Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetraphenylborate, and Sodium Bromide in Ethylene Glycol (1) + Water (2) Mixtures at (298.15, 303.15, 308.15, and 318....

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The electrical conductances of solutions of tetrabutylammonium bromide (Bu$_4$NBr), sodium tetraphenylborate (NaBPh$_4$), and sodium bromide (NaBr) in ethylene glycol (EG) (1) + water (2) mixed solvent media containing 0.10, 0.20, and 0.30 mass fractions of EG (w_1) have been reported at (298.15, 303.15, 308.15, and 318.15) 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 conductances have been estimated using tetrabutylammonium tetraphenylborate (Bu$_4$NBPh$_4$) as the "reference electrolyte". All of these three electrolytes are found to exist as free ions in the present solvent mixtures within the temperature range from (298.15 to 318.15) K. Although the association constants of the electrolytes do not vary significantly as a function of temperature, the limiting molar conductances of the electrolytes as well as the single-ion conductivity values increase appreciably with temperature.

Introduction

Studies on the transport properties of electrolytes in different solvent media are of considerable importance in obtaining information regarding the solvation and association behavior of ions in solutions. Earlier, we have investigated[1−11] these properties for a wide variety of electrolytes in different solvents in great detail. Solvent properties such as 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 equivalent conductivities of tetrabutylammonium bromide (Bu$_4$NBr), sodium tetraphenylborate (NaBPh$_4$), and sodium bromide (NaBr) in ethylene glycol (EG) (1) + water (2) mixtures containing 0.10, 0.20, and 0.30 mass fractions of EG (w_1) at (298.15, 303.15, 308.15, and 318.15) K in order to obtain precise temperature-dependent single-ion conductivities, since such data are relatively scarce in mixed solvent media.[12,13]

EG is a polar solvent with a clearly pronounced spatial network of hydrogen bonds[14] that is very sensitive to the influence of temperature and electrolytes. Addition of water to EG leads to the formation of hydrogen bonds with water molecules as well. This hydrogen-bond network defines the character of the molecular motion and, as a consequence, the dynamics of the ion−molecule interaction in electrolyte solutions. Therefore, it is interesting to study the solvation and association behavior of ions in EG (1) + water (2) mixtures as a function of temperature. However, a survey of the literature indicated that the electrical conductivities of electrolytes in these mixtures have not been studied in sufficient detail, in particular, as a function of temperature. Accascina and D'Aprano[15] investigated the electrical conductances of sodium bromide in

Table 1. Physical Properties of EG (1) + Water (2) Mixtures Containing 0.10, 0.20, and 0.30 Mass Fractions of EG at (298.15, 303.15, 308.15 and 318.15) K

T	ρ_0 g·cm^{-3}		η_0 mPa·s		ε^d
K	this work	lit.	this work	lit.	
	$w_1 = 0.10$				
298.15	1.00949		1.15197		75.65
303.15	1.00762	1.00800^a	1.01695	1.0185^a	73.84
308.15	1.00557		0.90783		72.07
318.15	1.00273		0.73813		68.68
	$w_1 = 0.20$				
298.15	1.02245		1.46935		72.68
303.15	1.02098	1.02078^a	1.30578	1.3166^a	71.07
308.15	1.01850		1.14938		69.47
318.15	1.01428		0.92431		66.27
	$w_1 = 0.30$				
298.15	1.03570		1.90253		69.77
303.15	1.03405	1.033528^b	1.65678		68.01
308.15	1.03166		1.46223		66.30
318.15	1.02673		1.16376		63.00
	$w_1 = 1.00$				
298.15	1.11045	1.10950^a	18.6352	18.6826^a	37.70
303.15	1.10447	1.10546^a	13.8621	13.8678^a	36.80
308.15	1.10013	1.09835^a	11.6634	11.6956^a	35.85
318.15	1.09215	1.09602^c	7.4532		34.21

^{a} From ref 16. ^{b} From ref 17. ^{c} From ref 15. ^{d} From ref 18.

ethylene glycol + water mixtures at 298.15 K. Triolo and D'Aprano[16] reported the electrical conductance of tetrabutylammonium bromide in ethylene glycol + water mixtures at 298.15 K.

Experimental Section

Ethylene glycol (E. Merck, India, 99 % pure) was dried over molecular sieves and fractionally distilled. The middle fraction was collected and redistilled. The physical properties of the purified

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Table 2. Molar Conductances and Corresponding Molarities of Electrolytes in EG (1) + Water (2) Mixtures Containing 0.10, 0.20, and 0.30 Mass Fractions of EG at (298.15, 303.15, 308.15 and 318.15) K

$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K		$T = 318.15$ K	
c	Λ	c	Λ	c	Λ	c	Λ
mol·dm^{-3}	S·cm^2·mol^{-1}	mol·dm^{-3}	S·cm^2·mol^{-1}	mol·dm^{-3}	S·cm^2·mol^{-1}	mol·dm^{-3}	S·cm^2·mol^{-1}
			$w_1 = 0.10$				
			Tetrabutylammonium Bromide				
0.00849	70.89	0.00847	78.84	0.00845	86.62	0.00843	102.85
0.01273	68.94	0.01271	76.90	0.01268	84.46	0.01264	100.40
0.02122	65.96	0.02118	73.81	0.02113	81.25	0.02107	96.36
0.02971	63.53	0.02965	71.31	0.02959	78.59	0.02950	93.10
0.03395	62.46	0.03389	70.15	0.03381	77.39	0.03371	91.70
0.03820	61.39	0.03812	69.12	0.03804	76.16	0.03792	90.28
0.04244	60.49	0.04236	68.03	0.04227	75.03	0.04214	89.11
0.05518	57.77	0.05506	65.35	0.05494	72.24	0.05477	85.42
			Sodium Bromide				
0.00847	99.36	0.00846	109.57	0.00844	120.19	0.00842	143.69
0.01271	98.20	0.01269	108.13	0.01266	118.58	0.01263	142.02
0.01695	96.89	0.01692	106.71	0.01689	117.07	0.01684	140.33
0.02119	96.04	0.02115	105.56	0.02111	115.91	0.02105	138.99
0.02543	95.15	0.02538	104.48	0.02533	114.74	0.02526	137.69
0.03391	93.41	0.03383	102.61	0.03376	112.67	0.03366	135.57
0.04239	92.01	0.04231	100.85	0.04222	110.83	0.04210	133.56
0.05087	90.80	0.05077	99.49	0.05067	109.37	0.05051	132.00
			Sodium Tetraphenylborate				
0.00780	52.83	0.00778	59.13	0.00777	65.40	0.00774	79.91
0.00910	52.52	0.00908	58.80	0.00906	65.08	0.00904	79.48
0.01040	52.24	0.01038	58.52	0.01036	64.78	0.01033	79.06
0.01170	51.98	0.01168	58.23	0.01165	64.49	0.01162	78.66
0.01300	51.73	0.01298	57.98	0.01295	64.24	0.01291	78.29
0.01430	51.50	0.01427	57.72	0.01425	63.99	0.01420	77.92
0.01560	51.27	0.01557	57.47	0.01554	63.74	0.01549	77.58
0.01690	51.06	0.01687	57.24	0.01684	63.52	0.01678	77.25
			$w_1 = 0.20$				
			Tetrabutylammonium Bromide				
0.00807	56.99	0.00806	64.27	0.00804	71.25	0.00801	89.71
0.01211	55.58	0.01209	62.46	0.01206	69.27	0.01201	87.04
0.02019	53.35	0.02016	59.76	0.02011	66.18	0.02002	82.69
0.02827	51.60	0.02822	57.61	0.02815	63.76	0.02803	79.18
0.03231	50.81	0.03225	56.56	0.03217	62.68	0.03204	77.60
0.03635	49.99	0.03628	55.60	0.03619	61.52	0.03604	76.19
0.0403	49.35	0.04031	54.76	0.04022	60.59	0.04004	74.69
0.05250	47.46	0.05239	52.42	0.05228	57.89	0.05205	71.09
			Sodium Bromide				
0.00789	79.66	0.00788	88.91	0.00786	98.11	0.00783	121.60
0.01184	78.72	0.01182	87.92	0.01179	97.07	0.01174	119.83
0.01579	77.99	0.01576	87.12	0.01572	96.07	0.01566	118.17
0.01973	77.38	0.01970	86.43	0.01966	95.36	0.01958	116.94
0.02368	76.73	0.02365	85.81	0.02359	94.71	0.02349	115.66
0.03158	75.59	0.03153	84.71	0.03145	93.36	0.03132	113.73
0.03947	74.70	0.03941	83.70	0.03932	92.28	0.03915	111.74
0.05132	73.20	0.05123	82.44	0.05111	90.79	0.05090	109.32
			Sodium Tetraphenylborate				
0.00842	43.11	0.00841	48.79	0.00839	54.48	0.00835	67.36
0.00982	42.85	0.00981	48.49	0.00978	54.14	0.00974	66.84
0.01123	42.59	0.01121	48.23	0.01118	53.82	0.01114	66.39
0.01263	42.37	0.01261	47.99	0.01258	53.51	0.01253	65.91
0.01404	42.12	0.01401	47.74	0.01398	53.23	0.01392	65.50
0.01544	41.92	0.01541	47.53	0.01537	52.96	0.01531	65.10
0.01684	41.71	0.01681	47.30	0.01677	52.69	0.01671	64.74
0.01825	41.52	0.01821	47.10	0.01817	52.45	0.01810	64.37
			$w_1 = 0.30$				
			Tetrabutylammonium Bromide				
0.00837	44.89	0.00836	50.25	0.00834	55.62	0.00830	68.55
0.01256	43.76	0.01254	49.02	0.01251	54.44	0.01245	66.91
0.02093	41.94	0.02090	47.19	0.02085	52.53	0.02075	64.19
0.02931	40.52	0.02925	45.61	0.02918	50.91	0.02905	62.17
0.03349	39.93	0.03343	44.98	0.03335	50.21	0.03320	61.12
0.03768	39.21	0.03761	44.33	0.03752	49.52	0.03735	60.23
0.04187	38.63	0.04179	43.79	0.04169	48.89	0.04150	59.46
0.05443	37.06	0.05432	42.12	0.05340	47.30	0.05396	57.10

Table 2 Continued

T = 298.15 K		T = 303.15 K		T = 308.15 K		T = 318.15 K	
c	Λ	c	Λ	c	Λ	c	Λ
mol·dm^{-3}	S·cm^2·mol^{-1}	mol·dm^{-3}	S·cm^2·mol^{-1}	mol·dm^{-3}	S·cm^2·mol^{-1}	mol·dm^{-3}	S·cm^2·mol^{-1}
			Sodium Bromide				
0.00732	65.27	0.00731	71.82	0.00729	80.50	0.00725	100.45
0.01464	63.85	0.01461	70.81	0.01458	79.06	0.01451	97.98
0.01830	63.29	0.01827	70.38	0.01823	78.49	0.01814	97.01
0.02196	62.80	0.02192	70.00	0.02187	77.94	0.02177	96.17
0.02928	61.92	0.02923	69.29	0.02916	77.04	0.02902	94.57
0.03660	61.12	0.03654	68.71	0.03645	76.19	0.03628	93.20
0.04393	60.47	0.04384	68.15	0.04374	75.43	0.04354	92.02
0.05125	59.81	0.05115	67.66	0.05103	74.79	0.05079	90.88
			Sodium Tetraphenylborate				
0.00753	35.07	0.00752	39.87	0.00750	44.51	0.00747	55.06
0.00875	34.86	0.00879	39.61	0.00875	44.22	0.00871	54.77
0.01005	34.68	0.01003	39.35	0.01000	43.95	0.00996	54.54
0.01130	34.48	0.01128	39.10	0.01126	43.68	0.01121	54.29
0.01256	34.31	0.01253	38.88	0.01251	43.45	0.01245	54.07
0.01382	34.16	0.01379	38.65	0.01376	43.20	0.01370	53.85
0.01507	34.00	0.01504	38.45	0.01501	42.99	0.01494	53.64
0.01633	33.85	0.01629	38.23	0.01626	42.79	0.01619	53.45

solvent were found to be in good agreement with the literature values.[17,18] Table 1 shows the comparison of the experimental values of density and viscosity of EG with literature data.[17,18] Triply distilled water with a specific conductance of less than 10^{-6} S·cm^{-1} at 298.15 K was used for the preparation of the mixed solvents. The densities and viscosities of EG (1) + water (2) mixed solvents used in this study at (298.15, 303.15, 308.15, and 318.15) K are reported in Table 1 along with those obtained from the literature.[19] The relative permittivities of EG (1) + water (2) mixtures obtained by regressing the relative permittivity data as a function of solvent composition from the literature[20] are included in Table 1.

All of these salts were of Fluka purum or puriss grade. Tetrabutylammonium bromide (Bu$_4$NBr) was purified by recrystallization from acetone, and the recrystallized salt was dried in vacuo at 333.15 K for 48 h. Sodium tetraphenylborate (NaBPh$_4$) was recrystallized 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}. The cell was calibrated by the method of Lind and co-workers[21] using aqueous potassium chloride solutions. The measurements were made in a water bath maintained within ± 0.01 K of the desired temperature. The details of the experimental procedure have been described earlier.[4,5] 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. The experimental uncertainties in density, viscosity, and conductivity were always within 0.02 %, 0.30 %, and 0.30 %,

respectively. The uncertainty of the solute molality was estimated to be $\pm 2 \times 10^{-5}$ mol·kg^{-1}.

Results and Discussion

The measured molar conductances (Λ) of electrolyte solutions as functions of molar concentration (c) in EG (1) + water (2) mixtures with mass fractions of 0.10, 0.20, and 0.30 of EG at (298.15, 303.15, 308.15, and 318.15) K are given in Table 2.

The conductance data have been analyzed by the 1978 Fuoss conductance−concentration equation.[22,23] For a given set of conductivity values (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

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

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

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

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

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

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

where RX is the relaxation field effect, EL is the electrophoretic countercurrent, γ is the fraction of unpaired ions, α is the fraction of contact-pairs, K_A is the overall pairing constant evaluated from the association constants of contact-pairs (K_S) and 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 is the reciprocal of 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 a Shedlovsky extrapolation[24] of the data. Input for the program is the set (c_j, Λ_j; $j = 1, ..., n$), n, ε, η, T, the initial value of Λ^0, and an instruction to cover a preselected range of R values.

Table 3. Derived Conductivity Parameters of Electrolytes in EG (1) + Water (2) Mixtures Containing 0.10, 0.20, and 0.30 Mass Fractions of EG at (298.15, 303.15, 308.15 and 318.15) K

T	Λ^0	K_A	R	
K	S·cm²·mol⁻¹	dm³·mol⁻¹	Å	$100\sigma/\Lambda^0$
		$w_1 = 0.10$		
		Tetrabutylammonium Bromide		
298.15	78.15 ± 0.05	7.12 ± 0.04	14.10	0.05
303.15	86.67 ± 0.03	6.23 ± 0.03	13.11	0.03
308.15	94.95 ± 0.08	5.68 ± 0.06	13.59	0.07
318.15	113.19 ± 0.06	6.05 ± 0.03	13.18	0.04
		Sodium Bromide		
298.15	105.75 ± 0.08	2.53 ± 0.04	10.32	0.08
303.15	116.96 ± 0.06	2.61 ± 0.03	9.99	0.05
308.15	128.34 ± 0.06	2.47 ± 0.03	9.62	0.05
318.15	153.31 ± 0.08	2.02 ± 0.03	9.30	0.06
		Sodium Tetraphenylborate		
298.15	57.25 ± 0.06	2.69 ± 0.01	14.20	0.06
303.15	63.83 ± 0.01	2.56 ± 0.02	17.53	0.01
308.15	70.52 ± 0.01	2.04 ± 0.02	16.11	0.09
318.15	86.54 ± 0.02	2.87 ± 0.02	17.11	0.01
		$w_1 = 0.20$		
		Tetrabutylammonium Bromide		
298.15	62.68 ± 0.03	6.47 ± 0.03	11.05	0.04
303.15	71.00 ± 0.05	7.72 ± 0.05	12.89	0.06
308.15	78.73 ± 0.06	7.87 ± 0.06	14.03	0.06
318.15	99.95 ± 0.05	9.64 ± 0.04	15.57	0.04
		Sodium Bromide		
298.15	84.16 ± 0.03	1.98 ± 0.02	12.42	0.05
303.15	94.11 ± 0.02	1.57 ± 0.01	9.68	0.02
308.15	103.90 ± 0.04	1.67 ± 0.02	10.38	0.04
318.15	130.09 ± 0.06	2.86 ± 0.02	8.49	0.05
		Sodium Tetraphenylborate		
298.15	46.96 ± 0.02	3.18 ± 0.03	13.96	0.02
303.15	53.00 ± 0.01	2.78 ± 0.03	14.21	0.01
308.15	59.40 ± 0.01	3.27 ± 0.02	14.29	0.01
318.15	74.37 ± 0.02	3.96 ± 0.03	9.76	0.01
		$w_1 = 0.30$		
		Tetrabutylammonium Bromide		
298.15	49.41 ± 0.05	6.75 ± 0.06	13.12	0.07
303.15	55.26 ± 0.03	5.93 ± 0.04	10.92	0.05
308.15	60.97 ± 0.03	5.27 ± 0.03	11.71	0.04
318.15	75.66 ± 0.05	6.31 ± 0.04	11.59	0.06
		Sodium Bromide		
298.15	69.15 ± 0.01	2.02 ± 0.01	8.73	0.02
303.15	75.49 ± 0.03	1.01 ± 0.02	11.73	0.05
308.15	85.02 ± 0.03	1.52 ± 0.02	10.57	0.04
318.15	107.02 ± 0.02	2.60 ± 0.01	8.94	0.02
		Sodium Tetraphenylborate		
298.15	38.01 ± 0.01	3.29 ± 0.04	14.11	0.02
303.15	43.34 ± 0.01	4.76 ± 0.03	17.01	0.01
308.15	48.62 ± 0.04	3.78 ± 0.04	11.79	0.02
318.15	59.31 ± 0.01	2.43 ± 0.03	16.81	0.01

In practice, calculations have been made by finding the values of Λ^0 and α that minimize the standard deviation, σ

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

for a sequence of R values and then plotting σ against R; the best-fit R corresponds to the minimum in the σ vs R curve. The values of Λ^0, K_A, and R obtained by this procedure are reported in Table 3. A representative plot (Figure 1) for Bu₄NBr in EG (1) + water (2) mixtures with $w_1 = 0.20$ at (298.15, 303.15, 308.15, and 318.15) K shows the variation of the experimental molar conductivity as a function of concentration along with the fitted profiles according to eqs 1 through 6.

In order to investigate the specific behavior of the individual ions comprising these electrolytes, it is necessary to split the
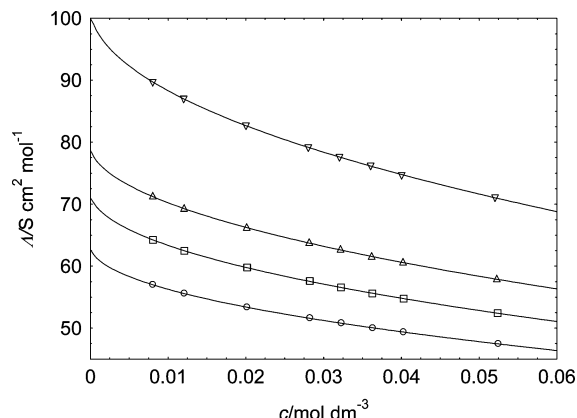
Figure 1. Variation of molar conductivity as a function of concentration for tetrabutylammonium bromide in EG (1) + water (2) with $w_1 = 0.20$. Experimental: ○, 298.15 K; □, 303.15 K; △, 308.15 K; and ▽, 318.15 K. The lines represent the calculations according to eqs 1 through 6.

Table 4. Limiting Ionic Molar Conductances in EG (1) + Water (2) Mixtures Containing 0.10, 0.20, and 0.30 Mass Fractions of EG at (298.15, 303.15, 308.15 and 318.15) K

T	$\lambda^0_\pm$			
	S·cm²·mol⁻¹			
K	Na⁺	Bu₄N⁺	Br⁻	Ph₄B⁻
		$w_1 = 0.10$		
298.15	42.93	15.33	62.82	14.32
303.15	47.69	17.40	69.27	16.14
308.15	52.59	19.20	75.75	17.93
318.15	64.12	24.00	89.19	22.42
		$w_1 = 0.20$		
298.15	34.65	13.17	49.51	12.31
303.15	38.56	15.45	55.55	14.44
308.15	42.87	17.70	61.03	16.53
318.15	53.01	22.87	77.08	21.35
		$w_1 = 0.30$		
298.15	29.19	9.45	39.96	8.82
303.15	32.18	11.95	43.31	11.16
308.15	36.75	12.70	48.27	11.87
318.15	45.81	14.45	61.21	13.50

limiting molar electrolyte conductances into their ionic components.

The limiting ionic conductivities (λ^0) have been evaluated from the division of the Λ^0 values of Bu₄NBPh₄ using the relationship

$$\lambda^0(\text{Bu}_4\text{N}^+) = 0.517\Lambda^0(\text{Bu}_4\text{NPh}_4\text{B}) \quad (8)$$

as described in the literature.[6,25]

The limiting molar conductivity (Λ^0) of the "reference electrolyte" Bu₄NBPh₄ was obtained by considering the Kohlrausch rule that allows the calculation of the Λ^0 value for a given electrolyte by the appropriate combination of others. The Λ^0 values of Bu₄NBr, NaBPh₄ and NaBr obtained in the present solvent media have been used to obtain the Λ^0 value of Bu₄NBPh₄ through the following equation:

$$\Lambda^0(\text{Bu}_4\text{NBPh}_4) = \Lambda^0(\text{Bu}_4\text{NBr}) + \Lambda^0(\text{NaPh}_4\text{B}) - \Lambda^0(\text{NaBr}) \quad (9)$$

The limiting ionic conductances calculated from the above equations are recorded in Table 4.

Limiting molar conducivities of sodium bromide and tetrabutylammonium bromide in some selected EG (1) + water (2) mixtures have also been reported earlier at 298.15 K.[15,16] A
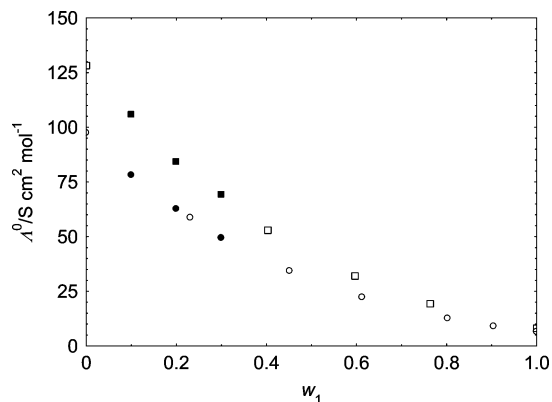
Figure 2. Limiting molar conductivities in EG (1) + water (2) mixtures at 298.15 K. Tetrabutylammonium bromide: ○, Accascina and D'Aprano;[25] ●, present study. Sodium bromide: □, D'Aprano and Triolo;[24] ■, present study.
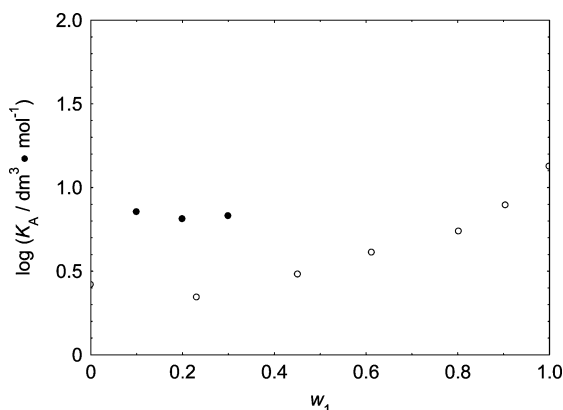

Figure 3. Association constants (as logarithm) of tetrabutylammonium bromide in EG (1) + water (2) at 298.15 K: ○, Accascina and D'Aprano;[25] ●, present study.

comparison of the Λ^0 values obtained in the present study with those from the literature (Figure 2) reveals a very good agreement.

The association constants for tetrabutylammonium bromide have been compared with those reported by D'Aprano and Triolo[16] in EG (1) + water (2) mixtures at 298.15 K in Figure 3. Although a direct comparison is not possible, because the solvent compositions are different in these two cases, our K_A values always appear to be higher than the literature values. It may be pointed out that the present analysis has been performed using Fuoss' 1978 equation,[20,21] whereas D'Aprano and Triolo[16] used a conductivity−concentration relationship developed prior to 1975 on the basis of a primitive model (rigid charged spheres of diameter a in a continuum). Discrepancies between theoretically derived values of the parameters based upon the previous models and parameters characteristic of real physical systems led Fuoss[22,23] to suggest a new model that eliminates a number of artifacts that are properties of the primitive model. The revised model always produced higher association constants[22] compared to those derived on the basis of the primitive models; e.g., the K_A values for LiCl, LiI, and CsBr in water at 298.15 K are reported to be 4.02, 3.69, and 1.96, respectively, following the Fuoss 1978 equation,[22] whereas the respective values were found to be 0.81, 0.62, and 0.695 on the basis of the primitive model.[27]

The association constants (K_A) listed in Table 3 for all these systems are practically negligible (i.e., $K_A < 10$). So, the numerical values of K_A (ranging between 1.01 and 9.64) should not be taken seriously.[26] One can only conclude that all of these
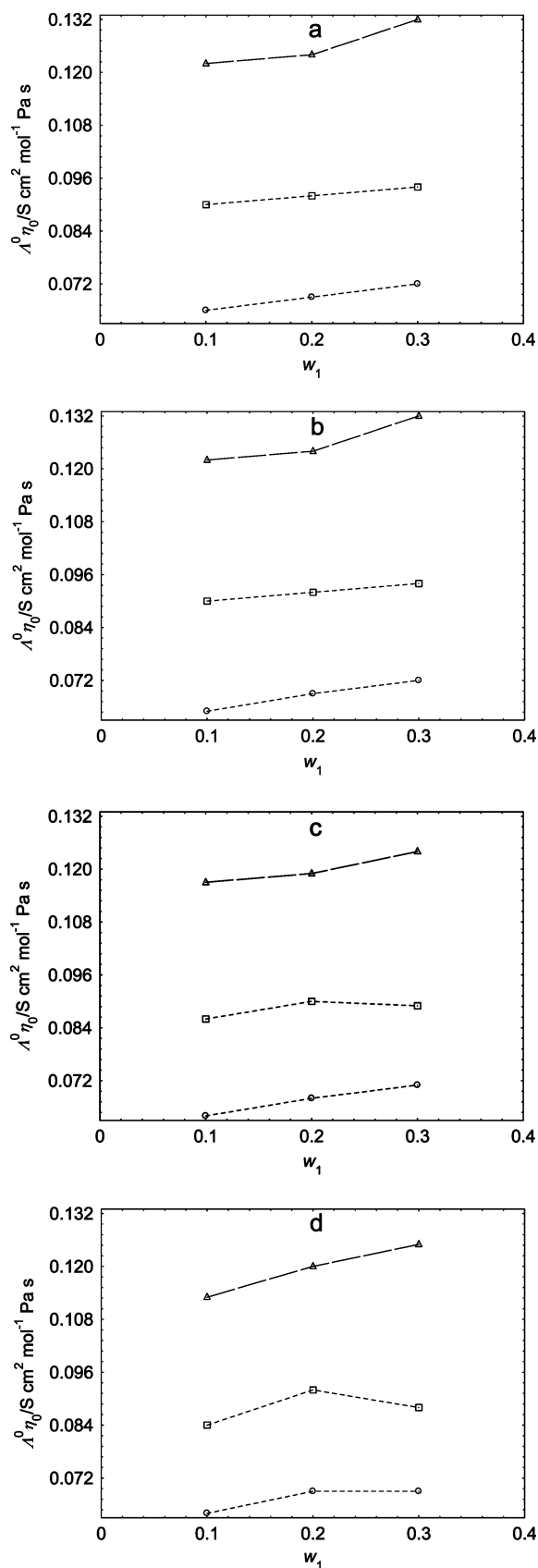

Figure 4. Walden products of ○, sodium tetraphenylborate; □, tetrabutylammonium bromide; and △, sodium bromide in EG (1) + water (2) at a, 298.15 K; b, 303.15 K; c, 308.15 K; and d, 318.15 K.

three electrolytes exist as free ions in the present EG (1) + water (2) solvent mixtures within the temperature range from (298.15 to 318.15) K. This is expected because the relative

permittivities of the solvent mixtures are fairly high[20] (63.00 $\leq \varepsilon \leq$ 75.65), thus promoting dissociation of electrolytes.

The association diameter (R) values for the salts under study in the EG (1) + water (2) mixtures are also reported in Table 3. No systematic trend in the R values for the salts has been observed. Because the best-fit conductivity parameters were found to be reproduced almost equally well over a wide range of arbitrarily chosen R values, a comprehensive correlation of the association diameter of the investigated systems could not be made in the present situation. This type of behavior has also been reported earlier.[25,26−29] The R values, deviate considerably from the sum of radii of the ions[12] constituting the electrolytes, thus indicating ionic solvation.

Figure 4 shows the variation of the Walden products as a function of the solvent composition at the temperatures investigated. The observed deviation from the ideal behavior with varying solvent composition demonstrates changed ion−solvent interactions, possibly due to the changing solvodynamic size of the ions.

In all the mixed solvent media, the limiting ionic equivalent conductances decreases in the order $\lambda^0_{Br^-} > \lambda^0_{Na^+} > \lambda^0_{Bu_4N^+} > \lambda^0_{Ph_4B^-}$ at each temperature, indicating that the sizes of these ions as they exist in solutions follow the order $Br^- < Na^+ < Bu_4N^+ < Ph_4B^-$. This is a manifestation of the solvation of, at least, the smaller ions (sodium and bromide) with higher surface charge densities. It is also observed that the limiting ionic molar conductances of all the ions decrease in going from 0.10 mass fraction of EG to 0.30 mass fraction of EG in the mixture at all temperatures investigated.

The limiting molar conductances of the electrolytes as well as the single-ion conductivity values increase appreciably with temperature. The effect of temperature on $\lambda^0_{Na^+}$ and $\lambda^0_{Br^-}$ ions is more pronounced compared to that on $\lambda^0_{Bu_4N^+}$ and $\lambda^0_{Ph_4B^-}$ in the present mixed solvent media.

Literature Cited

(1) Chakraborty, J. M.; Das, B. Electrical Conductances and Viscosities of Tetrabutylammonium Thiocyanate in Acetonitrile in the Temperature Range 25−45 °C. *Z. Phys. Chem.* **2004**, *218*, 219–230.

(2) Das, B.; Saha, N.; Hazra, D. K. Ionic Association and Conductances of Some Symmetrical Ttetraalkylammonium Salts in Methanol, Acetonitrile, and Methanol (1) + Acetonitrile (2) Mixtures at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 353–357.

(3) Das, B.; Saha, N. Electrical Conductances of Some Symmetrical Tetraalkylammonium Salts in Methanol, Acetonitrile, and Methanol (1) + Acetonitrile (2) Mixtures at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 2–5.

(4) Das, B.; Hazra, D. K. Studies on Viscosities, Conductances and Adiabatic Compressibilities of Some Tetraalkylammonium Perchlorates in 2-Methoxyethanol. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3470–3476.

(5) Das, B.; Hazra, D. K. Conductometric, Viscometric and Spectroscopic Investigations on the Solvation Phenomena of Alkali-Metal Ions and Ion Pairs in 2-Methoxyethanol. *J. Phys. Chem.* **1995**, *99*, 269–273.

(6) Das, B.; Hazra, D. K. Conductances of Selected Alkali Metal Salts in Aqueous Binary Mixtures of 2-Methoxyethanol at 25 °C. *J. Solution Chem.* **1998**, *27*, 1021–1030.

(7) Guha, C.; Chakraborty, J. M.; Karanjai, S.; Das, B. The Structure and Thermodynamics of Ion Association and Solvation of Some Thiocyanates and Nitrates in 2-Methoxyethanol Studied by Conductometry and FTIR Spectroscopy. *J. Phys. Chem. B* **2003**, *107*, 12814–12819.

(8) Victor, P. J.; Das, B.; Hazra, D. K. A Study on the Solvation Phenomena of Some Sodium Salts in 1,2-Dimethoxyethane from Conductance, Viscosity, Ultrasonic Velocity and FT-Raman Spectral Measurements. *J. Phys. Chem. A* **2001**, *105*, 5960–5964.

(9) Muhuri, P. K.; Das, B.; Hazra, D. K. Ionic Association of Some Lithium Salts in 1,2-Dimethoxyethane. A Raman Spectroscopic and Conductivity Study. *J. Phys. Chem. B* **1997**, *101*, 3329–3332.

(10) Haldar, P.; Das, B. Electrical Conductances of Tetrabutylammonium Bromide, Sodiumtetraphenylborate and Sodium Bromide in 2-Ethoxyethanol in the Temperature Range 35−50 °C. *Z. Phys. Chem* **2004**, *218*, 599–609.

(11) De, R.; Guha, C.; Das, B. Ion Association and Solvation Behaviour of Some 1−1 Electrolytes in 2-Ethoxyethanol Probed by Conductometric Study. *J. Solution Chem.* **2006**, *35*, 1505–1514.

(12) Covington, A. K.; Dickinson, T. *Physical Chemistry of Organic Solvent Systems*; Plenum Press: New York, 1973.

(13) Popovych, O.; Tomkins R. P. T. *Non Aquous Solution Chemistry*; Wiley-Interscience: New York, 1981.

(14) Lebed, A. V.; Kalugin, O. N.; Vyunnik, I. N. Properties of 1−1 Electrolytes Solutions in Ethylene Glycol at Tempereture from 5 to 175 °C. *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 2097–2101.

(15) Accascina, F.; D'Aprano, A. Electrical Conductance and Solvent-Solute Interactions. III. Sodium Bromide in Water−Ethylene Glycol Mixtures at 25°. *Ric. Sci.* **1966**, *36*, 257–260.

(16) Triolo, R.; D'Aprano, A. Electrical Conductance and Solvent-Solute Interactions. II. Tetrabutylammonium Bromide in Water-Ethylene Glycol Mixtures at 25°. *Ric. Sci.* **1964**, *7*, 443–450.

(17) Sakurai, M. Partial Molar Volumes of Ethylene Glycol and Water in Their Mixtures. *J. Chem. Eng. Data* **1991**, *36*, 422–427.

(18) Tsierkezos, N. G.; Molinou, I. E. Thermodynamic Properties of Water + Ethylene Glycol at 283.15, 293.15, 303.15, and 313.15 K. *J. Chem. Eng. Data* **1998**, *43*, 989–993.

(19) Lee, H.; Hong, W. H. Excess Volumes of Binary and Ternary Mixtures of Water, Methanol, and Ethylene Glycol. *J. Chem. Eng. Data* **1990**, *35*, 371–374.

(20) Åkerlöf, G. Dielectric Constants of Some Organic Solvent-Water Mixtures at Various Temperatures. *J. Am. Chem. Soc.* **1932**, *54*, 4125–4139.

(21) Lind, J. E., Jr.; Zwolenik, J. J.; Fuoss, R. M. Calibration of Conductance Cells at 25 °C with Aqueous Solutions of Potassium Chloride. *J. Am. Chem. Soc.* **1959**, *81*, 1557–1559.

(22) Fuoss, R. M. Paired Ions: Dipolar Pairs as Subset of Diffusion Pairs. *Proc. Natl. Acad. Sci.U.S.A.* **1978**, *75*, 16–20.

(23) Fuoss, R. M. Conductance−Concentration Function for the Paired Ion Model. *J. Phys. Chem.* **1978**, *82*, 2427–2440.

(24) Fuoss, R. M.; Shedlovsky, T. Extrapolation of Conductance Data for Weak Electrolytes. *J. Am. Chem. Soc.* **1949**, *71*, 1496–1498.

(25) Muhuri, P. K.; Hazra, D. K. Effect of Solvent Composition on Ionic Mobilities of Some Tetraalkylammonium and Common Ions in Propylene Carbonate + Methanol Media at 25 °C. *Z. Phys. Chem.* **1995**, *190*, 111–122.

(26) Mattina, C. F.; Fuoss, R. M. Conductance of Alkali Halides. XIII. Cesium Bromide, Lithium-7-Chloride, and Lithium-7-Iodide in Dioxane−Water Mixtures at 25°. *J. Phys. Chem.* **1975**, *79*, 1604–1610.

(27) Bahadur, L.; Ramanamurti, M. V. Conductance Studies in Amide−Water Mixtures. VI. Nitrates of Sodium, Potassium, and Ammonium in *N,N*-Dimethylformamide−Water Mixtures at 25 °C. *Can. J. Chem.* **1984**, *62*, 1051–1055.

(28) Islam, N.; Zaidi, S. B. A.; Ansari, A. A. Conductometric Studies of Ionic Association of Tetraalkylammonium Halides and Tetraphenylborate in *N,N*-Dimethylformamide−Methyl Ethyl Ketone at 25 °C. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 309–316.

(29) Srivastava, A.; Samant, R. A. Ionic Conductivity in Binary Solvent Mixtures. 1. Propylene Carbonate (20 Mass %) + Ethylene Carbonate at 25 °C. *J. Chem. Eng. Data* **1994**, *39*, 358–360.