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·cm^2·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 Shedlovšky 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.)

$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
$c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$	$c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$	$c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$
			$\mathrm{Pen_4NBr}$		
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
			$\mathrm{NaBPh_4}$		
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.)

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$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
$c/(\mathrm{mol \cdot dm^{-3}})$	$\Lambda/(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$	$c/(\mathrm{mol \cdot dm^{-3}})$	$\Lambda/(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$	$c/(\mathrm{mol \cdot dm^{-3}})$	$\Lambda/(\mathrm{S \cdot cm^2 \cdot mol^{-1}})$
$\mathrm{Pen_4NBr}$					
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
$\mathrm{NaBPh_4}$					
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.)

$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
$c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$	$c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$	$c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$
		T = 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.)

$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
$c/(\text{mol·dm}^{-3})$	$\Lambda/(\text{S·cm}^2\text{·mol}^{-1})$	$c/(\text{mol·dm}^{-3})$	$\Lambda/(\text{S·cm}^2\text{·mol}^{-1})$	$c/(\text{mol·dm}^{-3})$	$\Lambda/(\text{S·cm}^2\text{·mol}^{-1})$
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.)

$w_1 = 0.25$		$w_1 = 0.50$		$w_1 = 0.75$	
$c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$	$c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$	$c/(\mathrm{mol{\cdot}dm^{-3}})$	$\Lambda/(\mathrm{S{\cdot}cm^2{\cdot}mol^{-1}})$
		Pen_4NBr			
0.004947	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 / Å	$100\sigma / \Lambda^0$
$w_1 = 0.25$					
Et_4NBr					
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_4NBr					
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_4NBr					
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_4NBr					
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)	$R/\mathring{A}$	$100\sigma/\Lambda^0$
$w_1 = 0.25$					
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 / ($S \cdot cm^2 \cdot mol^{-1}$)	$-a_1$ / ($S \cdot cm^2 \cdot mol^{-1} \cdot K^{-1}$)	a_2 / ($S \cdot cm^2 \cdot mol^{-1} \cdot K^{-2}$)	σ / ($S \cdot cm^2 \cdot mol^{-1}$)
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

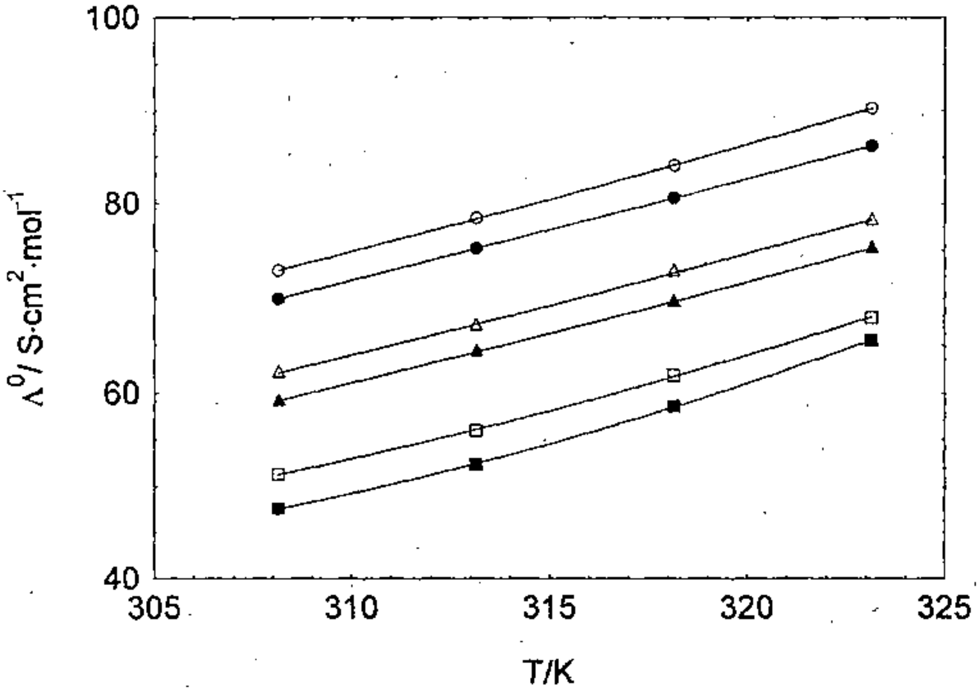

Figure 1. Temperature dependence of the limiting molar conductances of tetraethylammonium bromide (○, w_1 = 0.25; Δ, w_1 = 0.50; □, w_1 = 0.75) and tetrapropylammonium bromide (●, w_1 = 0.25; ▲, w_1 = 0.50; ■, w_1 = 0.75) in 2-ethoxyethanol- water mixtures.

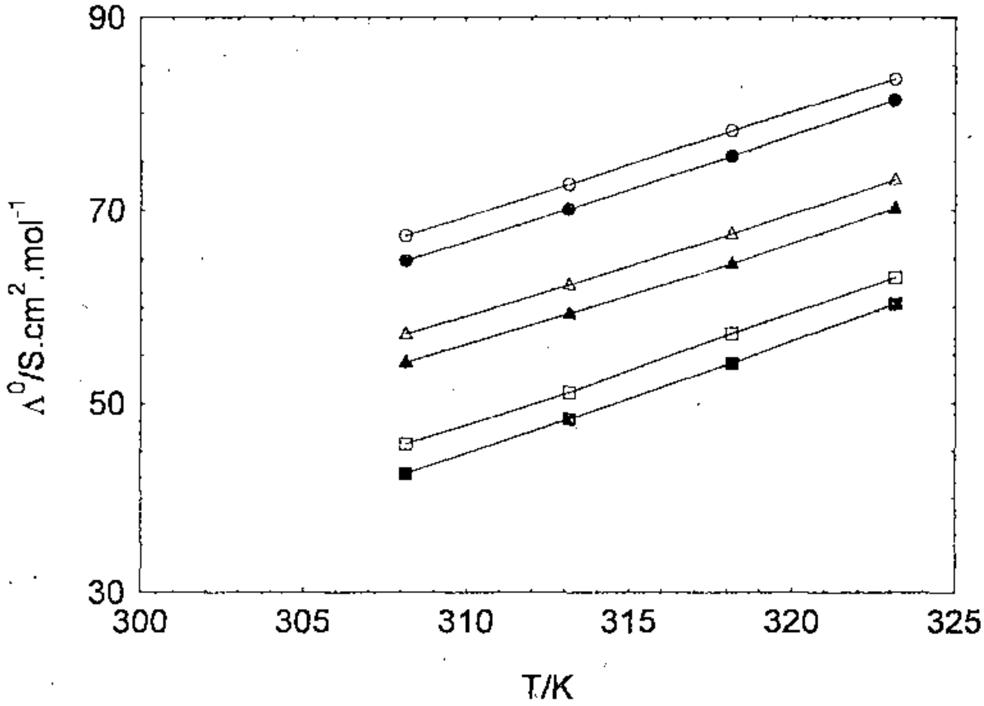

Figure 2. Temperature dependence of the limiting molar conductances of tetrabutylammonium bromide (○, w_1 = 0.25; △, w_1 = 0.50; □, w_1 = 0.75) and tetrapentylammonium bromide (●, w_1 = 0.25; ▲, w_1 = 0.50; ■, w_1 = 0.75) in 2-ethoxyethanol-water mixtures.

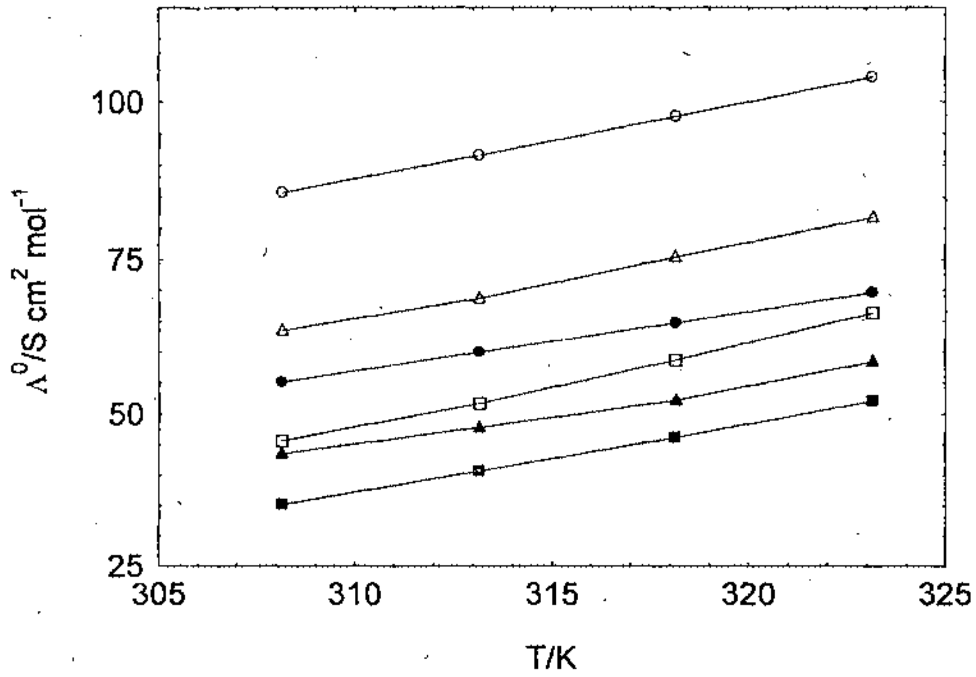

Figure 3. Temperature dependence of the limiting molar conductances of sodium bromide (○, $w_1 = 0.25$; △, $w_1 = 0.50$; □, $w_1 = 0.75$) and sodium tetraphenylborate (●, $w_1 = 0.25$; ▲, $w_1 = 0.50$; ■, $w_1 = 0.75$) in 2-ethoxyethanol-water mixtures.