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Conductimetric Studies of Ionic Association of Tetraalkylammonium Halides and Tetraphenylborate in *N,N*-Dimethylformamide-Methyl Ethyl Ketone Mixtures at 25 °C

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The molar conductivities of Et_4NBr, n-Pr_4NBr, n-Bu_4NBr, and n-Bu_4NBPh_4 have been measured in *N,N*-dimethylformamide-methyl ethyl ketone (DMF-MEK) mixtures ($34.5 \geqslant D \geqslant 20.10$) over the maximum concentration range ($2\times D^3\times 10^{-7}$ mol dm^{-3}) along with the densities and viscosities of the solvent mixtures at 25 °C. The conductance data have been analyzed by using the Fuoss-1978 (F78) conductance equation and the results compared with those obtained from the Justice (J) and the Fuoss-Onsager-Skinner (FOS) equations. The molar conductivities at infinite dilution (Λ_0), the thermodynamic association constant (K_A) and the distance or the ion-size parameter (R or $a°$) are evaluated from these data. A better fit of the parameters was provided by the F78 equation which yielded K_A and R values. The Λ_0 and the K_A values are found to increase with decrease in the dielectric constant of the medium and in a given solvent mixture they follow the order $Et_4NBr > n$-$Pr_4NBr > n$-$Bu_4NBr > n$-Bu_4NBPh_4.

Extensive studies on the electrolytic conductivities in various pure and mixed aprotic solvents have been made[1—8] to examine the magnitude and the nature of ion-ion and ion-solvent interactions in terms of the limiting molar conductance, the ion-size parameter and the ionic association constant. The solvent properties like the viscosity and the dielectric constant 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 study deals with the mixtures of *N,N*-dimethylformamide and methyl ethyl ketone (DMF-MEK) both of which are dipolar aprotic and in the pure state have no tendencies[9—11] to self-association through the dipole-dipole interactions. Recently,[12] it has been reported that the physical properties of DMF-MEK mixtures over the entire composition range show an ideal behavior for the physicochemical investigations in the cases of 1:1 electrolytes. Consequently, the investigation of conductance behavior of tetraalkylammonium halides and tetraphenylborate has been undertaken with a view to examining the suitability of the F78[13,14] conductance equation over those of the Justice[15] and the FOS[16] conductance equations.

Experimental

Methyl ethyl ketone was treated several times with saturated potassium carbonate solution to remove the acid impurities and the two layers thus obtained were separated. After removing most of the water by distillation, the ketone was dried over sodium sulfate and anhydrous potassium carbonate for several days. The decanted liquid was fractionally distilled several times until the measured density (0.7999 kg m^{-3}), viscosity (0.379 kg m^{-1} s^{-1}) and specific conductance: $(2—3.5)\times 10^{-8}$ S cm^{-1} at 25 °C were found to be comparable with those of the corresponding literature values.[12,17]

N,N-Dimethylformamide was purified by keeping it over anhydrous sodium carbonate for 24 hours and was then distilled under reduced pressure in a dry nitrogen atmosphere and the fraction distilling at 73 °C/57 mmHg (1 mmHg≈133.322 Pa) was collected. The purified solvent had a density: 0.9443 kg m^{-3}; viscosity: 0.795 kg m^{-1} s^{-1} and specific conductance: $(1—2)\times 10^{-7}$ S cm^{-1}, which agree well with those of the reported[18,19] values.

Tetrabutylammonium tetraphenylborate (n-Bu_4NBPh_4) was prepared[20] by dissolving sodium tetraphenylborate in conductivity water (2% solution) and filtered to remove a small amount of insoluble impurities. To this, an equivalent amount of tetrabutylammonium bromide in 2% aqueous solution was slowly added. The bulky white precipitate thus obtained was washed five times by decantation. After preliminary drying, the product was recrystallized four times from 1:3 water-acetone mixture and finally dried for several days at 40 °C and 10^{-4} mmHg pressure (mp 223—225 °C).

The pure samples of Et_4NBr, n-Pr_4NBr (both, Fluka, AG), and n-Bu_4NBr (Eastman, AG) procured from the supplier were used as such.

Conductance measurements were carried out by the IMPEDENCE BRIDGE, 1608-A (General Radio & Co., U.S.A.) at a constant frequency of 1 kHz with an accuracy of ±0.05—0.005%. The Pyrex conductivity cell (cell constant, 0.7891 cm^{-1}) having bright platinum disc electrodes was used. The cell was calibrated by the method of Lind and co-workers[21] using the decinormal potassium chloride solutions. The overall reproducibility of the conductance measurement was found to be within ca. ±0.025%.

The solvent mixtures were prepared by weight and in each case initially a concentrated electrolytic solution ($C_{max} = 2\times D^3\times 10^{-7}$)[22] of the salt was prepared and several solutions of different concentrations were prepared by the method of dilution. Dielectric constants of the solvent mixtures were taken from the literature.[12]

All the measurements were carried out in an atmosphere of pure and dry nitrogen at 25±0.01 °C in a thermostated oil bath.

Table 1. Properties of Solvent Mixtures at 25 °C

Solvent No.	$X_{\mathrm{DMF\%}}$	ρ / g cm^{-3}	η / cP[a]	D	q/Å[b]
1	00.00	0.7999 (0.79987)[c]	0.3790 (0.3795)[c]	18.01[c]	15.10
2	11.46	0.8157	0.419	20.10	13.94
3	22.55	0.8311	0.452	21.84	12.83
4	33.29	0.8456	0.487	23.53	11.90
5	43.70	0.8613	0.527	25.40	11.03
6	53.80	0.8768	0.569	27.40	10.23
7	73.10	0.9043	0.655	31.01	9.04
8	82.32	0.9179	0.699	32.95	8.50
9	91.29	0.9312	0.745	34.50	8.12
10	100.00	0.9443 (0.9440)[c]	0.795 (0.796)[c]	36.71[c]	—

a) 1 P=0.1 Pa s. b) Bjerrum distance. c) Ref. 35.

Results and Discussion

The physical properties of the solvents employed in computation are listed in Table 1. The molar conductivities, Λ(S cm^2 mol^{-1}) of dilute electrolytic solutions of varying concentrations, C(mol dm^{-3}) of $\mathrm{Et_4NBr}$, n-$\mathrm{Pr_4NBr}$, n-$\mathrm{Bu_4NBr}$, and n-$\mathrm{Bu_4NBPh_4}$ in mixtures of DMF–MEK are recorded at 25 °C (Table 2).

The concentration dependence of the above conductance data has been analyzed in terms of the F78 equation[13,14] and the parameters thus obtained are compared with those obtained by employing the J and the FOS equations.[15,16]

The F78 equation[13,14] based on the concept of diffusion controlled steady state approach is of the form,

$$\Lambda = [1 - \alpha(1 - \gamma)][\Lambda_0(1 + \Delta x/x) + \Delta\Lambda_e] \tag{1}$$

where Λ_0 is the limiting equivalent conductance, the term $\Delta x/x$ represents the relaxation effect, $\Delta\Lambda_e$ the electrophoretic effect, while γ denotes the fraction of solute present as free ions and α is the contact pair parameter. Both Δx and $\Delta\Lambda_e$ depend on the values of the diameter of the Gurney cosphere, R, the dielectric constant and the viscosity of the medium. The parameters and the auxilliary variables are related by a set of the following equations:

$$\begin{aligned} K_R &= (1 - \alpha)(1 - \gamma)/C\gamma^2 f^2 \\ &= (4\pi NR^3/3000)\exp(\beta/R) \end{aligned} \tag{2}$$

$$K_S = \alpha/(1 - \alpha) \tag{3}$$

The conductometric association constant, K_A is given by

$$K_A = (1 - \gamma)/C\gamma^2 f^2 = K_R/(1 - \alpha) \tag{4}$$

while the activity coefficient, f, is

$$-\ln f = \beta\kappa/2(1 + \kappa R) \tag{5}$$

in which $\beta = e^2/DkT$ and $\kappa^2 = 8\pi\beta\gamma n = \pi\beta NC/125$. The relevant terms have their usual significance. For this purpose, the PARACOND[23] computer program designed for the symmetrical electrolytes has been used.

Similarly, each set of conductance data has been analyzed using Justice's modification[15] of the Fuoss-Hsia equation[24] and the relevant constants derived by employing the Fernandez-Prini equation.[1] The Fuoss-Hsia equation is given by,

$$\begin{aligned} \Lambda = \Lambda_0 &- S(C\gamma)^{1/2} + E\gamma C\ln(C\gamma) \\ &+ J_1 C\gamma - J_2(C\gamma)^{3/2} - \Lambda C f_{\pm}^2 \gamma K_A \end{aligned} \tag{6}$$

where γ is the degree of dissociation, $f_{\pm}$ the mean molar activity coefficient, and all other terms have their usual significance. The thermodynamic association constant is given by

$$K_A = (1 - \gamma)/C\gamma^2 f_{\pm}^2 \tag{7}$$

in which the activity coefficient for the neutral ion pair is taken as unity. The activity coefficients are obtained using the Debye–Hückel equation,

$$\ln f_{\pm} = -A(\gamma C)^{1/2}/\{1 + BR_j(C\gamma)^{1/2}\}. \tag{8}$$

As proposed by Justice,[15] the distance parameter, R_j of Eq. 8 has been taken as the Bjerrum critical distance, q ($=e^2/2DkT$). The analysis of the data in terms of Eq. 6 has been carried out by a pit-mapping method[25] in which Λ_0, R_j, and K_A are varied until a minimum is located for the standard error of estimate. This latter quantity, σ_Λ is defined by

$$\sigma_\Lambda = \{\textstyle\sum(\Lambda_{\mathrm{obs}} - \Lambda_{\mathrm{calc}})^2/(N - 3)\}^{1/2}. \tag{9}$$

Finally, the above set of conductance data (Table 2) has been analyzed in terms of the FOS equation,[16]

$$\begin{aligned} \Lambda = \Lambda_0 &- S(C\gamma)^{1/2} + EC\gamma\log(6E'_1 C\gamma) \\ &+ LC\gamma - C\gamma f_{\pm}^2 \Lambda K_A \end{aligned} \tag{10}$$

for associated electrolytes. The symbols used have their usual meaning. Kay's computer program[26] based on the least square method of calculation is employed here.

The values of the best fit parameters of Λ_0, K_A, and the distance or the ion-size parameter (R or $a°$)

Table 2. Molar Conductivities, Λ(S cm^2 mol^{-1}) and Molar Concentrations, C(mol dm^{-3}) of Et_4NBr, n-Pr_4NBr, n-Bu_4NBr, and n-Bu_4NBPh_4 in DMF–MEK Mixtures at 25 °C

Et_4NBr		n-Pr_4NBr		n-Bu_4NBr		n-Bu_4NBPh_4	
$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
Solvent 2							
14.127	102.51	15.842	99.95	16.697	97.72	16.277	80.29
11.772	106.52	13.941	102.44	12.987	102.13	12.660	82.66
8.829	112.77	11.617	106.01	9.740	106.97	9.495	85.23
7.063	117.43	8.713	111.42	7.546	111.09	6.330	88.42
5.886	121.11	6.280	117.21	5.844	114.87	4.682	90.53
2.943	133.56	3.645	125.76	2.922	123.68	2.843	93.49
1.762	140.92	1.741	134.79				
Solvent 3							
17.453	97.38	17.246	96.16	14.889	94.08	20.432	74.75
15.177	100.29	14.996	98.81	12.947	96.06	17.945	76.02
12.467	104.35	12.318	102.45	10.635	98.71	13.051	78.93
9.696	109.41	9.077	107.91	8.272	101.93	10.246	80.95
6.981	115.67	6.898	112.51	5.956	105.78	8.512	82.39
3.491	127.17	5.174	116.95	2.978	112.42	5.932	85.01
2.327	132.67	3.449	122.52	1.489	117.16	3.589	88.04
Solvent 4							
24.743	94.68	23.315	89.48	25.470	86.16	25.351	71.52
21.516	97.44	19.429	92.41	16.621	92.36	21.126	73.23
18.328	100.56	15.753	95.66	12.994	95.71	17.484	74.92
14.996	104.39	12.953	98.57	10.526	98.41	13.000	77.44
12.372	108.05	8.831	103.91	8.475	101.01	9.219	80.08
8.837	113.91	5.251	110.14	5.129	106.31	5.548	83.42
5.438	121.52	2.913	115.79	3.570	109.51	2.533	87.33
2.472	131.16						
Solvent 5							
22.840	95.42	21.182	86.26	30.771	82.58	13.388	73.55
19.861	97.99	18.419	88.37	26.758	84.61	11.642	74.58
16.918	100.96	15.130	91.16	22.793	87.02	9.917	75.76
13.051	105.56	11.768	94.71	18.101	90.16	7.650	77.43
10.151	109.81	8.826	98.32	13.987	93.54	5.950	79.06
7.613	114.26	7.061	101.01	9.458	98.19	4.463	80.48
4.567	121.16	4.236	106.12	6.680	101.91	2.231	83.37
2.284	128.29	2.118	111.34	4.734	105.06	1.336	84.91
Solvent 6							
30.107	90.08	29.914	80.82	29.779	79.75	23.945	67.33
26.494	92.36	25.482	83.27	24.815	82.24	19.156	69.16
22.078	95.56	21.501	85.80	20.121	85.04	15.963	70.56
17.901	99.08	17.201	89.04	16.544	87.46	13.683	71.71
14.719	102.28	13.761	92.10	12.408	90.85	10.642	73.43
10.036	107.96	9.382	96.93	7.445	96.07	7.982	75.21
7.360	112.18	6.880	100.41	3.223	101.62	4.368	78.24
3.310	120.65	3.440	106.64			2.395	80.48
Solvent 7							
31.754	85.77	32.989	77.53	31.714	75.47	31.903	62.44
28.225	87.91	28.686	79.63	27.578	77.21	27.741	63.57
23.815	90.77	24.436	81.91	22.653	79.87	23.632	64.79
19.052	94.41	19.993	84.63	17.619	82.78	19.335	66.29
15.242	98.01	15.344	88.04	12.686	86.38	15.951	67.58
9.145	105.16	11.376	91.58	7.611	91.18	11.601	69.55
5.716	110.67	7.368	95.99	5.074	94.26	7.569	71.76
3.629	114.95	3.924	101.06	3.171	97.11	4.579	73.92
						3.187	75.17
Solvent 8							
28.677	80.63	29.444	75.89	22.086	71.51	17.945	62.57
24.580	82.91	26.767	77.07	17.436	73.71	15.834	63.34
19.118	86.44	23.555	78.63	13.251	75.89	13.459	64.28

Table 2. (Continued)

Et_4NBr		n-Pr_4NBr		n-Bu_4NBr		n-Bu_4NBPh_4	
$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
Solvent 8							
14.388	90.18	19.629	80.75	9.465	78.48	10.767	65.50
8.603	95.99	14.722	83.83	6.023	81.26	7.690	67.06
6.145	99.26	9.815	87.68	3.614	83.68	5.984	68.12
3.441	103.64	4.907	92.89	2.581	85.01	3.230	70.11
		2.181	96.73			1.795	71.49
Solvent 9							
31.214	78.28	28.693	73.66	28.587	69.05	22.468	60.52
26.755	80.19	24.594	75.12	23.823	70.65	18.617	61.66
20.809	83.13	19.129	77.63	17.867	72.97	14.480	63.04
14.406	87.01	14.346	80.12	12.994	75.24	10.860	64.45
8.644	91.58	7.173	84.96	10.210	76.77	7.082	66.24
5.402	94.86	4.304	87.56	5.105	80.25	4.287	67.87
3.745	96.91	3.311	88.63	3.576	81.59	2.603	69.11

corresponding to the minimum standard deviations from the relevant (F78, J and FOS) equations are listed in Tables 3-I, 3-II, and 3-III, respectively.

The above calculations have been carried out on a VAX-11/780 computer.

A comparison of the applicability of the above three equations to the conductance is made here. The computed values of Λ_0 for the salts under study in various DMF–MEK mixtures obtained using the F78, the J and the FOS equations are found to be close to each other. On the one hand, these Λ_0 show the usual decrease in their values with increase in the size of the ions in the order: $Et_4\overset{+}{N}>n\text{-}Pr_4\overset{+}{N}>n\text{-}Bu_4\overset{+}{N}>Ph_4B^-$ in accord with the trend in the behavior of their parent Λ values. On the other hand, the Λ_0 values are found to increase with decrease in the dielectric constant of the solvent mixtures. Such a situation has also been reported earlier for several pure[11,27] and mixed aprotic solvents[28,29] and has been attributed to a number of effects such as the solvent structure and the ion–solvent interactions. The solvent structure effects are apparently reflected by the viscosity behavior which is marked by its increase with increase in the mol% of DMF. The excess thermodynamic parameters[12] of the present system show an ideal mixing which suggest the absence of intermolecular interactions in DMF–MEX mixtures similar to those observed for the DMF–acetone system.[6]

The K_A values (Table 3) obtained using the F78 equation are found to be ca. 23.26% and ca. 30.38% higher than those obtained from the J and the FOS equations, respectively. An increase in the K_A values with decrease in the dielectric constant of the medium is in accordance with those reported earlier[27–33] for similar system. The applicability of the various theories of ion association can be examined in terms of the dependence of $\log K_A$ upon $1/D$ (Fig. 1). The nonlinearity of the plot suggests the applicability of the F78, FOS and Justice theories of ionic association.

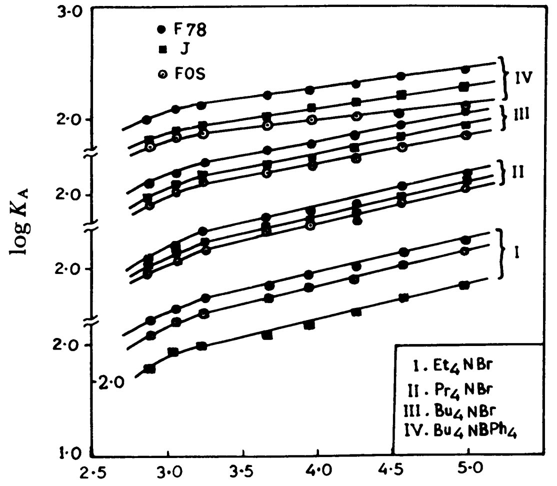

Fig. 1. $\log K_A$ vs. $100/D$.

Further, it is evident from Table 3 that the K_A values for all the salts in a given dielectric constant decrease with the increasing size of the cations in the order, $Et_4\overset{+}{N}>n\text{-}Pr_4\overset{+}{N}>n\text{-}Bu_4\overset{+}{N}\approx BPh_4^-$, similar to those observed earlier[11,30,34,35] due to apparent decrease in the ion–dipole interaction.

The distance or the ion-size parameter (R or a°) values obtained using different equations are compared with the crystallographic radii of the salts under study. The values of R_j or a° obtained using the J and the FOS equations in some of the solvent mixtures (Tables 3-II and 3-III) are less than the corresponding crystallographic radii of the ion pairs and are, therefore, not understandable. The F78 equation, on the other hand, predicts meaningful values of R as 11.40 to 17.55 Å in the media of $34.50\geqslant D\geqslant 20.10$ which are also more than the Bjerrum critical distance, q $(=e^2/2DkT)$ unlike the R_j or a° values (of J or the FOS equations) which are found to be less than the q values. It may, however, be noted that the J equation

Table 3-I. Best Fit Parameters for Et_4NBr, n-Pr_4NBr, n-Bu_4NBr, and n-Bu_4NBPh_4 in DMF–MEK Mixtures at 25 °C, Using the F78 Conductance Equation

Salt	Λ_0 S cm^{2}mol^{-1}	K_A dm^3 mol^{-1}	K_R	K_S	α	R Å	σ_Λ/%
			Solvent 9				
Et_4NBr	104.43±0.01	164.81	18.82	7.76	0.885	12.80	0.01
n-Pr_4NBr	94.51±0.04	143.48	21.09	5.80	0.853	13.65	0.04
n-Bu_4NBr	86.99±0.01	128.16	22.53	4.69	0.824	14.15	0.01
n-Bu_4NBPh_4	72.72±0.01	111.34	26.32	3.23	0.763	15.36	0.01
			Solvent 8				
Et_4NBr	113.09±0.03	223.98	16.62	12.48	0.926	11.40	0.03
n-Pr_4NBr	102.42±0.03	179.08	17.63	9.16	0.902	11.85	0.03
n-Bu_4NBr	90.23±0.05	159.54	21.46	6.34	0.864	13.35	0.06
n-Bu_4NBPh_4	74.74±0.01	127.15	27.46	3.63	0.784	15.30	0.02
			Solvent 7				
Et_4NBr	127.39±0.05	276.92	20.66	12.40	0.925	12.40	0.03
n-Pr_4NBr	111.51±0.05	233.44	23.09	9.11	0.901	13.30	0.03
n-Bu_4NBr	105.21±0.06	209.88	24.11	7.70	0.885	13.65	0.05
n-Bu_4NBPh_4	80.30±0.02	137.41	30.15	3.56	0.780	15.50	0.02
			Solvent 6				
Et_4NBr	134.02±0.04	308.08	27.32	10.27	0.911	13.20	0.02
n-Pr_4NBr	118.49±0.01	291.98	30.33	8.62	0.896	14.15	0.00
n-Bu_4NBr	112.29±0.03	244.59	31.17	6.85	0.872	14.40	0.02
n-Bu_4NBPh_4	85.92±0.01	165.90	34.17	3.85	0.794	15.24	0.01
			Solvent 5				
Et_4NBr	141.23±0.02	392.53	31.82	11.34	0.918	13.50	0.01
n-Pr_4NBr	121.00±0.05	327.13	35.22	8.28	0.892	14.50	0.03
n-Bu_4NBr	119.29±0.05	281.78	37.82	6.45	0.866	15.20	0.03
n-Bu_4NBPh_4	89.36±0.04	194.13	39.80	3.88	0.795	15.70	0.05
			Solvent 4				
Et_4NBr	146.95±0.05	462.65	38.29	11.08	0.917	14.10	0.02
n-Pr_4NBr	129.16±0.02	361.53	42.25	7.56	0.883	15.15	0.01
n-Bu_4NBr	123.04±0.02	322.51	43.88	6.35	0.864	15.55	0.01
n-Bu_4NBPh_4	94.56±0.01	213.59	46.66	3.58	0.782	16.20	0.01
			Solvent 3				
Et_4NBr	152.25±0.01	650.28	42.92	14.15	0.934	13.90	0.01
n-Pr_4NBr	143.83±0.02	552.89	45.91	11.04	0.917	14.70	0.006
n-Bu_4NBr	126.15±0.01	380.57	53.43	6.12	0.859	16.45	0.006
n-Bu_4NBPh_4	98.00±0.02	254.28	57.31	3.44	0.775	17.25	0.02
			Solvent 2				
Et_4NBr	161.05±0.01	823.58	52.02	14.83	0.936	14.35	0.005
n-Pr_4NBr	150.97±0.02	650.72	58.10	10.19	0.911	15.80	0.01
n-Bu_4NBr	142.45±0.04	540.16	61.16	7.83	0.886	16.45	0.02
n-Bu_4NBPh_4	103.41±0.02	284.32	66.78	3.26	0.765	17.55	0.014

yields higher values of R_j ($25.40 \geqslant D \geqslant 20.10$) than the crystallographic radii of the ion pairs. Although not too much can be deduced from the best-fit R values as they are particularly susceptible to the choice of conductance equation. However, some generalization can be made about the R values obtained from the F78 equation since this presupposes that ion pairs may be of solvent-separated or contact ion pair variety. For a contact ion pair (CIP), R is simply taken as the sum of the ionic radii whereas for the solvent separated ion pair (SSIP), $R=\bar{a}+ds$, where $\bar{a}$ is taken as the sum of the ionic radii and ds is the diameter of solvent molecules. The ds value estimated to be 4.98 Å for MEK and 5.03 Å for DMF. Consequently, the resultant association constant is greater for smaller ions than those for the larger ones because the smaller ion prefers to form an additional CIP with the formation of SSIP in DMF–MEK mixtures and it is apparent from Table 3-I that the SSIP formation constant, K_R increases and CIP formation constant, K_S

Table 3-II. Best Fit Parameters for $\mathrm{Et_4NBr}$, n-$\mathrm{Pr_4NBr}$, n-$\mathrm{Bu_4NBr}$, and n-$\mathrm{Bu_4NBPh_4}$ in DMF-MEK Mixtures at 25 °C, Using the J Conductance Equation

Salt	Λ_0	K_A	R_j	σ_Λ/%
	S cm^2 mol^{-1}	dm^3 mol^{-1}	Å	
		Solvent 9		
$\mathrm{Et_4NBr}$	104.40±0.01	134.53	2.43	0.01
n-$\mathrm{Pr_4NBr}$	94.42±0.05	107.06	5.98	0.05
n-$\mathrm{Br_4NBr}$	86.96±0.01	91.01	5.07	0.01
n-$\mathrm{Bu_4NBPh_4}$	72.72±0.01	69.029	4.46	0.01
		Solvent 8		
$\mathrm{Et_4NBr}$	113.06±0.04	197.48	1.79	0.03
n-$\mathrm{Pr_4NBr}$	102.37±0.03	149.45	5.24	0.03
n-$\mathrm{Bu_4NBr}$	90.30±0.06	127.15	3.48	0.05
n-$\mathrm{Bu_4NBPh_4}$	74.76±0.02	83.44	3.79	0.02
		Solvent 7		
$\mathrm{Et_4NBr}$	127.21±0.06	239.68	5.42	0.04
n-$\mathrm{Pr_4NBr}$	111.27±0.04	189.88	6.54	0.03
n-$\mathrm{Bu_4NBr}$	105.05±0.12	166.64	6.98	0.09
n-$\mathrm{Bu_4NBPh_4}$	80.28±0.03	87.73	6.80	0.03
		Solvent 6		
$\mathrm{Et_4NBr}$	133.86±0.04	261.70	7.28	0.02
n-$\mathrm{Pr_4NBr}$	118.39±0.01	241.44	6.83	0.01
n-$\mathrm{Bu_4NBr}$	110.58±0.16	157.49	7.73	0.12
n-$\mathrm{Bu_4NBPh_4}$	85.90±0.01	110.20	8.47	0.01
		Solvent 5		
$\mathrm{Et_4NBr}$	141.10±0.02	340.04	7.69	0.01
n-$\mathrm{Pr_4NBr}$	120.86±0.04	267.17	8.71	0.03
n-$\mathrm{Bu_4NBr}$	119.07±0.05	216.46	9.28	0.04
n-$\mathrm{Bu_4NBPh_4}$	89.34±0.05	128.41	9.96	0.05
		Solvent 4		
$\mathrm{Et_4NBr}$	146.70±0.04	396.24	9.44	0.02
n-$\mathrm{Pr_4NBr}$	129.05±0.02	293.08	9.52	0.02
n-$\mathrm{Bu_4NBr}$	122.88±0.01	249.46	10.19	0.01
n-$\mathrm{Bu_4NBPh_4}$	94.56±0.01	140.15	10.57	0.01
		Solvent 3		
$\mathrm{Et_4NBr}$	152.11±0.03	581.75	8.94	0.02
n-$\mathrm{Pr_4NBr}$	143.62±0.01	476.67	9.87	0.01
n-$\mathrm{Bu_4NBr}$	126.14±0.01	298.95	10.28	0.01
n-$\mathrm{Bu_4NBPh_4}$	97.94±0.02	162.05	11.87	0.02
		Solvent 2		
$\mathrm{Et_4NBr}$	160.83±0.01	739.32	10.27	0.005
n-$\mathrm{Pr_4NBr}$	150.83±0.02	558.91	10.93	0.01
n-$\mathrm{Bu_4NBr}$	142.23±0.02	440.31	11.94	0.014
n-$\mathrm{Bu_4NBPh_4}$	103.34±0.01	179.30	13.27	0.010

decrease with increasing the size of the cations in a given dielectric constant of the medium.

Thus, in view of the above findings the F78 equation seems to be better suited for explaining the conductance behavior of the present system. The successful applicability of this equation seems to stem from the consideration of the solvated radii of ions present in solution in the diffuse steady state and consequently gives significantly better fit parameters compared to the other available conductance equations.

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Table 3-III. Best Fit Parameters for Et$_4$NBr, n-Pr$_4$NBr, n-Bu$_4$NBr, and n-Bu$_4$NBPh$_4$ in DMF-MEK Mixtures at 25 °C, Using the FOS Conductance Equation

Salt	Λ_0	K_A	a°	σ_A/%
	S cm^2 mol^{-1}	dm^3 mol^{-1}	Å	
		Solvent 9		
Et$_4$NBr	104.40±0.05	129.69	6.41	0.02
n-Pr$_4$NBr	94.41±0.10	99.46	5.40	0.06
n-Bu$_4$NBr	86.95±0.02	84.51	5.86	0.01
n-Bu$_4$NBPh$_4$	72.72±0.01	66.17	7.22	0.01
		Solvent 8		
Et$_4$NBr	113.00±0.15	189.48	6.60	0.02
n-Pr$_4$NBr	102.40±0.06	142.92	6.35	0.04
n-Bu$_4$NBr	90.31±0.11	126.64	8.60	0.06
n-Bu$_4$NBPh$_4$	74.76±0.03	79.92	7.50	0.03
		Solvent 7		
Et$_4$NBr	127.20±0.16	230.27	6.38	0.06
n-Pr$_4$NBr	111.20±0.10	177.95	6.77	0.04
n-Bu$_4$NBr	105.10±0.15	159.49	6.68	0.09
n-Bu$_4$NBPh$_4$	80.26±0.05	79.10	6.80	0.04
		Solvent 6		
Et$_4$NBr	133.80±0.11	245.57	6.80	0.04
n-Pr$_4$NBr	118.30±0.05	226.36	7.07	0.02
n-Bu$_4$NBr	112.10±0.11	174.59	6.56	0.04
n-Bu$_4$NBPh$_4$	85.87±0.01	92.33	6.54	0.01
		Solvent 5		
Et$_4$NBr	141.10±0.07	320.13	7.25	0.03
n-Pr$_4$NBr	120.80±0.15	244.51	6.82	0.02
n-Bu$_4$NBr	118.90±0.18	186.17	6.63	0.06
n-Bu$_4$NBPh$_4$	89.32±0.08	105.38	6.07	0.06
		Solvent 4		
Et$_4$NBr	146.60±0.12	360.50	6.44	0.04
n-Pr$_4$NBr	128.90±0.09	256.36	6.44	0.03
n-Bu$_4$NBr	122.70±0.06	210.16	6.27	0.02
n-Bu$_4$NBPh$_4$	94.43±0.05	97.85	5.97	0.03
		Solvent 3		
Et$_4$NBr	152.00±0.09	545.70	7.85	0.04
n-Pr$_4$NBr	143.50±0.11	434.37	7.35	0.02
n-Bu$_4$NBr	126.10±0.04	259.24	7.40	0.02
n-Bu$_4$NBPh$_4$	97.74±0.08	101.88	5.78	0.03
		Solvent 2		
Et$_4$NBr	160.70±0.01	686.47	7.94	0.04
n-Pr$_4$NBr	150.70±0.10	502.16	7.61	0.03
n-Bu$_4$NBr	142.00±0.10	372.66	6.89	0.02
n-Bu$_4$NBPh$_4$	103.10±0.07	97.67	5.81	0.02

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