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Viscosity of Potassium Halides and Symmetrical Tetraalkylammonium Bromides in Acetonitrile + Water Mixtures at 298.15 K

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The viscosities of potassium halides, KCI and KBr, and tetraalkylammonium bromides, R_4NBr ($R = -CH_3$ through $n-C_5H_{11}$), in acetonitrile + water mixtures have been measured at 298.15 K and corresponding B-coefficients of the Jones−Dole equation have been calculated. From these B values, the ionic B-coefficients of R_4N^+ and Br^- ions have been determined, assuming that the equality $B_{K^+} = B_{Cl^-}$ holds for the different solvent mixtures.

1. Introduction

Transport properties of electrolyte solutions in mixed solvents have been widely used to analyze the ion−solvent interactions in conjugation with the nature of the solvent composition. Recently, we have reported (Nikam and Sawant, 1997) ionic partial molar volumes of R_4N^+ and Br^- ions in acetonitrile + water at 298.15 K. Viscosities of these salts in the same solvent mixtures at the same temperature are reported in the present communication. The reason for the choice of solutions is due to the fact that remarkable variations in the behavior of R_4N^+ ions are found when the solvent systems changes from pure water to systems containing organic cosolvent.

Table 1. Comparison of Densities and Viscosities of Acetonitrile + Water with Data from Literature at 298.15 K[e]

mole fraction of acetonitrile	d/g cm^3	η/mPa s	mole fraction of acetonitrile	d/g cm^3	η/mPa s
0	0.997 07	0.8903	0.3943	0.8678[b]	0.656[b]
	0.997 07[a]	0.8903[a]	0.3968		0.6514[c]
0.0466	0.981 05	0.8878	0.5015	0.8446[b]	0.563[b]
	(0.981 06)	(0.8876)			
			0.5048		0.5545[c]
0.1227	0.952 2[b]	0.940[b]	0.5064	0.84374	0.5976
				(0.84381)	(0.5980)
0.1586	0.938 57	0.8553			
	(0.938 52)	(0.8560)	0.5534		0.5171[c]
0.1823	0.927 5[c]		0.5979	0.8270[b]	0.495[b]
0.2157	0.918 2[b]	0.842[b]	0.6717	0.8155[c]	
0.2457		0.8151[c]	0.703	0.8109[c]	0.436[b]
0.2555		0.8010[c]	0.7374		0.4202[c]
0.2971		0.7545[c]	0.7929	0.7987[b]	0.402[b]
0.3013	0.891 8[b]	0.750[b]	0.7983	0.79788	0.3900
				(0.79783)	(0.3898)
0.3054	0.890 73	0.7602			
	(0.890 80)	(0.7600)	0.8000	0.7977[c]	
0.3492		0.6697[c]	0.8972	0.7865[b]	0.375[b]
0.3803	0.870 7[c]		0.8990	0.7862[c]	
0.3870		0.6606[c]	0.9559	0.7806[c]	
			1	0.77645	0.3405
					0.3406[d]

[a] Stokes and Mills, 1965. [b] Aminabhavi and Gopalakrishna, 1995. [c] Cunningham et al., 1967. [d] Lawrence et al., 1989. [e] Values in parentheses; an interpolated values at desired mole fractions of acetonitrile, are estimated from the Davis (1983) analytical model.

2. Experimental Section

Water was distilled in a Pyrex glass apparatus over alkaline $KMnO_4$, followed by further distillation over H_2SO_4. The electric conductance of distilled water varied between (7×10^{-7} and 9×10^{-7}) ohm^{-1} cm^{-1}. Commercially available acetonitrile (98% pure, E. Merck) was distilled over P_2O_5 and then over anhydrous Na_2CO_3. Finally, a third distillation of acetonitrile was carried out without any additive. Acetonitrile with a conductivity of about 5×10^{-8} ohm^{-1} cm^{-1} or less was collected in airtight amber-colored bottles. The purity of acetonitrile was checked by comparing its observed density, 0.776 45 g cm^{-3}, with that of literature, 0.776 49 g cm^{-3} (Riddick et al., 1986), at 298.15 K. All R_4NBr salts were from Fluka with a purity ranging between 98 and 99%. All these salts were recrystallized by the procedure described by Conway et al. (1966). Acetonitrile + water mixtures of compositions (0, 10, 30, 50, 70, 90, and 100) mass % acetonitrile corresponding to (0, 0.0466, 0.1586, 0.3054, 0.5064, 0.7983, and 1) mole fraction of acetonitrile were prepared by mixing a known mass of water and acetonitrile in a glass-stoppered flask. No attempt was made to monitor the relative humidity of the air to which the acetonitrile was exposed for a short period of time during preparation. However, any effect of humidity on the composition of acetonitrile was considered to be negligible. The uncertainty in mole fraction was less than ±0.0001. The recrystallized salts were dried at (100−110) °C in vacuum for 24 h prior to use. Owing to the hygroscopic nature of the bromides, these salts were stored in a vacuum desiccator over calcium chloride. Accurately known masses of recrystallized salts were dissolved in a particular solvent to give a concentration of 0.05 M. The uncertainty in the mass measurement was less than 0.02%. This served as the stock solution. Further concentrations were obtained by using a mass dilution technique. Salt concentrations varied from (0.002 to 0.05) M. The exact concentration of the salt solution was obtained either from measurement of halide ion concentration using Volahdr's method or by gravimetric analysis (Basseit et al., 1978; Kreshkov, 1970). The gravimetric analysis for the concentration determination of the salt was done by weighing small amounts of this solution into weighing bottles and drying them in an oven. The weighing bottle was then cooled in a desiccator and weighed to obtain the mass of the dry salt. The mass of the solution and dried salts were determined with an analytical balance accurate to 0.1 mg.

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Table 2. Viscosities and Densities at Concentration c of Various Salts in Different Mass Fractions w of Acetonitrile (A) + Water (B) at 298.15 K

c/mol dm^{-3}	d/g cm^{-3}	η/mPa s	c/mol dm^{-3}	d/g cm^{-3}	η/mPa s	c/mol dm^{-3}	d/g cm^{-3}	η/mPa s
				KCl				
				$w_A = 0$				
0.002 42	0.997 16	0.8905	0.015 39	0.997 78	0.8907	0.045 64	0.999 22	0.8907
0.005 33	0.997 30	0.8906	0.025 70	0.998 27	0.8907	0.055 17	0.999 67	0.8907
0.010 46	0.997 55	0.8906	0.035 83	0.998 76	0.8907			
				$w_A = 0.10$				
0.002 97	0.981 19	0.8883	0.015 70	0.991 81	0.8891	0.045 95	0.993 28	0.8899
0.005 84	0.991 33	0.8886	0.025 21	0.992 27	0.8894	0.055 88	0.993 76	0.8901
0.010 53	0.991 56	0.8888	0.035 74	0.992 78	0.8897			
				$w_A = 0.30$				
0.002 29	0.938 68	0.8561	0.015 46	0.939 34	0.8582	0.045 21	0.940 84	0.8616
0.005 12	0.938 83	0.8567	0.025 37	0.939 84	0.8594	0.055 44	0.941 35	0.8627
0.010 23	0.939 08	0.8575	0.035 40	0.940 35	0.8606			
				$w_A = 0.50$				
0.002 85	0.890 87	0.7640	0.015 78	0.891 54	0.7709	0.045 81	0.893 09	0.7822
0.005 36	0.891 00	0.7657	0.025 87	0.892 06	0.7750	0.055 92	0.893 61	0.7855
0.010 93	0.891 29	0.7687	0.035 60	0.892 57	0.7786			
				$w_A = 0.70$				
0.002 73	0.843 89	0.5991	0.015 68	0.844 59	0.6036	0.045 15	0.846 19	0.6128
0.005 94	0.844 06	0.6003	0.025 51	0.845 12	0.6068	0.055 26	0.846 74	0.6158
0.010 47	0.844 30	0.6019	0.035 92	0.845 69	0.6100			
				$w_A = 0.90$				
0.002 36	0.798 01	0.3910	0.015 71	0.798 77	0.3954	0.045 36	0.800 45	0.4042
0.005 45	0.798 19	0.3921	0.025 42	0.799 32	0.3983	0.055 57	0.801 03	0.4072
0.010 52	0.798 48	0.3938	0.035 53	0.799 90	0.4013			
				$w_A = 1$				
0.002 50	0.776 76	0.3365	0.015 35	0.777 50	0.3403	0.045 72	0.779 26	0.3489
0.005 41	0.776 93	0.3374	0.025 28	0.778 07	0.3431	0.055 73	0.779 83	0.3517
0.010 34	0.777 21	0.3388	0.035 79	0.778 68	0.3461			
				KBr				
				$w_A = 0$				
0.002 53	0.997 25	0.8904	0.015 30	0.998 30	0.8902	0.045 55	1.000 76	0.8892
0.005 36	0.997 48	0.8904	0.025 31	0.999 11	0.8899	0.055 28	1.001 55	0.8889
0.010 57	0.997 91	0.8903	0.035 34	0.999 93	0.8896			
				$w_A = 0.10$				
0.002 39	0.981 24	0.8882	0.015 46	0.982 33	0.8885	0.045 41	0.984 81	0.8884
0.005 32	0.981 49	0.8883	0.035 50	0.983 99	0.8885	0.055 44	0.985 64	0.8883
0.010 43	0.981 91	0.8885	0.035 50	0.983 99	0.8885			
				$w_A = 0.30$				
0.002 55	0.938 78	0.8560	0.015 32	0.939 86	0.8577	0.045 37	0.942 40	0.8606
0.005 58	0.939 04	0.8565	0.025 33	0.940 71	0.8587	0.055 10	0.943 23	0.8614
0.010 39	0.939 44	0.8571	0.035 36	0.941 56	0.8597			
				$w_A = 0.50$				
0.002 42	0.890 94	0.7612	0.015 68	0.892 08	0.7642	0.045 25	0.894 66	0.7700
0.005 41	0.891 20	0.7619	0.025 49	0.892 94	0.7662	0.055 64	0.895 56	0.7720
0.010 43	0.891 63	0.7631	0.035 46	0.893 80	0.7682			
				$w_A = 0.70$				
0.002 24	0.843 94	0.5985	0.015 49	0.845 12	0.6020	0.045 16	0.847 79	0.6091
0.005 25	0.844 21	0.5994	0.025 32	0.846 01	0.6044	0.055 77	0.848 74	0.6116
0.010 68	0.844 69	0.6008	0.035 23	0.846 90	0.6068			
				$w_A = 0.90$				
0.002 10	0.798 08	0.3908	0.015 35	0.799 30	0.3944	0.045 22	0.802 08	0.4020
0.005 51	0.798 39	0.3917	0.025 48	0.800 24	0.3970	0.055 53	0.803 04	0.4046
0.010 14	0.798 82	0.3930	0.035 39	0.801 16	0.3995			
				$w_A = 1$				
0.002 56	0.776 85	0.3364	0.015 51	0.778 08	0.3401	0.045 88	0.780 93	0.3482
0.005 87	0.777 17	0.3374	0.025 94	0.779 05	0.3429	0.055 79	0.781 86	0.3509
0.010 80	0.777 64	0.3388	0.035 25	0.779 93	0.3454			
				$[CH_3]_4NBr$				
				$w_A = 0$				
0.002 61	0.997 15	0.8908	0.015 72	0.997 68	0.8923	0.045 53	0.998 86	0.8951
0.005 49	0.997 27	0.8912	0.025 45	0.998 06	0.8932	0.055 59	0.999 27	0.8960
0.010 32	0.997 46	0.8917	0.035 32	0.998 46	0.8942			
				$w_A = 0.10$				
0.002 72	0.981 47	0.8883	0.015 24	0.993 39	0.8897	0.045 08	0.998 00	0.8926
0.005 09	0.981 84	0.8886	0.025 94	0.985 04	0.8908	0.055 09	0.999 52	0.8935
0.010 71	0.992 70	0.8892	0.035 91	0.996 58	0.8918			

Table 2 (Continued)

c/mol dm^{-3}	d/g cm^{-3}	η/mPa s	c/mol dm^{-3}	d/g cm^{-3}	η/mPa s	c/mol dm^{-3}	d/g cm^{-3}	η/mPa s
$w_A = 0.30$								
0.002 21	0.938 68	0.8559	0.015 73	0.939 82	0.8583	0.045 63	0.940 34	0.8630
0.005 79	0.938 86	0.8566	0.025 21	0.939 82	0.8598	0.055 39	0.941 33	0.8645
0.010 34	0.939 08	0.8574	0.035 12	0.940 32	0.8614			
$w_A = 0.50$								
0.002 11	0.891 05	0.7609	0.015 77	0.893 16	0.7643	0.045 68	0.897 77	0.7712
0.005 64	0.891 59	0.7618	0.025 34	0.894 63	0.7665	0.055 29	0.899 25	0.7733
0.010 38	0.892 33	0.7630	0.035 22	0.89615	0.7686			
$w_A = 0.70$								
0.002 64	0.843 91	0.5988	0.015 17	0.844 75	0.6028	0.045 11	0.846 73	0.6117
0.005 29	0.844 09	0.5997	0.025 76	0.845 45	0.6060	0.055 99	0.847 38	0.6145
0.010 92	0.844 46	0.6015	0.035 42	0.846 08	0.6088			
$[C_2H_5]_4NBr$								
$w_A = 0$								
0.002 81	0.997 15	0.8915	0.015 59	0.997 60	0.8960	0.045 93	0.998 66	0.9060
0.005 72	0.997 25	0.8926	0.025 15	0.997 93	0.8992	0.055 28	0.998 99	0.9061
0.010 52	0.997 42	0.8943	0.035 42	0.998 29	0.9026			
w_A 0.10								
0.002 15	0.980 96	0.8887	0.015 19	0.990 43	0.8931	0.045 07	0.877 92	0.9026
0.005 03	0.980 85	0.8897	0.025 81	0.980 00	0.8965	0.055 05	0.978 78	0.9059
0.010 28	0.990 63	0.8915	0.035 63	0.979 60	0.8996			
$w_A = 0.30$								
0.002 74	0.938 49	0.8565	0.015 20	0.938 12	0.8605	0.045 66	0.937 23	0.8696
0.005 37	0.938 41	0.8574	0.025 44	0.937 83	0.8636	0.055 90	0.937 93	0.8726
0.010 21	0.938 27	0.8589	0.035 84	0.937 52	0.8667			
$w_A = 0.50$								
0.002 22	0.890 69	0.7613	0.015 91	0.890 47	0.7659	0.045 01	0.889 99	0.7746
0.005 11	0.890 65	0.7624	0.025 85	0.990 30	0.7689	0.055 08	0.889 82	0.7775
0.010 73	0.890 55	0.7642	0.035 54	0.890 14	0.7718			
$w_A = 0.70$								
0.002 81	0.843 73	0.5988	0.015 29	0.843 70	0.6028	0.045 81	0.843 62	0.6117
0.005 73	0.843 72	0.5998	0.025 32	0.843 67	0.6057	0.055 68	0.843 59	0.6146
0.010 92	0.843 71	0.6014	0.035 61	0.843 65	0.6088			
$w_A = 0.90$								
0.002 22	0.797 91	0.3907	0.015 54	0.798 08	0.3940	0.045 82	0.798 47	0.4011
0.005 33	0.797 95	0.3916	0.025 65	0.798 21	0.3964	0.055 86	0.798 60	0.4034
0.010 39	0.798 01	0.3928	0.035 68	0.798 34	0.3988			
$w_A = 1$								
0.002 72	0.776 68	0.3364	0.015 34	0.776 95	0.3395	0.045 33	0.777 60	0.3466
0.005 43	0.776 74	0.3371	0.025 13	0.777 16	0.3419	0.054 80	0.777 81	0.3489
0.010 79	0.776 85	0.3384	0.035 67	0.777 39	0.3444			
$[C_3H_7]_4NBr$								
$w_A = 0$								
0.002 11	0.997 11	0.8919	0.015 32	0.997 44	0.9016	0.045 25	0.998 13	0.9236
0.005 52	0.997 18	0.8944	0.025 54	0.997 68	0.9091	0.055 77	0.998 43	0.9314
0.010 93	0.997 31	0.8984	0.035 42	0.997 93	0.9164			
$w_A = 0.10$								
0.002 61	0.981 13	0.8898	0.015 55	0.981 55	0.8978	0.045 92	0.982 53	0.9158
0.005 84	0.981 24	0.8918	0.025 84	0.981 88	0.9039	0.055 39	0.982 84	0.9213
0.010 45	0.981 39	0.8947	0.035 33	0.982 19	0.9096			
$w_A = 0.30$								
0.002 28	0.938 68	0.8568	0.015 34	0.939 27	0.8632	0.045 43	0.941 65	0.8772
0.005 53	0.938 82	0.8584	0.025 14	0.939 72	0.8678	0.055 91	0.941 06	0.8817
0.010 78	0.939 06	0.8610	0.035 03	0.940 17	0.8724			
$w_A = 0.50$								
0.002 38	0.890 88	0.7614	0.015 59	0.891 67	0.7668	0.045 44	0.893 48	0.7783
0.005 75	0.891 07	0.7628	0.025 37	0.892 27	0.7706	0.055 15	0.894 06	0.7820
0.010 55	0.891 37	0.7648	0.035 64	0.892 88	0.7745			
$w_A = 0.70$								
0.002 91	0.843 96	0.5988	0.015 23	0.844 90	0.6031	0.045 27	0.847 19	0.6133
0.005 22	0.844 14	0.5996	0.025 85	0.845 72	0.6068	0.055 69	0.848 01	0.6169
0.010 84	0.844 57	0.6016	0.035 30	0.846 44	0.6100			
$w_A = 0.90$								
0.002 51	0.798 11	0.3909	0.015 44	0.799 33	0.3947	0.045 28	0.802 13	0.4028
0.005 59	0.798 41	0.3919	0.025 66	0.800 29	0.3975	0.055 61	0.803 10	0.4055
0.010 88	0.798 90	0.3934	0.035 50	0.801 21	0.4001			
$w_A = 1$								
0.002 19	0.776 85	0.3363	0.015 12	0.778 17	0.3401	0.045 87	0.781 35	0.3486
0.005 18	0.777 16	0.3372	0.025 49	0.800 29	0.3430	0.055 12	0.782 29	0.3510
0.010 79	0.777 73	0.3389	0.035 23	0.780 24	0.3456			

Table 2 (Continued)

c/mol dm^{-3}	d/g cm^{-3}	η/mPa s	c/mol dm^{-3}	d/g cm^{-3}	η/mPa s	c/mol dm^{-3}	d/g cm^{-3}	η/mPa s
$[C_4H_9]_4NBr$								
$w_A = 0$								
0.002 16	0.997 10	0.8927	0.015 73	0.997 44	0.9071	0.045 38	0.998 17	0.9380
0.005 38	0.997 18	0.8963	0.025 54	0.997 68	0.9173	0.055 61	0.998 43	0.9485
0.010 67	0.997 31	0.9018	0.035 74	0.997 93	0.9279			
$w_A = 0.10$								
0.002 66	0.980 26	0.8907	0.015 92	0.976 42	0.9030	0.045 11	0.967 92	0.9293
0.005 28	0.979 51	0.8932	0.025 24	0.973 71	0.9114	0.055 55	0.994 89	0.9386
0.010 55	0.977 99	0.8981	0.035 22	0.970 80	0.9204			
$w_A = 0.30$								
0.002 29	0.938 67	0.8575	0.015 35	0.939 26	0.8674	0.045 31	0.940 61	0.8892
0.005 17	0.938 80	0.8598	0.025 91	0.939 72	0.8750	0.055 12	0.941 05	0.8963
0.010 88	0.939 06	0.8641	0.035 73	0.940 18	0.8823			
$w_A = 0.50$								
0.002 76	0.890 96	0.7622	0.015 23	0.891 66	0.7696	0.045 39	0.893 52	0.7870
0.005 72	0.891 08	0.7640	0.025 15	0.892 27	0.7754	0.055 33	0.894 13	0.7927
0.020 78	0.891 39	0.7670	0.035 44	0.892 91	0.7813			
$w_A = 0.70$								
0.002 57	0.844 20	0.5991	0.015 55	0.844 96	0.6053	0.045 77	0.847 33	0.6192
0.005 78	0.844 60	0.6007	0.025 78	0.845 76	0.6101	0.055 81	0.848 12	0.6238
0.010 92	0.844 60	0.6032	0.035 69	0.846 54	0.6146			
$w_A = 0.90$								
0.002 51	0.798 12	0.3911	0.015 34	0.799 35	0.3955	0.045 17	0.802 22	0.4054
0.005 47	0.798 41	0.3921	0.025 53	0.780 33	0.3989	0.055 32	0.803 19	0.4087
0.010 73	0.798 91	0.3939	0.035 38	0.801 28	0.4022			
$w_A = 1$								
0.002 24	0.776 85	0.3364	0.015 57	0.778 20	0.3409	0.045 53	0.781 39	0.3504
0.005 07	0.777 15	0.3374	0.025 03	0.779 24	0.3439	0.055 03	0.782 39	0.3533
0.010 27	0.777 70	0.3392	0.035 19	0.780 31	0.3471			
$[C_5H_{11}]_4NBr$								
$w_A = 0$								
0.002 09	0.997 09	0.8935	0.015 61	0.997 34	0.9119	0.045 93	0.997 90	0.9522
0.005 42	0.997 15	0.8981	0.023 04	0.997 47	0.9218	0.055 98	0.998 08	0.9655
0.010 33	0.997 24	0.9119	0.034 94	0.997 70	0.9377			
$w_A = 0.10$								
0.002 29	0.981 10	0.8912	0.015 59	0.981 43	0.9087	0.045 55	0.982 17	0.9471
0.005 25	0.981 18	0.8951	0.025 23	0.981 67	0.9087	0.056 32	0.982 43	0.9608
0.010 11	0.981 30	0.9016	0.035 22	0.981 91	0.9339			
$w_A = 0.30$								
0.002 48	0.938 67	0.8585	0.015 79	0.939 22	0.8735	0.045 76	0.940 46	0.9062
0.005 38	0.938 79	0.8619	0.025 78	0.938 63	0.8844	0.056 13	0.940 88	0.9173
0.010 42	0.939 00	0.8675	0.035 32	0.940 03	0.8948			
$w_A = 0.50$								
0.002 57	0.890 89	0.7625	0.015 71	0.891 67	0.7724	0.045 32	0.893 44	0.7940
0.005 39	0.891 05	0.7646	0.025 64	0.892 26	0.7797	0.055 76	0.894 07	0.8016
0.010 66	0.891 37	0.7687	0.035 19	0.892 84	0.7867			
$w_A = 0.70$								
0.002 39	0.843 93	0.5994	0.015 92	0.844 99	0.6076	0.045 19	0.847 29	0.6247
0.005 23	0.844 15	0.6011	0.025 22	0.845 72	0.6130	0.055 90	0.848 13	0.6309
0.010 83	0.844 59	0.6045	0.035 61	0.846 54	0.6191			
$w_A = 0.90$								
0.002 34	0.798 10	0.3911	0.015 22	0.799 36	0.3964	0.045 55	0.802 32	0.4083
0.005 53	0.798 42	0.3925	0.025 59	0.800 30	0.4006	0.055 28	0.803 27	0.4121
0.010 71	0.798 92	0.3946	0.035 31	0.801 32	0.4044			
$w_A = 1$								
0.002 21	0.776 85	0.3365	0.015 13	0.778 23	0.3413	0.045 68	0.781 50	0.3521
0.005 37	0.777 20	0.3378	0.025 38	0.779 33	0.3450	0.055 32	0.782 50	0.3553
0.010 28	0.777 72	0.3396	0.035 46	0.780 41	0.3485			

The solutions were stored in dark-colored amber bottles that were kept in a dry box.

Densities of solvent mixtures and salt solutions were determined using a 15 cm^3 double-arm pycnometer (Nikam and Sawant, 1997). The pycnometer was calibrated using conductivity water with 0.997 07 g cm^{-3} as its density at 298.15 K. 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 minimum to attain thermal equilibrium. The position of the liquid levels in the two arms were recorded with the help of a traveling microscope that could be read to ±0.01 mm. The estimated accuracy of density measurements of solutions was ±0.000 01 g cm^{-3} as reported earlier (Nikam and Sawant, 1997).

The viscosity measurements were made using a commercial capillary viscometer of an Ostwald−Sprengel type. The viscometer was clamped vertically in the bath, and 20.00 cm^3 of the solution was added from a pipet. The viscometer was calibrated with water using the viscosity and density values reported by Stokes and Mills (1965). Viscosity values were determined using the relation (Wright,

Table 3. Ionic *B*-Coefficient of Ions in Acetonitrile (A) + Water (B) at 298.15 K on the Basis of $B_{K^+} = B_{Cl^-}$ [e]

	B^+/dm^3 mol^{-1}						
w_A	$K^+ = Cl^-$	Br^-	$[CH_3]_4N^+$	$[C_2H_5]_4N^+$	$[C_3H_7]_4N^+$	$[C_4H_9]_4N^+$	$[C_5H_{11}]_4N^+$
0	−0.007	−0.043	0.130	0.392	0.867	1.190	1.500
	−0.007[a]	−0.042[a]	0.143[b]	0.385[b]	0.889[b]	1.190[b]	
		−0.04[c]	0.12[c]	0.38[c]	0.86[b]	1.28[b]	
0.10	−0.001	−0.035	0.125	0.373	0.668	1.013	1.439
0.20	0.007[b]	−0.010[b]	0.110[b]	0.328[b]	0.586[b]	0.854[b]	
0.30	0.041	0.028[b]	0.134	0.294	0.482	0.781	1.203
0.40	0.090[b]	0.053[b]	0.166[b]	0.269[b]	0.493[b]	0.697[b]	
0.50	0.126	0.090	0.187	0.258	0.390	0.635	0.833
0.60	0.172[b]	0.118[b]	0.204[b]	0.250[b]	0.459[b]	0.601[b]	
0.70	0.222	0.132	0.314	0.318	0.417	0.596	0.804
0.80	0.284[b]	0.183[b]	0.240[b]	0.367[b]	0.484[b]	0.585[b]	
0.90	0.351	0.259		0.293	0.392	0.547	0.702
1	0.395	0.364		0.296	0.405	0.528	0.631
	0.43[c]	0.35[c]		0.33[d]	0.39[d]	0.500[d]	0.67[d]

[a] Bhattacharyya, 1995. [b] Kumar et al., 1989. [c] Kay et al., 1966. [d] Lawrence et al., 1989. [e] For refs. *a*, *b*, and *c*, all B_i values are of the $B_{K^+} = B_{Cl^-}$ method. For ref *d*, all B_i values are of a different method.

1961; Mulcahy, 1984)

$$\eta = d(Kt - L/t) \tag{1}$$

where η is the viscosity, d is the density of the liquid, t is the flow time, and K and L are the constants for a given viscometer. The flow time was measured with an electronic stopwatch with an accuracy of ±0.01 s. The maximum and minimum flow times were about 800 and 150 s, respectively. At least three repetitions of each data set reproducible to 0.05 s were obtained, and the results were averaged. The K and L were obtained by measuring the flow times of pure water at three temperatures (298.15, 303.15, and 308.15) K at which dynamic viscosities are known. Linear regression analysis of a plot of $\eta t/d$ against t^2 for pure water at three temperatures provides estimates of $K = 3.063\,395 \times 10^{-5}$ cm^2 s^{-2} and $L = -0.919\,74$ cm^2, as slope and intercept of the plot, with a correlation coefficient of 0.999. Knowledge of K and L allows determination of viscosities from the flow times and densities for acetonitrile + water and solutions of salts using eq 1. The estimated accuracy of experimental viscosities was ±0.1%. Comparison of measured densities and viscosities of acetonitrile + water mixtures at 298.15 K with those of literature values (Cunningham et al., 1967; Davis, 1983; Stokes and Mills, 1965; Lawrence et al., 1989; Aminabhavi and Gopalakrishna, 1995) is given in Table 1. Table 2 includes the experimental densities and viscosities for salt solutions at 298.15 K.

3. Results and Discussion

The viscosities of dilute salt solutions were analyzed by the Jones−Dole equation (Jones and Dole, 1929)

$$\eta_r = \eta/\eta_0 = 1 + Ac^{1/2} + Bc \tag{2}$$

where η and η_0 are the viscosities of the solution and solvent, respectively, and c is the concentration in molarity, A is the ion-ion interaction parameter that can be calculated from Debye−Huckel theory, and B reflects the effects of ion−solvent interactions. When $(\eta_r - 1)/c^{1/2}$ is plotted against $c^{1/2}$ for the electrolytes, straight lines are obtained with intercept equal to A, and the slopes yield the viscosity B-coefficient.

The B-coefficient of KCI, KBr, and R_4NBr, obtained by a computerized least-squares method, were used to calculate ionic B-coefficients of R_4NBr using the assumption $B_{K^+} = B_{Cl^-}$ (Kaminsky, 1957). Ionic B-coefficients of K^+, Cl^-, Br^-, and R_4N^+ ions along with literature values (Kay et al., 1966; Kumar et al., 1986; Lawrence et al., 1989; Bhattacharyya, 1995) are listed in Table 3.

Table 4. $B^+ - 0.025\ \bar{V}_2^{\circ+}$ Values of R_4N^+ Ions in Acetonitrile (A) + Water (B) at 298.15 K

	$B^+ - 0.0025\bar{V}_2^{\circ+}$/dm^3 mol^{-1}				
w_A	$[CH_3]_4N^+$	$[C_2H_5]_4N^+$	$[C_3H_7]_4N^+$	$[C_4H_9]_4N^+$	$[C_5H_{11}]_4N^+$
0	−0.073	0.036	0.035	0.527	0.683
0.10	−0.079	0.016	0.151	0.348	0.616
0.30	−0.074	−0.062	−0.036	0.111	0.373
0.50	−0.026	−0.097	−0.131	−0.041	−0.049
0.70	0.093	−0.036	−0.105	−0.087	−0.045
0.90		−0.103	−0.175	−0.189	−0.205
1		−0.109	−0.176	−0.248	−0.299

The difference $B^+ - 0.0025\bar{V}_2^{\circ+}$ is used as a criterion for determining the net structural effects of R_4N^+ ions (Desnoyers and Perrron, 1972). According to these authors, a negative value for the difference term would correspond to an overall structure breaker, while a positive value would indicate a structure maker. The values of $\bar{V}_2^{\circ+}$ (cm^3 mol^{-1}), calculated by the method as described by Conway et al. (1966), are taken from our previous data (Nikam and Sawant, 1977). Table 4 indicates that the difference term is positive for R_4N^+ ions in water−rich solutions and negative in acetonitrile−rich solution except for $[CH_3]_4N^+$ ion, suggesting structure-making, structure-breaking behavior of R_4N^+ ions, respectively.

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