Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetraphenylborate, and Sodium Bromide in *N*,*N*-Dimethylformamide (1) + Water (2) Mixtures at (308.15, 313.15, 318.15, and 323.15) K

Ramesh Sharma, Binod Sharma, Deepankar Pradhan, and Sanjay Dahal

Department of Chemistry, Sikkim Manipal Institute of Technology, Majhitar, Sikkim 737 132, India

Chanchal Das*

Department of Chemistry, Sikkim Government College, Gangtok, Sikkim 737 102, India

The electrical conductances of solutions of tetrabutylammonium bromide (Bu_4NBr), sodium tetraphenylborate ($NaBPh_4$), and sodium bromide (NaBr) in *N*,*N*-dimethylformamide (DMF) (1) + water (2) mixed solvent media containing (0.10, 0.20, and 0.40) mass fraction of DMF have been reported at (308.15, 313.15, 318.15, and 323.15) K. The conductance data have been analyzed by 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 limiting ionic conductances have been estimated from an appropriate division of the limiting molar conductivity of the "reference electrolyte" Bu_4NBPh_4. All of these three electrolytes are found to exist as free ions in the present solvent mixtures within the temperature range from (308.15 to 323.15) K. Although association constants of the electrolytes do not vary significantly as a function of temperature, the limiting molar conductances of electrolytes as well as single-ion conductivity values increase appreciably with temperature.

Introduction

Studies on transport properties are important in understanding the nature of molecular interactions in binary mixtures. The measurement of the electrical conductance of electrolytes in a binary solvent mixture provides valuable information about its transport properties. Conductometric properties of electrolyte solutions in the *N*,*N*-dimethylformamide (DMF) (1) + water (2) mixture have been a subject of interest for many years. Singh et al.[1] have published conductance data for some 1:1 electrolytes in the DMF + water mixture at 298.15 K. Bahadur and Ramanamurti[2] have reported on conductivities of some nitrate salts in the DMF + water mixture at 298.15 K. Szejgis et al.[3] have published their results on the conductivity properties of some alkali metal iodides in the DMF + water mixture at 298.15 K. Very recently, conductance data of quinolinium dichromate in the DMF + water mixture have been reported by Radhika and Manikyamba.[4] 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 the temperature. Therefore, it is interesting to study the solvation and association behavior of ions in DMF (1) + water (2) mixture as a function of temperature. The present paper reports the equivalent conductivities of tetrabutylammonium bromide (Bu_4NBr), sodium tetraphenylborate ($NaBPh_4$), and sodium bromide (NaBr) in DMF (1) + water (2) mixtures containing (0.10, 0.20, and 0.40) mass fraction of DMF at (308.15, 313.15, 318.15, and 323.15) K to obtain precise temperature-dependent single-ion conductivities.

Values of equivalent or molar conductance of an electrolyte at infinite dilution (Λ^0), ionic association constant (K_A), and the association diameter (R) can be obtained from conductance data as a function of concentration by using an appropriate equation. Several equations and approaches are available for the analysis of the conductance data, depending on the precision required. The selection of an equation for the determination of Λ^0, K_A, and R is open to debate.[5,6] In this paper conductance data have been analyzed by the Fuoss 78 conductance−concentration equation,[7,8] which is based on a more realistic physical picture than the primitive model.

Experimental Section

DMF (Merck, India, 99 % pure) was dried over molecular sieves and distilled under reduced pressure fractionally. The middle fraction was collected and redistilled. The physical properties of the purified solvent were found to be in good agreement with the literature values.[9,10] Table 1 shows the comparison of experimental values of density and viscosity of DMF with literature data.[9,10] The relative permittivities of pure DMF at different temperatures were obtained from the literature[11] and are included in Table 1. Triply distilled water with a specific conductance of less than $10^{-6}\ S\cdot cm^{-1}$ at 308.15 K was used for the preparation of the mixed solvents. The densities and viscosities of DMF (1) + water (2) 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 DMF (1) + water (2) mixtures at the experimental temperatures were obtained with the equations as described in the literature.[12] The relative permittivity values of the mixed solvents were calculated using the density and relative permittivity data of the pure solvents from literature and the densities of the mixed solvents and are given in Table 1.

All of the salts were of 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

---

* Corresponding author. E-mail: cdaschem@gmail.com.

10.1021/je1008813

Table 1. Physical Properties of DMF (1) + Water (2) Mixtures Containing (0.10, 0.20, and 0.40) Mass Fractions of DMF at (308.15, 313.15, 318.15, and 323.15) K

	ρ_0/g·cm^{-3}		η_0/mPa·s		
T/K	this work	lit.	this work	lit.	ε^a
			$w_1 = 0.10$		
308.15	0.99190		0.95256		74.28
313.15	0.98959		0.86976		72.75
318.15	0.98859		0.79598		71.27
323.15	0.98564		0.73179		69.83
			$w_1 = 0.20$		
308.15	0.99044		1.16339		73.11
313.15	0.98874		1.06719		71.62
318.15	0.98761		0.97459		70.16
323.15	0.98491		0.89386		68.74
			$w_1 = 0.40$		
308.15	0.98719		1.53943		70.03
313.15	0.98490		1.39177		68.61
318.15	0.98381		1.24013		67.23
323.15	0.98092		1.09601		65.87
			$w_1 = 1.00$		
308.15	0.93492	0.93571^b	0.71025	0.7063^c	35.78^d
313.15	0.93085	0.93073^b	0.66907	0.6683^c	34.94^d
318.15	0.92612	0.92598^b	0.64015	0.6330^c	34.16^d
323.15	0.92204	0.92114^b	0.59989	0.6004^c	33.36^d

[a] Calculated with the equations as described in ref 12. [b] From ref 9. [c] From ref 10. [d] From ref 11.

dried under vacuum at 353.15 K for 72 h. Sodium bromide (NaBr) was dried in vacuo for 72 h immediately prior to use and was used without further purification.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 1.15 cm^{-1} and having an uncertainty of 0.1 %. The cell was calibrated by the method of Lind et al.[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.[14−16] 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. Kinematic viscosities were measured using a suspended-level Ubbelohde-type viscometer.

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 relative uncertainties in density, viscosity, and conductivity were always within 0.01 %, 0.01 %, and 0.10 %, respectively. The uncertainty of the solute molality was estimated to be ± $2 \cdot 10^{-5}$ mol·kg^{-1}.

Results and Discussion

The measured molar conductances (Λ) of electrolyte solutions as functions of molar concentration (c) in DMF (1) + water (2) mixtures with mass fractions of 0.10, 0.20, and 0.40 of DMF 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.[7,8] For a given set of conductivity values (c), (c_j, Λ_j; $j = 1, ..., n$), three adjustable parameters, the limiting molar conductivity (Λ^0), association constant (K_A), and the association diameter (R), are derived from the following set of equations

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

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

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

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

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

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

where RX is the relaxation field effect, EL is the electrophoretic countercurrent, γ is the fraction of unpaired ions, α is the fraction of contact-pairs, K_A is the overall pairing constant evaluated from the association constant of contact-pairs, K_S, of solvent-separated pairs, K_R, ε is the relative permittivity of the solvent, e is the electronic charge, k_B is the Boltzmann constant, k^{-1} is the radius of the ion atmosphere, c is the molar concentration of the solution, f is the activity coefficient, T is the temperature in absolute scale, and β is twice the Bjerrum distance. The computations were performed on a computer using the program as suggested by Fuoss. The initial Λ^0 values for the iteration procedure were obtained from Shedlovsky extrapolation[17] of the data. Input for the program is the set (c_j, Λ_j; $j = 1, ..., n$), n, ε, η, T, initial value of Λ^0, and an instruction to cover a preselected range of R values.

In practice, calculations are performed by finding the values of Λ^0 and α which minimize the standard deviation, σ,

$$\sigma = [\sum [\Lambda_j(\mathrm{calcd}) - \Lambda_j(\mathrm{obsd})]^2/(n - 2)]^{1/2} \tag{7}$$

for a sequence of R values and then plotting σ against R; the best-fit R corresponds to the minimum in σ(%) versus R curve. However, for all of these electrolytes investigated, since a preliminary scan using a unit increment of R values from 4 to 20 produced no significant minima in the σ(%) versus 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[8]

$$d = 1.183(M/\rho_0)^{1/3} \tag{8}$$

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. A representative plot (Figure 1) for $NaBPh_4$ in DMF (1) + water (2) mixtures with $w_1 = 0.20$ at (308.15, 313.15, 318.15, and 323.15) 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.

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.

Table 2. Equivalent Conductances and Corresponding Molarities of Electrolytes in DMF (1) + Water (2) Mixtures at (308.15, 313.15, 318.15, and 323.15) K

$T = 308.15$ K		$T = 313.15$ K		$T = 318.15$ K		$T = 323.15$ K	
c / $\mathrm{mol \cdot dm^{-3}}$	Λ / $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$	c / $\mathrm{mol \cdot dm^{-3}}$	Λ / $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$	c / $\mathrm{mol \cdot dm^{-3}}$	Λ / $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$	c / $\mathrm{mol \cdot dm^{-3}}$	Λ / $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$
$w_1 = 0.10$							
Bu_4NBr							
0.01000	84.657	0.00998	94.459	0.00997	104.388	0.00994	113.883
0.02000	82.778	0.01995	92.226	0.01993	101.802	0.01987	111.349
0.02500	81.822	0.02494	91.106	0.02492	100.600	0.02484	110.001
0.03000	81.005	0.02993	90.282	0.0299	99.199	0.02981	108.731
0.03500	79.930	0.03492	88.942	0.03488	97.997	0.03478	107.513
0.04000	78.889	0.03991	87.750	0.03986	96.805	0.03977	105.993
0.04500	77.957	0.04482	86.581	0.04477	95.799	0.04464	104.567
0.05000	77.111	0.04989	85.435	0.04983	94.351	0.04969	103.182
NaBr							
0.01000	124.557	0.00997	137.465	0.00996	151.032	0.00993	164.186
0.02000	122.278	0.01995	135.118	0.01993	148.572	0.01987	162.079
0.02500	121.422	0.02494	134.012	0.02491	147.155	0.02484	160.499
0.03000	120.219	0.02993	133.318	0.02990	146.531	0.02981	159.191
0.03500	119.373	0.03492	132.115	0.03488	145.038	0.03478	158.187
0.04000	118.239	0.03991	130.852	0.03987	143.637	0.03974	156.621
0.04500	117.201	0.04498	129.496	0.04485	142.062	0.04471	155.616
0.05000	116.211	0.04988	128.642	0.04983	141.301	0.04968	153.809
$NaBPh_4$							
0.00750	71.296	0.00748	78.492	0.00748	86.010	0.00745	93.501
0.00800	71.121	0.00798	78.204	0.00797	85.909	0.00795	93.380
0.00850	71.099	0.00848	78.102	0.00847	85.701	0.00845	93.293
0.00900	70.930	0.00898	77.917	0.00897	85.643	0.00894	93.128
0.00950	70.902	0.00948	77.861	0.00947	85.492	0.00944	93.009
0.01000	70.757	0.00998	77.710	0.00997	85.302	0.00994	92.835
0.01500	69.538	0.01497	76.295	0.01495	84.086	0.01491	91.446
0.02000	68.378	0.01996	74.984	0.01994	82.819	0.01988	89.996
$w_1 = 0.20$							
Bu_4NBr							
0.00978	74.422	0.00976	82.433	0.00978	90.530	0.00976	98.795
0.01998	72.206	0.01995	80.049	0.02006	88.163	0.02000	96.314
0.02508	71.263	0.02503	79.163	0.02521	87.272	0.02513	95.185
0.02978	70.091	0.02972	78.087	0.03001	85.991	0.02989	93.874
0.03487	69.038	0.03481	77.044	0.03517	85.025	0.03506	92.869
0.03997	68.052	0.03990	75.893	0.04037	83.807	0.04025	91.761
0.04506	67.171	0.04497	74.745	0.04559	82.696	0.04545	90.434
0.05016	65.989	0.05006	73.623	0.05083	81.367	0.05067	89.122
NaBr							
0.00989	111.118	0.00987	123.353	0.00986	135.059	0.00983	146.927
0.01977	109.054	0.01973	120.603	0.01971	132.217	0.01965	144.611
0.02493	107.707	0.02428	119.362	0.02425	130.855	0.02418	143.035
0.02966	106.521	0.02960	117.790	0.02956	128.819	0.02948	141.388
0.03481	105.132	0.03475	116.183	0.03470	127.504	0.03460	139.295
0.03997	104.074	0.03989	115.008	0.03984	125.881	0.03973	137.415
0.04470	103.359	0.04461	114.099	0.04455	124.329	0.04442	136.642
0.04986	101.596	0.04976	112.550	0.04969	122.761	0.04954	134.827
$NaBPh_4$							
0.00748	63.405	0.00747	70.161	0.00746	77.269	0.00742	84.668
0.00804	63.045	0.00803	69.873	0.00802	77.088	0.00800	84.532
0.00849	62.897	0.00848	69.623	0.00847	77.013	0.00844	84.440
0.00905	62.689	0.00903	69.538	0.00902	76.683	0.00900	84.031
0.00949	62.599	0.00948	69.333	0.00947	76.483	0.00944	83.814
0.00994	62.264	0.00993	69.207	0.00991	76.237	0.00989	83.542
0.01497	60.769	0.01494	67.650	0.01494	74.413	0.01488	81.567
0.01999	59.001	0.01997	65.763	0.01995	72.509	0.01988	79.799
$w_1 = 0.40$							
Bu_4NBr							
0.00992	57.853	0.00990	65.051	0.00989	71.690	0.00986	79.007
0.01984	56.175	0.01979	63.151	0.01977	70.048	0.01971	77.271
0.02480	55.339	0.02474	62.416	0.02471	69.144	0.02463	76.604
0.02976	54.596	0.02969	61.557	0.02966	68.269	0.02957	75.632
0.03513	53.794	0.03505	60.770	0.03500	67.338	0.03489	74.896
0.04009	52.873	0.03999	60.007	0.03994	66.346	0.03981	74.094
0.04505	51.995	0.04494	59.090	0.04488	65.534	0.04474	73.153
0.05001	51.184	0.04989	58.133	0.04982	64.639	0.04966	72.310
NaBr							
0.00975	86.469	0.00973	97.310	0.00972	108.074	0.00969	118.714
0.02058	83.725	0.02056	93.969	0.02051	105.128	0.02045	115.526
0.02492	82.679	0.02486	93.133	0.02483	103.908	0.02476	114.211
0.03033	81.455	0.03026	91.728	0.03023	102.238	0.03014	112.563
0.03467	80.663	0.03459	91.086	0.03455	101.472	0.03444	111.779
0.04008	79.030	0.03999	89.668	0.03994	100.040	0.03982	110.376
0.04442	78.225	0.04434	88.503	0.04406	98.797	0.04413	109.140
0.04983	76.569	0.04972	87.111	0.04966	96.985	0.04951	107.476

Table 2. Continued

$T = 308.15$ K		$T = 313.15$ K		$T = 318.15$ K		$T = 323.15$ K	
$\frac{c}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{\Lambda}{\mathrm{S \cdot cm^2 \cdot mol^{-1}}}$	$\frac{c}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{\Lambda}{\mathrm{S \cdot cm^2 \cdot mol^{-1}}}$	$\frac{c}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{\Lambda}{\mathrm{S \cdot cm^2 \cdot mol^{-1}}}$	$\frac{c}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{\Lambda}{\mathrm{S \cdot cm^2 \cdot mol^{-1}}}$
			$NaBPh_4$				
0.00754	51.952	0.00752	58.786	0.00751	65.711	0.00741	72.161
0.00807	51.837	0.00805	58.695	0.00804	65.500	0.00801	72.040
0.00842	51.792	0.00840	58.616	0.00839	65.388	0.00836	71.917
0.00894	51.710	0.00892	58.489	0.00891	65.257	0.00889	71.736
0.00947	51.534	0.00945	58.364	0.00944	65.034	0.00941	71.662
0.01000	51.316	0.00997	58.254	0.00996	65.007	0.00993	71.581
0.01508	50.419	0.01510	56.884	0.01508	63.456	0.01503	70.039
0.02000	49.209	0.01995	55.607	0.01992	62.105	0.01986	68.701

Table 3. Derived Conductivity Parameters of Electrolytes in DMF (1) + Water (2) Mixtures at (308.15, 313.15, 318.15, and 323.15) K

$\frac{T}{\mathrm{K}}$	$\frac{\Lambda^0}{\mathrm{S \cdot cm^2 \cdot mol^{-1}}}$	$\frac{K_A}{\mathrm{dm^3 \cdot mol^{-1}}}$	$\frac{R}{\mathrm{Å}}$	$\frac{\sigma^a}{\%}$
		$w_1 = 0.10$		
		Bu_4NBr		
308.15	92.28 ± 0.45	2.40 ± 0.25	9.99	0.39
313.15	103.18 ± 0.58	2.72 ± 0.30	9.99	0.46
318.15	113.85 ± 0.48	2.76 ± 0.22	10.00	0.34
323.15	124.32 ± 0.70	2.67 ± 0.29	10.00	0.45
		NaBr		
308.15	133.52 ± 0.49	1.30 ± 0.18	5.94	0.31
313.15	147.29 ± 0.65	1.20 ± 0.22	5.94	0.38
318.15	161.96 ± 0.75	1.27 ± 0.23	5.95	0.39
323.15	176.05 ± 0.85	1.14 ± 0.23	5.95	0.41
		$NaBPh_4$		
308.15	77.05 ± 0.13	1.95 ± 0.21	9.49	0.13
313.15	84.89 ± 0.10	2.33 ± 0.15	9.49	0.09
318.15	92.65 ± 0.10	1.47 ± 0.13	9.50	0.09
323.15	100.84 ± 0.15	1.56 ± 0.18	9.50	0.18
		$w_1 = 0.20$		
		Bu_4NBr		
308.15	81.61 ± 0.43	3.74 ± 0.30	10.08	0.41
313.15	90.11 ± 0.50	3.37 ± 0.31	10.09	0.44
318.15	98.70 ± 0.54	2.97 ± 0.29	10.09	0.44
323.15	107.53 ± 0.51	2.82 ± 0.25	10.09	0.38
		NaBr		
308.15	119.94 ± 0.66	2.35 ± 0.29	6.03	0.44
313.15	133.07 ± 0.55	2.55 ± 0.22	6.04	0.33
318.15	146.22 ± 0.82	2.78 ± 0.31	6.04	0.44
323.15	158.88 ± 0.02	2.40 ± 0.35	6.04	0.52
		$NaBPh_4$		
308.15	69.71 ± 0.15	6.03 ± 0.30	9.58	0.15
313.15	76.72 ± 0.19	5.00 ± 0.33	9.59	0.18
318.15	84.72 ± 0.15	5.26 ± 0.23	9.59	0.12
323.15	92.57 ± 0.12	4.80 ± 0.18	9.59	0.09
		$w_1 = 0.40$		
		Bu_4NBr		
308.15	63.61 ± 0.40	4.01 ± 0.36	10.31	0.48
313.15	71.04 ± 0.34	3.39 ± 0.27	10.31	0.38
318.15	78.34 ± 0.43	3.09 ± 0.30	10.31	0.43
323.15	85.77 ± 0.37	2.25 ± 0.22	10.32	0.35
		NaBr		
308.15	94.44 ± 0.68	4.06 ± 0.42	6.26	0.54
313.15	105.48 ± 0.52	3.47 ± 0.28	6.26	0.37
318.15	117.43 ± 0.74	3.37 ± 0.36	6.26	0.48
323.15	128.50 ± 0.60	2.90 ± 0.26	6.27	0.36
		$NaBPh_4$		
308.15	56.47 ± 0.13	3.99 ± 0.31	9.81	0.18
313.15	64.05 ± 0.13	4.45 ± 0.27	9.81	0.15
318.15	71.48 ± 0.10	4.41 ± 0.18	9.81	0.11
323.15	78.23 ± 0.14	3.42 ± 0.23	9.82	0.14

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

In the absence of accurate transport number data for the system in the temperature range investigated here, we have used the "reference electrolyte" method for the division of Λ^0 into their ionic components. Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) has been used as the "reference electrolyte".[18] This electrolyte was used as the "reference electrolyte" also by Fuoss and Hirsch[19] to evaluate the limiting ionic conductances in several organic solvents. We have divided the Λ^0 values of Bu_4NBPh_4 into ionic components using the following relationships.[20]

$$\Lambda^0(Bu_4NBPh_4) = \lambda^0(Bu_4N^+) + \lambda^0(Ph_4B^-) \qquad (9)$$

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

$$\lambda^0(Bu_4N^+) = 0.517\Lambda^0(Bu_4NBPh_4) \qquad (11)$$

The ionic radii (r) values have been taken from the literature.[21,22] The limiting molar conductivity (Λ^0) of the "reference electrolyte" Bu_4NBPh_4 was obtained by considering the Kohlrausch rule which allows the calculation of Λ^0 value for a given electrolyte by the appropriate combination of others. The Λ^0 values of Bu_4NBr, $NaBPh_4$, and NaBr obtained in this medium have been used to obtain the Λ^0 value of Bu_4NBPh_4 through the following equation

$$\Lambda^0(Bu_4NBPh_4) = \Lambda^0(Bu_4NBr) + \Lambda^0(NaBPh_4) - \Lambda^0(NaBr) \qquad (12)$$

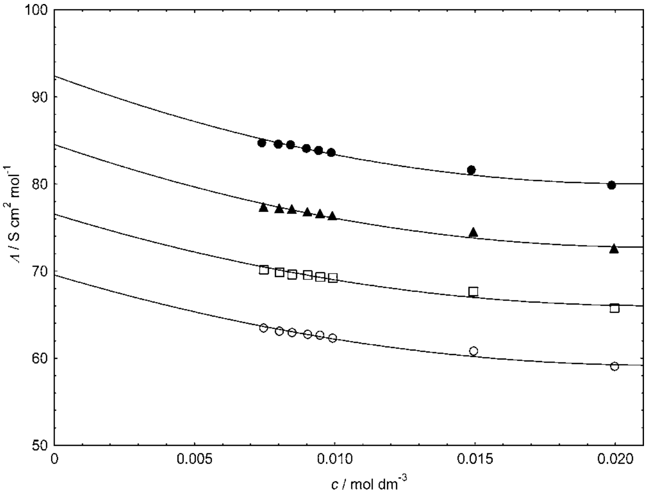

Figure 1. Variation of molar conductivity as a function of concentration for sodium tetraphenylborate in DMF (1) + water (2) with $w_1 = 0.20$. Experimental: ○, 308.15 K; □, 313.15 K; ▲, 318.15 K; and ●, 323.15 K. The lines represent the calculations according to eqs 1 through 6.

Table 4. Limiting Ionic Conductances in DMF (1) + Water (2) Mixtures Containing (0.10, 0.20, and 0.40) Mass Fractions of DMF at (308.15, 313.15, 318.15, and 323.15) K

	$\lambda^0_\pm$/S·cm^2·mol^{-1}			
T/K	Na^+	Bu_4N^+	Br^-	Ph_4B^-
		$w_1 = 0.10$		
308.15	59.75	18.51	73.77	17.30
313.15	65.19	21.08	82.10	19.70
318.15	71.13	23.02	90.83	21.52
323.15	77.12	25.39	98.93	23.72
		$w_1 = 0.20$		
308.15	54.55	16.22	65.39	15.16
313.15	60.41	17.45	72.66	16.31
318.15	66.75	19.23	79.47	17.97
323.15	72.66	21.31	86.22	19.91
		$w_1 = 0.40$		
308.15	44.09	13.26	50.35	12.38
313.15	49.75	15.31	55.73	14.30
318.15	55.83	16.74	61.60	15.65
323.15	61.08	18.35	67.42	17.15

The limiting ion 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., $K_A < 10$). So, the numerical values of K_A should not be taken seriously.[2] One can only conclude that all of these electrolytes exist as free ions in the present DMF (1) + water (2) solvent mixtures within the temperature range of (308.15 to 323.15) K. This is expected because the relative permittivity of the solvent mixtures are fairly high ($65.87 \leq \varepsilon \geq 74.28$), thus promoting the dissociation of electrolytes.

Figure 2 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 charged ion—solvent interactions, possibly due to the changing solvodynamic size of the ions.

In all of the mixed solvent media, the limiting ionic equivalent conductances (λ^0) decreases in the order $\lambda^0_{Br^-} > \lambda^0_{Na^+} > \lambda^0_{Bu_4N^+} > \lambda^0_{Ph_4B^-}$ at each temperature range, indicating that the sizes of these ions as they exist in solution 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 equivalent conductances of all of the ions decrease in going from 0.10 mass fraction of DMF to 0.40 mass fraction of DMF in the mixture at all temperatures investigated.

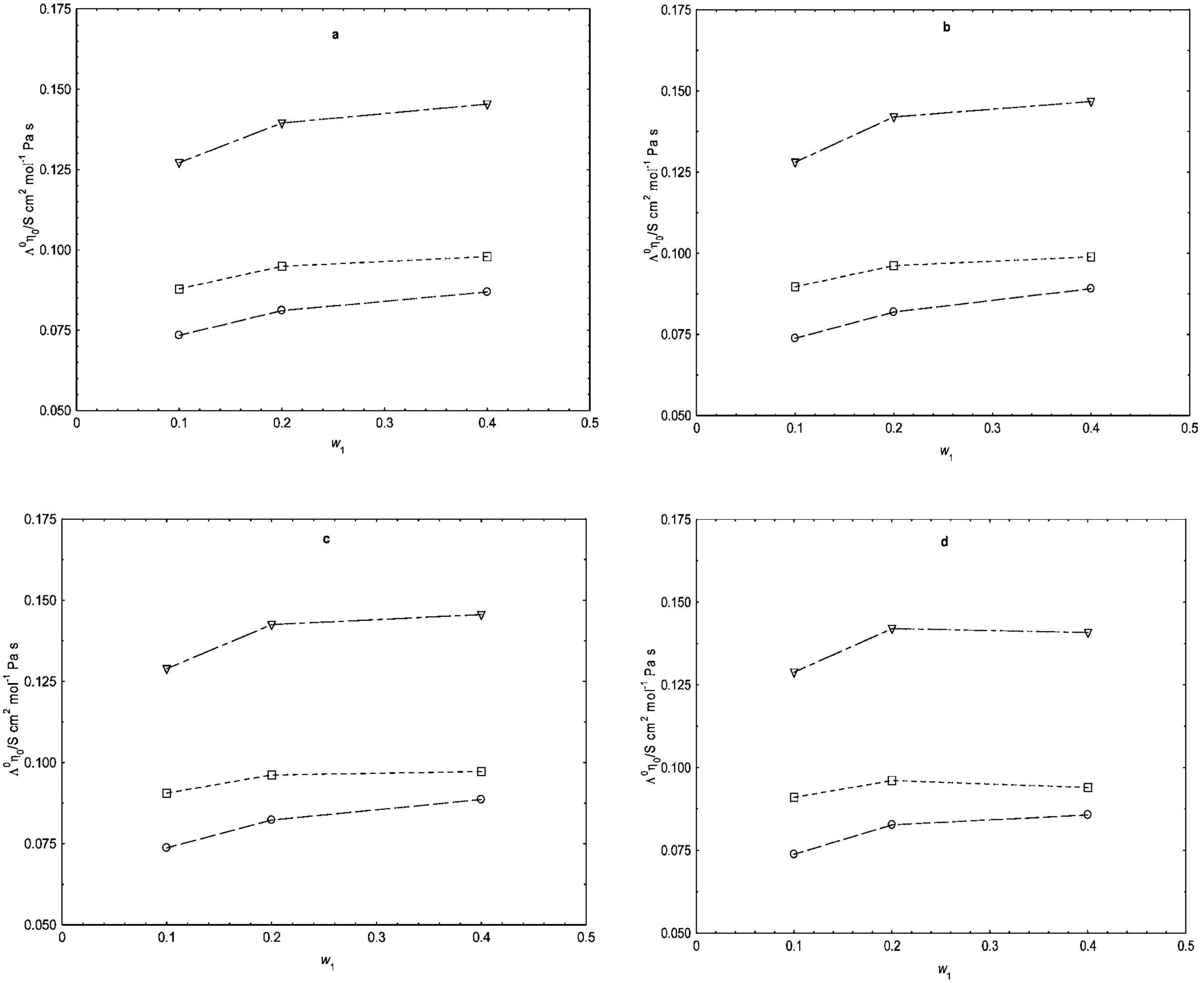

Figure 2. Walden products of: ○, sodium tetraphenylborate; □, sodium tetrabutylammonium bromide; and △, sodium bromide in DMF (1) + water (2) at a, 308.15 K; b, 313.15 K; c, 318.15 K; and d, 323.15 K.

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

Acknowledgment

The authors are grateful to Prof. Bijan Das, Department of Chemistry, North Bengal University, for his valuable suggestions.

Literature Cited

(1) Singh, D.; Bahadur, L.; Ramanamurti, M. V. Conductance studies in amide-water mixtures. II. Sodium salts in *N*,*N*-dimethylformamide-water mixtures at 35 °C. *J. Solution Chem.* **1977**, *6*, 703–715.

(2) 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*, 1051–1056.

(3) Szejgis, A.; Bald, A.; Gregorowicz, J. Conductivity study on some alkali metal iodides in aqueous *N*,*N*-dimethylformamide solutions at 298.15 K. *Monatsh. Chem.* **1997**, *128*, 1093–1100.

(4) Radhika, V.; Manikyamba, P. Conductance and solvation behavior of quinolinium dichromate in binary mixtures of water with *N*,*N*-dimethylformamide. *J. Chem. Eng. Data* **2008**, *53*, 2766–2769.

(5) Safonova, L. P.; Sakharov, D. V.; Shmukler, L. E.; Kolker, A. M. Conductance studies of 1−1 electrolytes in *N*,*N*-dimethylformamide at various temperatures. *Phys. Chem. Chem. Phys.* **2001**, *3*, 819–823.

(6) Safonova, L. P.; Kolker, A. M. Conductometry of electrolyte solutions. *Russ. Chem. Rev.* **1992**, *61*, 959–973.

(7) Fuoss, R. M. Paired ions: dipolar pairs as subset of diffusion pairs. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 16–20.

(8) Fuoss, R. M. Conductance-concentration functions for the paired ion model. *J. Phys. Chem.* **1978**, *82*, 2427–2440.

(9) Marcheselli, L.; Marchetti, A.; Tagliazucchi, M.; Tassi, L.; Tosi, G. *N*,*N*-dimethylformamide---2-methoxyethanol solvent system: Densities and excess molar volumes at different temperatures. *J. Chem. Soc., Faraday Trans.* **1992**, *21*, 3159–3163.

(10) Akhtar, S.; Omar Faruk, A. N. M.; Saleh, M. A. Viscosity of aqueous solutions of formamide, *N*-methylformamide and *N*,*N*-dimethylformamide. *Phys. Chem. Liq.* **2001**, *39*, 383–399.

(11) Marchetti, A.; Preti, C.; Tagliazucchi, M.; Tassi, L.; Tosi, G. The *N*,*N*-dimethylformamide + ethane-1,2-diol solvent system. Dielectric constant, refractive index and related properties at various temperatures. *J. Chem. Eng. Data* **1991**, *36*, 365–368.

(12) Pal, M.; Bagchi, S. Ultraviolet-visible spectrophotometric determination of ion-association constants for alkylpyridinium iodides. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 961–972.

(13) 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.

(14) Das, C.; Das, B. Effect of tetraalkylammonium salts on the micellar behavior of lithium dodecyl sulfate: A conductometric and tensiometric study. *J. Mol. Liq.* **2008**, *137*, 152–158.

(15) Das, C.; Chakraborty, T.; Ghosh, S.; Das, B. Mixed micellization of anionic-nonionic surfactants in aqueous media: A physicochemical study with theoretical consideration. *Colloid Polym. Sci.* **2008**, *286*, 1143–1155.

(16) Sharma, R.; Pradhan, B.; Subba, D.; Das, C. Electrical conductances of tetrabutylammonium bromide, sodium tetraphenylborate and sodium bromide in *N*,*N*-dimethylformamide at (308.15, 313.15, 318.15, and 323.15) K. *J. Chem. Eng. Data* **2009**, *54*, 2902–2905.

(17) Fuoss, R. M.; Shedlovsky, T. Extrapolation of conductance data for weak electrolytes. *J. Am. Chem. Soc.* **1949**, *71*, 1496–1498.

(18) Krumgalz, B. S. Separation of limiting equivalent conductances into ionic contribution in non-aqueous solution by indirect methods. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 571–587.

(19) Fuoss, R. M.; Hirsch, E. Single ion conductances in non-aqueous solvents. *J. Am. Chem. Soc.* **1960**, *82*, 1013–1017.

(20) 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.

(21) Gill, D. S. Evaluation of solvated radii of ions in non-aqueous solvents. *Electrochem. Acta* **1979**, *24*, 701–703.

(22) Gill, D. S.; Sekhri, M. B. New approach to the evaluation of single-ion conductances in pure and mixed non-aqueous solvents [Part 2]. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 119–125.

Received for review August 26, 2010. Accepted October 11, 2010.

JE1008813