Ionic Association and Conductances of Some Symmetrical Tetraalkylammonium Salts in Methanol, Acetonitrile, and Methanol (1) + Acetonitrile (2) Mixtures at 298.15 K

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Electrical conductance measurements are reported for tetrahexylammonium bromide (Hex_4NBr), tetraheptylammonium bromide (Hep_4NBr), and tetrabutylammonium tetraphenylborate (Bu_4NPh_4B) in methanol, acetonitrile, and methanol (1) + acetonitrile (2) binary mixtures at 298.15 K. The conductance data have been analyzed by the Fuoss conductance−concentration equation in terms of the limiting molar conductance ($\Lambda°$), the association constant (K_A), and the distance of closest approach of ions (R). Single-ion conductivities have been determined on the basis of tetrabutylammonium tetraphenylborate as the reference electrolyte. The results have been interpreted in terms of ion−ion and ion−solvent interactions.

Introduction

Extensive studies on the electrical conductivities in various mixed organic solvents have been performed in recent years (Muhuri and Hazra, 1995; Srivastava and Samant, 1994; Doe et al., 1990; Taniewska-Osinska et al., 1989; Islam et al., 1989; Papadopopulos, 1989; Niazi, 1988) to examine the nature and magnitude of ion−ion and ion−solvent interactions. Such solvent properties as the viscosity and the relative permittivity have also been taken into consideration, which help determine the extent of ion association and the solute−solvent interactions.

Very recently, we have repoted (Das and Saha, 2000) the results of conductance measurements on four symmetrical tetraalkylammonium bromides, viz., tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), and tetrapentylammonium bromide (Pen_4NBr) in methanol, acetonitrile, and methanol (1) + acetonitrile (2) ranging in composition from 0.20 to 0.80 mole fraction of methanol at 298.15 K. We have now extended this work to study the conductometric behavior of the next two higher homologues, tetrahexylammonium bromide (Hex_4NBr) and tetraheptylammonium bromide (Hep_4NBr), along with that of the salt tertabutylammonium tetraphenylborate (Bu_4NPh_4B) in the same solvent systems at 298.15 K. The salt tertabutylammonium tetraphenylborate has been used as a “reference electrolyte” to estimate the single-ion conductivities.

Experimental Section

Methanol (E. Merck, India, uvasol grade, 99.5% pure) was dried over molecular sieves and distilled fractionally. The middle fraction was collected and redistilled. The purified solvent had a density of 0.786 54 $g·cm^{-3}$ and a viscosity of 0.545 mPa·s at 298.15 K. These values agree well with the literature values (Doe et al., 1984).

Acetonitrile (E. Merck, India, 99% pure) was distilled with P_2O_5 and then redistilled over CaH_2. The purified solvent had a density of 0.776 86 $g·cm^{-3}$ and a coefficient of viscosity of 0.345 mPa·s at 298.15 K; these values are also found to be in good agreement with literature values (Moumouzias et al., 1991; Singh et al., 1994).

The purities as checked by gas chromatography were found to be >99.8% for methanol and >99.5% for acetonitrile.

Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described earlier by us (Das and Hazra, 1991; Muhuri et al., 1996). Tetrabutylammonium tetraphenylborate was prepared and purified as reported in the literature (Srivastava and Samant, 1994).

A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion of molality to molarity was done using the density values.

The densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (298.15, 308.15, and 318.15) K with doubly distilled water and benzene. Details have been described earlier (Das and Hazra, 1993, 1995a; Saha et al., 1995).

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip type cell (cell constant = 0.751 cm^{-1}) with an accuracy of 0.01%. The cell was calibrated by the method of Lind and co-workers (Lind et al., 1959) using aqueous potassium chloride solutions. Measurements were made in an oil bath maintained at (298.15 ± 0.005) K, as described earlier (Das and Hazra, 1992, 1995b). Several independent solutions were prepared, and conductance measurements were performed with each of these to ensure the reproducibility of the results. Corrections were made for the specific conductances of the solvent.

The experimental values of the densities (ρ), the viscosities (η), and the relative permittivities (ϵ) of methanol (1) + acetonitrile (2) at 298.15 K are not available at the relevant compositions in which conductance measurements have been carried out. The available values of ρ and η (from Saha et al., 1995) and those of ϵ (from Gill and Chauhan, 1984) are, therefore, plotted against the mole fraction of methanol, and the values of ρ, η, and ϵ at all the desired compositions have been generated from the smooth master curves and are given in Table 1.

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Table 1. Densities (ρ), Viscosities (η), and Relative Permittivities (ϵ) for Methanol (1) + Acetonitrile (2) at 298.15 K

x_1[a]	ρ/g·cm^{-3} [b]	η/mPa·s[b]	ϵ[c]
0.00	0.77686	0.346	35.95
0.20	0.77952	0.334	35.47
0.40	0.78212	0.343	34.92
0.60	0.78465	0.373	34.30
0.80	0.78680	0.435	33.58
1.00	0.78654	0.545	32.62

[a] x_1 is the mole fraction of methanol. [b] From Saha et al., 1995. [c] From Gill and Chauhan, 1984.

Results

Molar conductances (Λ) of electrolyte solutions as a function of molar concentration (c) are given in Table 2 in different solvent mixtures at 298.15 K.

The conductance data have been analyzed by the 1978 Fuoss conductance–concentration equation (Fuoss, 1978a,b). For a given set of conductivity values (c_j, Λ_j; $j = 1, ..., n$), three adjustable parameters, the limiting molar conductivity ($\Lambda°$), the association constant (K_A), and the distance of closest approach of ions (R), are derived from the following set of equations:

$$\Lambda = p[\Lambda°(1 + R_X) + E_L] \tag{1}$$

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

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

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

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

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

where R_X is the relaxation field effect, E_L is the electrophoretic countercurrent, k^{-1} is the radius of the ion atmosphere, ϵ is the relative permittivity of the solvent, e is the electron charge, k_B is the Boltzmann constant, γ is the fraction of solute present as unpaired ion, c is the molarity of the solution, f is the activity coefficient, T is the absolute temperature, and β is twice the Bjerrum distance. The computations were performed on a computer using the program suggested by Fuoss. The initial $\Lambda°$ values for the iteration procedure were obtained from Shedlovsky extrapolation 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 $\Lambda°$, and an instruction to cover a preselected range of R values.

In practice calculations are performed by finding the values of $\Lambda°$ and α that minimize the standard deviation, σ,

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

for a sequence of R values and then plotting σ against R; the best-fit R corresponds to the minimum of the σ versus R curve. First, approximate runs over a fairly wide range of R values are made to locate the minimum, and then a fine scan around the minimum is made. Finally, with this minimizing value of R, the corresponding $\Lambda°$ and K_A are calculated.

The values of $\Lambda°$, K_A, and R obtained by this procedure are reported in Table 3.

Discussion

The conductances of solutions of Bu_4NPh_4B in acetonitrile and methanol have also been reported earlier by other workers (Accascina et al., 1959; Barthel et al., 1990; Berns and Fuoss, 1960; Brown and Fuoss, 1960; Coetzee and Cunningham, 1965; Coplan and Fuoss, 1964). They analyzed their data with equations different from the one used in the present analysis. Conductance data of sufficient precision with the exception of the works mentioned above for any of the systems investigated here do not exist in the literature. Consequently, we compared the $\Lambda°$, and K_A values for the above-mentioned systems with those from the present work (Table 3). It has been observed that the values of $\Lambda°$ calculated from the previous conductance equations do not differ significantly from the values of $\Lambda°$ calculated from the 1978 Fuoss conductance–concentration equation. The values of K_A obtained from our work are, however, generally higher. This discrepancy may be attributed to the different models used for analysis of the experimental data. We have reanalyzed the literature experimental data with the 1978 Fuoss conductance equation, and the results are included in Table 3 for comparison. In each case a better fit of the conductance data to the 1978 Fuoss equation than to the previous equations has been observed. The $\Lambda°$ and K_A values in methanol are found to be in good agreement with our results. In acetonitrile, however, though our $\Lambda°$ value agrees well with the redetermined $\Lambda°$ values from literature conductance data, our K_A value exhibits fair agreement with those obtained after redetermination.

The limiting ionic conductivities have been evaluated from division of the $\Lambda°$ values of Bu_4NPh_4B using the following relationship:

$$\lambda^0(Bu_4N^+) = 1.07\lambda^0(Ph_4B^-) \tag{8}$$

as described earlier by us (Das and Hazra, 1998; Muhuri and Hazra, 1995) in conjunction with our recently reported $\Lambda°$ values of Bu_4NBr in the same solvent mixtures (Das and Saha, 2000). The values of the limiting ionic conductivity ($\lambda^\circ_\pm$) in methanol, acetonitrile, and methanol (1) + acetonitrile (2) mixtures calculated using the above equation are given in Table 4. Also included in this table are the λ°_+ values for Et_4N^+, Pr_4N^+, Bu_4N^+, and Pen_4N^+ ions obtained from the division of the $\Lambda°$ values of their bromide salts taken from our earlier work (Das and Saha, 2000).

The $\lambda°$ value of the bromide ion decreases gradually from pure acetonitrile to pure methanol, apparently because of the decrease in the relative permittivity of the medium with increasing methanol content. The $\lambda°$ value of each of the tetraalkylammonium ions, on the other hand, goes through a maximum at a mole fraction of 0.2 of methanol in the mixture on passing from acetonitrile to methanol. This indicates simultaneous control of the viscosity of the medium on the ionic conductivities along with the relative permittivity.

The association constants (K_A) in Table 3 indicate that the salts Hex_4NBr and Hep_4NBr are slightly associated in acetonitrile and methanol (1) + acetonitrile (2) mixtures. Tetrabutylammonium tetraphenylborate is, on the other hand, found to be somewhat more associated. In a given solvent mixture, the extent of association is always higher with Hex_4NBr compared to Hep_4NBr, similar to those observed earlier, due to an apparent decrease in the ion–

Table 2. Molar Conductances (Λ) and Corresponding Molarities (c) of Tetraalkylammonium Bromides in Methanol (1) + Acetonitrile (2) at 298.15 K

10^4c/mol·dm^{-3}	Λ/S·cm^2·mol^{-1}	10^4c/mol·dm^{-3}	Λ/S·cm^2·mol^{-1}	10^4c/mol·dm^{-3}	Λ/S·cm^2·mol^{-1}	10^4c/mol·dm^{-3}	Λ/S·cm^2·mol^{-1}
			$x_1 = 0.00$				
Hex_4NBr		Hep_4NBr		Bu_4NPh_4B		Bu_4NPh_4B	
4.625	143.83	4.700	140.31	4.611	112.99	40.121	99.73
7.510	141.82	7.523	138.40	7.030	111.33	45.001	98.62
10.245	140.21	10.315	136.82	10.002	109.66		
15.004	137.92	14.988	134.63	15.002	107.37		
19.989	135.92	19.966	132.70	19.568	105.61		
25.133	134.07	25.105	130.91	25.666	103.60		
30.206	132.50	30.008	129.45	30.106	102.30		
34.946	131.15	35.001	128.07	34.413	101.14		
40.213	129.75	40.117	126.75				
45.882	128.41	45.994	125.42				
			$x_1 = 0.20$				
Hex_4NBr		Hep_4NBr		Bu_4NPh_4B			
4.616	136.29	4.536	132.46	4.532	114.21		
10.103	132.72	9.885	129.03	10.063	110.30		
12.109	131.68	12.212	127.86	12.125	109.14		
15.118	130.29	14.996	126.61	14.998	107.69		
20.302	128.21	20.108	124.61	20.108	105.42		
25.218	126.50	25.103	122.92	25.033	103.53		
29.815	125.06	30.000	121.45	29.987	101.82		
35.216	123.53	35.014	120.07	34.959	100.27		
40.028	122.28	40.123	118.79	40.103	98.80		
45.002	121.07	44.982	117.66	44.999	97.50		
			$x_1 = 0.40$				
Hex_4NBr		Hep_4NBr		Bu_4NPh_4B		Bu_4NPh_4B	
4.502	130.58	4.515	126.84	4.506	109.42	44.001	92.99
10.300	126.87	10.118	123.33	10.110	105.47		
12.012	126.00	11.998	122.41	12.031	104.39		
14.992	124.65	15.009	121.07	15.246	102.77		
20.038	122.65	20.004	119.16	20.103	100.63		
25.075	120.92	24.996	117.50	25.214	98.67		
30.192	119.36	30.036	116.01	29.999	97.03		
34.996	118.02	35.034	114.67	35.112	95.44		
40.102	116.72	39.981	113.45	40.008	94.05		
43.998	115.79	44.033	112.52				
			$x_1 = 0.60$				
Hex_4NBr		Hep_4NBr		Bu_4NPh_4B			
4.301	120.83	4.403	116.73	4.410	101.79		
10.007	117.35	10.010	113.42	9.985	97.96		
12.103	116.35	11.173	112.42	11.996	96.86		
15.008	115.11	14.999	111.26	14.998	95.38		
19.988	113.29	20.011	109.44	20.013	93.24		
25.120	111.60	25.021	107.92	25.102	91.30		
30.004	110.22	29.998	106.53	30.080	89.67		
34.996	108.92	34.996	105.27	34.998	88.19		
40.015	107.73	40.130	104.10	40.021	86.80		
42.990	107.06	43.002	103.46	42.998	86.03		
			$x_1 = 0.80$				
Hex_4NBr		Hep_4NBr		Bu_4NPh_4B			
4.003	104.90	4.019	100.85	4.213	87.59		
9.499	101.87	9.533	97.94	9.546	84.17		
12.518	100.60	12.501	96.74	12.506	82.71		
15.016	99.67	14.998	95.86	15.111	81.56		
19.982	98.07	20.103	94.25	20.008	79.63		
25.009	96.60	25.212	92.93	24.990	77.98		
30.107	95.34	30.246	91.71	30.145	76.41		
34.998	94.22	35.013	90.68	34.868	75.12		
37.500	93.67	37.498	90.17	37.488	74.45		
40.006	93.18	39.990	89.70	40.011	73.85		
			$x_1 = 1.00$				
Hex_4NBr		Hep_4NBr		Bu_4NPh_4B			
3.504	82.33	3.512	80.43	4.101	70.00		
5.499	81.28	5.208	79.55	7.456	68.03		
7.512	80.35	7.509	78.50	10.017	66.77		
10.016	79.38	9.996	77.56	16.104	64.34		
14.002	78.09	15.012	75.98	18.266	63.60		
20.018	76.46	20.006	74.71	20.004	63.04		
22.506	75.87	22.516	74.12	25.106	61.54		
24.300	75.47	25.123	73.56	29.982	60.24		
30.117	74.26	30.017	72.56	34.808	59.15		
34.791	73.43	35.011	71.70				

Table 3. Derived Conductivity Parameters for Tetraalkylammonium Bromides in Methanol (1) + Acetonitrile (2) at 298.15 K

x_1	Λ°/S·cm^2·mol^{-1}	K_A/dm^{-3}·mol^{-1}	R/Å	$100\sigma/\Lambda^\circ$
		Hex_4NBr		
0.00	151.44 ± 0.02	25.86	15.50	0.02
0.20	143.95 ± 0.01	27.70	15.90	0.01
0.40	138.01 ± 0.01	29.12	16.10	0.01
0.60	127.63 ± 0.01	30.31	16.30	0.01
0.80	110.66 ± 0.01	32.06	16.80	0.02
1.00	86.75 ± 0.01	34.43	16.70	0.02
		Hep_4NBr		
0.00	147.85 ± 0.02	25.11	15.60	0.02
0.20	139.93 ± 0.01	26.95	15.80	0.01
0.40	134.16 ± 0.01	28.31	16.00	0.01
0.60	123.49 ± 0.02	29.65	16.20	0.01
0.80	106.48 ± 0.01	30.39	16.50	0.01
1.00	84.79 ± 0.01	34.20	17.10	0.02
		Bu_4NPh_4B		
0.00	120.10 ± 0.01	33.31	16.30	0.01
	(119.40,[a] 119.26,[b] 119.46,[c] 119.44,[d] 120.02[e])	(26.15,[a] 20.19,[b] 22.78,[c] 21.73,[d] 15.47[e])		
0.20	121.90 ± 0.01	44.65	17.20	0.01
0.40	117.02 ± 0.01	48.61	17.60	0.01
0.60	108.97 ± 0.03	53.79	18.00	0.01
0.80	93.85 ± 0.01	60.35	18.00	0.01
1.00	75.24 ± 0.02 (75.92[f])	72.98 (71.61[f])	19.80	0.02

[a] Values obtained from recalculation of the data from Accascina et al. (1959) using the Fuoss conductance equation. [b] Values obtained from recalculation of the data from Brown and Fuoss (1960) using the Fuoss conductance equation. [c] Values obtained from recalculation of the data from Berns and Fuoss (1960) using the Fuoss conductance equation. [d] Values obtained from recalculation of the data from Coetzee and Cunningham (1965) using the Fuoss conductance equation. [e] Values obtained from recalculation of the data from Barthel et al. (1990) using the Fuoss conductance equation. [f] Values obtained from recalculation of the data from Coplan and Fuoss (1964) using the Fuoss conductance equation.

Table 4. Limiting Ionic Conductances ($\lambda^\circ_\pm$) in Methanol (1) + Acetonitrile (2) at 298.15 K

	x_1					
ion	0.00	0.20	0.40	0.60	0.80	1.00
Et_4N^+	85.53	88.62	86.94	81.91	72.39	59.62
Pr_4N^+	71.11	72.09	70.49	65.28	57.12	45.26
Bu_4N^+	62.08	63.01	60.49	56.33	48.51	38.89
Pen_4N^+	56.54	57.42	56.04	51.18	43.85	34.78
Hex_4N^+	51.44	51.96	50.28	46.33	40.25	30.77
Hep_4N^+	47.85	47.94	46.43	42.19	36.07	28.81
Ph_4B^-	58.02	58.89	56.53	52.64	45.34	36.35
Br^-	100.00	91.99	87.73	81.30	70.41	55.98

dipole interaction (Kay et al., 1965; Islam et al., 1989). For each salt, however, ionic association increases slowly with increasing methanol content in the solvent mixtures. This is quite expected due to the gradual decrease in the relative permittivity of the medium with increasing amount of methanol in the mixtures.

It can be seen from Table 3 and our earlier work (Das and Saha, 2000) that the distances of closest approach of ions (R) for the tetraalkylammonium bromide salts vary from 15.50 to 17.10 Å for the $R_4N^+Br^-$ ion pairs in different solvent mixtures. Although not too much can be deduced from the best-fit R values, since the conductivity parameters are reproduced almost equally well over a wide range of arbitrarily chosen R values, some generalizations can be made about the R values obtained from the 1978 Fuoss equation because this presupposes that ion pairs may be of solvent-separated or contact variety. The sums of the crystallographic radii (a) for Et_4NBr to Hep_4NBr are 5.80 to 7.68 Å. The diameters (d) of methanol + acetonitrile were calculated as described earlier by us (Das and Hazra, 1998). For the present solvent system, the values of R vary from 3.75 (methanol) to 4.37 (acetonitrile) Å. The values of R are, thus, always higher than $a + d$, which has a maximum value of 12.05 Å for Hep_4NBr in acetonitrile, indicating that $R_4N^+Br^-$ ion pairs are solvent separated in all the solvent media investigated. Such large values of R for tetraalkylammonium salts have also been observed in different pure and mixed solvents (Islam et al., 1989; Muhuri and Hazra, 1991, 1995; Srivastava and Samant, 1994).

The Stokes' radii of the tetraalkylammonium ions are found to be smaller than their corresponding crystallographic radii. This is physically unacceptable. They seem to indicate that the ionic radii on the basis of the Stokes' law do not appear to be correct. This probably arises from the fact that the electrolytic solutions are different from the model which underlies the Stokes' law. We have, therefore, estimated the actual radii of the ions in solution using the Stokes' law as modified by Gill (Gill and Sekhri, 1982). The results indicate poor solvation of the large tetraalkylammonium ions, particularly in the methanol-rich region, and strong solvation of the bromide ion in the pure as well as mixed solvents.

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