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Partial Molal Volumes of Uni-univalent Electrolytes in Methanol + Water. 3. Sodium Iodide and Potassium Iodide

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Densities of methanol + water + sodium iodide and + potassium iodide were measured at 15, 25, 35, and 45 °C. The apparent molal volumes of the electrolytes in these mixtures were calculated, and the apparent molol volumes at infinite dilution and partial molal thermal expansions were evaluated.

Introduction

As a continuation in the series of the determination of the partial molal volumes of the electrolytes in methanol + water (*7*, *8*), the densities of the solutions of methanol + water + sodium iodide and + potassium iodide were measured at 15, 25, 35, and 45 °C. The apparent molal volumes and thermal expansion of these electrolytes in the mixtures were derived. The partial molal volume and thermal expansion of an electrolyte give us useful information concerning the structure and the interactions in the solution.

Experimental Section

Densities of the solutions were measured relative to densities of the mixed solvents with an oscillating-tube densimeter (Anton Paar, DMA 60) operated in a phase-locked loop mode using two measuring cells (DMA 601). The precision of the density measurements was estimated to be $\pm 2 \times 10^{-6}$ g·cm^{-3}. Details of the apparatus and procedure have been described previously (*6*). The temperature of the cells was maintained within ±0.002 K by using a quartz temperature controller. The densimeter was calibrated at each measurement with water (*1*) and dry air.

Suprapur sodium iodide and potassium iodide were obtained from E. Merck Co. Ltd. These electrolytes were used without further purification. Spectro grade methanol, obtained from Nacalai Tesque Inc., was used without further purification for all experiments. The water content of the methanol, determined using the Karl-Fischer method, was less than 0.01 mass %. Doubly distilled water through a quartz still was used for calibration of the cells. The deionized water was used to make the mixtures of methanol and water.

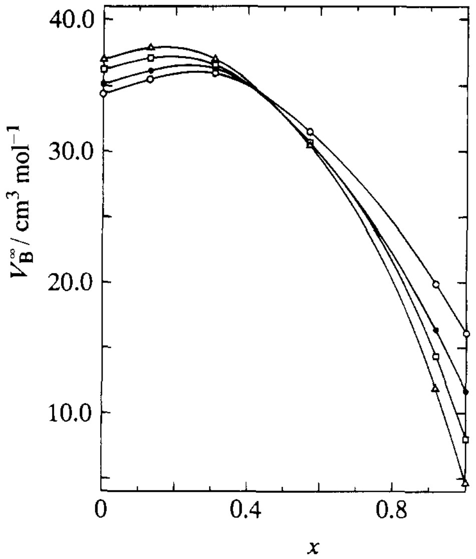

Figure 1. Partial molal volumes of sodium iodide at infinite dilution in x methanol + $(1 - x)$ water at various temperatures: ○, 15 °C; ●, 25 °C; □, 35 °C; △, 45 °C.

Results and Discussion

Observed densities ϱ of the solutions of sodium iodide and potassium iodide at various temperatures are given in Tables 1 and 2, respectively, where x is the mole fraction of methanol in the mixed solvent and m is the molality of the electrolyte. The apparent molal volumes of the electrolyte $V_{B\varphi}$ were calculated from

$$V_{B\varphi} = 1000(\varrho_0 - \varrho)/m\varrho\varrho_0 + M_B/\varrho \qquad (1)$$

where ϱ_0 is the density of the solvent and M_B is the molal mass of the electrolyte.

We assumed that the apparent molal volume depends on the concentration of the electrolyte as follows:

$$V_{B\varphi} = V_{B\varphi}^\infty + A_v m^{1/2} + b_v m \qquad (2)$$

The value of the partial molal volumes V_B for each electrolyte can be calculated from

$$V_B = V_{B\varphi}^\infty + (3A_v/2)m^{1/2} + 2b_v m \qquad (3)$$

where $V_{B\varphi}^\infty$, A_v, and b_v are the apparent molal volume of the electrolyte at infinite dilution, the Debye–Hückel

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Table 1. Densities of Solutions ϱ and Apparent Molal Volumes $V_{B\varphi}$ for NaI in x Methanol + (1 − x) Water

m/(mol·kg^{-1})	ϱ/(g·cm^{-3}	$V_{B\varphi}$/(cm^3·mol^{-1})	m/(mol·kg^{-1})	ϱ/(g·cm^{-3}	$V_{B\varphi}$/(cm^3·mol^{-1}	m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})
				x = 0.129				
				t = 15.00 °C				
0.0000	0.966 986		0.0404	0.971 479	35.93	0.1691	0.985 653	36.27
0.0058	0.967 630	35.59	0.0696	0.974 710	36.02	0.2275	0.992 028	36.36
0.0204	0.969 255	35.79	0.1160	0.979 821	36.16			
				t = 25.00 °C				
0.0000	0.963 127		0.0665	0.970 445	36.65	0.2141	0.986 515	36.98
0.0126	0.964 524	36.40	0.1025	0.974 386	36.79	0.2906	0.994 766	37.06
0.0313	0.966 586	36.55	0.1615	0.980 819	36.89			
				t = 35.00 °C				
0.0000	0.958 565		0.0684	0.963 764	23.90	0.2730	0.979 067	23.30
0.0117	0.959 461	23.52	0.1230	0.967 870	24.05	0.4182	0.98 789	24.43
0.0301	0.960 860	23.72	0.2231	0.975 365	24.24			
				t = 45.00 °C				
0.0000	0.953 402		0.0980	0.963 932	38.60	0.3116	0.986 538	38.89
0.0170	0.955 239	38.19	0.1611	0.970 653	38.73	0.4181	0.997 672	38.94
0.0470	0.958 472	38.43	0.2321	0.978 170	38.82			
				x = 0.307				
				t = 15.00 °C				
0.0000	0.929 883		0.0507	0.935 338	36.51	0.1840	0.949 561	36.75
0.0071	0.930 653	36.15	0.1069	0.941 353	36.68	0.3101	0.962 905	36.76
0.0280	0.932 900	36.43	0.1333	0.944 169	36.71			
				t = 25.00 °C				
0.0000	0.923 498		0.0666	0.930 603	36.99	0.2156	0.946 342	37.17
0.0153	0.925 132	36.64	0.1068	0.934 868	37.07	0.2723	0.952 295	37.16
0.0313	0.926 839	36.83	0.1614	0.940 632	37.15			
				t = 35.00 °C				
0.0000	0.916 743		0.0286	0.919 774	37.13	0.0862	0.925 860	37.34
0.0110	0.917 909	36.87	0.0430	0.921 301	37.17	0.1281	0.930 255	37.41
0.0172	0.918 575	37.02	0.0622	0.923 332	37.28			
				t = 45.00 °C				
0.0000	0.909 578		0.1142	0.921 487	38.20	0.2561	0.936 154	38.23
0.0285	0.912 564	37.88	0.1616	0.926 398	38.25	0.3483	0.945 639	38.14
0.0536	0.915 193	38.04	0.1952	0.929 872	38.25			
				x = 0.571				
				t = 15.00 °C				
0.0000	0.874 916		0.0435	0.879 530	32.57	0.1937	0.895 341	32.84
0.0079	0.875 762	31.89	0.0804	0.883 429	32.70	0.2742	0.903 770	32.75
0.0196	0.877 003	32.25	0.1328	0.888 942	32.83			
				t = 25.00 °C				
0.0000	0.866 791		0.0688	0.874 062	32.04	0.1657	0.884 216	32.31
0.0100	0.867 856	31.26	0.1045	0.877 808	32.17	0.2137	0.889 228	32.33
0.0385	0.870 865	31.80	0.1355	0.881 053	32.28			
				t = 35.00 °C				
0.0000	0.858 392		0.0724	0.865 982	32.13	0.2487	0.884 256	32.52
0.0129	0.859 757	31.47	0.1154	0.870 454	32.37	0.3711	0.896 889	32.39
0.0430	0.862 910	31.95	0.1763	0.876 765	32.48			
				t = 45.00 °C				
0.0000	0.849 884		0.0650	0.856 651	32.07	0.2810	0.878 854	32.52
0.0119	0.851 135	31.01	0.1208	0.862 407	32.34	0.4008	0.891 116	32.37
0.0344	0.853 477	31.78	0.1884	0.869 359	32.50			
				x = 0.917				
				t = 15.00 °C				
0.0000	0.809 557		0.0432	0.814 181	21.62	0.1323	0.823 670	22.02
0.0078	0.810 399	20.71	0.0658	0.816 597	21.78	0.1839	0.829 160	22.00
0.0223	0.811 957	21.23	0.0956	0.819 768	21.96			
				t = 25.00 °C				
0.0000	0.800 480		0.0934	0.810 538	19.03	0.1799	0.819 778	19.36
0.0145	0.802 051	17.68	0.1176	0.813 123	19.19	0.2291	0.825 032	19.38
0.0391	0.804 709	18.43	0.1471	0.816 272	19.3			
				t = 35.00 °C				
0.0000	0.791 278		0.0490	0.796 567	17.01	0.1019	0.802 219	17.74
0.0142	0.792 823	15.96	0.0605	0.797 796	17.23	0.1264	0.804 826	17.94
0.0327	0.794 812	16.64	0.0755	0.799 402	17.45			
				t = 45.00 °C				
0.0000	0.781 958		0.0471	0.787 035	15.25	0.3567	0.819 784	17.44
0.0075	0.782 783	12.94	0.0847	0.791 052	15.93	0.4090	0.825 297	17.44
0.0257	0.784 744	14.48	0.2250	0.805 897	17.16			

Table 1 (Continued)

m/(mol·kg^{-1})	ϱ/(g·cm^{-3}	$V_{B\varphi}$/(cm^3·mol^{-1})	m/(mol·kg^{-1})	ϱ/(g·cm^{-3}	$V_{B\varphi}$/(cm^3·mol^{-1}	m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})
				x = 1.000				
				t = 15.00 °C				
0.0000	0.795 907		0.0361	0.799 802	17.82	0.0774	0.804 243	18.21
0.0054	0.796 497	16.91	0.0521	0.801 519	18.02	0.1037	0.807 062	81.31
0.0257	0.798 685	17.64	0.0578	0.802 133	18.08			
				t = 25.00 °C				
0.0000	0.786 499		0.0322	0.790 021	13.82	0.1405	0.801 741	14.90
0.0071	0.787 280	12.72	0.0600	0.793 032	14.31	0.2094	0.809 182	15.00
0.0165	0.788 312	13.34	0.0926	0.796 564	14.65			
				t = 35.00 °C				
0.0000	0.77 038		0.0629	0.783 923	11.39	0.1588	0.794 320	12.33
0.0145	0.778 642	9.84	0.0939	0.787 298	11.75	0.2244	0.801 420	12.58
0.0352	0.780 905	10.68	0.0629	0.783 923	11.39	0.1588	0.794 320	12.33
0.0352	0.780 905	10.68	0.1246	0.790 625	12.13			
				t = 45.00 °C				
0.0000	0.767 462		0.0488	0.772 827	8.45	0.2052	0.789 742	10.62
0.0107	0.768 655	6.43	0.0850	0.776 773	9.25	0.3023	0.800 193	11.04
0.0278	0.770 538	7.66	0.1349	0.782 170	10.01			

Table 2. Densities of Solutions ϱ and Apparent Molal Volumes $V_{B\varphi}$ for KI in x Methanol + (1 − x) Water

m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})
				x = 0.129				
				t = 15.00 °C				
0.0000	0.966 991		0.0912	0.977 597	46.84	0.2241	0.992 832	47.11
0.148	0.968 717	46.50	0.1420	0.983 440	46.97	0.2925	1.000 587	47.20
0.0304	0.970 545	46.63	0.1744	0.987 164	47.03			
				t = 25.00 °C				
0.0000	0.963 122		0.0612	0.970 167	47.90	0.1615	0.981 587	48.15
0.0088	0.964 144	47.56	0.0934	0.973 845	48.00	0.2192	0.988 105	48.23
0.0345	0.967 105	47.81	0.1270	0.977 678	48.08			
				t = 35.00 °C				
0.0000	0.958 771		0.0296	0.961 210	34.51	0.1136	0.968 064	34.85
0.0070	0.959 349	34.28	0.0496	0.962 844	34.62	0.1614	0.971 935	34.97
0.0164	0.960 120	34.41	0.0786	0.965 220	34.74			
				t = 45.00 °C				
0.0000	0.953 399		0.0577	0.959 919	49.44	0.1852	0.974 156	49.75
0.0147	0.955 072	49.17	0.1151	0.966 353	49.62	0.2175	0.977 720	49.81
0.0425	0.958 212	49.37	0.1549	0.970 785	49.72			
				x = 0.307				
				t = 15.00 °C				
0.0000	0.929 887		0.0582	0.936 529	46.14	0.1829	0.950 629	46.30
0.0122	0.931 290	45.84	0.0928	0.940 455	46.22	0.2337	0.956 339	46.31
0.0345	0.933 831	46.06	0.1446	0.946 315	46.29			
				t = 25.00 °C				
0.0000	0.923 489		0.0489	0.929 021	46.69	0.1281	0.937 929	46.86
0.0123	0.924 890	46.44	0.0676	0.931 129	46.75	0.1967	0.945 589	46.89
0.0313	0.927 043	46.61	0.0909	0.933 760	46.81			
				t = 35.00 °C				
0.0000	0.916 748		0.0344	0.920 614	47.31	0.1203	0.930 175	47.53
0.0055	0.917 368	46.77	0.0562	0.923 046	47.38	0.1569	0.934 237	47.55
0.0166	0.918 617	47.18	0.0820	0.925 918	47.47			
				t = 45.00 °C				
0.0000	0.909 577		0.0322	0.913 161	47.89	0.1223	0.923 098	48.18
0.0061	0.910 257	47.51	0.0527	0.915 422	48.00	0.1761	0.928 986	48.22
0.0164	0.911 404	47.77	0.0778	0.918 204	48.10			
				x = 0.571				
				t = 15.00 °C				
0.0000	0.874 912		0.0691	0.882 719	41.65	0.1786	0.795 019	41.70
0.0132	0.876 410	41.11	0.0975	0.885 918	41.70	0.2458	0.902 542	41.58
0.0420	0.879 671	41.56	0.1231	0.888 790	41.74			
				t = 25.00 °C				
0.0000	0.866 789		0.0343	0.870 658	41.05	0.1036	0.878 434	41.40
0.0058	0.867 450	40.45	0.0512	0.872 564	41.19	0.1333	0.881 742	41.44
0.0199	0.869 042	40.90	0.0703	0.874 707	41.30			

Table 2 (Continued)

$m/(\mathrm{mol{\cdot}kg^{-1}})$	$\varrho/(\mathrm{g{\cdot}cm^{-3}})$	$V_{B\varphi}/(\mathrm{cm^3{\cdot}mol^{-1}})$	$m/(\mathrm{mol{\cdot}kg^{-1}})$	$\varrho/(\mathrm{g{\cdot}cm^{-3}})$	$V_{B\varphi}/(\mathrm{cm^3{\cdot}mol^{-1}})$	$m/(\mathrm{mol{\cdot}kg^{-1}})$	$\varrho/(\mathrm{g{\cdot}cm^{-3}})$	$V_{B\varphi}/(\mathrm{cm^3{\cdot}mol^{-1}})$
				$x = 0.571$				
				$t = 35.00$ °C				
0.0000	0.858 388		0.0409	0.862 985	40.73	0.1126	0.870 969	41.09
0.0069	0.859 163	39.97	0.0571	0.864 797	40.84	0.1475	0.874 844	41.14
0.0194	0.860 574	40.47	0.0839	0.867 782	41.00			
				$t = 45.00$ °C				
0.0000	0.849 880		0.0304	0.853 276	40.36	0.0719	0.857 888	40.73
0.0050	0.850 441	39.82	0.0407	0.854 430	40.48	0.0963	0.860 593	40.84
0.0128	0.851 311	40.00	0.0543	0.855 941	40.61			
				$x = 0.917$				
				$t = 15.00$ °C				
0.0000	0.809 564		0.0223	0.812 117	30.68	0.0801	0.818 681	31.14
0.0052	0.810 163	29.95	0.0358	0.183 650	30.85	0.0962	0.820 504	31.17
0.0133	0.811 088	30.46	0.0593	0.816 316	31.07			
				$t = 25.00$ °C				
0.0000	0.800 480		0.0222	0.803 033	27.67	0.0564	0.806 943	28.25
0.0044	0.800 986	26.87	0.0334	0.804 320	27.93	0.0802	0.809 657	28.44
0.0127	0.801 949	27.39	0.0420	0.805 298	28.07			
				$t = 35.00$ °C				
0.000	0.791 280		0.0335	0.795 138	25.69	0.0931	0.801 942	26.52
0.0104	0.792 481	24.90	0.0456	0.796 522	25.96	0.1242	0.805 483	26.71
0.0218	0.793 796	25.35	0.0656	0.798 806	26.25			
				$t = 45.00$ °C				
0.0000	0.781 954		0.0393	0.786 473	24.20	0.1142	0.794 976	25.35
0.0070	0.782 767	22.58	0.0642	0.789 314	24.71	0.1355	0.797 391	25.52
0.0220	0.784 493	23.63	0.0891	0.792 138	25.10			
				$x = 1.000$				
				$t = 15.00$ °C				
0.0000	0.795 904		0.0289	0.799 233	26.88	0.0733	0.804 308	27.21
0.0096	0.797 012	26.38	0.0414	0.800 663	27.03	0.0982	0.807 162	27.22
0.0183	0.798 013	26.68	0.0538	0.802 077	27.13			
				$t = 25.00$ °C				
0.0000	0.786 498		0.0360	0.790 682	23.35	0.1450	0.803 235	23.94
0.0090	0.787 548	22.16	0.0715	0.794 777	23.74	0.1830	0.807 615	23.87
0.0221	0.789 071	23.09	0.1012	0.798 189	23.91			
				$t = 35.00$ °C				
0.0000	0.777 040		0.0454	0.782 319	20.78	0.0976	0.788 347	21.45
0.0066	0.777 815	19.15	0.0595	0.783 955	21.02	0.1201	0.790 941	21.59
0.0234	0.779 768	20.21	0.0798	0.786 296	21.30			
				$t = 45.00$ °C				
0.0000	0.767 464		0.0306	0.771 032	18.10	0.0824	0.777 013	19.37
0.0062	0.768 187	16.57	0.0500	0.773 281	18.72	0.1099	0.780 166	19.73
0.0166	0.769 412	17.48	0.0619	0.774 651	19.00			

Table 3. Partial Molal Volumes of the Electrolytes at Infinite Dilution $V_{B\varphi}^{\infty}$ in x Methanol + $(1 - x)$ Water

	$V_{B\varphi}^{\infty}/(\mathrm{cm^3{\cdot}mol^{-1}})$						
t/°C	$x = 0.000$	$x = 0.129$	$x = 0.307$	$x = 0.571$	$x = 0.917$	$x = 1.000$	
				NaI			
15.00	34.38[a]	35.49 ± 0.08	35.94 ± 0.01	31.50 ± 0.01	19.90 ± 0.10	16.11 ± 0.19	
25.00	35.15[a]	36.15 ± 0.04	36.30 ± 0.04	30.68 ± 0.08	16.38 ± 0.07	11.69 ± 0.10	11.8[b]
35.00	36.24[a]	37.10 ± 0.03	36.57 ± 0.05	30.69 ± 0.05	14.38 ± 0.08	8.03 ± 0.06	
45.00	37.00[a]	37.87 ± 0.03	37.32 ± 0.02	30.43 ± 0.05	11.92 ± 0.10	4.66 ± 0.07	
				KI			
15.00	43.99[a]	46.27 ± 0.04	45.56 ± 0.01	40.58 ± 0.01	29.35 ± 0.14	25.40 ± 0.09	
25.00	45.34[a]	47.38 ± 0.07	46.10 ± 0.05	40.02 ± 0.12	26.12 ± 0.18	21.20 ± 0.09	21.4[c]
35.00	46.28[a]	48.10 ± 0.06	46.67 ± 0.10	39.50 ± 0.11	23.53 ± 0.08	17.97 ± 0.16	
45.00	46.92[a]	48.85 ± 0.04	47.27 ± 0.09	39.24 ± 0.15	21.34 ± 0.13	15.15 ± 0.15	

[a] Reference 4. [b] Reference 9. [c] Reference 2.

constant, and the constants which are related to the nonelectrical parts of solute–solvent interactions, respectively. At infinite dilution, the apparent molal volume $V_{B\varphi}^{\infty}$ is equal to the partial molal volume V_B^{∞}. In the Debye–Hückel theory, the value of A_v is independent of the electrolyte. We have the values of A_v for the mixtures at 25 °C (*5*). We have used the A_v which were given in Table 4 of ref 8. In that table, the values were calculated as an average of the observed A_v for sodium chloride, potassium chloride, sodium bromide, potassium bromide, sodium iodide, and potassium iodide. From the plots of $V_{B\varphi} - A_v m^{1/2}$ vs m, the values of $V_{B\varphi}^{\infty}$ and b_v were evaluated, and the values are listed in Tables 3 and 4, respectively. In these tables, $V_{B\varphi}^{\infty}$ and b_v for pure water were taken from

Table 4. Apparent Molal Volume Concentration Dependence Constants b_v in x Methanol + (1 + x) Water

	b_v/(cm^3·kg·mol^{-2})						
t/°C	x = 0.000	x = 0.129	x = 0.307	x = 0.571	x = 0.917	x = 1.000	
				NaI			
15.00	−0.042[a]	−0.6 ± 0.5	−3.2 ± 0.1	−7.2 ± 0.1	−13.9 ± 0.8	−16.4 ± 2.7	
25.00	−0.430[a]	−1.3 ± 0.2	−3.5 ± 0.2	−7.4 ± 0.5	−13.8 ± 0.4	−15.9 ± 0.7	−5.5[b]
35.00	−0.736[a]	−1.5 ± 0.2	−3.9 ± 0.6	−8.0 ± 0.2	−13.9 ± 0.8	−15.9 ± 0.4	
45.00	−1.028[a]	−1.9 ± 0.1	−4.7 ± 0.1	−7.9 ± 0.2	−13.5 ± 0.3	−15.6 ± 0.3	
				KI			
15.00	0.042[a]	−0.7 ± 0.2	−3.5 ± 0.1	−8.4 ± 0.1	−16.1 ± 2.0	−20.0 ± 1.3	
25.00	−0.305[a]	−1.1 ± 0.4	−3.9 ± 0.4	−8.5 ± 1.3	−16.5 ± 3.3	−19.2 ± 0.7	−3.8[c]
35.00	−0.580[a]	−1.5 ± 0.3	−3.7 ± 0.9	−8.7 ± 1.0	−16.9 ± 0.9	−19.0 ± 1.9	
45.00	−0.785[a]	−1.8 ± 0.3	−4.5 ± 0.7	−9.8 ± 2.2	−16.1 ± 1.3	−19.3 ± 2.0	

[a] Reference 4. [b] Reference 3. [c] Reference 2. In refs 2 and 3, values of b_v were calculated from the plots of molarity. Listed values were calculated by the authors from the molality plots.

Table 5. Difference of Partial Molal Volumes at Infinite Dilution of the Two Electrolytes $\delta V_{B\varphi}$ in x Methanol + (1 − x) Water

	$\delta V_{B\varphi}$/(cm^3·mol^{-1})					
t/°C	x = 0.000	x = 0.129	x = 0.307	x = 0.571	x = 0.917	x = 1.000
			NaCl−KCl			
15.00	−9.61	−10.41	−10.33	−9.48	−9.80	−9.23
25.00	−10.19	−10.81	−10.42	−9.24	−9.58	−9.60
35.00	−10.04	−10.60	−10.20	−9.02	−9.43	−10.01
45.00	−9.92	−10.15	−9.92	−8.36	−9.26	−10.41
			NaBr−KBr			
15.00	−9.61	−10.23	−10.31	−9.61	−9.68	−9.32
25.00	−10.19	−10.54	−10.43	−9.05	−9.52	−9.59
35.00	−10.04	−10.80	−10.24	−8.78	−9.46	−9.92
45.00	−9.92	−10.63	−9.96	−8.13	−9.61	−10.38
			NaI−KI			
15.00	−9.61	−10.78	−9.61	−9.08	−9.45	−9.28
25.00	−10.19	−11.23	−9.81	−9.35	−9.74	−9.50
35.00	−10.04	−11.00	−10.11	−8.81	−9.14	−9.93
45.00	−9.92	−10.98	−10.26	−8.81	−9.42	−10.49
			NaCl−NaBr			
15.00	−7.46	−7.25	−6.79	−6.43	−7.91	−8.29
25.00	−6.92	−6.97	−6.56	−6.14	−6.19	−5.92
35.00	−7.16	−6.99	−7.03	−6.22	−5.38	−4.99
45.00	−7.53	−7.47	−7.83	−7.01	−4.96	−4.55
			KCl−KBr			
15.00	−7.46	−7.07	−6.77	−6.57	−7.78	−8.38
25.00	−6.92	−6.70	−6.57	−5.95	−6.13	−5.91
35.00	−7.16	−7.19	−7.07	−5.98	−5.41	−4.90
45.00	−7.53	−7.95	−7.87	−6.77	−5.31	−4.52
			NaBr−NaI			
15.00	−11.34	−12.74	−13.51	−11.76	−10.43	−9.46
25.00	−11.61	−13.17	−14.06	−12.04	−10.82	−10.16
35.00	−11.80	−13.82	−14.23	−12.91	−11.61	−10.17
45.00	−11.88	−14.04	−14.38	−12.95	−11.65	−10.00
			KBr−KI			
15.00	−11.34	−13.30	−12.81	−11.23	−10.20	−9.42
25.00	−11.61	−13.86	−13.43	−12.34	−11.05	−10.07
35.00	−11.80	−14.02	−14.10	−12.95	−11.29	−10.19
45.00	−11.88	−14.38	−14.68	−13.64	−11.45	−10.11

ref 4. Observed $V_{B\varphi}^{\infty}$ and b_v in pure methanol at 25 °C were compared with the values evaluated from the literature (*2, 3, 9*). In these tables, the maximum errors for $V_{B\varphi}^{\infty}$ and b_v were also listed, respectively. They were correlated to the reading errors of the densimeter and the mass measurements. In Table 3, the observed V_B^{∞} values for each electrolyte in pure methanol at 25 °C are consistent within experimental error with those taken from the literature. However, the absolute value of b_v given in Table 4 is larger than the literature values. Table 5 shows the differences between the two V_B^{∞} values of the solutions which have a common ion. For lithium chloride, sodium chloride, potassium chloride, sodium bromide, and potassium bromide, V_B^{∞} values in the mixtures were determined previously (*7, 8*). If the additivity rule holds for the partial molal volumes of the electrolyte in the solutions, the values in this table should be identical at each temperature and for the each solvent composition. In the table, the value agree within ±1 cm^3·mol^{-1}.

In Figures 1 and 2, V_B^{∞} values for sodium iodide and potassium iodide were plotted against x at various temperatures, respectively. In Figure 3, V_B^{∞} values at 25 °C were plotted against x for each electrolyte solution.

Table 6. Partial Molal Thermal Expansion of the Electrolytes in x Methanol + $(1 - x)$ Water

	$(\partial V_B^\infty/\partial T)_P/(\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-1}})$					
t/°C	$x = 0.000$	$x = 0.129$	$x = 0.307$	$x = 0.571$	$x = 0.917$	$x = 1.000$
			NaI			
15.00	0.091	0.073 ± 0.007	0.014 ± 0.001	−0.075 ± 0.002	−0.340 ± 0.008	−0.458 ± 0.017
25.00	0.090	0.078 ± 0.005	0.034 ± 0.002	−0.046 ± 0.001	−0.286 ± 0.008	−0.046 ± 0.011
35.00	0.089	0.084 ± 0.003	0.054 ± 0.002	−0.018 ± 0.005	−0.233 ± 0.007	−0.354 ± 0.007
45.00	0.088	0.089 ± 0.001	0.074 ± 0.002	0.010 ± 0.008	−0.179 ± 0.007	−0.302 ± 0.003
			KI			
15.00	0.151	0.111 ± 0.008	0.053 ± 0.005	−0.068 ± 0.006	−0.345 ± 0.016	−0.443 ± 0.016
25.00	0.115	0.093 ± 0.004	0.056 ± 0.004	−0.053 ± 0.005	−0.293 ± 0.011	−0.374 ± 0.011
35.00	0.080	0.075 ± 0.002	0.058 ± 0.005	−0.038 ± 0.008	−0.240 ± 0.008	−0.305 ± 0.009
45.00	0.044	0.058 ± 0.002	0.061 ± 0.009	−0.023 ± 0.016	−0.188 ± 0.007	−0.237 ± 0.012

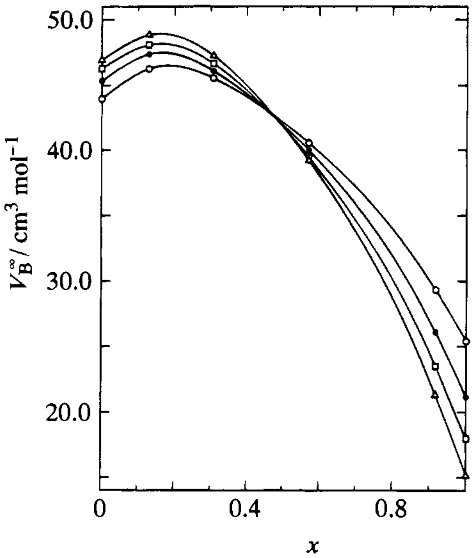

Figure 2. Partial molal volumes of potassium iodide at infinite dilution in x methanol + $(1 - x)$ water at various temperatures: ○, 15 °C; ●, 25 °C; □, 35 °C; △, 45 °C.

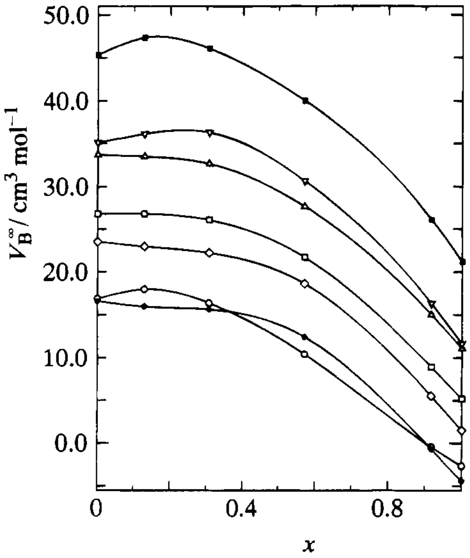

Figure 3. Partial molal volumes of electrolytes at infinite dilution in x methanol + $(1 - x)$ water at 25 °C: ▽, NaI; ■, KI; ○, LiCl(*7*); ●, NaCl(*7*); □, KCl(*7*); ◇, NaBr(*8*); △, KBr(*8*).

The partial molal thermal expansions of the electrolytes $(\partial V_B^\infty/\partial T)_p$ are given in Table 6. In the table, the maximum errors are also shown. They are caused by the maximum errors in Table 3. In Tables 3 and 4, both V_B^∞ and the thermal expansion decrease with an increase in temperature or with an increase in methanol concentration. The same tendency was observed in solutions of lithium chloride, sodium chloride, potassium chloride, sodium bromide, and potassium bromide.

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