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,....., 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 crystallographic 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].

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

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

The 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:

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

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

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

$$\Delta G_{308.15}^0 = a_0 \tag{16}$$

$$\Delta S_{308.15}^0 = a_1 \tag{17}$$

$$\Delta H_{308.15}^0 = a_0 + 308.15a_1 \tag{18}$$

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:

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

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:

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

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_4NBr	
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	4.5 303	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	Λ^0 / Scm^2mol^{-1}	K_A / dm^3mol^{-1}	R / Å	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	Λ^0 / Scm^2mol^{-1}	K_A / dm^3mol^{-1}	R / Å	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	$\Delta H^0_{308.15} / \mathrm{Jmol}^{-1}$
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
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