Ionic Viscosity *B*-Coefficients of Tetraalkyl Ammonium Chlorides in (0 to 100) Mass % Water + Methanol at 298.15 K

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The viscosities of tetraalkylammonium chlorides, R_4NCl (R = $-CH_3$ through n-C_4H_9), have been measured in (0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100) mass % aqueous methanol at 298.15 K. By using the Jones−Dole equation, the corresponding *B*-coefficients have been calculated. The ionic *B*-values have been determined using the "reference electrolyte" KCl. Solvation number (n_s) values have been used to discuss the solvation of ions.

1. Introduction

The viscometric method is known to give valuable information regarding ion−solvent interactions, which are the controlling forces in dilute solutions where ion−ion interactions are absent. Viscosities of R_4NCl in (0 to 100) mass % aqueous methanol at 298.15 K are reported in the present communication. The variations of the solvational properties are reflected in the viscosity *B*-coefficients of ions. Although a number of extensive viscometric studies have been made in various solvents with different electrolytes, the literature provides no information regarding the viscometric studies of R_4NCl in the complete range of aqueous methanol. This led us to undertake the present investigation, and the results are reported in this article.

2. Experimental Section

Water was distilled in a Pyrex glass apparatus with traces of $KMnO_4$, followed by successive distillations. The electric conductance of distilled water was ~7 × 10^{-6} $S\cdot cm^{-1}$. Methanol (Glaxo, Excel-R Purity 99.5%) was directly used without further purification. The purity of methanol was checked by comparing its observed density 0.78662 $g\cdot cm^{-3}$ with that of 0.78662 $g\cdot cm^{-3}$ reported[1] earlier at 298.15 K.

Water + methanol mixtures of compositions (10, 20, 30, 40, 50, 60,70, 80 and 90) mass % methanol were prepared by mixing an appropriate mass of water and methanol in glass stoppered flask. Due to the hygroscopic nature of the chlorides, these salts were stored in a vacuum desiccator over calcium chloride.

Tetra methylammonium chloride (Loba Chem, purity 98%), tetraethylammonium chloride (Merck-Schuchardt, purity > 97%), and tetraphenyl and tetrabutylammonium chlorides (Fluka Chemika, purity >97% and >98%, respectively), were used after purification.[2] The recrystallized salts were dried at (60 to 80) °C in vacuo for 2 days prior to use.

Accurately known mass of recrystallized salts were dissolved in a particular solvent to give a concentration of 0.05 M. This served as the stock solution. Further solutions of known concentration were obtained by using a mass dilution technique. Salts concentration varied from 0.0033 M to 0.0481 M. The exact concentration of the salt solution was obtained either from measurement of halide ion concentration using Volahrd's method or by gravimetric analysis.[3,4] The solutions were stored in dark amber colored bottles, which are kept in a drybox. Densities were determined by using ~15 cm^3 bicapillary pycnometer as described[5,6] earlier. The pycnometer was calibrated using conductivity water with (0.99706, 0.99570, 0.99405, 0.99208) $g\cdot cm^{-3}$ as its density at (298.15, 303.15, 308.15, and 313.15) K, respectively. The pycnometer filled with air-bubble free experimental liquids was kept in a transparent walled water bath (maintained constant to ±0.01 K) for 10 to 15 min to attain thermal equilibrium. The positions of the liquid levels in the two arms were recorded with the help of a travelling microscope which could be read to ±0.01 mm. The estimated uncertainty of density measurements of solvent and salt solutions was ±0.00001 $g\cdot cm^{-3}$.

Table 1. Comparison of Measured Densities (*d*) and Viscosities (*η*) of Water (1) + Methanol (2) at 298.15 K

		$d/(g\ cm^{-3})$		$\eta/(mPa\cdot s)$	
w_2	x_2	exptl	lit.[a]	exptl	lit.[a]
0.0	0.0000	0.99706	0.99705	0.8944	0.8949
0.1	0.0588	0.97984	0.97973	1.1635	1.158
0.2	0.1233	0.96431	0.96451	1.3817	1.400
0.3	0.1943	0.94886	0.94869	1.5393	1.531
0.4	0.2727	0.93156	0.93134	1.5870	1.593
0.5	0.3599	0.91192	0.91185	1.5201	1.510
0.6	0.4576	0.89041	0.89013	1.3855	1.403
0.7	0.5675	0.86718	0.86706	1.2040	1.190
0.8	0.6922	0.84244	0.84217	0.9984	1.006
0.9	0.8350	0.81546	0.81528	0.7759	0.767
1.0	1.0000	0.78662	0.78662	0.5490	0.541

[a] From ref 1.

The viscosity measurements were made using a suspended level Ubbelohde viscometer.[7,8] The viscometer was clamped vertically in the bath, and 20 cm^3 of the solution was added from a burette. The viscometer was calibrated with water using the viscosity and density values reported by Marsh.[9] Viscosity values were determined using the relation

$$\eta_1/\eta_2 = d_1 t_1/d_2 t_2 \tag{1}$$

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Table 2. Densities (d) and Viscosities (η) of Me_4NCl, Et_4NCl, n-Pr_4NCl and n-Bu_4NCl in Water (1) + Methanol (2) at 298.15 K

	Me_4NCl		Et_4NCl		n-Pr_4NCl		n-Bu_4NCl			Me_4NCl		Et_4NCl		n-Pr_4NCl		n-Bu_4NCl	
c/mol dm^{-3}	d/g cm^{-3}	η/mPa s	d/g cm^{-3}	η/mPa s	d/g cm^{-3}	η/mPa s	d/g cm^{-3}	η/mPa s	c/mol dm^{-3}	d/g cm^{-3}	η/mPa s	d/g cm^{-3}	η/mPa s	d/g cm^{-3}	η/mPa s	d/g cm^{-3}	η/mPa s
$w_2 = 0.0$																	
0.0033	0.99707	0.8954	0.99712	0.8954	0.99703	0.8970	0.99707	0.8970	0.0309	0.99716	0.8995	0.99759	0.9042	0.99674	0.9182	0.99717	0.9259
0.0081	0.99709	0.8963	0.99721	0.8969	0.99698	0.9007	0.99709	0.9018	0.0352	0.99717	0.9001	0.99766	0.9056	0.99670	0.9215	0.99718	0.9305
0.0145	0.99711	0.8972	0.99732	0.8990	0.99691	0.9056	0.99711	0.9084	0.0395	0.99719	0.9006	0.99772	0.9070	0.99666	0.9248	0.99720	0.9351
0.0195	0.99712	0.8980	0.99740	0.9006	0.99686	0.9095	0.99713	0.9137	0.0443	0.99720	0.9012	0.99780	0.9086	0.99661	0.9285	0.99721	0.9403
0.0244	0.99714	0.8986	0.99749	0.9021	0.99681	0.9132	0.99714	0.9189	0.0481	0.99721	0.9017	0.99786	0.9098	0.99657	0.9314	0.99723	0.9444
$w_2 = 0.1$																	
0.0033	0.97986	1.1645	0.97987	1.1644	0.97982	1.1662	0.97985	1.1650	0.0309	0.98003	1.1699	0.98019	1.1755	0.97973	1.1919	0.98000	1.1976
0.0081	0.97989	1.1655	0.97993	1.1662	0.97981	1.1706	0.97988	1.1700	0.0352	0.98006	1.1707	0.98024	1.1774	0.97972	1.1960	0.98002	1.2031
0.0145	0.97993	1.1668	0.98000	1.1688	0.97979	1.1765	0.97991	1.1774	0.0395	0.98008	1.1715	0.98029	1.1791	0.97970	1.2000	0.98004	1.2085
0.0195	0.97996	1.1678	0.98006	1.1708	0.97977	1.1812	0.97994	1.1834	0.0443	0.98011	1.1723	0.98035	1.1811	0.97968	1.2046	0.98007	1.2147
0.0244	0.98000	1.1687	0.98012	1.1728	0.97975	1.1858	0.97996	1.1895	0.0481	0.98013	1.1730	0.98039	1.1827	0.97967	1.2082	0.98009	1.2196
$w_2 = 0.2$																	
0.0033	0.96434	1.3825	0.96434	1.3826	0.96432	1.3847	0.96432	1.3832	0.0309	0.96457	1.3886	0.96458	1.3957	0.96437	1.4144	0.96440	1.4196
0.0081	0.96438	1.3836	0.96438	1.3847	0.96432	1.3897	0.96433	1.3887	0.0352	0.96460	1.3895	0.96461	1.3978	0.96437	1.4191	0.96441	1.4257
0.0145	0.96444	1.3850	0.96443	1.3877	0.96434	1.3965	0.96435	1.3970	0.0395	0.96463	1.3904	0.96465	1.4000	0.96438	1.4238	0.96443	1.4319
0.0195	0.96448	1.3861	0.96448	1.3901	0.96434	1.4020	0.96437	1.4037	0.0443	0.96467	1.3915	0.96469	1.4024	0.96439	1.4291	0.96444	1.4388
0.0244	0.96452	1.3872	0.96452	1.3925	0.96435	1.4073	0.96438	1.4105	0.0481	0.96470	1.3923	0.96473	1.4043	0.96440	1.4333	0.96445	1.4443
$w_2 = 0.3$																	
0.0033	0.94890	1.5402	0.94891	1.5401	0.94889	1.5419	0.94888	1.5404	0.0309	0.94922	1.5480	0.94936	1.5547	0.94917	1.5730	0.94904	1.5988
0.0081	0.94896	1.5495	0.94899	1.5495	0.94894	1.5495	0.94891	1.5495	0.0352	0.94927	1.5492	0.94943	1.5571	0.94921	1.5779	0.94907	1.5853
0.0145	0.94903	1.5434	0.94910	1.5457	0.94901	1.5541	0.94895	1.5548	0.0395	0.94932	1.5505	0.94950	1.5595	0.94925	1.5830	0.94910	1.5919
0.0195	0.94909	1.5448	0.94918	1.5484	0.94906	1.5598	0.94898	1.5619	0.0443	0.94938	1.5518	0.94958	1.5622	0.94930	1.5886	0.94913	1.5993
0.0244	0.94915	1.5462	0.94926	1.5511	0.94910	1.5654	0.94901	1.5691	0.0481	0.94943	1.5529	0.94964	1.5644	0.94934	1.5931	0.94915	1.6052
$w_2 = 0.4$																	
0.0033	0.93160	1.5831	0.93161	1.5824	0.93158	1.5845	0.93159	1.5827	0.0309	0.93192	1.5925	0.93200	1.5964	0.93175	1.6161	0.93179	1.6197
0.0081	0.93165	1.5848	0.93168	1.5846	0.93161	1.5897	0.93162	1.5882	0.0352	0.93197	1.5940	0.93206	1.5988	0.93178	1.6212	0.93182	1.6259
0.0145	0.93172	1.5870	0.93177	1.5878	0.93165	1.5970	0.93167	1.5965	0.0395	0.93203	1.5954	0.93213	1.6011	0.93180	1.6262	0.93185	1.6323
0.0195	0.93178	1.5887	0.93184	1.5903	0.93168	1.6027	0.93170	1.6034	0.0443	0.93209	1.5970	0.93219	1.6038	0.93183	1.6320	0.93188	1.6395
0.0244	0.93184	1.5904	0.93191	1.5929	0.93171	1.6085	0.93174	1.6103	0.0481	0.93214	1.5982	0.93225	1.6059	0.93185	1.6365	0.93191	1.6451
$w_2 = 0.5$																	
0.0033	0.91199	1.5211	0.91199	1.5211	0.91197	1.5233	0.91197	1.5209	0.0309	0.91286	1.5302	0.91266	1.5369	0.91242	1.5541	0.91242	1.5548
0.0081	0.91212	1.5227	0.91211	1.5236	0.91205	1.5285	0.91205	1.5259	0.0352	0.91302	1.5316	0.91276	1.5395	0.91249	1.5590	0.91249	1.5605
0.0145	0.91231	1.5248	0.91226	1.5272	0.91215	1.5356	0.91215	1.5335	0.0395	0.91318	1.5330	0.91287	1.5421	0.91256	1.5639	0.91256	1.5663
0.0195	0.91247	1.5264	0.91238	1.5301	0.91223	1.5412	0.91223	1.5398	0.0443	0.91337	1.5346	0.91298	1.5451	0.91263	1.5694	0.91264	1.5729
0.0244	0.91263	1.5280	0.91250	1.5330	0.91231	1.5468	0.91231	1.5461	0.0481	0.91352	1.5359	0.91307	1.5474	0.91270	1.5737	0.91270	1.5781
$w_2 = 0.6$																	
0.0033	0.89048	1.3867	0.89051	1.3865	0.89049	1.3884	0.89049	1.3860	0.0309	0.89117	1.3962	0.89134	1.4015	0.89118	1.4160	0.89118	1.4148
0.0081	0.89060	1.3884	0.89065	1.3889	0.89061	1.3931	0.89061	1.3902	0.0352	0.89128	1.3976	0.89146	1.4040	0.89128	1.4204	0.89128	1.4197
0.0145	0.89076	1.3906	0.89084	1.3923	0.89077	1.3995	0.89077	1.3967	0.0395	0.89139	1.3991	0.89159	1.4064	0.89139	1.4247	0.89139	1.4247
0.0195	0.89088	1.3923	0.89099	1.3951	0.89089	1.4045	0.89089	1.4020	0.0443	0.89151	1.4007	0.89174	1.4092	0.89151	1.4296	0.89151	1.4303
0.0244	0.89100	1.3939	0.89114	1.3978	0.89101	1.4094	0.89101	1.4074	0.0481	0.89161	1.4020	0.89185	1.4114	0.89161	1.4335	0.89160	1.4348
$w_2 = 0.7$																	
0.0033	0.86727	1.2051	0.86733	1.2059	0.86728	1.2065	0.86730	1.2078	0.0309	0.86801	1.2142	0.86861	1.2216	0.86817	1.2300	0.86832	1.2395
0.0081	0.86740	1.2067	0.86755	1.2086	0.86744	1.2105	0.86748	1.2133	0.0352	0.86813	1.2156	0.86881	1.2241	0.86831	1.2337	0.86848	1.2444
0.0145	0.86757	1.2088	0.86785	1.2123	0.86764	1.2159	0.86772	1.2206	0.0395	0.86825	1.2171	0.86900	1.2265	0.86844	1.2375	0.86864	1.2493
0.0195	0.86770	1.2105	0.86808	1.2151	0.86780	1.2202	0.86790	1.2264	0.0443	0.86838	1.2186	0.86923	1.2293	0.86860	1.2416	0.86882	1.2548
0.0244	0.86784	1.2121	0.86831	1.2179	0.86796	1.2244	0.86808	1.2320	0.0481	0.86848	1.2199	0.86940	1.2315	0.86872	1.2449	0.86896	1.2592
$w_2 = 0.8$																	
0.0033	0.84257	0.9999	0.84264	1.0000	0.84257	1.0007	0.84262	1.0006	0.0309	0.84362	1.0093	0.84404	1.0134	0.84365	1.0203	0.84405	1.0238
0.0081	0.84275	1.0016	0.84290	1.0023	0.84276	1.0041	0.84287	1.0045	0.0352	0.84379	1.0107	0.84424	1.0155	0.84381	1.0233	0.84427	1.0275
0.0145	0.84299	1.0038	0.84324	1.0054	0.84301	1.0086	0.84320	1.0098	0.0395	0.84395	1.0121	0.84444	1.0176	0.84398	1.0264	0.84450	1.0312
0.0195	0.84318	1.0055	0.84349	1.0079	0.84320	1.0122	0.84346	1.0140	0.0443	0.84414	1.0136	0.84465	1.0199	0.84417	1.0298	0.84475	1.0353
0.0244	0.84337	1.0071	0.84373	1.0103	0.84339	1.0156	0.84371	1.0182	0.0481	0.84429	1.0149	0.84481	1.0218	0.84432	1.0325	0.84494	1.0386
$w_2 = 0.9$																	
0.0033	0.81560	0.7769	0.81568	0.7773	0.81562	0.7775	0.81567	0.7776	0.0309	0.81682	0.7844	0.81747	0.7884	0.81688	0.7922	0.81741	0.7946
0.0081	0.81581	0.7783	0.81600	0.7793	0.81583	0.7800	0.81597	0.7805	0.0352	0.81701	0.7855	0.81774	0.7901	0.81708	0.7946	0.81768	0.7973
0.0145	0.81609	0.7800	0.81642	0.7819	0.81613	0.7835	0.81638	0.7844	0.0395	0.81721	0.7866	0.81801	0.7918	0.81728	0.7969	0.81795	0.8000
0.0195	0.81631	0.7813	0.81674	0.7838	0.81636	0.7861	0.81669	0.7875	0.0443	0.81743	0.7879	0.81831	0.7937	0.81750	0.7995	0.81825	0.8030
0.0244	0.81653	0.7827	0.81705	0.7858	0.81658	0.7888	0.81700	0.7906	0.0481	0.81760	0.7899	0.81855	0.7951	0.81767	0.8015	0.81849	0.8054
$w_2 = 1.0$																	
0.0033	0.78677	0.5500	0.78686	0.5500	0.78680	0.5502	0.78888	0.5516	0.0309	0.78807	0.5561	0.78888	0.5578	0.78836	0.5604	0.78902	0.5658
0.0081	0.78699	0.5511	0.78722	0.5514	0.78707	0.5520	0.78725	0.5543	0.0352	0.78828	0.5570	0.78919	0.5590	0.78860	0.5620	0.78935	0.5679
0.0145	0.78729	0.5526	0.78768	0.5532	0.78743	0.5543	0.78774	0.5576	0.0395	0.78849	0.5580	0.78951	0.5602	0.78885	0.5636	0.78969	0.5699
0.0195	0.78753	0.5537	0.78805	0.5546	0.78772	0.5562	0.78813	0.5602	0.0443	0.78872	0.5590	0.78986	0.5615	0.78912	0.5654	0.79006	0.5722
0.0244	0.78776	0.5547	0.78841	0.5559	0.78799	0.5580	0.78815	0.5626	0.0481	0.78891	0.5598	0.79013	0.5626	0.78933	0.5668	0.79036	0.5740

where η_1, d_1, t_1 and η_2, d_2, t_2 are viscosity, density, and flow time of solvent and solution, respectively. The flow time was measured with an electronic stop watch (accuracy of ±0.01 s). A viscometer was selected having a flow time of 250 to 300 s for redistilled water at 298.15 K. The estimated uncertainly (relative to water) of experimental viscosities was ±0.001 mPa·s. Comparison of measured densities (d) and viscosities (η) of (0 to 100) mass % aqueous methanol at 298.15 K is given in Table 1. Densities (d) and viscosities (η) of Me_4NCl, Et_4NCl, n-Pr_4NCl, and n-Bu_4NCl at various concentrations in 0−100 wt % aqueous methanol at 298.15 K is reported in Table 2.

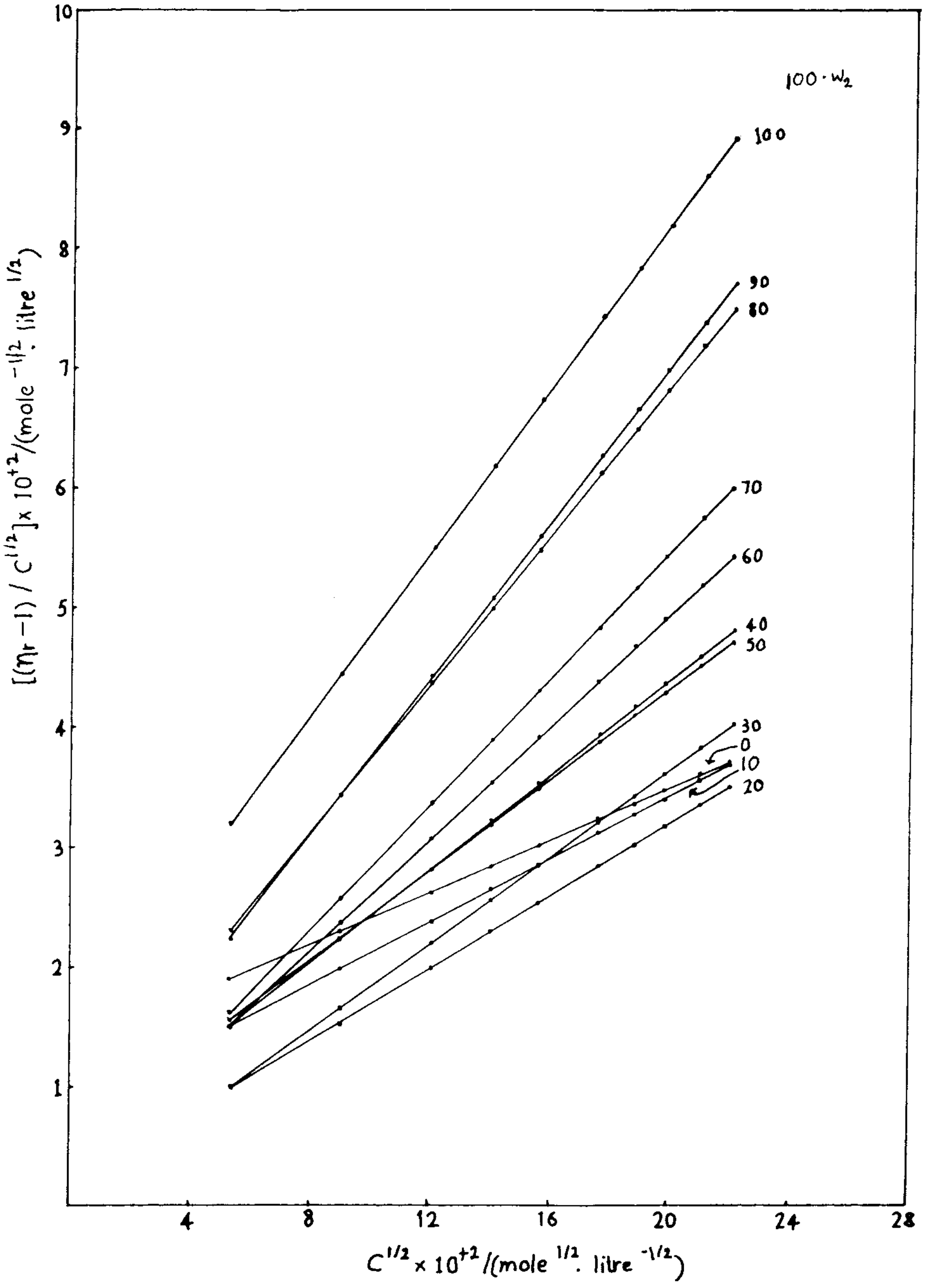

Figure 1. Plots of $(\eta_r - 1)/c^{1/2}$ vs $c^{1/2}$ for Me_4NCl in (0 to 100) mass % methanol at 298.15 K.

3. Results and Discussion

The relative viscosities (η_r) of solutions of R_4NCl in water, methanol and methanol + water mixtures are measured at 298.15 K and analyzed with the help of the Jones−Dole equation[10]

$$\eta_r = (\eta/\eta_0) = 1 + AC^{1/2} + BC \qquad (2)$$

where η and η_0 are the viscosities of the solution and the solvent respectively and c is the molar concentration. "A" is the measure of long-range Coulombic forces between ions, while "B" reflects the effect of ion−solvent interactions. The values of A and B for all electrolytes in (0 to 100) mass % aqueous methanol at 298.15 K are tabulated in Table 3.

The plots of $[(\eta/\eta_0) - 1]/c^{1/2}$ vs $c^{1/2}$ for all electrolytes in the whole composition range of aqueous methanol at 298.15 K are found to be straight lines with intercept equal to A, and the slopes yield the viscosity B-coefficient. The representative plots for Me_4NCl are shown in Figure 1. The B-coefficients are obtained by a computerized least-squares method.

The ionic B-coefficients ($B^{\pm}$) are calculated by the method adopted by Kaminsky[11] using the equation of the form,

$$B(K^+) = B(Cl^-) = {}^1/_2 B(KCl) \qquad (3)$$

This method depends on the reference electrolyte (KCl) for which cation−solvent and anion−solvent interactions may be considered to be equal in pure water and pure methanol.[12] Ionic B-coefficients in (0 to 100) mass % aqueous methanol of R_4N^+ and Cl^- ions at 298.15 K are shown in Table 4. Ionic B-values for Me_4N^+ and Et_4N^+, first increase with increase of methanol, reach a maximum in solution

Table 3. Parameters of Jones−Dole Equations A and B for Me_4NCl, Et_4NCl, *n*-Pr_4NCl, and *n*-Bu_4NCl in Water (1) + Methanol (2) at 298.15 K

	Me_4NCl		Et_4NCl		*n*-Pr_4NCl		*n*-Bu_4NCl	
w_2	$A/dm^{3/2}\cdot mol^{-1/2}$	$B/dm^3\cdot mol^{-1}$	$A/dm^{3/2}\cdot mol^{-1/2}$	$B/dm^3\cdot mol^{-1}$	$A/dm^{3/2}\cdot mol^{-1/2}$	$B/dm^3\cdot mol^{-1}$	$A/dm^{3/2}\cdot mol^{-1/2}$	$B/dm^3\cdot mol^{-1}$
0.0	0.0131 ± 0.00004	0.1098 ± 0.0003	−0.0015 ± 0.00004	0.3650 ± 0.0003	0.0003 ± 0.00007	0.8584 ± 0.0004	−0.0220 ± 0.00005	1.2636 ± 0.0003
		0.116^a		0.373^a		0.793^a		1.27^b
0.1	0.0070 ± 0.0001	0.1377 ± 0.0002	−0.0085 ± 0.0001	0.3824 ± 0.0007	−0.0076 ± 0.00004	0.8336 ± 0.0002	−0.0478 ± 0.00006	1.2205 ± 0.0003
0.2	0.0012 ± 0.00003	0.1539 ± 0.0002	−0.0112 ± 0.00006	0.3911 ± 0.0004	−0.0094 ± 0.00003	0.8193 ± 0.0002	−0.0478 ± 0.00004	1.1598 ± 0.0002
0.3	−0.0006 ± 0.00007	0.1863 ± 0.0004	−0.0135 ± 0.00002	0.4005 ± 0.0001	−0.0167 ± 0.00005	0.8026 ± 0.0003	−0.0525 ± 0.00004	1.1296 ± 0.0002
0.4	0.0038 ± 0.00004	0.2001 ± 0.0003	−0.0143 ± 0.000009	0.3828 ± 0.00005	−0.0144 ± 0.00005	0.7854 ± 0.0003	−0.0500 ± 0.00003	1.0615 ± 0.0002
0.5	−0.0013 ± 0.00005	0.2222 ± 0.0003	−0.0136 ± 0.00003	0.4353 ± 0.0002	−0.0075 ± 0.00003	0.7674 ± 0.0002	−0.0495 ± 0.00005	1.0189 ± 0.0003
0.6	0.0011 ± 0.00003	0.2425 ± 0.0002	−0.0133 ± 0.00003	0.4492 ± 0.0002	−0.0068 ± 0.00006	0.7507 ± 0.0004	−0.0491 ± 0.00004	0.9634 ± 0.0002
0.7	0.0001 ± 0.00003	0.2740 ± 0.0002	−0.0003 ± 0.00001	0.4754 ± 0.00006	−0.0061 ± 0.00004	0.7340 ± 0.0002	0.0002 ± 0.00007	0.9521 ± 0.0004
0.8	0.0087 ± 0.000008	0.3033 ± 0.00005	−0.0002 ± 0.00004	0.4877 ± 0.0003	−0.0010 ± 0.00005	0.7143 ± 0.0003	−0.0133 ± 0.00003	0.8978 ± 0.0002
0.9	0.0061 ± 0.00004	0.3234 ± 0.0002	0.0052 ± 0.00003	0.4948 ± 0.0002	−0.0020 ± 0.00003	0.6976 ± 0.0002	−0.0072 ± 0.00003	0.8262 ± 0.0002
1.0	0.0110 ± 0.00003	0.3578 ± 0.00002	0.0028 ± 0.00002	0.5004 ± 0.0001	−0.0014 ± 0.00003	0.6817 ± 0.0002	0.0373 ± 0.00007	0.7772 ± 0.0004
								0.878^c

[a] From ref 15. [b] From ref 16. [c] From ref 17.

Table 4. Ionic *B*-Coefficients of R_4N^+ and Cl^- Ions in Water (1) + Methanol (2) at 298.15 K

	ionic *B*-coefficients/$dm^3\cdot mol^{-1}$				
w_2	Me_4N^+	Et_4N^+	*n*-Pr_4N^+	*n*-Bu_4N^+	Cl^-
0.0	0.1167	0.3719	0.8653.	1.2705	−0.0069
	0.12^a	0.38^a	0.86^a	1.266^b	-0.007^b
0.1	0.1387	0.3834	0.8346	1.2215	−0.0010
0.2	0.1671	0.4043	0.8325	1.1730	−0.0132
0.3	0.1949	0.4091	0.8112	1.1382	−0.0086
0.4	0.2017	0.3844	0.7870	1.0631	−0.0016
0.5	0.1669	0.3800	0.7121	0.9636	0.0553
0.6	0.1282	0.3349	0.6364	0.8491	0.1143
0.7	0.0966	0.2980	0.5566	0.7747	0.1774
0.8	0.0552	0.2396	0.4662	0.6497	0.2481
0.9	0.0250	0.1964	0.3992	0.5278	0.2984
1.0	−0.0388	0.1038	0.2851	0.3806	0.3966
	-0.03^c	0.12^c	0.30^c	0.40^c	0.382^c

[a] From ref 18. [b] From ref 19. [c] From ref 12.

Table 5. Radii (R^+) and Solvation Number (n_s) of Me_4N^+, Et_4N^+, *n*-Pr_4N^+, and *n*-Bu_4N^+ Ions in Water (1) + Methanol (2) at 298.15 K

		w_2				
ions	$R^+/Å^a$	0.0	0.1	0.2	0.3	0.4
Me_4N^+	3.47	0.2711	0.7124	1.2239	1.6553	1.6593
Et_4N^+	4.00	4.6912	4.6475	4.7730	4.5589	3.8289
n-Pr_4N^+	4.52	14.0455	12.5599	11.7544	10.6209	9.4894
n-Bu_4N^+	4.94	21.4548	19.1418	17.0291	15.3149	12.9972

		w_2					
ions	$R^+/Å^a$	0.5	0.6	0.7	0.8	0.9	1.0
Me_4N^+	3.47	0.9877	0.3462	−0.1049	−0.5987	−0.8719	−1.4068
Et_4N^+	4.00	3.4796	2.5497	1.8429	0.9675	0.3994	−0.5519
n-Pr_4N^+	4.52	7.6114	5.9119	4.3500	2.8605	1.8472	0.5326
n-Bu_4N^+	4.94	10.4738	7.9846	6.3209	4.2338	2.4845	0.7779

[a] From ref 12.

in 40 and 30 mass % aqueous methanol, respectively, and then further decrease with an increase in methanol. Ionic *B*-values for *n*-Pr_4N^+ and *n*-Bu_4N^+ continuously decrease with increase of the methanol content in solution.

An analysis of *B*-coefficients can be made on the basis of Einstein's equation[13]

$$B_{\pm} = 2.5 \times (4/3)\, \pi\, (R_{\pm}{}^3 N/1000) \qquad (4)$$

where $R_{\pm}$ is the radius of the ion assumed as a rigid sphere moving in a continuum and 2.5 is the shape factor for a sphere. The number (n_s) of solvent molecules bound to the ion in the primary sphere of solvation can be calculated[14] by combining the Jones−Dole equation with Einstein's

$$B_{\pm} = 2.5/1000(V_i + n_s V_s) \qquad (5)$$

where V_i represents the bare ion molar volume and is related to the crystallographic radius r_c of the ion and V_s is the solvent molar volume. The values of R_+ and n_s are shown in Table 5. The negative values of solvation numbers listed are physically unacceptable. They seem to indicate that the determination of solvation number on the basis of eq 5 does not appear to be correct. This is probably due to the fact that the electrolytic solutions are different from the mode that underlines eq 5.

The solvation numbers of R_4N^+ ions decrease with increase of methanol in solutions, suggesting preferential solvation of these ions by water through ion−dipole interactions.

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