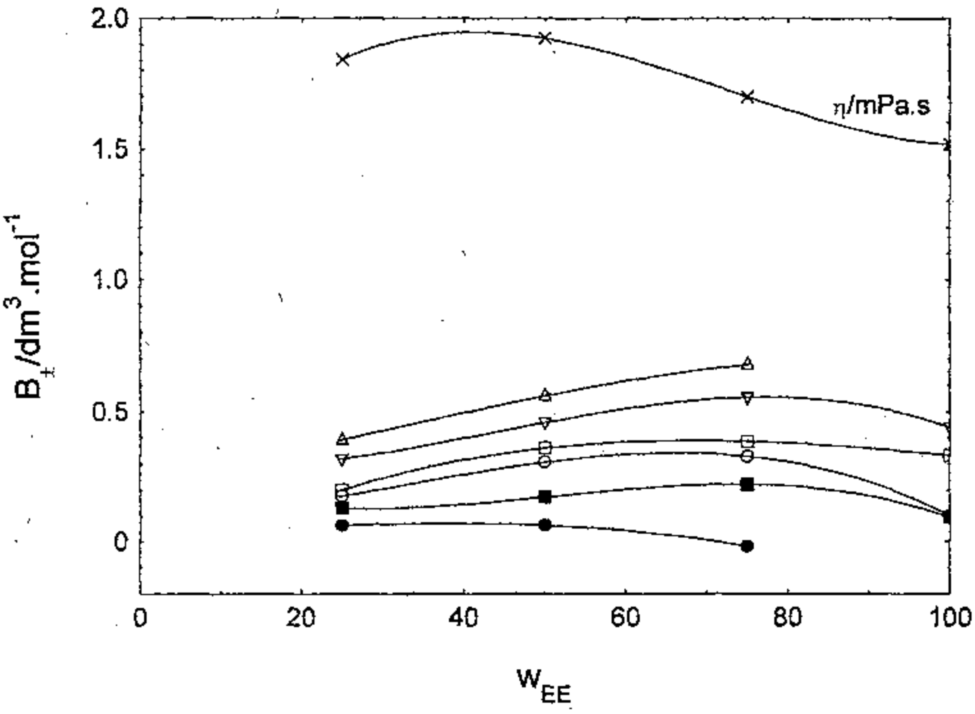

Fig. 4. Solvent composition dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures at 308.15 K: Na^+ (●), Br^- (■), Et_4N^+(○), Pr_4N^+(□), Bu_4N^+(∇), Ph_4B^-(Δ).

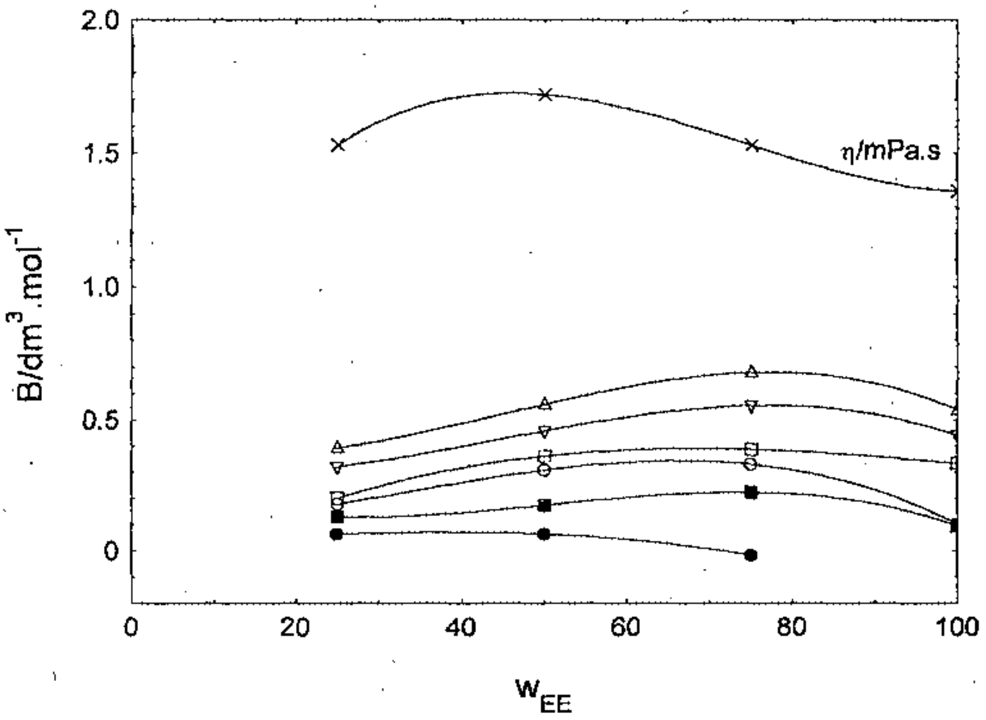

Fig. 5. Solvent composition dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures at 313.15 K: Na^+ (●), Br^- (■), Et_4N^+(○), Pr_4N^+(□), Bu_4N^+(∇), Ph_4B^- (Δ).

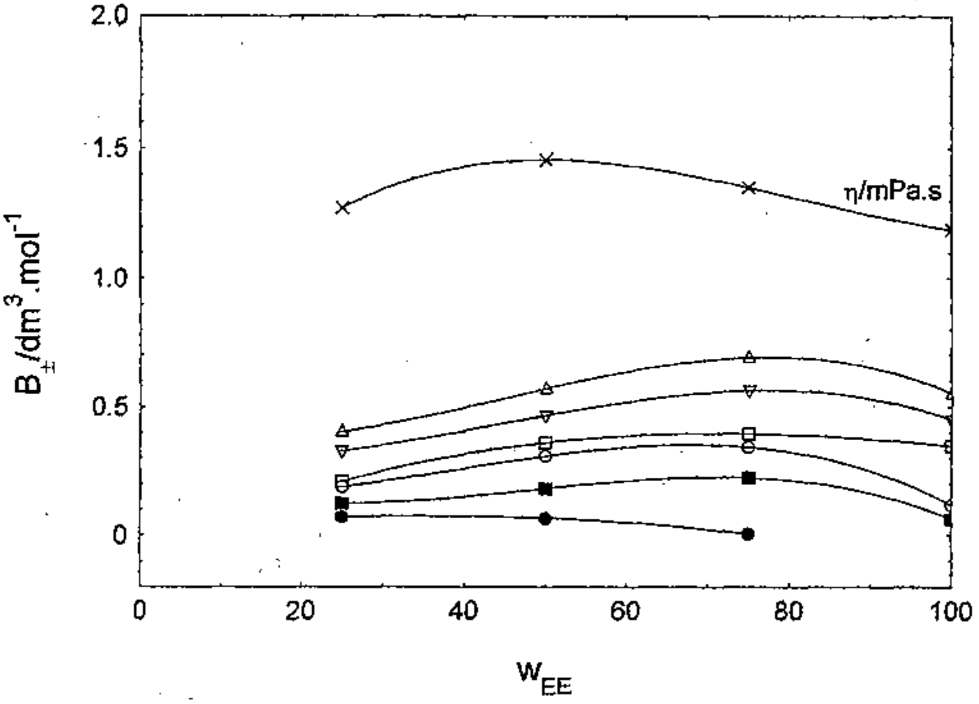

Fig. 6. Solvent composition dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures at 318.15 K: Na^+ (●), Br^- (■), Et_4N^+(○), Pr_4N^+(□), Bu_4N^+(∇), Ph_4B^- (Δ).

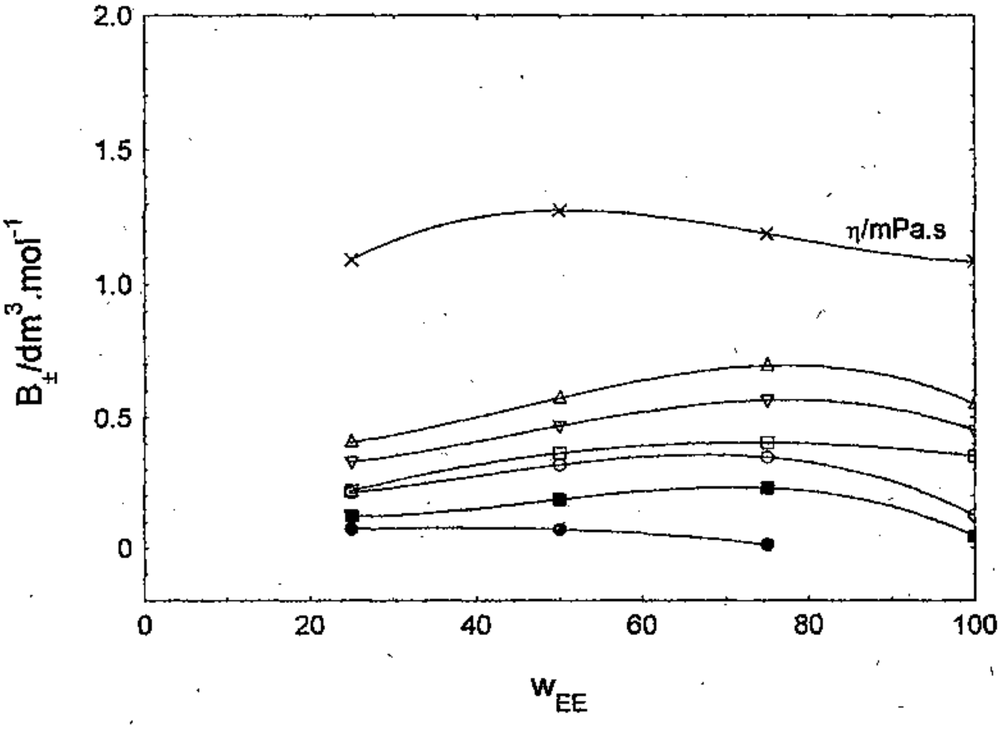

Fig. 7. Solvent composition dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures at 323.15 K: Na^+ (●), Br^- (■), Et_4N^+(○), Pr_4N^+(□), Bu_4N^+(∇), Ph_4B^-(Δ).

CHAPTER VII

Concluding Remarks

Symmetrical tetraalkylammonium and alkali metal salts show numerous interesting properties that are now being actively investigated in many laboratories. Most of the present day knowledge on non-aqueous solutions has come from studies on various thermodynamic properties *e.g.*, apparent molal volumes, adiabatic compressibilities, heat capacities etc. as well as on transport properties *e.g.*, conductance, viscosity and transference numbers. We, therefore, determined the thermodynamic and transport properties of some tetraalkylammonium and alkali metal salts in 2-ethoxyethanol and its binary mixtures with water from their measurements of conductances and viscosities since these are potentially capable of yielding more precise information on the nature of interactions taking place in solutions.

The viscosity *B*-coefficients give us quantitative values of the ion solvent interactions, but still we have no unambiguous method of division of *B*-coefficients into ionic *B*-values in all solvents. The use of Bu_4NBPh_4 appears to be sound but we lack sufficient data measured in different solvents to arrive at a definite conclusion. It is desirable to use different methods of division of *B* values to have reasonably consistent ionic *B*-values.

Accurate B_{ion}-values would give the solvation number of ions. It is known that

$$B_{ion} = B_{ion}^{Einst} + B_{ion}^{str} + B_{ion}^{Disord}$$

but it is not possible to calculate the individual constituents like B_{ion}^{Einst} etc. so that the effect of charges on the nature of solvation can be properly explored. Efforts should be made to know at least B_{ion}^{Einst} values experimentally.

Similarly, different methods are to be used to find out the limiting conductances of the ions from the limiting equivalent conductances of electrolytes. Proper evaluation of the limiting equivalent conductance, Λ^0, the single-ion conductances, $\lambda_{\pm}^0$, the ionic association constant, K_A, and the ion-size parameter a^0 and their dependence on the relative permittivities would be of great help in determining ion-ion and ion-solvent interactions. However, the variation of $\lambda_{\pm}^0$ values for ions depend not only on their solvodynamic entity but also their movement through different solvents. This aspect needs consideration and further study.

However, it is necessary to remember that ion-solvent interactions are very complex in nature. There are strong electrical forces between the ions and the solvents and it is not really possible to separate them all. Nevertheless, if careful judgments are used, valid conclusions can be drawn in many cases from viscosity and conductivity measurements relating to degree of structure and order of system.

More extensive studies of the different thermodynamic and transport properties of electrolytes will be of immense help in understanding the nature of ion-solvent interactions and the role of solvents in different chemical processes.

List of Papers Derived (so far) from this Dissertation:

1. Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetraphenylborate and Sodium Bromide in 2-Ethoxyethanol in the Temperature Range 35-50° C, P. Haldar and B. Das, *Z. Phys. Chem.*, **218**, 599 (2004).

2. Conductometric Study of Some Tetraalkylammonium Bromides in 2-Ethoxyethanol in the Temperature Range 35-50° C, P. Haldar and B. Das, *Z. Phys. Chem.*, **218**, 1129 (2004).

3. Viscocities of Some Tetraalkylammonium Bromides in 2-Ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K, P. Haldar and B. Das, *Can. J. Chem.*, **83**, 499 (2005).

4. Electrical Conductances of Tetraethylammonium Bromide and Tetrapropylammonium Bromide in 2-Ethoxyethanol (1) + Water (2) Mixtures at (308.15, 313.15, 318.15 and 323.15) K, P. Haldar and B. Das, *J. Chem. Eng. Data*, **50**, 1768 (2005).

5. Electrical Conductances of Sodium Bromide and Sodium Tetraphenylborate in 2-Ethoxyethanol + Water Mixtures at 308.15, 313.15, 318.15 and 323.15 K, P. Haldar and B. Das, *J. Mol. Liq.*, 2006, *in Press.*