J. Chem. Eng. Data **2004,** *49,* 1771−1774 **1771**

Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetraphenylborate, and Sodium Bromide in Acetonitrile (1) + Water (2) Mixtures at (308.15, 313.15, and 318.15)K

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The electrical conductances of solutions of tetrabutylammonium bromide (Bu_4NBr), sodium tetraphenylborate ($NaBPh_4$), and sodium bromide (NaBr) in acetonitrile (1) + water (2) mixed-solvent media containing 0.20 and 0.40 volume fractions of acetonitrile have been reported at (308.15, 313.15, 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 conductance have been estimated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as the "reference electrolyte". These three electrolytes are found to exist as free ions in both solvent mixtures in the temperature range of (308.15 to 318.15) K. Besides the relative permittivity and the viscosity of the media, specific interactions of the ions with the solvent media have been found to exhibit a profound influence on their mobilities. Although the association constants of the electrolytes do not vary significantly as a function of temperature, the limiting equivalent 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 great importance in obtaining information as to the solvation and association behavior of ions in solutions. We have investigated[1−7] 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 that enabled many to interpret the unique structure of the solvent. The present paper reports the molar conductivities of tetrabutylammonium bromide (Bu_4NBr), sodium tetraphenylborate ($NaBPh_4$), and sodium bromide (NaBr) in acetonitrile (1) + water (2) mixtures at (308.15, 313.15, and 318.15) K in order to obtain precise temperature-dependent single-ion conductivities because such data are practically nonexistent in mixed-solvent media.

Experimental Section

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorus pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.76570 g·cm^{-3} and a coefficient of viscosity of 0.3126 mPa·s at 308.15 K; these values are in good agreement with the literature values.[8] 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. The physical properties of acetonitrile (1) + water (2) mixed solvents used in this study at (308.15, 313.15, and 318.15) K are reported in Table 1. The relative permittivities of acetonitrile (1) + water (2) mixtures at the experimental temperatures were obtained with the equations as described in the literature[9] using the literature density and relative permittivity data of the pure solvents[8,10] and the densities of the mixed solvents given in Table 1.

Table 1. Properties of Acetonitrile (1) + Water (2) Mixtures Containing 0.20 and 0.40 Volume Fractions of Acetonitrile at (308.15, 313.15, and 318.15) K

T/K	ρ_0/g·cm^3	η_0/mPa·s	ϵ
	$\phi_1 = 0.20$		
308.15	0.96485	0.9067	67.94
313.15	0.96200	0.7833	66.38
318.15	0.95912	0.6984	64.84
	$\phi_1 = 0.40$		
308.15	0.92362	0.8200	60.07
313.15	0.91730	0.6803	58.57
318.15	0.91542	0.5611	57.32

All of these salts were Fluka purum or puriss grade. Tetrabutylammonium bromide (Bu_4NBr) 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 with a cell constant of 1.15 cm^{-1} and having an uncertainty of 0.01%. The cell was calibrated by the method of Lind and co-workers[11] 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.[12,13] 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

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10.1021/je049794d CCC: $27.50

Table 2. Equivalent Conductances and Corresponding Molarities of Electrolytes in Acetonitrile (1) + Water (2) Mixtures Containing 0.20 and 0.40 Volume Fractions of Acetonitrile at (308.15, 313.15, and 318.15) K

T = 308.15 K		T = 313.15 K		T = 318.15 K	
c/mol·dm^3	Λ/S·cm^2·mol^{-1}	c/mol·dm^3	Λ/S·cm^2·mol^{-1}	c/mol·dm^3	Λ/S·cm^2·mol^{-1}
		$\phi_1 = 0.20$			
		Bu_4NBr			
0.00755	114.66	0.00754	123.50	0.00751	135.88
0.01510	108.72	0.01509	117.49	0.01502	129.20
0.02264	104.17	0.02263	112.88	0.02252	124.09
0.03019	100.33	0.03018	108.99	0.03003	119.77
0.03773	96.95	0.03772	105.57	0.03754	115.96
0.04528	93.89	0.04527	102.47	0.04505	112.52
0.06073	88.46	0.06037	96.97	0.06006	106.42
0.07547	83.67	0.07539	92.14	0.07513	101.02
		$NaPh_4B$			
0.00667	77.71	0.00664	85.96	0.00664	94.69
0.00858	76.93	0.00854	84.91	0.00854	93.73
0.01145	75.91	0.01139	83.50	0.01139	92.45
0.01431	75.02	0.04244	82.26	0.01423	91.32
0.01907	73.71	0.01898	80.44	0.01898	89.67
0.02861	71.51	0.02847	77.40	0.02847	86.90
0.03814	69.65	0.03796	74.83	0.03796	84.54
0.04768	68.02	0.04745	72.57	0.04745	82.50
		NaBr			
0.00809	140.96	0.00808	152.61	0.00808	166.62
0.01618	135.56	0.01615	147.07	0.01610	160.70
0.02428	131.41	0.02423	142.81	0.02415	156.14
0.03237	127.91	0.03230	139.22	0.03220	152.29
0.04046	124.83	0.04037	136.06	0.04024	148.90
0.04856	122.05	0.04845	133.20	0.04805	145.93
0.06474	117.11	0.06458	128.13	0.06440	140.40
0.08093	112.75	0.08071	123.67	0.08050	135.60
		$\phi_1 = 0.40$			
		Bu_4NBr			
0.00752	106.67	0.00750	116.27	0.00747	124.04
0.01597	101.39	0.01499	111.04	0.01494	118.85
0.02256	98.22	0.02249	107.01	0.02242	114.86
0.03007	95.14	0.02999	103.63	0.02988	111.51
0.03759	92.41	0.03748	100.64	0.03735	108.55
0.04510	89.95	0.04498	97.95	0.04483	105.87
0.05263	87.69	0.05248	95.64	0.05229	103.41
0.06766	83.60	0.06747	90.99	0.06723	98.97
		$NaPh_4B$			
0.00773	76.32	0.00771	84.39	0.00769	91.89
0.00994	75.48	0.00991	83.47	0.00989	90.97
0.01326	74.38	0.01322	82.28	0.01319	89.78
0.01658	73.41	0.01652	81.23	0.01648	88.73
0.02210	71.99	0.02203	79.68	0.02197	87.18
0.03315	69.60	0.03304	77.09	0.03295	84.60
0.04419	67.59	0.04406	74.91	0.04394	82.41
0.05524	65.82	0.05507	72.99	0.05493	80.49
		NaBr			
0.00739	125.25	0.00737	138.12	0.00735	151.61
0.01181	123.55	0.01178	136.03	0.01175	149.26
0.01772	121.72	0.01776	133.79	0.01763	146.72
0.02363	120.18	0.02356	131.89	0.02351	144.58
0.02954	118.82	0.02945	130.22	0.02939	142.70
0.04432	115.92	0.04417	126.66	0.04408	138.70
0.05909	113.48	0.05889	123.67	0.05877	135.32
0.07386	111.33	0.07361	121.03	0.07347	132.34

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.

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

Results and Discussion

The measured molar conductances (Λ) of electrolyte solutions as functions of molar concentration (c) in acetonitrile (1) + water (2) mixtures with volume fractions of 0.20 and 0.40 of acetonitrile at (308.15, 313.15, and 318.15) K are given in Table 2.

The conductance data have been analyzed by the 1978 Fuoss conductance−concentration equation.[14,15] For a given set of conductivity values (c_j, Λ_j; j = 1, ..., n), three adjustable parameters—the limiting molar conductivity

(Λ^0), the association constant (K_A), and the association diameter (R)—are derived from the following set of equations:

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

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

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

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

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

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

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, 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 on the absolute scale; and β is twice the Bjerrum distance. The computations were performed on a computer using the program suggested by Fuoss. The initial Λ^0 values for the iteration procedure were obtained from a Shedlovsky extrapolation[16] of the data. Input for the program is the set (c_j, Λ_j; $j = 1, ..., n$), n, ϵ, η, T, and 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 that minimize the standard deviation, σ,

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

for a sequence of R values and then plotting σ against R; the best-fit R corresponds to the minimum in the σ versus R curve.

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

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 conductivities have been evaluated from the division of the Λ^0 values of Bu_4NBPh_4 using the following relationship:

$$\lambda^0(Bu_4N^+) = 0.517\Lambda^0(Bu_4NPh_4B) \tag{8}$$

as described in the literature.[17,18]

The limiting molar conductivity (Λ^0) of the “reference electrolyte” Bu_4NBPh_4 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 Bu_4NBr, $NaBPh_4$, and NaBr obtained in the present solvent media have been used to obtain the Λ^0 value of Bu_4NBPh_4 through the following equation:

$$\Lambda^0(Bu_4NBPh_4) = \Lambda^0(Bu_4NBr) + \Lambda^0(NaPh_4B) - \Lambda^0(NaBr) \tag{9}$$

Table 3. Derived Conductivity Parameters of Electrolytes in Acetonitrile (1) + Water (2) Mixtures Containing 0.20 and 0.40 Volume Fractions of Acetonitrile at (308.15, 313.15, and 318.15) K

T/K	Λ^0/S·cm^2·mol^{-1}	K_A/dm^3·mol^{-1}	R/Å	σ%^{a}
		$\phi_1 = 0.20$		
		Bu_4NBr		
308.15	125.96 ± 0.07	9.24 ± 0.04	16.47	0.05
313.15	135.50 ± 0.06	8.30 ± 0.03	14.77	0.03
318.15	149.27 ± 0.06	8.46 ± 0.03	14.85	0.03
		$NaPh_4B$		
308.15	84.16 ± 0.01	3.65 ± 0.01	11.24	0.02
313.15	94.05 ± 0.08	5.59 ± 0.08	12.11	0.03
318.15	102.92 ± 0.02	3.80 ± 0.02	11.50	0.03
		NaBr		
308.15	152.27 ± 0.04	5.51 ± 0.01	10.76	0.02
313.15	164.80 ± 0.02	4.97 ± 0.01	10.20	0.01
318.15	179.96 ± 0.02	4.81 ± 0.01	10.07	0.01
		$\phi_1 = 0.40$		
		Bu_4NBr		
308.15	117.52 ± 0.01	7.40 ± 0.01	12.11	0.01
313.15	128.59 ± 0.01	7.31 ± 0.01	11.97	0.01
318.15	137.35 ± 0.05	6.13 ± 0.02	11.09	0.03
		$NaPh_4B$		
308.15	84.06 ± 0.06	3.64 ± 0.03	10.55	0.04
313.15	93.26 ± 0.04	3.29 ± 0.03	10.50	0.05
318.15	101.79 ± 0.06	2.38 ± 0.04	10.47	0.07
		NaBr		
308.15	133.97 ± 0.07	1.92 ± 0.03	9.11	0.03
313.15	148.54 ± 0.08	2.29 ± 0.03	9.13	0.06
318.15	163.69 ± 0.10	2.27 ± 0.03	9.19	0.07

[a] $\sigma\% = 100\sigma/\Lambda^0$.

Table 4. Limiting Ionic Conductances in Acetonitrile (1) + Water (2) Mixtures Containing 0.20 and 0.40 Volume Fractions of Acetonitrile at (308.15, 313.15, and 318.15) K

	$\lambda^0_{\pm}$/S·cm^2·mol^{-1}			
T/K	Na^+	Bu_4N^+	Br^-	Ph_4B^-
		$\phi_1 = 0.20$		
308.15	56.21	29.90	96.06	27.95
313.15	62.77	33.47	102.03	31.28
318.15	68.03	37.34	111.93	34.89
		$\phi_1 = 0.40$		
308.15	51.40	34.95	82.57	32.66
313.15	57.84	37.89	90.70	35.42
318.15	65.34	39.00	98.35	36.45

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

The association constants (K_A) listed in Table 3 for all of these systems are practically negligible (i.e., $K_A < 10$). Therefore, the numerical values of K_A should not be taken seriously.[19] One can only conclude that these three electrolytes exist as free ions in both solvent mixtures in the temperature range of (308.15 to 318.15) K. This is expected because the relative permittivities of the solvent mixtures are fairly high ($57.32 \leq \epsilon \leq 67.94$).

The co-sphere diameter (R) values for all of the salts under study in the acetonitrile (1) + water (2) mixtures are also reported in Table 3. No systematic trend in R values for the salts studied has been observed. Because the best-fit conductivity parameters are reproduced equally well over a wide range of arbitrarily chosen R values, a comprehensive correlation of the co-sphere diameter of the studied systems could not be made in the present situation. This type of behavior has also been reported earlier.[18,20,21]

In both 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 $Br^- < Na^+ < Bu_4N^+ < Ph_4B^-$. Another interesting observation is that the limiting ionic equivalent conductances of Na^+ and Br^- ions decrease in going from 0.20 volume fraction of acetonitrile to 0.40 volume fraction of acetonitrile in the mixture at all temperatures investigated, whereas those for Bu_4N^+ and Ph_4B^- ions exhibit an increase in going from 0.20 to 0.40 volume fraction of acetonitrile in the mixture. This indicates that besides the relative permittivity and the viscosity of the media the specific interaction of the ions with the solvent media has a profound influence on their mobilities.

Although the association constants of the electrolytes do not vary significantly as a function of temperature, the limiting equivalent conductances of the electrolytes as well as the single-ion conductivity values increase appreciably with temperature.

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Received for review May 31, 2004. Accepted August 9, 2004. We thank the University of North Bengal for financial assistance.

JE049794D