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Viscosity *B*-Coefficients of 1:1 Electrolytes in Acetonitrile-Water Mixtures at 25 and 35 °C

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Viscosity *B*-coefficients of the Jones-Dole equation were determined for KCl, KBr, KI, NaBr, CsI, Me_4NBr, Et_4NBr, *n*-Pr_4NI, *n*-Bu_4NBr, and $Na[BPh_4]$ at 25 and 35 °C in various acetonitrile–H_2O mixtures. The *B*-coefficients were split into the ionic components and a comparison was made among different methods available. The effective flow volume, V_e° obtained from $B=2.5\,V_e^\circ$ was compared with the crystal ionic volume, V_{cryst}° and the ionic partial molar volume, $\overline{V}_{\text{ion}}^\circ$ determined from the density experiments simultaneously carried out. Ion-solvent and solvent-solvent interactions were discussed in terms of the above parameters.

Microviscosity determination of electrolytes in aqueous solutions as well as in nonaqueous solutions have been carried out in order to throw light on the nature of ion-solvent interactions. Recently, such measurements have also been reported for water-organic binary solvent system. In a previous communication,[1] we have tried to evaluate the nature of ion-solvent interactions in DMF–H_2O binary solvent. We found that the use of a large number of electrolytes of known behavior provided useful information on the effects induced by the cosolvent on the 'water-structure'. Interesting results were obtained by previous workers on the viscosity and transport properties of electrolytes in pure acetonitrile.[2] Recently some works have been reported on the ultrasonic,[3] transport,[4] and thermodynamic[5] properties of the binary mixture of acetonitrile–H_2O system. However, no work has been reported on the viscosity of electrolytes in acetonitrile–H_2O solvent system. We therefore, thought it timely to extend our previous work[1] to this solvent system. In this paper we report the viscosity and density data of large number of uni-univalent electrolytes in various acetonitrile–H_2O mixtures at 25 and 35 °C. The primary objective of this study is to investigate the nature of ion-solvent interactions and hence throw light on the nature of effects induced by acetonitrile on the 'water-structure'.

Experimental

KCl, KBr (BDH, AR), KI, NaBr (E. Merck), CsI (Sisco, >99% pure), and $Na[BPh_4]$ (Sigma) were used without further purification. Laboratory grade Me_4NBr (Fluka, USA) and Et_4NBr (BDH) were purified as described elsewhere.[6] *n*-Pr_4NBr and *n*-Bu_4NBr (Fluka, puriss) were purified as described by Conway et al.[7] *n*-Pr_4NI (Fluka, puriss) was recrystallized from acetone (E. Merck) by adding ether. The salts were stored in vacuum desiccator and dried for 3 to 4 h at 100 °C prior to use. Acetonitrile was purified as described elsewhere.[8] Its density, viscosity, and refractive index at 25 °C compared well with the reported values.[9] Laboratory grade distilled water was redistilled over $KMnO_4$ in an all glass unit. Freshly distilled water was used to make all solutions.

Densities of the solutions were measured using a 45 ml single stem capillary pycnometer having a capillary diameter of 1.5 mm and were vacuum corrected. The values are precise to $5\times10^{-5}\,\text{g cm}^{-3}$. Viscosity of dilute solutions were measured using an Ubbelohde suspended level viscometer having a fall time of 1130.2 s for water at 25 °C. The kinetic energy correction term for the viscometer fell in the region of experimental error and, therefore, was neglected. All measurements were carried out in a thermostatic water bath with an accuracy of ±0.01 °C. The relative viscosities determined were precise to 0.05%.

Results and Discussion

The relative viscosity of KCl, KBr, KI, NaBr, CsI, Me_4NBr, Et_4NBr, *n*-Pr_4NI, and *n*-Bu_4NBr at 25 and 35 °C and for $Na[BPh_4]$ at 25 °C were determined in 20, 40, 60, and 80% weight percent acetonitrile–H_2O binary mixtures corresponding to 0.099, 0.226, 0.397, and 0.637 mol fraction of acetonitrile. Viscosity data were analyzed by the Jones-Dole equation:[10]

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

Plots of $(\eta_r-1)/C^{1/2}$ vs. $C^{1/2}$ for observed viscosity data were found to be linear. The least square values of *A*, *B*, and δ, the RMS deviation of the experimental and calculated relative viscosity values are presented in Table 1. The *B*-coefficients of KCl, KBr, KI, NaBr, CsI, and Me_4NBr increase with increase in acetonitrile concentration of the binary solvent. Et_4NBr has a *B*-value fairly constant and increases only at higher acetonitrile concentration. However, for each composition of the solvent the *B*-value changes in the order KCl>KBr>KI>CsI and NaBr>KBr. The *B*-value of *n*-Pr_4NI and *n*-Bu_4NBr shows an initial decrease with increase in acetonitrile concentration, reaches a minimum between 40 and 60% acetonitrile concentration, and then increases with further increase in acetonitrile concentration. It has been observed[1] that *n*-Pr_4NBr behaved in a qualitatively similar fashion in DMF–H_2O mixtures. However, *n*-

Table 1. Least Square Values of Coefficients A($dm^{3/2}\,mol^{-1/2}$) and B($dm^3\,mol^{-1}$) of Eq. 1

% Acetonitrile[a]	Temp/°C		KCl	KBr	KI	CsI	NaBr	Me_4NBr	Et_4NBr	n-Pr_4NI	n-Bu_4NBr	$Na[BPh_4]$
0[b]	25	A	0.005	0.005	0.005	0.004	—	0.007	0.008	—	0.008	—
		B	−0.0140	−0.0490	−0.076	−0.118	0.053	0.101	0.343	0.82	1.148	—
	35	A	0.006	0.005	0.005	0.007	0.007	—	—	—	—	—
		B	0.0098	−0.026	−0.0485	−0.103	0.067	0.100	0.320	0.73	1.12	—
20	25	A	0.018	0.017	0.008	0.005	0.005	0.008	0.007	0.009	0.016	0.024
		B	0.015	−0.003	−0.031	−0.076	0.081	0.100	0.318	0.548	0.844	1.96
		$\delta\times10^4$	0.68	1.67	1.17	2.20	0.66	1.16	1.26	1.44	1.44	1.03
	35	A	0.020	0.014	0.016	0.015	0.008	0.009	0.006	0.013	0.012	—
		B	0.030	0.016	−0.012	−0.054	0.115	0.120	0.322	0.485	0.736	—
		$\delta\times10_4$	1.22	0.83	1.77	1.44	0.91	0.97	0.91	1.59	1.57	—
40	25	A	0.016	0.011	0.012	0.012	0.012	0.006	0.012	0.012	0.013	0.033
		B	0.181	0.143	0.071	0.052	0.193	0.219	0.322	0.474	0.750	1.77
		$\delta\times10^4$	1.05	2.48	2.09	0.49	2.72	1.61	0.76	0.58	2.76	0.89
	35	A	0.022	0.021	0.004	0.011	0.009	0.010	0.008	0.017	0.020	—
		B	0.196	0.163	0.106	0.081	0.234	0.247	0.320	0.393	0.626	—
		$\delta\times10^4$	1.52	3.97	2.26	1.55	2.61	3.73	2.75	2.38	0.00	—
60	25	A	0.020	0.016	0.015	0.021	0.031	0.010	0.019	0.005	0.009	0.017
		B	0.344	0.290	0.211	0.172	0.306	0.322	0.368	0.498	0.719	1.50
		$\delta\times10^4$	1.48	0.87	1.75	1.04	1.57	1.34	2.97	1.82	3.14	2.20
	35	A	0.020	0.013	0.013	0.016	0.017	0.008	0.027	0.018	0.021	—
		B	0.387	0.315	0.243	0.215	0.346	0.337	0.344	0.467	0.647	—
		$\delta\times10^4$	2.07	2.44	2.24	0.61	2.20	2.08	3.53	2.75	1.00	—
80	25	A	0.029	0.014	0.016	0.040	0.013	0.023	0.010	0.010	0.017	0.015
		B	0.508	0.417	0.372	0.300	0.490	0.403	0.530	0.602	0.748	1.12
		$\delta\times10^4$	0.73	1.00	2.48	0.73	1.55	1.59	2.42	1.90	1.75	1.57
	35	A	0.041	0.024	0.012	0.028	0.014	0.016	0.027	0.012	0.020	—
		B	0.552	0.468	0.413	0.338	0.540	0.434	0.473	0.587	0.719	—
		$\delta\times10^4$	0.76	1.31	2.28	2.05	2.14	2.51	1.31	2.11	1.99	—

a) Weight % AN. b) Values of A and B for pure water (except for data of CsI; $10^4\delta=2.00$ and NaBr; $10^4\delta=1.11$ at 35 °C) from Refs. 14, 19, and 20.

Bu_4NBr did not exhibit a minimum in DMF–H_2O solvent system.

In order to get an accurate information about the ion-solvent interactions, it is necessary to evaluate the contribution of the individual ionic species to the viscosity B-coefficients. However, no absolute method of such a computation is available even for pure water solvent. The most popular method of dividing the viscosity B-coefficients into ionic components arises from the observation that K^+ and Cl^- ions behave very similarly in ionic mobility and, therefore, it is likely that $B_{K^+}=B_{Cl^-}$. This method was used by Gurney[11)] and subsequently by Kaminsky[12)] and others. However, the method has never been free of criticism. Nightingale[13)] considered that from mobility grounds RbCl or CsCl should have been more appropriate than KCl. Subsequently Desnoyers and Perron[14)] proposed a splitting method in which they assumed that Et_4N^+ ion is neither a structure-breaker nor a structure-former. By assuming the hydrodynamic volume to be equal to the partial molar volume, they calculated the B_{ion} value for Et_4N^+ ion to be 0.3593 $dm^3\,mol^{-1}$. Using this value the B_{ion} values calculated for other ions in water showed comparable values to those obtained by the method of Kaminsky, i.e., $B_{K^+}=B_{Cl^-}$. Very recently Jenkins and Pritchett[15)] made use of Krumgalz's suggestions alternative to Gurney's assumption and came to the conclusion that $B_{Cs^+}=B_{I^-}$ is a more reasonable approximation.

In the light of the above discussions it is imperative that any method of splitting B-coefficients into the ionic components for binary solvent system is not likely to be free of the criticisms which apply in pure water. We, therefore, decided to compare the B_{ion} values obtained by the various methods from the experimental B-values. Table 2 lists the B_{ion} values obtained by three different methods, i.e., (i) on the basis of $B_{K^+}=B_{Cl^-}$; (ii) assuming $B_{Et_4N^+}=0.3593$ $dm^3\,mol^{-1}$ and (iii) by using $B_{Cs^+}=B_{I^-}$.

From Table 2 we find that the B_{ion} values obtained by methods (i) and (iii) are comparable only in water and low concentration of acetonitrile. However, with increasing acetonitrile concentration the values by the above two methods deviate beyond experimental error. Also, B_{ion} values obtained by method (ii) do not agree in any rate either with those obtained by method (i) or (iii). Interesting results are obtained in 80% acetonitrile concentration where all the three methods give close results for B_{ion} with a deviation of $\pm 0.032\ dm^3\ mol^{-1}$ between methods (i) and (iii) and the results by method (ii) falling in between. This close agreement is surprising considering the large magnitude of the B_{ion} values of alkali and halide ions and also the normally large values of tetraalkylammonium ions.

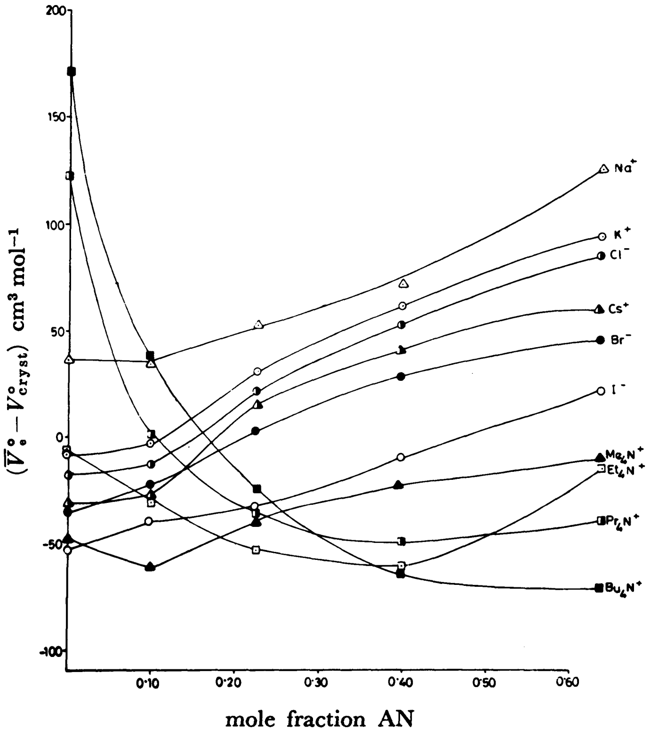

Fig. 1. Variation of $(\overline{V}^\circ_e - V^\circ_{cryst})$ with mole fraction of acetonitrile (AN) at 25 °C. B_{ion} on basis of $B_{K^+} = B_{Cl^-}$.

Eagland and Pilling⁶⁾ considered that $B = 2.5\,V^\circ_e$, where V°_e is the volume fraction of the solute molecules together with solvent molecules which are immobilized by the solute molecules because of the primary hydration. Like B_{ion}, $\overline{V}^\circ_e$ (for ion) would be sensitive to ion-dipole and structure-breaking effects. It would, therefore, be interesting to have a close look at the interaction effects by substracting V°_{cryst} from $\overline{V}^\circ_e$ values where V°_{cryst} is the crystal ionic volume derived from Pauling crystal radii. Figures 1—3 show the values of $(\overline{V}^\circ_e - V^\circ_{cryst})$ obtained by methods (i)—(iii), respectively. It is interesting to note that $(\overline{V}^\circ_e - V^\circ_{cryst})$ values for Na^+, K^+, Cs^+, Cl^-, Br^-, and I^- in Fig. 1 increase slowly with increase in acetonitrile concentration of the binary solvent upto about 40% of acetonitrile followed by a steep increase with further increase of acetonitrile concentration. For n-Pr_4N^+ and n-Bu_4N^+, $(\overline{V}^\circ_e - V^\circ_{cryst})$ values steeply decrease initially with increase in acetonitrile concentration and finally show a slight increase for n-Pr_4N^+ only at 80% acetonitrile concentration. The behaviors of the above electrolytes are identical in Fig. 3. Me_4N^+ and Et_4N^+ show a more regular change in Fig. 3 compared to Fig. 1 (probably due to small experimental errors involved). However, a somewhat different trend is observed in Fig. 2; for K^+, Cs^+, and Me_4N^+ ions $(\overline{V}^\circ_e - V^\circ_{cryst})$ values first increase upto 60% acetonitrile concentration and then decrease at 80% acetonitrile concentration, and for Cl^-, Br^-, and I^- ions the values first decrease and then increase. A

Table 2. Ionic B-coefficients at 25 °C

% Acetonitrile		Na^+	K^+	Cs^+	Cl^-	Br^-	I^-	Me_4N^+	Et_4N^+	n-Pr_4N^+	n-Bu_4N^+	$[BPh_4]^-$
0	i	0.095	−0.007	−0.049	−0.007	−0.042	−0.069	0.143	0.385	0.889	1.190	—
	ii	0.069	−0.033	−0.075	0.019	−0.016	−0.043	0.117	—	0.863	1.164	—
	iii	0.085	−0.017	−0.059	0.003	−0.032	−0.059	0.133	0.375	0.879	1.180	—
20	i	0.091	0.007	−0.038	0.007	−0.010	−0.038	0.110	0.328	0.586	0.854	1.87
	ii	0.123	0.039	−0.006	−0.025	−0.042	−0.070	0.142	—	0.618	0.886	1.84
	iii	0.091	0.007	−0.038	0.007	−0.010	−0.038	0.110	0.328	0.586	0.854	1.87
40	i	0.140	0.090	0.071	0.090	0.053	−0.019	0.166	0.269	0.493	0.697	1.63
	ii	0.231	0.181	0.162	0.000	−0.038	−0.110	0.257	—	0.584	0.788	1.54
	iii	0.095	0.045	0.026	0.136	0.098	0.026	0.121	0.224	0.448	0.652	1.68
60	i	0.188	0.172	0.133	0.172	0.118	0.039	0.204	0.250	0.459	0.601	1.31
	ii	0.298	0.282	0.243	0.062	0.008	−0.071	0.314	—	0.569	0.711	1.20
	iii	0.141	0.125	0.086	0.219	0.165	0.086	0.157	0.203	0.412	0.554	1.36
80	i	0.327	0.254	0.182	0.254	0.163	0.118	0.240	0.367	0.484	0.585	0.793
	ii	0.319	0.246	0.174	0.262	0.171	0.126	0.232	—	0.476	0.577	0.801
	iii	0.295	0.222	0.150	0.286	0.195	0.150	0.208	0.335	0.452	0.553	0.825

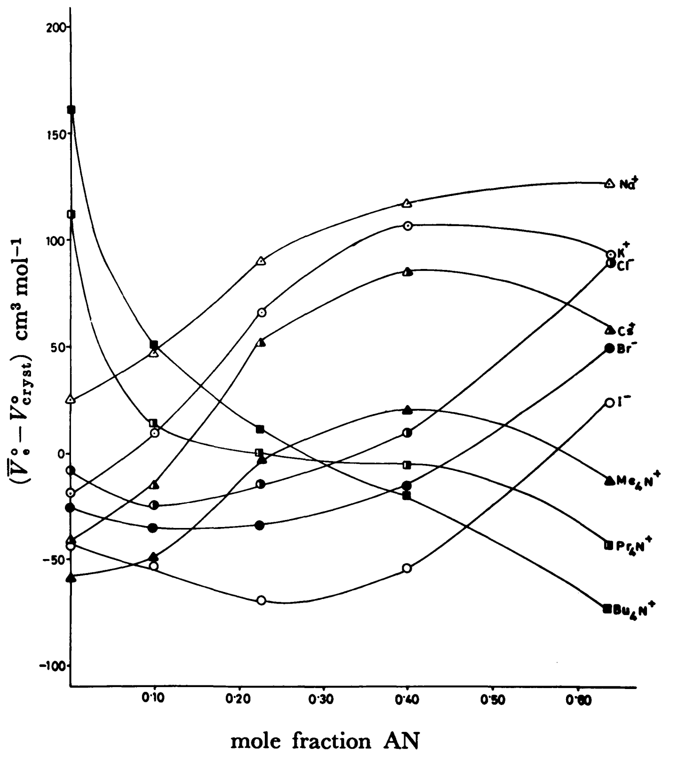

Fig. 2. Variation of $(\bar{V}_e^\circ - V_{\text{cryst}}^\circ)$ with mole fraction of acetonitrile (AN) at 25 °C. B_{ion} on the basis of $B_{\text{Et}_4\text{N}^+} = 0.3593$ mol⁻¹ dm³.

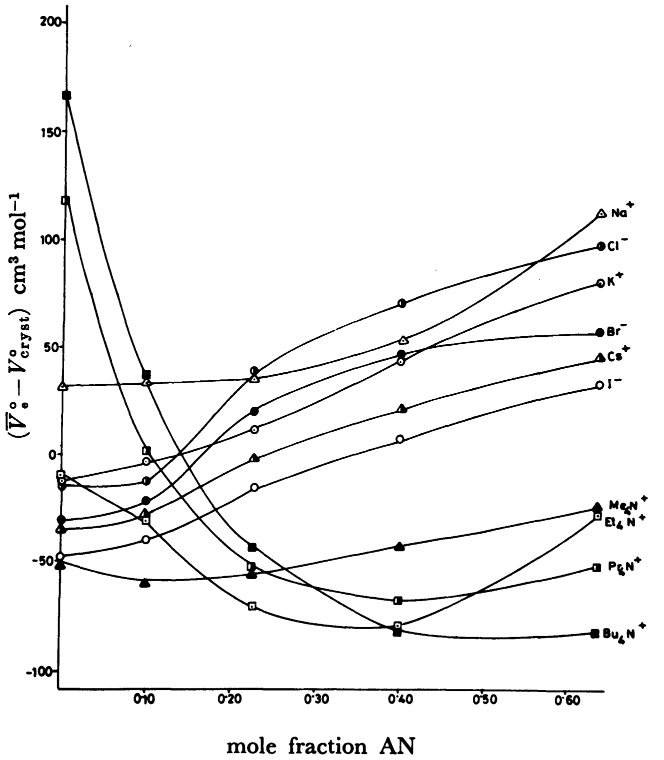

Fig. 3. Variation of $(\bar{V}_e^\circ - V_{\text{cryst}}^\circ)$ with mole fraction of acetonitrile (AN) at 25 °C. B_{ion} on basis of $B_{\text{Cs}^+} = B_{\text{I}^-}$.

Table 3. $\Delta B/\Delta T$ Coefficients in Acetonitrile-Water Mixtures in the Range 25—35 °C

$(\Delta B/\Delta T)$/dm³ mol⁻¹ K⁻¹	% Acetonitrile				
	0	20	40	60	80
KCl	0.0024	0.0016	0.0015	0.0043	0.0044
KBr	0.0023	0.0019	0.0020	0.0025	0.0051
KI	0.0027	0.0019	0.0035	0.0032	0.0041
CsI	0.0015	0.0022	0.0030	0.0043	0.0038
NaBr	0.0014	0.0034	0.0041	0.0040	0.0050
Me_4NBr	−0.0001	0.0020	0.0028	0.0015	0.0031
Et_4NBr	−0.0023	0.0004	−0.0002	−0.0024	−0.0057
n-Pr_4NI	−0.0090	−0.0063	−0.0081	−0.0031	−0.0015
n-Bu_4NBr	−0.0028	−0.0108	−0.0124	−0.0072	−0.0029

decrease of $(\bar{V}_e^\circ - V_{\text{cryst}}^\circ)$ for K^+, Cs^+, and Me_4N^+ ions with increase in acetonitrile concentration cannot be explained in view of the fact that all these ions have a stronger electrostriction in acetonitrile relative to water.[16] Therefore, $B_{\text{Et}_4\text{N}^+}$ probably cannot be taken as a constant for the splitting in this solvent. It is however, not possible to comment on the relative merit of methods (i) and (iii) without a detailed knowledge of the actual interactions taking place. But, for all practical purposes, both methods give B_{ion} values which are very close, particularly for mixtures of extreme composition (20 and 80% acetonitrile), so that a qualitative distinction is not possible.

It has been observed by earlier workers[17] that addition of acetonitrile to water breaks the ice-like structure of water liberating free water molecules thereby decreasing the structure. Therefore, B-values of the structure-breaking electrolytes should increase and that of the structure-forming electrolytes should decrease with the addition of acetonitrile as is observed in Table 1. However, in reality the picture does not seem to be so simple since $\Delta B/\Delta T$ for KCl, KBr, KI, and Et_4NBr first decreases and then increases with acetonitrile concentration (Table 3). In the case of NaBr, CsI, and Me_4NBr $\Delta B/\Delta T$ increases with acetonitrile concentration increasing. $\Delta B/\Delta T$ for n-

Table 4. Differences in *B*-Coefficients of Two Salts with a Common Ion

ΔB/dm^3 mol^{-1}	Temp/°C	% Acetonitrile				
		0	20	40	60	80
(KCl–KBr)	25	0.036	0.017	0.038	0.054	0.091
	35	0.036	0.014	0.033	0.072	0.084
(KCl–KI)	25	0.062	0.045	0.110	0.133	0.136
	35	0.058	0.042	0.090	0.144	0.139
(KI–CsI)	25	0.042	0.045	0.020	0.039	0.072
	35	0.054	0.042	0.025	0.028	0.075
(NaBr–KBr)	25	0.102	0.084	0.050	0.016	0.073
	35	0.093	0.099	0.071	0.031	0.072

Pr_4NI and n-Bu_4NBr which is negative for the entire composition of the solvent mixture studied, shows a maximum negative value between 20 and 40% acetonitrile concentration. Therefore, solute-solvent interactions sensitive to temperature change exist at all the studied concentrations. This suggests preferential solvation of the electrolytes by acetonitrile molecules.

Table 4 shows a similarly interesting trend in the data on the differences in *B*-coefficients of two alkali salts with either the cation or the anion as the common member. This observation is common to both the temperatures studied. In both cases the difference observed in pure water first decreases and then increases with the concentration of acetonitrile upto the highest concentration studied. The difference between the halide ions which are normally small in water are surprisingly high in 80% acetonitrile. However, the differences between the alkali cations which are significantly high in water relative to halides are not so prominent in 80% acetonitrile as in case of halides. A decrease in the intermediate region is probably due to a decrease in overall structure of the solvent. Increase on the other hand indicates increase in ion-dipole interactions, probably with free water molecules.

The apparent molar volumes (ϕ_v) of the electrolytes were calculated by using the density data. The limiting apparent molar volume, ϕ_v° ($=\overline{V}^\circ$) was then calculated by the least square method. In order to calculate the ionic partial molar volumes, the $\overline{V}^\circ$ values, for Me_4NBr, Et_4NBr, n-Pr_4NBr, and n-Bu_4NBr were plotted against respective r^3 [r=ionic radii of the ammonium ions[18)]] and the intercept gave the values for Br^- ions. With increasing acetonitrile, the ionic partial molar volumes decrease and become negative for chloride and bromide ions but are positive for Na^+, K^+, Cs^+, and I^- ions. Not much change is observed in the case of tetraalkylammonium ions. Because of electrostriction it is not possible to make a comparison of the *B*-values with the $\overline{V}^\circ$ values of the alkali and halide ions with respect to acetonitrile concentration, though such a comparison is possible in the case of the tetraalkylammonium and tetraphenylborate ions. Table 5 shows the $\overline{V}^\circ_{\text{ion}}$ and the $(B/\overline{V}^\circ)_{\text{ion}}$ values of the electrolytes vs. acetonitrile concentration. The ratio increases for Me_4N^+ alone but decreases for Et_4N^+, n-Pr_4N^+, n-Bu_4N^+, and $[BPh_4]^-$ ions. Marginal increase is observed for Et_4N^+ and n-Pr_4N^+ ions in 80% acetonitrile concentration. It is interesting to note that for Me_4N^+ and Et_4N^+ ions, the ratio tends to the ideal value (2.5) at 80% acetonitrile concentration.

Table 5. Ionic Partial Molar Volumes $\overline{V}^\circ_{\text{ion}}$ (dm^3 mol^{-1}) and $(B/\overline{V}^\circ)_{\text{ion}}$[a)] Values of Different Ions in Acetonitrile–H_2O Mixtures at 25°C

Ion		% Acetonitrile				
		0	20	40	60	80
Cl^-	$\overline{V}^\circ_{\text{ion}}$	0.013	0.003	−0.001	−0.004	−0.009
Br^-	$\overline{V}^\circ_{\text{ion}}$	0.020	0.008	0.006	0.001	−0.003
I^-	$\overline{V}^\circ_{\text{ion}}$	0.031	0.022	0.018	0.014	0.007
Na^+	$\overline{V}^\circ_{\text{ion}}$	0.004	0.016	0.016	0.023	0.024
K^+	$\overline{V}^\circ_{\text{ion}}$	0.014	0.023	0.027	0.030	0.030
Cs^+	$\overline{V}^\circ_{\text{ion}}$	0.027	0.038	0.036	0.041	0.042
Me_4N^+	$\overline{V}^\circ_{\text{ion}}$	0.094	0.101	0.102	0.102	0.104
	$(B/\overline{V}^\circ)_{\text{ion}}$	1.521	1.089	1.628	2.000	2.308
Et_4N^+	$\overline{V}^\circ_{\text{ion}}$	0.154	0.161	0.162	0.163	0.162
	$(B/\overline{V}^\circ)_{\text{ion}}$	2.500	2.037	1.661	1.534	2.265
n-Pr_4N^+	$\overline{V}^\circ_{\text{ion}}$	0.220	0.232	0.229	0.233	0.230
	$(B/\overline{V}^\circ)_{\text{ion}}$	4.041	2.526	2.153	1.970	2.104
n-Bu_4N^+	$\overline{V}^\circ_{\text{ion}}$	0.280	0.297	0.300	0.300	0.303
	$(B/\overline{V}^\circ)_{\text{ion}}$	4.250	2.875	2.323	2.003	1.931
$[BPh_4]^-$	$\overline{V}^\circ_{\text{ion}}$	—	0.279	0.281	0.270	0.269
	$(B/\overline{V}^\circ)_{\text{ion}}$	—	6.703	5.801	4.852	2.948

a) Values of B_{ion} on the basis of $B_{K^+}=B_{Cl^-}$.

We may therefore, say that acetonitrile destroys the ice-like structure of water. Ionic *B*-coefficients of simple monovalent ions are large in acetonitrile–H_2O solvent mixture due to the participation of acetonitrile molecules in the solvation process and small for large tetraalkylammonium ions because of the disappearance of hydrophobic hydration.

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