Conductance Studies of NaCl, KCl, NaBr, NaI, NaBPh$_4$, and Bu$_4$NI in Water + 2-Ethoxyethanol Mixtures at 298.15 K

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The electrical conductances of solutions of sodium chloride (NaCl), potassium chloride (KCl), sodium bromide (NaBr), sodium iodide (NaI), sodium tetraphenylborate (NaBPh$_4$), and tetrabutylammonium iodide (Bu$_4$NI) in water (1) + 2-ethoxyethanol (2) mixtures containing (0.01, 0.025, 0.05, 0.075, 0.10, 0.15, and 0.20) mol fractions of 2-ethoxyethanol have been measured at 298.15 K. The conductance data have been analyzed by the Fuoss−Justice equation. The individual limiting ionic conductivities of Na$^+$, K$^+$, Bu$_4$N$^+$, BPh$_4^-$, I$^-$, Cl$^-$, and Br$^-$ ions have been determined using the Fuoss−Hirsch assumption. The dependencies of the limiting molar conductances, Λ_o, and Walden products, $\Lambda_o\eta$, versus mixed solvent composition have been discussed.

Introduction

Mixed water−organic solvents are a subject of very intensive investigations carried out by many research centers all over the world. A knowledge of their structures and properties is very important on account of their application in various areas of chemistry and modern technologies. Alkoxyethanols, popularly called by the trade name cellosolves, are the perfect solvents of many substances, and they are commonly used in industry as a component of solvents and as coemulgators and stabilizers of emulsions, paints, lacquers, and plastics. Cellosolves are nonionic amphiphile molecules, very effective as surfactants. In addition, they are used as additives to gasoline due to their octane-enhancing and pollution-reducing properties.[1,2] The possibilities of the applications of alkoxyethanols are known fairly well, while the properties of these solvents and their aqueous and nonaqueous mixtures are not yet fully understood.

Ion−ion and ion−solvent interactions are connected with the physicochemical properties of these mixtures and with the intermolecular interactions existing in these solutions. The conductometric investigations made in this paper allow us to determine the values of parameters as the limiting molar conductances and the association constants. The values of Λ_o may provide information about ion−solvent interactions, while knowledge of the association constant is essential for studies performed in solvents with low relative permittivity.

The electrical conductance of the solutions of Bu$_4$NBr, NaBPh$_4$, and NaBr in 2-ethoxyethanol have been reported in the temperature range from (308.15 to 323.15) K by Haldar and Das.[3] The same measurements have been made in the 2-ethoxyethanol (1) + water (2) mixtures containing (0.25, 0.50, and 0.75) mass fractions of 2-ethoxyethanol.[4,5] Sodium bromide and tetrabutylammonium bromide exist essentially in the form of free ions, and sodium tertraphenylborate is slightly associated in aqueous 2-ethoxyethanol solutions over the entire temperature range. Ion−solvent interactions are very weak for the tertrabutylammonium ion. The solvation of the Br$^-$ and Na$^+$ ions was found to be gradually weakened as the 2-ethoxyethanol content of the medium increases.

Table 1. Experimental and Literature Densities, ρ, Viscosities, η, and Refractive Indices, n_D, of 2-Ethoxyethanol at 298.15 K

ρ/g·cm^{-3}		η/mPa·s		n_D	
exptl	lit.	exptl	lit.	exptl	lit.
0.92527	0.92520^{a,b} 0.925028^c	1.8450	1.850^a 1.8277^d	1.4056	1.4057^a 1.4051^b

[a] Ref 32. [b] Ref 33. [c] Ref 1. [d] Ref 5.

In the literature, we can find only several papers on the conductometric investigations of aqueous solutions of alkoxyethanols. These papers concern mainly the aqueous solutions of 2-methoxyethanol.[6−10] Analyzing the conductometric data available in the literature, we can notice very large discrepancies. The differences between the values obtained by various authors are as high as 100 %. Analyzing the physicochemical property data of cellosolves and their aqueous mixtures, we can also notice that the results are not always consistent. Therefore, analysis of the literature data prompted us to carry out more systematic and extensive conductometric and physicochemical property studies in aqueous mixtures of 2-alkoxyethanols. In this paper, we present conductometric studies of NaCl, KCl, NaBr, NaI, NaBPh$_4$, and Bu$_4$NI in water (1)-rich 2-ethoxyethanol (2) mixtures at 298.15 K.

Experimental Section

Chemicals. 2-Ethoxyethanol (Fluka, puriss p.a. ≥ 99.5 %) was dried over freshly activated molecular sieves of type 4A (Sigma) for several days before use and next double distilled. The measured density, viscosity, and refractive index of the pure solvent agreed well with those values published in the literature (Table 1).

The salts were of puriss grade and were used without further purification (with the exception of Bu$_4$NI). Sodium chloride (Merck) was dried at 373.15 K. Potassium chloride, sodium bromide, and sodium iodide were from Merck and were dried in vacuo at 353.15 K. Sodium tetraphenylborate (Fluka) was dried in vacuo at 353.15 K. Tetrabutylammonium iodide was of Aldrich purum grade and was purified by recrystallization from acetone and dried in vacuo at 333.15 K.

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Table 2. Densities, ρ, Viscosities, η, and Relative Permittivities, ε_r, of Water (1) + 2-Ethoxyethanol (2) Mixtures at 298.15 K

x_2	ρ/g·cm^3	η/mPa·s	ε_r
0.0100	0.99708	1.0530	75.90
0.0250	0.99726	1.3193	72.42
0.0500	0.99822	1.7841	67.10
0.0750	0.99835	2.2245	62.30
0.1000	0.99723	2.6075	57.99
0.1500	0.99235	3.1639	50.62
0.2000	0.98604	3.4627	44.65

Double distilled, deionized, and degassed water with a specific conductance better than $0.5 \cdot 10^{-6}$ S·cm^{-1} was used for the preparation of the mixed solvents. All the solutions were prepared by mass using an analytical balance (Sartorius RC 210D) with an uncertainty of $\pm 1 \cdot 10^{-5}$ g. The uncertainty of composition of mixtures was 0.0001 as mole fraction.

Measurements. The details of the measuring procedure of conductance are presented elsewhere.[11,12] Conductance measurements were performed in the solutions containing (0.01, 0.025, 0.05, 0.075, 0.10, 0.15, and 0.20) mol fractions of 2-ethoxyethanol (2), usually for (7 to 12) molar concentrations of salts, with the use of a Precise Component Analyzer type 6430B (Wayne-Kerr, UK). All conductance values were the result of an extrapolation to infinite frequency. All data were corrected with the specific conductance of the solvent. The temperature was kept constant within 0.003 K (Ultra Thermostat UB 20F with Through-flow cooler DLK 25, Lauda, Germany). The uncertainty of the measured values of conductivity was 0.03 %.

The experimental procedure for densimetric measurements was similar to those described previously,[12] and only the details of the procedure were modified. Measurements of density were carried out using a bicapillary pycnometer with a volume of about 30 cm^3. The pycnometer was calibrated with extra pure water, previously degassed ultrasonically. The pycnometer was thermostatted using a precise thermostat (Julabo, MHF 32, Germany) with a temperature stability better than 0.01 K. The temperature was controlled by a calibrated digital thermometer (Anton Paar, DT 100-20) with an uncertainty of ± 0.01 K. The uncertainty in the density measurements was $2 \cdot 10^{-5}$ g·cm^{-3}.

The experimental procedure for viscosimetric measurements was described in our previous papers.[11,12] Viscosities were measured with a AVS 350 viscosimeter (Schott Geräte, Germany). The viscosimeter filled with the liquid was placed vertically in a glass-sided water thermostat. An electronic stopwatch with a precision of 0.01 s was used for flow time measurements. The temperature was kept constant using a precision thermostat Julabo F32 (Julabo Labortechnik GmbH, Germany). The uncertainty in the viscosity measurements was better than 0.05 %.

The refractive indices (Na-D line, at $\lambda = 589$ nm) were measured using an automatic precision refractometer (DR 5000 Krüss). The uncertainty in the refractive index measurements was $2 \cdot 10^{-5}$.

Results and Discussion

The physical properties (densities, dynamic viscosities, and relative permittivities) of water (1) + 2-ethoxyethanol (2) mixtures are summarized in Table 2. Viscosity data were interpolated for the full composition on the basis of our experimental data. The densities and relative permittivities were interpolated on the basis of literature data.[13]

The experimental molar conductances, Λ, and corresponding molarities, c, for the investigated salts in the mixed solvent are collected in Table 3.

The conductance data were analyzed using the Fuoss–Justice equation[14,15] in the form

$$\Lambda = \alpha[\Lambda_o - S(\alpha c)^{1/2} + E(\alpha c)\ln(\alpha c) + J(\alpha c) + J_{3/2}(\alpha c)^{3/2}] \quad (1)$$

together with

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

and

$$\ln y_\pm = -(A\alpha^{1/2}c^{1/2})/(1 + BR\alpha^{1/2}c^{1/2}) \quad (3)$$

In these equations, Λ_o is the limiting molar conductance; α is the dissociation degree of an electrolyte; K_A is the ionic association constant; R is the distance parameter of ions; $y_\pm$ is the activity coefficient of ions on the molar scale; and A and B are the coefficients of the Debye–Hückel equation. The analytical form of the parameters S, E, J, and $J_{3/2}$ was presented previously.[16−18] The values of Λ_o, K_A, and R were obtained using the well-known procedure given by Fuoss.[15]

The values of density, dynamic viscosity, and relative permittivity necessary for the calculation are collected in Table 2. The values of Λ_o, K_A, R, and the Walden products, $\Lambda_o\eta$, for the investigated salts in water (1) + 2-ethoxyethanol (2) mixtures are collected in Table 4. The limiting molar conductances for salts in water were taken from ref 19.

As seen from Table 4, NaI and $NaBPh_4$ are not associated in the mixed solvent media, and for the remaining salts the association constants are practically negligible (the values of K_A are very small and may be neglected[4,5]). One can assume that these electrolytes exist essentially as free ions in the examined water (1) + 2-ethoxyethanol (2) mixtures. The K_A values increase with an increasing amount of 2-ethoxyethanol (2) in the mixture because the relative permittivity of the medium decreases.

Values in Table 4 demonstrate that slight additions of 2-ethoxyethanol (2) to water (1) cause an intensive decrease of the Λ_o value, and the decrease of these values is greater for larger water contents. The order of Λ_o values over the whole composition range is the same as in the water

$$\Lambda_o(NaBPh_4) < \Lambda_o(Bu_4NI) < \Lambda_o(NaCl) \approx \Lambda_o(NaI) \approx \Lambda_o(NaBr) < \Lambda_o(KCl)$$

The above order can be easily explained considering ion size. The largest ions (BPh_4^- and Bu_4N^+) are practically unsolvated in solution, but due to their large size, the ionic mobility is small.[4,5,11,20,21] The slight differences in the limiting conductances of sodium chloride, sodium bromide, and sodium iodide seem to indicate that the effective sizes of these anions are almost the same. The value of Λ_o for potassium chloride is larger than for sodium chloride due to the larger crystallographic radii of the potassium ion. It causes the electric field intensity around the potassium ion to be smaller. The interactions with solvent dipoles are very weak, and the effective size of this ion is smaller than the sodium ion. Thereby, the mobility of the potassium ion becomes greater than that of the sodium ion, and the limiting conductance of KCl is higher than that of NaCl.

A decrease of Λ_o values observed during the addition of the organic solvent to water can be explained by changes of macroscopic viscosity. From simple hydrodynamic models it follows that the ionic mobility decreases as the viscosity increases, which is observed in the examined composition range. Therefore, a more reasonable analysis is consideration of the changes of the Walden product values, $\Lambda_o\eta$, versus composition of the mixture. The

Table 3. Molar Conductances, Λ, and Corresponding Molarities, *c*, for NaCl, KCl, NaBr, NaI, $NaBPh_4$, and Bu_4NI in Water (1) + 2-Ethoxyethanol (2) Mixtures at 298.15 K

$x_2 = 0.0100$		$x_2 = 0.0250$		$x_2 = 0.0500$		$x_2 = 0.0750$		$x_2 = 0.1000$		$x_2 = 0.1500$		$x_2 = 0.2000$	
$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ	$c \cdot 10^4$	Λ
$mol \cdot dm^{-3}$	$S \cdot cm^2 \cdot mol^{-1}$	$mol \cdot dm^{-3}$	$S \cdot cm^2 \cdot mol^{-1}$	$mol \cdot dm^{-3}$	$S \cdot cm^2 \cdot mol^{-1}$	$mol \cdot dm^{-3}$	$S \cdot cm^2 \cdot mol^{-1}$	$mol \cdot dm^{-3}$	$S \cdot cm^2 \cdot mol^{-1}$	$mol \cdot dm^{-3}$	$S \cdot cm^2 \cdot mol^{-1}$	$mol \cdot dm^{-3}$	$S \cdot cm^2 \cdot mol^{-1}$
NaCl													
17.715	107.94	13.929	90.41	24.154	69.12	16.432	56.68	19.086	48.02	15.868	38.29	37.841	31.26
24.946	107.31	20.912	89.84	35.415	68.57	24.229	56.28	27.034	47.68	23.091	37.96	53.155	30.78
35.777	106.56	31.194	89.10	50.208	68.02	36.522	55.76	37.150	47.33	34.857	37.53	67.227	30.44
50.804	105.74	60.114	87.89	64.341	67.57	51.933	55.26	52.171	46.89	49.728	37.09	81.642	30.11
65.658	105.07	74.678	87.20	78.291	67.18	66.061	54.88	81.241	46.20	63.398	36.76	96.373	29.84
79.946	104.52	87.970	86.90	92.270	66.89	80.456	54.54	95.351	45.94	77.298	36.46	109.81	29.61
93.498	104.04	101.49	86.50	105.29	66.60	93.881	54.26	108.89	45.71	91.046	36.20	122.85	29.40
		114.91	86.15	118.25	66.34	107.00	54.01	122.49	45.48	103.74	35.98	135.61	29.22
						120.42	53.78			117.05	35.78		
KCl													
35.376	126.74	6.0021	107.54	13.663	82.57	19.265	66.07	5.2886	56.92	12.062	44.28	22.035	36.98
50.828	125.85	11.040	106.76	22.160	81.96	27.032	65.64	11.422	56.35	21.228	43.76	31.217	36.55
65.231	125.15	21.220	105.78	30.758	81.48	38.637	65.11	29.224	55.32	29.228	43.39	42.824	36.11
79.938	124.53	28.970	105.22	42.773	80.94	54.079	64.57	41.907	54.74	40.737	42.97	59.114	35.60
93.555	124.03	39.448	104.61	58.734	80.33	69.366	64.14	72.957	53.73	57.588	42.47	75.278	35.19
108.00	123.54	55.904	103.86	73.721	79.86	83.715	63.78	87.294	53.36	72.285	42.11	89.426	34.88
121.38	123.13	70.640	103.28	88.102	79.45	98.161	63.43	102.89	52.99	87.177	41.79	105.30	34.58
		86.718	102.76	102.95	79.07	111.68	63.14	116.96	52.71	101.45	41.52	119.18	34.34
		100.73	102.36	117.12	78.76	127.40	62.85	129.33	52.45	115.56	41.27	131.85	34.13
		116.68	101.96	132.69	78.36					129.22	41.05		
		124.19	101.64										
NaBr													
21.301	108.81	21.545	90.353	20.743	68.85	22.764	55.72	9.7186	47.95	7.7771	38.64	11.007	33.06
31.699	108.02	29.961	89.833	29.292	68.43	31.781	55.34	20.270	47.39	17.078	38.16	19.505	32.64
45.119	107.23	42.994	89.155	41.334	68.00	42.435	54.99	31.018	46.97	29.694	37.67	29.851	32.26
61.035	106.50	59.441	88.516	57.880	67.48	61.111	54.51	40.166	46.67	43.065	37.30	40.527	31.95
76.579	105.89	74.020	88.017	76.106	67.01	78.002	54.58	54.204	46.32	54.589	37.05	55.538	31.58
90.555	105.42	89.471	87.557	91.042	66.68	93.451	53.88	71.897	45.96	74.034	36.66	69.964	31.29
104.63	104.97	103.92	87.185	106.95	66.38	108.44	53.64	87.363	45.67	88.442	36.40	85.871	31.00
119.34	104.56	118.57	86.840	121.11	66.12	122.93	53.42	102.26	45.47	105.68	36.15	101.19	30.77
132.92	104.19	131.24	86.564			137.87	53.21	117.27	45.25	123.40	35.92	118.94	30.53
								132.45	45.04	139.24	35.73	134.10	30.34
								148.01	44.89	155.59	35.57	150.06	30.16
NaI													
17.051	106.95	5.7070	88.88	31.978	65.39	25.162	52.85	7.8141	45.45	7.9004	36.53	12.988	31.61
25.190	106.32	10.950	88.33	45.714	64.91	36.283	52.45	15.356	45.06	16.857	36.11	22.702	31.26
34.270	105.74	25.162	87.48	61.054	64.52	50.713	52.08	25.223	44.67	26.678	35.79	32.987	30.93
47.943	105.07	36.283	87.04	77.010	64.12	66.709	51.76	35.672	44.34	35.572	35.55	46.240	30.62
63.102	104.47	50.713	86.54	94.106	63.93	84.433	51.47	46.413	44.09	48.723	35.26	61.013	30.33
76.829	103.99	66.709	86.01	111.44	63.64	101.58	51.22	61.996	43.78	64.426	34.99	76.987	30.07
90.704	103.57	84.433	85.59	126.63	63.43	119.10	51.00	80.322	43.46	81.600	34.74	91.751	29.86
103.85	103.20	101.58	85.26	141.59	63.24	134.59	50.83	96.321	43.25	96.232	34.56	107.33	29.66
116.73	102.71	119.10	84.93	156.29	63.07	150.16	50.67	111.12	43.11	113.52	34.38	123.11	29.48
		134.59	84.66					124.84	42.98	128.31	34.24	137.41	29.34
		150.16	84.42					139.60	42.88	144.20	34.10		
$NaBPh_4$													
7.8917	59.82	4.4280	49.69	10.056	37.88	10.885	30.85	13.913	26.43	11.983	21.66	13.044	19.03
12.165	59.42	8.6841	49.30	15.468	37.65	17.571	30.61	21.928	26.27	19.004	21.53	18.825	18.89
16.813	59.08	15.055	48.90	21.309	37.47	22.902	30.45	31.756	26.10	25.203	21.42	27.047	18.74
23.424	58.68	20.821	48.61	28.947	37.26	31.856	30.25	44.057	25.93	32.936	21.30	34.009	18.63
31.258	58.25	28.858	48.32	38.091	37.06	42.754	30.04	55.370	25.80	42.316	21.18	41.761	18.54
39.262	57.94	37.889	48.02	49.017	36.87	53.306	29.87	64.438	25.72	52.036	21.07	49.856	18.43
46.727	57.65	47.145	47.78	58.486	36.72	63.310	29.73	74.313	25.62	61.643	20.98	55.632	18.37
54.207	57.39	56.323	47.57	69.911	36.58	75.070	29.58	84.270	25.54	70.586	20.91	66.593	18.27
61.304	57.19	65.993	47.38	79.622	36.47	85.455	29.46	92.876	25.48	79.708	20.84	76.902	18.16
67.758	57.01	75.232	47.23	91.106	36.35	96.485	29.35	104.16	25.41	91.867	20.76	86.482	18.06
		85.056	47.05	101.29	36.29							96.355	17.98
		94.053	46.92									105.31	17.90
Bu_4NI													
7.3345	80.89	3.8928	65.55	12.696	46.99	15.858	36.64	4.4934	31.77	14.638	25.02	20.200	22.28
11.258	80.23	7.6174	64.97	18.725	46.48	21.641	36.30	9.5889	31.36	19.964	24.76	26.474	22.04
15.750	79.61	12.541	64.38	24.252	46.09	28.967	35.97	15.351	31.00	25.440	24.58	33.513	21.80
20.721	79.03	17.014	63.89	31.109	45.68	35.226	35.72	22.807	30.66	32.492	24.33	39.699	21.61
26.904	78.38	22.356	63.39	37.972	45.35	42.738	35.43	29.219	30.42	39.105	24.16	44.934	21.45
33.086	77.79	28.213	62.91	45.026	45.06	49.153	35.20	37.656	30.11	46.067	23.94	51.254	21.26
39.739	77.22	34.852	62.41	52.230	44.75	55.332	34.99	44.066	29.87	52.040	23.77	57.118	21.10
45.646	76.75	41.249	61.96	58.588	44.47	63.259	34.74	51.700	29.63	58.522	23.62	63.020	20.95
51.157	76.34	46.906	61.62	62.608	44.31			58.255	29.43	63.956	23.48		
56.636	75.94	54.350	61.20	67.803	44.10			64.401	29.28				
								69.279	29.15				

changes of the Walden product connected with the change of the mixture composition result from ion−solvent interactions. The values of $\Lambda_o \eta$ increase clearly during the addition of a small amount of 2-ethoxyethanol (2) to water (1) (see Table 4). At about $x_2 =$ 0.75 to 0.10 we can see a maximum of $\Lambda_o \eta$. From an analysis of the relationship $\Lambda_o \eta = f(x_2)$, we can see the differences between conductometric properties of sodium and potassium halides and the salts containing the large ions ($NaBPh_4$ and Bu_4NI). The changes of the Walden product are clearly visible for NaCl, NaBr, NaI, and KCl.

Table 4. Limiting Molar Conductances, Λ_o, Association Constants, K_A, Parameters, R, and Walden Products, $\Lambda_o\eta$, for NaCl, KCl, NaBr, NaI, $NaBPh_4$, and Bu_4NI in Water (1) + 2-Ethoxyethanol (2) Mixtures at 298.15 K[a]

x_2	Λ_o $S\cdot cm^2\cdot mol^{-1}$	K_A $dm^3\cdot mol^{-1}$	R Å	$\Lambda_o\eta\cdot 10^{-2}$ $S\cdot cm^2\cdot mol^{-1}\cdot mPa\cdot s$	Λ_o $S\cdot cm^2\cdot mol^{-1}$	K_A $dm^3\cdot mol^{-1}$	R Å	$\Lambda_o\eta\cdot 10^{-2}$ $S\cdot cm^2\cdot mol^{-1}\cdot mPa\cdot s$
		NaCl				KCl		
0.0000	126.59	–	–	1.127	149.95	–	–	1.335
0.0100	111.16 ± 0.02	0.59 ± 0.08	3.8	1.170	131.53 ± 0.01	0.27 ± 0.05	3.6	1.385
0.0250	92.82 ± 0.05	0.73 ± 0.06	3.8	1.225	108.85 ± 0.02	0.24 ± 0.05	3.7	1.436
0.0500	71.58 ± 0.02	0.41 ± 0.04	3.8	1.276	84.67 ± 0.01	1.03 ± 0.06	4.3	1.509
0.0750	58.53 ± 0.01	1.07 ± 0.09	4.1	1.301	68.24 ± 0.02	1.23 ± 0.06	4.2	1.517
0.1000	49.87 ± 0.01	1.25 ± 0.09	4.2	1.301	57.98 ± 0.02	2.81 ± 0.08	4.3	1.512
0.1500	39.90 ± 0.02	2.17 ± 0.08	4.4	1.262	45.78 ± 0.01	2.55 ± 0.09	4.6	1.448
0.2000	33.76 ± 0.02	4.36 ± 0.11	4.5	1.169	39.05 ± 0.02	4.69 ± 0.11	4.8	1.352
		NaBr				NaI		
0.0000	128.38	–	–	1.143	126.92	–	–	1.130
0.0100	112.27 ± 0.02	0.25 ± 0.06	3.7	1.182	109.96 ± 0.02	–	3.7	1.158
0.0250	93.30 ± 0.02	0.23 ± 0.06	3.7	1.231	90.38 ± 0.01	–	3.9	1.192
0.0500	71.15 ± 0.01	0.31 ± 0.05	3.8	1.268	67.98 ± 0.02	–	4.3	1.212
0.0750	57.77 ± 0.01	0.16 ± 0.04	4.1	1.285	54.85 ± 0.01	–	4.1	1.220
0.1000	49.18 ± 0.01	0.32 ± 0.03	4.2	1.283	46.51 ± 0.02	–	4.1	1.213
0.1500	39.74 ± 0.01	0.41 ± 0.03	4.1	1.257	37.55 ± 0.01	–	4.3	1.188
0.2000	34.35 ± 0.01	0.78 ± 0.04	3.9	1.188	32.94 ± 0.01	–	4.3	1.140
		$NaBPh_4$				Bu_4NI		
0.0000	69.98	–	–	0.623	96.26	–	–	0.857
0.0100	61.57 ± 0.01	–	5.4	0.648	83.09 ± 0.02	6.58 ± 0.11	4.3	0.875
0.0250	50.77 ± 0.01	–	6.2	0.670	66.85 ± 0.01	6.85 ± 0.14	4.3	0.882
0.0500	39.08 ± 0.01	–	7.5	0.697	48.76 ± 0.02	7.26 ± 0.16	6.9	0.869
0.0750	31.93 ± 0.01	–	8.2	0.706	38.35 ± 0.01	7.85 ± 0.16	8.7	0.853
0.1000	27.45 ± 0.01	–	10.4	0.716	32.56 ± 0.01	8.92 ± 0.15	9.3	0.849
0.1500	22.56 ± 0.01	–	11.0	0.713	26.32 ± 0.01	9.95 ± 0.21	11.5	0.833
0.2000	19.92 ± 0.01	0.31 ± 0.03	11.4	0.702	23.85 ± 0.01	10.50 ± 0.19	12.5	0.826

[a] In all cases, $\Delta R = 0.5\cdot 10^{-8}$ cm.

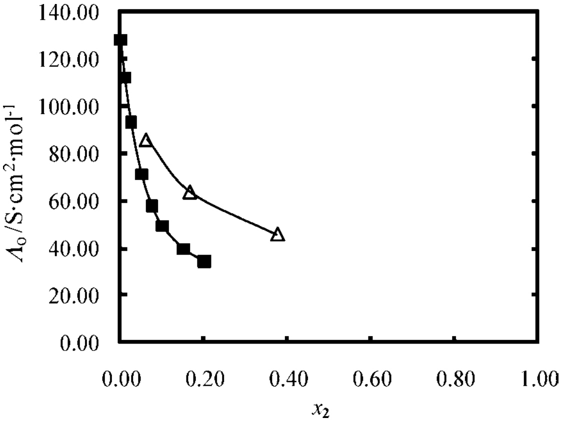

Figure 1. Limiting molar conductance, Λ_o, of NaBr as a function of the mole fraction, x_2, in water (1) + 2-ethoxyethanol (2) mixtures: Δ, ref 4 (at 308.15 K); ■, this work (at 298.15 K).

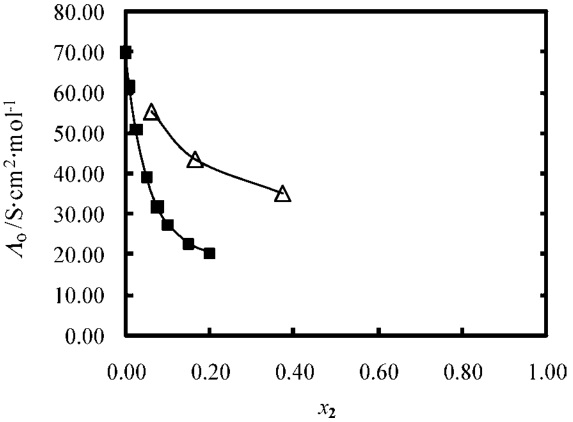

Figure 2. Limiting molar conductance, Λ_o, of $NaBPh_4$ as a function of the mole fraction, x_2, in water (1) + 2-ethoxyethanol (2) mixtures: Δ, ref 4 (at 308.15 K); ■, this work (at 298.15 K).

In the literature, we can find papers on conductometric studies in 2-ethoxyethanol (1) + water (2),[4,5,20] but only ref 4 concerns the electrolytes (NaBr and $NaBPh_4$) investigated by us. However, the values of the limiting molar conductance obtained in that paper are higher than ours (see Figures 1 and 2) because the measurements were carried out at 308.15 K.

It is well-known that the Walden product values depend on changes in temperature to a very small degree.[22] Therefore, the relationships $\Lambda_o\eta = f(x_2)$ obtained in this paper and on the basis of data from ref 4 should be similar. Unfortunately, Figures 3 and 4 show significant differences between experimental and literature data. However, one should pay attention to the fact that the values of viscosity from ref 4 differ from other literature data.[23,24] The viscosities at 308.15 K for $x_2 = 0.06247$, 0.16660, and 0.37488 are (1.8430, 1.9234, and 1.7002) mPa·s (ref 4), respectively, and (1.4691, 2.1823, and 2.3420) mPa·s (from ref 23). Thus, the results differ considerably. For $x_2 = 0.06247$, the value from ref 4 is about 25 % higher than from ref 23. For $x_2 = 0.16660$ and $x_2 = 0.37488$, the values are, respectively, 10 % and 30 % lower.

The single-ion conductances were obtained on the basis of the Fuoss−Hirsch assumption[25]

$$\lambda_o(Bu_4N^+) = \lambda_o(BPh_4^-) = [\Lambda_o(Bu_4NI) + \Lambda_o(NaBPh_4)\text{-}\Lambda_o(NaI)]/2 \quad (4)$$

The dependencies $\lambda_o^+ = f(x_2)$ and $\lambda_o^- = f(x_2)$ are presented in Figures 5 and 6, respectively. The factors having an influence on these dependencies are the macroscopic viscosity and the effective size of ions. The values of limiting ionic conductances decrease with an increase of the macroscopic viscosities and of the effective ion size. Therefore, it is no wonder that in the case of the large ions (Bu_4N^+ and BPh_4^-) the values of λ_o are the smallest.

The changes of the values of $\lambda_o^{\pm}\eta$ as a function of the mixed solvent composition are independent from the changes of the

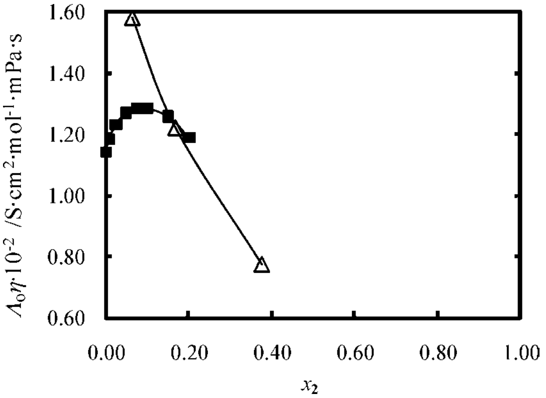

Figure 3. Walden product, $\Lambda_o\eta$, of NaBr as a function of the mole fraction, x_2, in water (1) + 2-ethoxyethanol (2) mixtures: Δ, ref 4 (at 308.15 K); ■, this work (at 298.15 K).

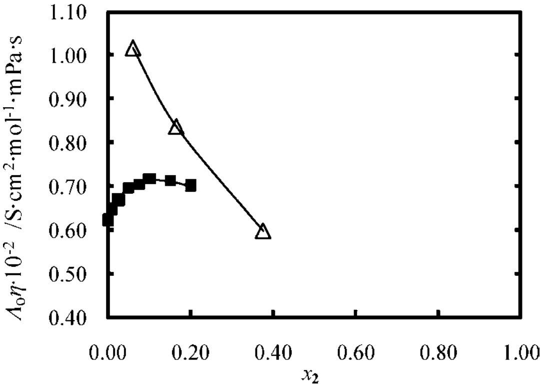

Figure 4. Walden product, $\Lambda_o\eta$, of $NaBPh_4$ as a function of the mole fraction, x_2, in water (1) + 2-ethoxyethanol (2) mixtures: Δ, ref 4 (at 308.15 K); ■, this work (at 298.15 K).

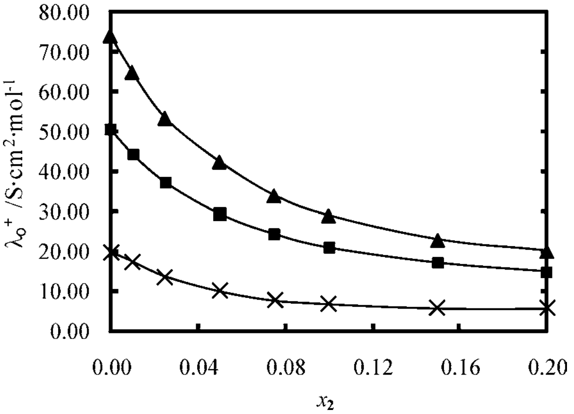

Figure 5. Limiting ionic conductances of the individual cations, λ_o^+, as a function of the mole fraction, x_2, in water (1) + 2-ethoxyethanol (2) mixtures at 298.15 K: ▲, K^+; ■, Na^+; ×, Bu_4N^+.

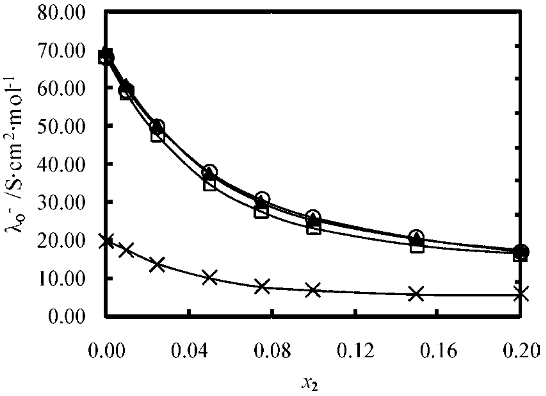

Figure 6. Limiting ionic conductances of the individual anions, λ_o^-, as a function of the mole fraction, x_2, in water (1) + 2-ethoxyethanol (2) mixtures at 298.15 K: ○, Cl^-; ▲, Br^-; □, I^-; ×, BPh_4^-.

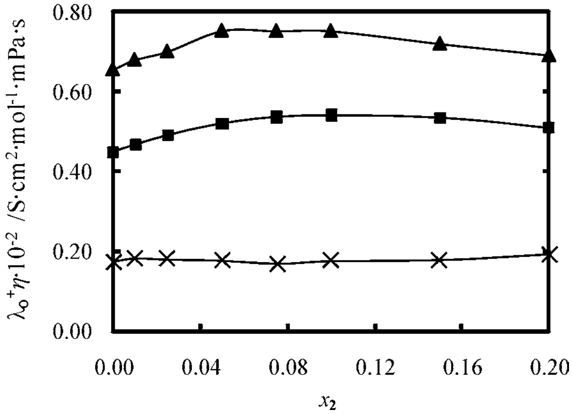

Figure 7. Walden product for cations, $\lambda_o^+\eta$, as a function of the mole fraction, x_2, in water (1) + 2-ethoxyethanol (2) mixtures at 298.15 K: ▲, K^+; ■, Na^+; ×, Bu_4N^+.

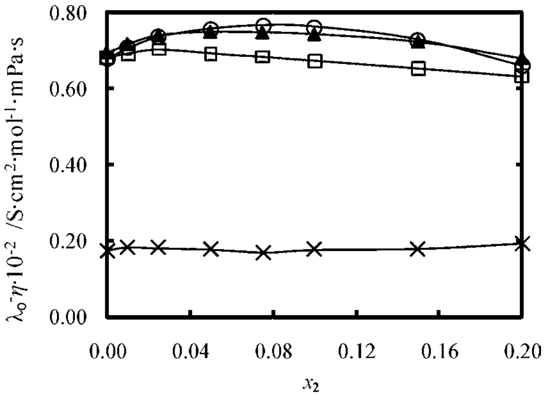

Figure 8. Walden product for anions, $\lambda_o^-\eta$, as a function of the mole fraction, x_2, in water (1) + 2-ethoxyethanol (2) mixtures at 298.15 K: ○, Cl^-; ▲, Br^-; □, I^-; ×, BPh_4^-.

macroscopic viscosity. Thus, the difference between the values of $\lambda_o^\pm\eta$ for different ions may provide information about the differences in the ion−solvent interactions. The dependencies $\lambda_o^+\eta = f(x_2)$ and $\lambda_o^-\eta = f(x_2)$ are presented in Figures 7 and 8, respectively.

As can be seen in Figures 7 and 8, the addition of small amounts of 2-ethoxyethanol (2) to water (1) leads to an increase of the values of the ionic Walden product for the cations K^+ and Na^+ and the anions Cl^-, Br^-, and I^-, but they remain almost constant for Bu_4N^+ and BPh_4^-. The big organic ions having small surface charge density are practically unsolvated in the solution, and this is why there are constant values of the Walden product. In the course of the dependence $\lambda_o^\pm\eta = f(x_2)$ for smaller ions, we can see a maximum. This phenomenon can be observed in other mixtures of water with organic cosolvents.[11,12,26−31] It can be explained by the assumption of the preferential solvation of these ions by the water dipoles, as was proposed by Kay, who named it "sorting effect".[29] Preferential solvation of ions in the case when small amounts of 2-ethoxyethanol (2) are added to water (1) can lead to a change of the microscopic viscosity (around the ion) to a smaller extent than macroscopic viscosity, which is used for the calculation of the values of the Walden products. It can lead to an excess of the mobility of ions, which causes the presence of the maximum on the dependence of $\lambda_o^\pm\eta = f(x)$. Greater amounts of 2-ethoxyethanol (2) added to water

(1) cause the values of the ionic Walden product to stabilize and next decrease insignificantly (what we can see for anions). This is probably caused by the fact that the ions are gradually presolvated by cellosolve molecules, which leads to an increase of the effective radii of the ions and decreases their mobility.

Conclusions

The electrical conductances of solutions of sodium chloride, potassium chloride, sodium bromide, sodium iodide, sodium tetraphenylborate, and tetrabutylammonium iodide have been measured in aqueous 2-ethoxyethanol (2) mixtures containing (0.01, 0.025, 0.05, 0.075, 0.10, 0.15, and 0.20) mol fractions of 2-ethoxyethanol (2) at 298.15 K. The limiting molar conductances, Λ_o, and Walden products, $\Lambda_o\eta$, have been determined. The conductometric data available in the literature have been compared with the data obtained by us. The changes of the dependence $\lambda_o^{\pm}\eta = f(x)$ have been analyzed based on the “sorting effect” proposed by Kay. In the range of compositions containing a large amount of water (1), slight additions of 2-ethoxyethanol (2) do not cause significant changes in the hydration shells of ions.

Supporting Information Available:

Tables 1, SM1, and SM2 and experimental data summaries for the tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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