Limiting Ionic Partial Molar Volumes and Viscosities of Cs^+, Na^+, $(C_4H_9)_4N^+$, Cl^-, Br^-, $I,^-$, and BPh_4^- in Aqueous Acetone at 308.15 K

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Densities and viscosities of CsX ($X = Cl^-$, Br^-, I^-) NaBr, $(C_4H_9)_4NBr$, and $NaBPh_4$ in (0, 0.2, 0.4, 0.6, and 0.8) weight fraction (w_1) acetone + water have been measured over the whole composition range at 308.15 K. From the densities, apparent and limiting partial molar volumes of the electrolytes and ions in their mixtures have been evaluated. The viscosity data have been analyzed with the help of the Jones−Dole equation, and the corresponding viscosity B coefficients have been calculated. The ionic B coefficients have been determined using the reference electrolyte $NaBPh_4$.

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1. Introduction

The nature of ion−solvent interactions in aqueous and nonaqueous solutions has been successfully elucidated from the volumetric and viscometric behavior of electrolytes.[1,2] A knowledge of this property is very important in many practical problems concerning energy transport, mass transport, and fluid flow. In the present paper, we report apparent and limiting ionic partial molar volumes and viscosities of CsX ($X = Cl^-$, Br^-, I^-), NaBr, $(C_4H_9)_4NBr$, and $NaBPh_4$ in acetone + water mixtures at 308.15 K to determine the effect of the variation of limiting ionic partial molar volumes and viscosity B coefficients with acetone content for a given electrolyte.

2. Experimental Section

Water was distilled in quick-fit 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} $\Omega^{-1}\cdot cm^{-1}$. Acetone was purified[3] by refluxing with $KMnO_4$ for 2 h. The solution was cooled, and Na_2CO_3 was added to it. Two hours later it was filtered and distilled. The distillate was further distilled and preserved over anhydrous $CaCl_2$ in a vacuum desiccator. The purity of acetone was checked by comparing its observed density ($0.78442\ g\cdot cm^{-3}$) to that of $0.7844\ g\cdot cm^{-3}$ at 298.15 K reported in the literature[3].

CsCl, CsBr, and CsI were of analar grade, from the SAS chemical company, Bombay, with a purity greater than 99%; $NaBPh_4$ was from E. Merck with a purity greater than 99.5%; NaBr was from Loba Chemie Indoaustranal company with a purity greater than 99%; and $(C_4H_9)_4NBr$ was from Fluka Chemie, AG, CH-9470 assay greater than 98% (Br). All of these electrolytes were vacuum-dried and used without further purification.

Acetone + water mixtures of compositions (0, 0.2, 0.4, 0.6, and 0.8) weight fraction of acetone were prepared by mixing known masses of water and acetone in glass-stoppered flasks. No attempts were made to monitor the relative humidity of the air to which the acetone was exposed for a short period of time during preparation. However, any effect of humidity on the composition of acetone was considered to be negligible.

Accurately known masses of electrolytes were dissolved in a particular solvent to give concentration of 0.05 M. This served as the stock solution. Additional concentrations were obtained by using a mass dilution technique. Electrolyte concentrations varied from (0.005 to 0.05) M. The exact concentration of the electrolyte solution was obtained either from the measurement of halide ion concentration using the Volahrds method or by gravimetric analysis.[4,5] Densities were determined by using 15-cm^3 bicapillary pycnometer as described earlier.[6] The pycnometer was calibrated using conductivity water with $0.99705\ g\cdot cm^{-3}$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 to attain thermal equilibrium. The positions of the liquid levels in the two arms were recorded with the help of a travelling microscope that could be read to 0.01 mm. The estimated accuracy of the density measurements of solvent and electrolyte solutions was $0.00005\ g\cdot cm^{-3}$.

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

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \tag{1}$$

where η_1, ρ_1, t_1 and η_2, ρ_2, t_2 are the viscosity, density, and flow time of the 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 uncertainty in the experimental viscosities (relative to water) was ±0.1%.

3. Results and Discussion

The observed densities, ρ, and viscosities, η, of the solutions, which are the mean of three or four series of

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Table 1. Densities, ρ, Apparent Molar Volumes, V_ϕ, and Viscosities, η, for CsX, $(C_4H_9)_4NBr$, NaBr, and $NaBPh_4$ in Acetone (1) + Water (2) at T = 308.15 K

C mol·dm^{-3}	$\rho \times 10^{-3}$ kg·m^{-3}	$V_\phi \times 10^6$ m^3·mol^{-1}	η mPa·s	C mol·dm^{-3}	$\rho \times 10^{-3}$ kg·m^{-3}	$V_\phi \times 10^6$ m^3·mol^{-1}	η mPa·s	C mol·dm^{-3}	$\rho \times 10^{-3}$ kg·m^{-3}	$V_\phi \times 10^6$ m^3·mol^{-1}	η mPa·s
					CsCl						
	$w_1 = 0$				$w_1 = 0.2$				$w_1 = 0.4$		
0.0053	0.99471	40.56	0.7232	0.0052	0.96485	38.91	0.9913	0.0092	0.92992	39.51	1.0347
0.0108	0.99541	40.64	0.7233	0.0098	0.96545	39.00	0.9941	0.0158	0.93079	39.69	1.0403
0.0150	0.99595	40.69	0.7233	0.0165	0.96633	39.09	0.9975	0.0188	0.93118	39.76	1.0426
0.0199	0.99657	40.73	0.7233	0.0217	0.96700	39.15	0.9999	0.0235	0.93180	39.85	1.0462
0.0250	0.99723	40.78	0.7233	0.0267	0.96766	39.20	1.0020	0.0294	0.93257	39.96	1.0505
0.0300	0.99786	40.81	0.7232	0.0327	0.96844	39.25	1.0044	0.0328	0.93301	40.02	1.0529
0.0348	0.99848	40.85	0.7232	0.0387	0.96922	39.30	1.0068	0.0391	0.93384	40.11	1.0574
0.0413	0.99930	40.89	0.7232	0.0413	0.96956	39.32	1.0078	0.0423	0.93425	40.16	1.0596
	$w_1 = 0.6$				$w_1 = 0.8$						
0.0096	0.88617	37.64	0.8560	0.0056	0.83366	36.05	0.5239				
0.0133	0.88666	37.77	0.8595	0.0084	0.83405	36.19	0.5261				
0.0179	0.88728	37.90	0.8638	0.0125	0.83462	36.37	0.5291				
0.0224	0.88789	38.02	0.8678	0.0172	0.83526	36.55	0.5324				
0.0273	0.88855	38.13	0.8720	0.0223	0.83596	36.71	0.5359				
0.0314	0.88909	38.22	0.8755	0.0296	0.83696	36.91	0.5407				
0.0372	0.88987	38.33	0.8803	0.0340	0.83757	37.02	0.5436				
0.0404	0.89030	38.39	0.8829	0.0379	0.83810	37.11	0.5461				
					CsBr						
	$w_1 = 0$				$w_1 = 0.2$				$w_1 = 0.4$		
0.0098	0.99605	47.20	0.7230	0.0050	0.96501	46.34	0.9872	0.0051	0.92958	46.01	1.0265
0.0151	0.99703	47.24	0.7229	0.0100	0.96585	46.42	0.9886	0.0100	0.93041	46.16	1.0291
0.0201	0.99804	47.28	0.7228	0.0150	0.96669	46.49	0.9899	0.0150	0.93126	46.28	1.0316
0.0256	0.99904	47.32	0.7226	0.0200	0.96753	46.54	0.9912	0.0201	0.93212	46.39	1.0342
0.0300	1.00005	47.34	0.7225	0.0250	0.96837	46.59	0.9924	0.0250	0.93295	46.47	1.0365
0.0352	1.00104	47.37	0.7223	0.0296	0.96914	46.63	0.9935	0.0350	0.93464	46.63	1.0413
0.0398	1.00202	47.40	0.7222	0.0350	0.97004	46.68	0.9948	0.0374	0.93505	46.66	1.0424
0.0450	1.00303	47.42	0.7220	0.0405	0.97096	46.72	0.9961	0.0422	0.93586	46.73	1.0447
	$w_1 = 0.6$				$w_1 = 0.8$						
0.0092	0.88646	44.84	0.8501	0.0084	0.83437	43.44	0.5226				
0.0134	0.88719	44.98	0.8528	0.0130	0.83518	43.62	0.5249				
0.0179	0.88796	45.10	0.8557	0.0168	0.83585	43.75	0.5268				
0.0226	0.88878	45.22	0.8586	0.0211	0.83661	43.88	0.5290				
0.0268	0.88950	45.31	0.8612	0.0254	0.83736	43.99	0.5311				
0.0318	0.89036	45.41	0.8642	0.0300	0.83817	44.11	0.5334				
0.0358	0.89105	45.49	0.8666	0.0330	0.83870	44.18	0.5349				
0.0402	0.89180	45.56	0.8693	0.0370	0.83940	44.26	0.5368				
					CsI						
	$w_1 = 0$				$w_1 = 0.2$				$w_1 = 0.4$		
0.0100	0.99605	58.65	0.7228	0.0098	0.96618	57.26	0.9881	0.0115	0.93110	56.34	1.0283
0.0149	0.99703	58.69	0.7226	0.0150	0.96724	57.32	0.9893	0.0141	0.93163	56.39	1.0294
0.0199	0.99804	58.73	0.7223	0.0194	0.96814	57.36	0.9903	0.0163	0.93209	56.44	1.0303
0.0249	0.99904	58.76	0.7221	0.0242	0.96912	57.41	0.9913	0.0186	0.93257	56.48	1.0313
0.0299	1.00005	58.79	0.7218	0.0294	0.97018	57.45	0.9924	0.0210	0.93306	56.52	1.0323
0.0348	1.00104	58.81	0.7215	0.0339	0.97110	57.48	0.9934	0.0236	0.93360	56.57	1.0333
0.0397	1.00202	58.84	0.7212	0.0387	0.97208	57.51	0.9944	0.0257	0.93404	56.60	1.0342
0.0447	1.00303	58.86	0.7209	0.0435	0.97306	57.54	0.9954	0.0282	0.93455	56.64	1.0352
	$w_1 = 0.6$				$w_1 = 0.8$						
0.0113	0.88725	55.66	0.8501	0.0105	0.83514	54.59	0.5237				
0.0138	0.88777	55.74	0.8515	0.0124	0.83555	54.66	0.5247				
0.0156	0.88815	55.78	0.8525	0.0147	0.83604	54.74	0.5259				
0.0179	0.88864	55.84	0.8538	0.0169	0.83651	54.81	0.5270				
0.0202	0.88912	55.89	0.8551	0.0190	0.83696	54.87	0.5280				
0.0224	0.88958	55.94	0.8564	0.0211	0.83741	54.92	0.5290				
0.0246	0.89004	55.99	0.8576	0.0233	0.83788	54.98	0.5301				
0.0268	0.89050	56.03	0.8588	0.0253	0.83830	55.03	0.5311				
					$(C_4H_9)_4NBr$						
	$w_1 = 0$				$w_1 = 0.2$				$w_1 = 0.4$		
0.0100	0.99423	303.81	0.7316	0.0098	0.96443	306.51	0.9964	0.0094	0.92905	308.09	1.0334
0.0151	0.99434	303.67	0.7358	0.0145	0.96456	306.45	1.0015	0.0140	0.92922	308.13	1.0383
0.0198	0.99444	303.56	0.7397	0.0193	0.96469	306.40	1.0067	0.0195	0.92942	308.18	1.0441
0.0250	0.99455	303.46	0.7440	0.0243	0.96483	306.36	1.0121	0.0232	0.92955	308.20	1.0479
0.0296	0.99465	303.37	0.7478	0.0289	0.96495	306.32	1.0170	0.0276	0.92971	308.23	1.0525
0.0345	0.99475	303.29	0.7519	0.0336	0.96508	306.29	1.0220	0.0329	0.92990	308.27	1.0581
0.0394	0.99486	303.21	0.7559	0.0385	0.96521	306.25	1.0272	0.0375	0.93006	308.29	1.0628
0.0444	0.99496	303.13	0.7600	0.0431	0.96534	306.22	1.0321	0.0416	0.93021	308.31	1.0671

Table 1. (Continued)

C	$\rho \times 10^{-3}$	$V_\phi \times 10^6$	η	C	$\rho \times 10^{-3}$	$V_\phi \times 10^6$	η	C	$\rho \times 10^{-3}$	$V_\phi \times 10^6$	η
mol·dm^{-3}	kg·m^{-3}	m^3·mol^{-1}	mPa·s	mol·dm^{-3}	kg·m^{-3}	m^3·mol^{-1}	mPa·s	mol·dm^{-3}	kg·m^{-3}	m^3·mol^{-1}	mPa·s
					$(C_4H_9)_4NBr$ (Continued)						
	$w_1 = 0.6$				$w_1 = 0.8$						
0.0089	0.88532	307.04	0.8504	0.0084	0.83346	305.51	0.5217				
0.0138	0.88557	307.20	0.8543	0.0126	0.83374	305.73	0.5236				
0.0179	0.88577	307.32	0.8575	0.0168	0.83403	305.93	0.5255				
0.0222	0.88599	307.42	0.8609	0.0173	0.83406	305.95	0.5257				
0.0266	0.88621	307.52	0.8644	0.0253	0.83459	306.25	0.5293				
0.0314	0.88645	307.62	0.8682	0.0293	0.83486	306.39	0.5311				
0.0356	0.88665	307.70	0.8715	0.0356	0.83528	306.58	0.5339				
0.0406	0.88690	307.79	0.8755	0.0406	0.83561	306.72	0.5362				
					NaBr						
	$w_1 = 0$				$w_1 = 0.2$				$w_1 = 0.4$		
0.0108	0.99487	24.98	0.7240	0.0098	0.96495	23.72	0.9883	0.0095	0.92949	22.32	1.0276
0.0151	0.99521	25.02	0.7243	0.0150	0.96537	23.78	0.9895	0.0142	0.92988	22.44	1.0295
0.0203	0.99561	25.06	0.7246	0.0194	0.96572	23.83	0.9905	0.0188	0.93025	22.53	1.0313
0.0249	0.99597	25.10	0.7249	0.0251	0.96617	23.88	0.9918	0.0238	0.93066	22.62	1.0332
0.0304	0.99640	25.13	0.7252	0.0295	0.96652	23.92	0.9928	0.0290	0.93108	22.71	1.0352
0.0348	0.99674	25.15	0.7254	0.0337	0.96686	23.95	0.9937	0.0333	0.93143	22.77	1.0368
0.0402	0.99716	25.18	0.7257	0.0389	0.96727	23.99	0.9948	0.0391	0.93190	22.85	1.0390
0.0465	0.99765	25.21	0.7261	0.0445	0.96772	24.03	0.9960	0.0422	0.93215	22.89	1.0401
	$w_1 = 0.6$				$w_1 = 0.8$						
0.0098	0.88570	20.70	0.8485	0.0090	0.8337	20.70	0.5219				
0.0136	0.88602	20.82	0.8502	0.0133	0.8340	20.82	0.5236				
0.0183	0.88641	20.94	0.8523	0.0168	0.8344	20.94	0.5249				
0.0230	0.88681	21.05	0.8544	0.0224	0.8348	21.05	0.5269				
0.0266	0.88711	21.13	0.8560	0.0255	0.8351	21.13	0.5280				
0.0314	0.88751	21.22	0.8581	0.0295	0.8355	21.22	0.5294				
0.0351	0.88782	21.29	0.8597	0.0337	0.8358	21.29	0.5309				
0.0404	0.88826	21.38	0.8620	0.0378	0.8362	21.38	0.5324				
					$NaBPh_4$						
	$w_1 = 0$				$w_1 = 0.2$				$w_1 = 0.4$		
0.0100	0.99460	287.26	0.7317	0.0114	0.96490	288.79	0.9996	0.0110	0.92960	280.94	1.0370
0.0128	0.99476	287.15	0.7340	0.0134	0.96503	288.74	1.0020	0.0130	0.92977	280.94	1.0394
0.0148	0.99487	287.08	0.7356	0.0155	0.96516	288.70	1.0044	0.0149	0.92992	280.94	1.0418
0.0176	0.99503	286.99	0.7379	0.0175	0.96529	288.66	1.0067	0.0168	0.93008	280.95	1.0441
0.0198	0.99516	286.92	0.7397	0.0193	0.96540	288.63	1.0088	0.0186	0.93022	280.95	1.0463
0.0228	0.99533	286.84	0.7421	0.0216	0.96555	288.59	1.0115	0.0202	0.93035	280.95	1.0483
0.0256	0.99549	286.76	0.7444	0.0237	0.96569	288.56	1.0139	0.0224	0.93053	280.95	1.0510
0.0291	0.99570	286.67	0.7472	0.0251	0.96578	288.54	1.0155	0.0250	0.93074	280.96	1.0542
	$w_1 = 0.6$				$w_1 = 0.8$						
0.0108	0.88592	276.92	0.8547	0.0101	0.83406	271.58	0.5246				
0.0125	0.88608	276.97	0.8565	0.0117	0.83425	271.66	0.5256				
0.0143	0.88626	277.02	0.8584	0.0135	0.83445	271.73	0.5268				
0.0161	0.88643	277.06	0.8603	0.0151	0.83464	271.79	0.5278				
0.0178	0.88660	277.10	0.8621	0.0169	0.83485	271.85	0.5290				
0.0194	0.88675	277.14	0.8637	0.0184	0.83502	271.90	0.5300				
0.0226	0.88706	277.20	0.8671	0.0211	0.83533	271.98	0.5317				
0.0247	0.88726	277.24	0.8693	0.0234	0.83560	272.05	0.5332				

many measurements of CsX solutions at 308.15 K, are given in Table 1 along with the mass % values of acetone in the mixed solvent. The apparent molar volumes, V_ϕ, of the electrolytes were calculated from the densities using the equation

$$V_\phi = \frac{M}{\rho_o} - \frac{1000(\rho - \rho_o)}{C\rho_o} \tag{2}$$

where ρ_o is the density of water or acetone + water solvent, ρ is the density of electrolyte solutions, and M is the molecular weight of the electrolyte. The values of V_ϕ for electrolytes are given in the Table 1. V_ϕ for each electrolyte varied linearly with $C^{1/2}$ over the concentration range studied. The limiting partial molar volume, $V°_\phi$, of these electrolytes was obtained by computerized least-squares fitting of the results, with a correlation coefficient greater than 0.999, to the Masson equation[9]

$$V_\phi = V_\phi° + S^*_v C^{1/2} \tag{3}$$

where S^*_v is the experimental slope. The values of $V_\phi°$ and S^*_v are presented in Table 2. Figure 1 shows a representative plot of $V_\phi°$ versus $C^{1/2}$ for CsCl in all solvents. Similar plots are obtained for the other electrolytes.

The S^*_v values shown in Table 2 are positive for the solutions of electrolytes in water and acetone + water mixtures, indicating ion−ion interactions in solvent media.[10]

The S^*v values decrease as the size of CsX increases; it appears that the dielectric constant[11] of the solvent medium and the size of the X^- ion play an important role in the determination of S^*v values.

$V_\phi°$ is regarded as a measure of solute−solvent interactions. The $V_\phi°$ values in water and acetone + water

Table 2. Limiting Partial Molar Volumes, V_ϕ°, Experimental Slopes, S^*v, and Standard Deviation, σ, of CsCl, CsBr, CsI, $(C_4H_9)_4NBr$, NaBr, and $NaBPh_4$ in Acetone + Water at T = 308.15 K

electrolyte	w_1	$V_\phi^\circ \times 10^6$ / $m^3 \cdot mol^{-1}$	$S^*v \times 10^3$ / $dm^3 \cdot L^{1/2} \cdot mol^{-3/2}$	σ
CsCl	0	40.38	2.51	0.003
	0.2	38.69	3.11	0.003
	0.4	38.95	5.89	0.003
	0.6	36.93	7.27	0.002
	0.8	35.38	8.89	0.004
CsBr	0	47.00	1.98	0.003
	0.2	46.13	2.92	0.003
	0.4	45.63	5.37	0.003
	0.6	44.18	6.91	0.003
	0.8	42.68	8.19	0.003
CsI	0	58.46	1.90	0.002
	0.2	57.01	2.57	0.003
	0.4	55.80	4.97	0.003
	0.6	54.98	6.42	0.003
	0.8	53.79	7.81	0.003
$(C_4H_9)_4NBr$	0	304.42	−6.35	0.021
	0.2	306.77	−2.64	0.003
	0.4	307.88	1.89	0.020
	0.6	306.39	7.00	0.002
	0.8	304.49	11.02	0.005
NaBr	0	24.77	2.06	0.004
	0.2	23.45	2.77	0.004
	0.4	21.81	5.27	0.002
	0.6	20.04	6.65	0.003
	0.8	20.04	6.81	0.011
$NaBPh_4$	0	288.10	−8.33	0.002
	0.2	289.30	−4.81	0.003
	0.4	280.90	0.36	0.003
	0.6	276.30	6.00	0.003
	0.8	270.71	8.78	0.003

mixtures are shown in Table 2 for all CsX along with reference electrolytes.

Limiting ionic partial molar volumes have been calculated following the method suggested by Conway et al.[12] Following this procedure, the V_ϕ° values for CsX in water and acetone + water were plotted against the molecular weight of the corresponding X^- ions using an equation of the form

$$V_\phi^\circ = V_\phi^\circ(Cs^+) + b(\text{mol wt of } X^-) \qquad (4)$$

where b is a constant and $V_\phi^\circ(Cs^+)$ is the limiting ionic partial molar volumes of the Cs^+ ion. An excellent linear relationship was observed for all electrolytes in all solvents with a correlation coefficient greater than 0.999.

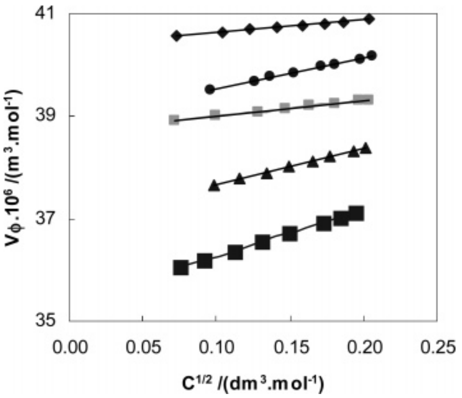

Figure 1. Plot of apparent molar volume V_ϕ versus $C^{1/2}$ for cesium chloride in w_1 = 0 (◆), w_1 = 0.2 (■), w_1 = 0.4 (●), w_1 = 0.6 (▲), and w_1 = 0.8 (■).

Table 3. Ionic Partial Molar Volumes in Various Acetone (1) + Water (2) Mixtures at T = 308.15 K

	$V_\phi^{0\pm} \times 10^6/m^3 \cdot mol^{-1}$						
w_1	Na^+	Cs^+	Cl^-	Br^-	I^-	BPh_4^-	$(C_4H_9)_4 N^+$
0	10.37	32.60	7.78	14.4	25.86	277.73	290.02
0.2	8.38	31.06	7.63	15.07	25.95	280.92	291.70
0.4	8.06	31.88	7.07	13.75	23.92	272.84	294.13
0.6	5.25	29.39	7.54	14.79	25.59	271.05	291.60
0.8	2.89	27.66	7.72	15.02	26.13	267.81	289.47

Table 4. Parameters of Jones−Dole Equation A and B and Standard Deviation, σ, for CsCl, CsBr, CsI, $(C_4H_9)_4NBr$, NaBr, and $NaBPh_4$ in Acetone (1) + Water (2) at T = 308.15 K

electrolyte	w_1	A / $dm^{3/2} \cdot mol^{-1/2}$	B / $dm^3 \cdot mol^{-1}$	σ
CsCl	0	0.0063	−0.0259	0.0002
	0.2	0.0680	0.2150	0.0002
	0.4	0.0720	0.4950	0.0002
	0.6	0.0786	0.7750	0.0002
	0.8	0.0760	1.048	0.0002
CsBr	0	0.0057	−0.0560	0.0002
	0.2	0.0117	0.2095	0.0002
	0.4	0.0188	0.4100	0.0002
	0.6	0.0222	0.6590	0.0003
	0.8	0.0258	0.9110	0.0004
CsI	0	0.0070	−0.0966	0.0002
	0.2	0.0084	0.1940	0.0002
	0.4	0.0084	0.3740	0.0002
	0.6	0.0089	0.6370	0.0002
	0.8	0.0185	0.8920	0.0006
$(C_4H_9)_4NBr$	0	0.0072	1.1180	0.0003
	0.2	0.0082	1.0610	0.0002
	0.4	0.0082	0.9930	0.0004
	0.6	0.0030	0.9280	0.0002
	0.8	0.0013	0.8620	0.0006
NaBr	0	0.0065	0.0618	0.0002
	0.2	0.0110	0.1900	0.0002
	0.4	0.0141	0.3280	0.0001
	0.6	0.0164	0.4700	0.0003
	0.8	0.0240	0.6150	0.0006
$NaBPh_4$	0	0.0116	1.0840	0.0002
	0.2	0.0169	1.1090	0.0002
	0.4	0.0076	1.1700	0.0002
	0.6	0.0042	1.2260	0.0002
	0.8	0.0039	1.2390	0.0007

Table 3 represents the values of V_ϕ°(ion). $V_\phi^\circ(X^-)$ values show a systematic increase as the size of X^- increases. In general, the $V_\phi^\circ(Cs^+)$ values decreases with an increase in the acetone content of the solvent mixture, whereas $V_\phi^\circ(X^-)$ in general increases with the acetone content in the acetone + water mixture.

The viscosities of cesium halides, $(C_4H_9)_4NBr$, NaBr, and $NaBPh_4$ are analyzed with the help of the Jones−Dole[13] equation

$$\eta_r = \left(\frac{\eta}{\eta_o}\right) = 1 + AC^{1/2} + BC \qquad (5)$$

where η and η_o 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, whereas B reflects the effect of ion−solvent interactions. Plots of $[(\eta/\eta_o) - 1]/C^{1/2}$ versus $C^{1/2}$ for all of the electrolytes over the whole composition range of aqueous acetone are found to be straight lines with intercepts equal to A, and the slopes give the Jones−Dole viscosity B coefficients. Figure 2 shows a representative plot for CsCl in all solvents. Similar plots are obtained for the other electrolytes. The A and B coefficients obtained with a computerized least-squares method are listed in Table

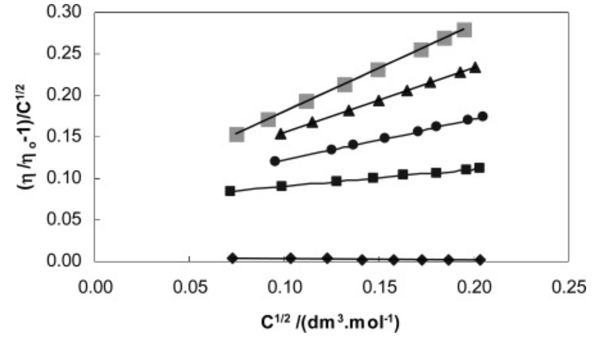

Figure 2. Plot of $[(\eta/\eta_o) - 1]/C^{1/2}$ versus $C^{1/2}$ for cesium chloride in $w_1 = 0$ (◆), $w_1 = 0.2$ (■), $w_1 = 0.4$ (●), $w_1 = 0.6$ (▲), and $w_1 = 0.8$ (■).

Table 5. Ionic *B* Coefficients of Na^+, Cs^+, Cl^-, Br^-, I^-, BPh_4^-, and Bu_4N^+ Ions in Acetone (1) +Water (2) Mixtures at *T* = 308.15 K

	B/dm^3·mol^{-1}						
w_1	Na^+	Cs^+	Cl^-	Br^-	I^-	BPh_4^-	$(C_4H_9)_4\,N^+$
0	−0.0943	−0.2121	0.1862	0.1561	0.1155	1.1783	0.9619
0.2	0.0189	0.0384	0.1766	0.1711	0.1556	1.0901	0.8899
0.4	0.1597	0.2417	0.2533	0.1683	0.1323	1.0103	0.8247
0.6	0.2988	0.4878	0.2872	0.1712	0.1492	0.9272	0.7568
0.8	0.4209	0.7169	0.3311	0.1941	0.1751	0.8181	0.6679

4.The viscosity *B* coefficients are negative for aqueous CsCl, CsBr, and CsI solutions, suggesting the structure-breaking tendencies of these electrolytes in pure water. The *B* values in these systems increase with increasing acetone content in the solvent mixtures, indicating that the solute−solvent interactions increase with the decrease in the dielectric constant of the solvent system. The *B* values are in the order CsCl < CsBr < CsI, which is in agreement with the intrinsic ionic volume order $Cl^- < Br^- < I^-$. This means that as the electrolyte molar volume increases solute−solvent interaction increases.

To have a better understanding of ion−solvent interactions, it is necessary to split the viscosity *B* coefficient into the individual ionic *B* coefficients. This has been done in the present study using $(C_4H_9)_4NBr$, NaBr, and $NaBPh_4$ as the reference electrolytes, assuming that[14]

$$\frac{B(\mathrm{BPh_4}^-)}{B(\mathrm{Bu_4N}^+)} = \frac{r^3(\mathrm{BPh_4}^-)}{r^3(\mathrm{Bu_4N}^+)} = \left(\frac{5.35}{5.00}\right)^3$$

$$B(\mathrm{Bu_4NBPh_4}) = B(\mathrm{BPh_4}^-) + B(\mathrm{Bu_4N}^+) \qquad (6)$$

where *r* is the ionic radius. The solubility of Bu_4NBPh_4 is very low in aqueous acetone at room temperature; therefore, the above method could not be employed. The ionic *B* coefficient is therefore obtained from the relation[15]

$$B(\mathrm{Bu_4NBPh_4}) = B(\mathrm{Bu_4NBr}) + B(\mathrm{NaBPh_4}) - B(\mathrm{NaBr}) \quad (7)$$

Therefore, the Jones−Dole viscosity *B* coefficients were determined for Bu_4NBr, $NaBPh_4$, and NaBr; using eq 7, the *B* coefficient of Bu_4NBPh_4 was calculated; and from eq 6, the *B* coefficient of Bu_4N^+ was calculated, which enabled us to get the ionic B coefficient of Br^- and hence the ionic *B* coefficient of all of the other ions could be calculated. The ionic *B* coefficients for all cations and anions are listed in Table 5. The small negative *B* values of cations and small positive values of halide (Cl^-, Br^- and I^-) ions in water are due to the breakdown of the tetrahedral structure of water and the formation of strongly structured solvated ions. As the acetone content in the solvent mixture increases, these *B* values of small ions increase. Small ions have values that are considerably higher in acetone than in water and can reasonably be ascribed to increased ion−solvent interactions through charge-transfer phenomena.

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Literature Cited

(1) Millero, F. J. In *The Partial Molal Volumes of Electrolytes in Aqueous Solutions. In Water and Aqueous Solutions (Structure, Thermodynamics and Transport Processes)*; Horne, R. A., Ed.; Wiley-Interscience: New York, 1972; Chapter 13.
(2) Nikam, P. S.; Sawant, A. B. Viscosity of Potassium Halides and Symmetrical Tetra Alkyl Ammonium Bromides in Acetonitrile + Water Mixtures at 298.15 K. *J. Chem. Eng. Data* **1997**, *42*, 1151−1156.
(3) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed; Techniques of Chemistry; Wiley-Interscience, New York, 1986; Vol. 2.
(4) Kreshkov, A. P. *Fundamentals of Analytical Chemistry*, 3rd ed; Khimiya: Moscow, 1970; Vol. 2.
(5) Nikam, P. S.; Nikumbh, A. B. Ionic Viscosity *B*-Coefficients of Tetraalkyl Ammonium Chlorides in (0 to 100) Mass % Water + Methanol at 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 400−404.
(6) Nikam, P. S.; Jagdale, B. S.; Sawant, A. B.; Hasan, M. Ultrasonic Study of Binary Liquid Mixtures of Benzonitrile with Alkanols (C_1−C_3) at Various Temperatures. *Acoust. Lett.* **1999**, *22*, 199−203.
(7) Nikam, P. S.; Kharat, S. J. Densities and Viscosities of Binary Mixtures of *N,N*-Dimethylformamide with Benzyl Alcohol and Acetophenone at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **2003**, *48*, 1291−1295.
(8) Marsh, K. N. Recommended Reference Materials for the Realisation of Physicochemical Properties; Blackwell Scientific Publications: Oxford, UK, 1987.
(9) Masson, D. O. Solute Molecular Volumes in Relation to Solvation and Ionization. *Philos. Mag.* **1929**, *8*, 218−235.
(10) Nikam P. S.; Sawant A. B. Limiting Ionic Partial Molar Volumes of R_4N^+ and Br^- in Aqueous Acetonitrile at 298.15 K. *J. Chem. Eng. Data* **1997**, *42*, 585−589.
(11) Nikam P. S.; Sawant A. B. Volumetric behaviour of R_4N^+ and Br^- ions in acetonitrile + water at 303.15 K. *J. Mol. Liq.* **1998**, *75*, 199−209.
(12) Conway, B. E.; Verrall, R. E.; Desnoyers, J. E. Partial Molal Volumes of Tetraalkylammonium Halides and Assignment of Individual Ionic Contributions. *J. Chem. Soc., Faraday Trans.* **1966**, *62*, 2736−2749.
(13) Jones, G.; Dole, M. The Viscosity of Aqueous Solutions of Strong Electrolytes with Special Reference to Barium Chloride. *J. Am. Chem. Soc*. **1929**, *51*, 2950−2964.
(14) Gill D. S.; Chauhan M. S.; Sekhri M. B. Conductance and Viscosity Measurements of Tetrabutylammonium Tetraphenylboride in Nonaqueous Solvents at 25 °C. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 3461−3466.
(15) Nandi, D.; Hazra, D. K. Viscosities of Alkali-Metal Chlorides and Bromides in 2-Methoxyethanol at 25 and 35 °C. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 4227−4236.

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