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Partial Molal Volumes of Uni-univalent Electrolytes in Methanol + Water. 2. Sodium Bromide and Potassium Bromide

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

Introduction

As a series of the determination of the partial molal volumes of the electrolytes in methanol + water mixtures (*9*), the densities of the solutions of methanol + water + sodium bromide and + potassium bromide were measured at 15, 25, 35 and 45 °C. The apparent molal volumes, partial molal volumes, and thermal expansion of these electrolytes in the mixtures were determined.

Experimental Section

The densities of the solutions were measured relative to the 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 earlier (*8*). The temperature of the cells was maintained within ±0.002 °C by using a constructed quartz temperature controller. The densimeter was calibrated at each measurement with water (*5*) and dry air.

Suprapur sodium bromide and potassium bromide were obtained from E. Merck Co. Ltd. These electrolytes were used without further purification. Spectrograde methanol, obtained from Nacalai Tesque Inc., was used without further purification for all experiments. The water content of the methanol, determined by 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. The mixture was degassed before use to prevent the formation of bubbles in the density-measuring cell during an experiment.

Results and Discussion

The observed densities ϱ of the solutions of sodium bromide and potassium bromide 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 molecular weight of the electrolyte.

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

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

The values of the partial molal volumes V_B for each electrolyte given in Tables 1 and 2 were calculated from eq 3, where $V^{\infty}_{B\varphi}$, A_v, and b_v are the apparent molal volume

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

of the electrolyte at infinite dilution, the Debye–Hückel constant, and a constant which is related to the nonelectrical parts of solute–solvent interactions, respectively. At infinite dilution, the apparent molal volume $V^{\infty}_{B\varphi}$ is equal to the partial molal volume V^{∞}_{B}. In the Debye–Hückel theory, the value of A_v is kept constant with variation of the electrolyte. Usually, observed apparent molal volumes were calculated using the A_v, calculated from the pressure dependence of the permittivity and the isothermal compressibility of the mixed solvents. However, we can calculate the values of A_v for the mixtures only at 25 °C (*6*). We have treated the apparent molal volumes as follows: (i) The concentration dependencies of the observed apparent molal volumes were fitted to eq 2, and the values of A_v were obtained. (ii) The averages of A_v for various electrolyte solutions of the same solvent composition and the same temperature were obtained. (iii) The values were checked to determine that the standard deviations were small. (iv) The concentration dependence of the apparent molal volumes were fitted by eq 2, in which the values of A_v were fixed to that average. (v) Then, the values of $V^{\infty}_{B\varphi}$ and b_v were determined. The resulting values of $V^{\infty}_{B\varphi}$, A_v, and b_v are listed in Tables 3–5, respectively. In the tables, $V^{\infty}_{B\varphi}$, A_v, and b_v in pure water and in pure methanol at 25 °C were taken from the literature (*1–4*,

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Table 1. Densities of the Solutions ϱ, Apparent Molal Volumes $V_{b\varphi}$, and Partial Molal Volumes V_B for NaBr in x Methanol + $(1 - x)$ Water

m/ (mol·kg^{-1})	ϱ/ (g·cm^{-3})	$V_{B\varphi}$/ (cm^3·mol^{-1})	V_B/ (cm^3·mol^{-1})	m/ (mol·kg^{-1})	ϱ/ (g·cm^{-3})	$V_{B\varphi}$/ (cm^3·mol^{-1})	B_B/ (cm^3·mol^{-1})	m/ (mol·kg^{-1})	ϱ/ (g·cm^{-3})	$V_{B\varphi}$/ (cm^3·mol^{-1})	V_B/ (cm^3·mol^{-1})
$x = 0.129$											
t = 15.00 °C											
0.0000	0.966 987		22.75	0.0676	0.972 234	23.29	23.56	0.2095	0.983 114	23.69	24.14
0.0105	0.967 808	22.96	23.07	0.1030	0.974 961	23.42	23.74	0.3627	0.994 710	23.97	24.56
0.0389	0.970 009	23.17	23.37	0.1475	0.978 379	23.54	23.93				
t = 25.00 °C											
0.0000	0.963 122		22.98	0.0570	0.967 520	23.53	23.74	0.2253	0.980 360	23.94	24.34
0.0074	0.963 695	23.13	23.27	0.1333	0.973 363	23.75	24.08	0.2253	0.980 360	23.94	24.34
0.0324	0.965 630	23.40	23.57	0.1695	0.976 119	23.84	24.20				
t = 35.00 °C											
0.0000	0.958 565		23.28	0.0684	0.963 764	23.90	24.14	0.2730	0.979 067	24.30	24.63
0.0117	0.959 461	23.52	23.68	0.1230	0.967 870	24.05	24.35	0.4182	0.989 789	24.43	24.74
0.0301	0.960 860	23.72	23.89	0.2231	0.975 365	24.24	24.57				
t = 45.00 °C											
0.0000	0.953 399		23.83	0.0974	0.960 759	24.58	24.86	0.2876	0.974 955	24.89	25.18
0.0173	0.954 718	24.16	24.35	0.1345	0.963 543	24.67	24.97	0.3579	0.980 161	24.95	25.21
0.0715	0.958 809	24.50	24.75	0.1763	0.966 667	24.76	25.06				
$x = 0.307$											
t = 15.00 °C											
0.0000	0.929 882		22.44	0.0726	0.935 363	23.22	23.48	0.2382	0.947 722	23.58	23.95
0.0091	0.930 574	22.66	22.87	0.1082	0.938 034	23.32	23.64	0.3259	0.954 216	23.68	24.03
0.0452	0.933 302	23.08	23.31	0.1768	0.943 155	23.49	23.84				
t = 25.00 °C											
0.0000	0.923 498		22.24	0.0432	0.926 754	22.88	23.12	0.1810	0.937 045	23.29	23.59
0.0081	0.924 113	22.52	22.68	0.0756	0.929 187	23.03	23.32	0.2838	0.944 671	23.41	23.64
0.0241	0.925 320	22.74	22.94	0.1190	0.932 430	23.16	23.47				
t = 35.00 °C											
0.0000	0.916 742		22.34	0.0415	0.919 850	23.01	23.26	0.1083	0.924 820	23.27	23.59
0.0077	0.917 322	22.59	22.79	0.0590	0.921 158	23.10	23.38	0.1470	0.927 691	23.36	23.68
0.0176	0.918 062	22.84	22.99	0.0841	0.923 023	23.20	23.50				
t = 45.00 °C											
0.0000	0.909 579		22.63	0.0644	0.914 350	23.46	23.77	0.1663	0.921 831	23.75	24.02
0.0160	0.910 772	23.10	23.31	0.0955	0.916 642	23.59	23.90	0.2229	0.925 966	23.82	24.03
0.0385	0.912 436	23.31	23.59	0.1304	0.919 198	23.68	23.98				
$x = 0.571$											
t = 15.00 °C											
0.0000	0.874 917		19.74	0.0648	0.879 700	20.98	21.44	0.2228	0.891 239	21.51	21.81
0.0093	0.875 606	20.29	20.54	0.1068	0.882 784	21.22	21.67	0.2946	0.896 450	21.57	21.72
0.0276	0.876 966	20.64	21.00	0.1560	0.886 378	21.38	21.79				
t = 25.00 °C											
0.0000	0.866 788		18.64	0.0392	0.869 701	19.83	20.30	0.0982	0.874 036	20.31	20.88
0.0096	0.867 502	19.24	19.57	0.0547	0.870 844	19.98	20.51	0.1389	0.877 013	20.50	21.06
0.0230	0.868 498	19.60	19.99	0.0781	0.872 563	20.18	20.74				
t = 35.00 °C											
0.0000	0.858 390		17.78	0.0581	0.862 695	19.25	19.82	0.1707	0.870 932	19.87	20.37
0.0107	0.859 188	18.61	18.83	0.0951	0.865 414	19.52	20.12	0.2296	0.875 218	20.02	20.39
0.0310	0.860 694	18.84	19.41	0.1323	0.868 133	19.72	20.29				
t = 45.00 °C											
0.0000	0.849 884		17.48	0.0295	0.852 064	18.69	19.20	0.0767	0.855 517	19.25	19.89
0.0059	0.850 320	18.06	18.34	0.0468	0.853 335	18.94	19.53	0.1102	0.857 955	19.48	20.13
0.0146	0.850 966	18.37	18.77	0.0584	0.854 186	19.08	19.69				
$x = 0.917$											
t = 15.00 °C											
0.0000	0.809 563		9.48	0.0272	0.811 630	11.02	11.63	0.0932	0.816 597	11.87	12.61
0.0061	0.810 031	10.19	10.63	0.0461	0.813 056	11.37	12.07	0.1199	0.818 596	12.05	12.75
0.0163	0.810 806	10.77	11.24	0.0686	0.814 752	11.66	12.40				
t = 25.00 °C											
0.0000	0.800 475		5.55	0.0242	0.802 355	7.29	8.05	0.0584	0.804 981	8.06	9.00
0.0088	0.801 163	6.68	7.18	0.0343	0.803 137	7.59	8.42	0.0790	0.806 558	8.35	9.33
0.0171	0.801 806	7.06	7.72	0.0463	0.804 058	7.84	8.74				
t = 35.00 °C											
0.0000	0.791 278		2.77	0.0572	0.795 727	5.76	6.91	0.1464	0.802 555	6.93	8.21
0.0161	0.792 540	4.58	5.27	0.0819	0.797 627	6.15	7.43	0.1892	0.805 805	7.26	8.46
0.0344	0.793 973	5.08	6.20	0.1074	0.799 577	6.52	7.82				
t = 45.00 °C											
0.0000	0.781 955		0.27	0.0602	0.786 650	3.93	5.50	0.1372	0.792 539	5.38	7.27
0.0081	0.782 598	1.56	2.46	0.0865	0.788 664	4.65	6.26	0.1787	0.795 684	5.84	7.83
0.0316	0.784 435	3.26	4.30	0.1119	0.790 610	4.98	6.82				

Table 1 (Continued)

m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})	m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	B_B/(cm^3·mol^{-1})	m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})
$x = 1.000$											
$t = 15.00$ °C											
0.0000	0.795 905		6.65	0.0289	0.798 120	8.35	9.04	0.0813	0.802 087	9.11	9.85
0.0090	0.796 597	7.68	8.16	0.0488	0.799 633	8.74	9.48	0.1040	0.803 808	9.29	9.97
0.0197	0.797 416	8.14	8.72	0.0626	0.800 672	8.92	9.67				
$t = 25.00$ °C											
0.0000	0.786 496		1.54	0.0604	0.791 217	4.46	5.49	0.1870	0.800 966	5.64	6.63
0.0107	0.787 346	2.77	3.55	0.0939	0.793 804	4.92	6.04	0.2236	0.803 769	5.79	6.67
0.0318	0.788 997	3.86	4.69	0.1324	0.796 769	5.31	6.40				
$t = 35.00$ °C											
0.0000	0.772 469		−2.14	0.0837	0.779 029	1.86	3.33	0.2566	0.792 308	3.52	4.85
0.0218	0.774 200	0.01	1.14	0.1244	0.782 169	2.45	4.00	0.3838	0.802 028	3.95	4.77
0.0527	0.776 618	1.27	2.52	0.1862	0.786 914	3.08	4.58				
$t = 45.00$ °C											
0.0000	0.767 460		−5.35	0.0278	0.769 689	−2.29	−0.93	0.0764	0.773 523	−0.63	1.29
0.0076	0.768 074	−3.74	−2.88	0.0379	0.770 496	−1.83	−0.31	0.1045	0.775 711	−0.02	2.06
0.0181	0.768 920	−2.76	−1.68	0.0555	0.771 886	−1.21	0.53				

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

m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{b\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})	m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})	m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})
$x = 0.129$											
$t = 15.00$ °C											
0.0000	0.966 991		32.98	0.0561	0.971 684	33.45	33.69	0.1676	0.980 908	33.79	34.17
0.0075	0.967 618	33.18	33.25	0.0834	0.973 955	33.56	33.84	0.2361	0.986 513	33.94	34.37
0.0242	0.969 025	33.29	33.46	0.1202	0.976 996	33.67	34.00				
$t = 25.00$ °C											
0.0000	0.963 121		33.52	0.0562	0.967 776	34.07	34.30	0.2166	0.980 888	34.50	34.92
0.0110	0.964 035	33.72	33.88	0.0921	0.970 732	34.19	34.49	0.3270	0.989 790	34.67	35.16
0.0273	0.965 390	33.92	34.08	0.1665	0.976 820	34.39	34.77				
$t = 35.00$ °C											
0.0000	0.958 771		34.08	0.0296	0.961 210	34.51	34.70	0.1136	0.968 064	34.85	35.18
0.0070	0.959 349	34.28	34.40	0.0496	0.962 844	34.62	34.86	0.1614	0.971 935	34.97	35.34
0.0164	0.960 120	34.41	34.55	0.0786	0.965 220	34.74	35.03				
$t = 45.00$ °C											
0.0000	0.953 407		34.46	0.0475	0.957 277	35.05	35.30	0.1671	0.966 904	35.46	35.86
0.0073	0.954 001	34.67	34.82	0.0780	0.959 743	35.19	35.50	0.2063	0.970 032	35.54	35.96
0.0258	0.955 517	34.92	35.10	0.1249	0.963 518	35.35	35.71				
$x = 0.307$											
$t = 15.00$ °C											
0.0000	0.929 881		32.75	0.0557	0.934 432	33.38	33.60	0.1927	0.945 505	33.66	33.86
0.0118	0.930 851	33.02	33.21	0.0918	0.937 358	33.49	33.73	0.2662	0.951 403	33.71	33.84
0.0268	0.932 077	33.24	33.40	0.1329	0.940 681	33.58	33.81				
$t = 25.00$ °C											
0.0000	0.923 496		32.67	0.0774	0.929 780	33.43	33.68	0.2125	0.940 636	33.66	33.84
0.0108	0.924 376	32.96	33.15	0.1312	0.934 114	33.56	33.80	0.2937	0.947 117	33.69	33.78
0.0325	0.926 146	33.23	33.43	0.1730	0.937 469	33.62	33.84				
$t = 35.00$ °C											
0.0000	0.916 744		32.58	0.0365	0.919 700	33.20	33.43	0.1029	0.925 051	33.46	33.75
0.0067	0.917 292	32.81	33.00	0.0544	0.921 152	33.29	33.56	0.1447	0.928 395	33.55	33.83
0.0187	0.918 265	33.07	33.23	0.0748	0.922 792	33.38	33.66				
$t = 45.00$ °C											
0.0000	0.909 573		32.59	0.0584	0.914 266	33.51	33.74	0.2073	0.926 102	33.84	34.17
0.0085	0.910 261	32.77	33.11	0.1165	0.918 907	33.68	34.01	0.2588	0.930 167	33.88	34.18
0.0331	0.912 238	33.34	33.52	0.1637	0.922 652	33.80	34.12				
$x = 0.571$											
$t = 15.00$ °C											
0.0000	0.874 917		29.36	0.0413	0.878 255	30.36	30.68	0.0990	0.882 883	30.63	30.93
0.0103	0.875 756	29.89	30.16	0.0545	0.879 318	30.42	30.78	0.1168	0.884 309	30.67	30.94
0.0262	0.877 036	30.19	30.50	0.0800	0.881 357	30.57	30.90				
$t = 25.00$ °C											
0.0000	0.866 787		27.69	0.0328	0.869 460	28.72	29.12	0.0739	0.872 786	29.07	29.49
0.0097	0.867 584	28.31	28.59	0.0448	0.870 429	28.86	29.27	0.0963	0.874 594	29.17	29.57
0.0204	0.868 450	28.55	28.90	0.0577	0.871 474	28.96	29.39				

Table 2 (Continued)

m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{b\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})	m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})	m/(mol·kg^{-1})	ϱ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})
$x = 0.571$											
$t = 35.00$ °C											
0.0000	0.858 395		26.56	0.0320	0.861 008	27.70	28.13	0.1097	0.867 293	28.28	28.73
0.0075	0.859 010	27.13	27.44	0.0483	0.862 330	27.88	28.36	0.1586	0.871 227	28.42	28.78
0.0194	0.859 980	27.50	27.87	0.0630	0.863 523	28.02	28.50				
$t = 45.00$ °C											
0.0000	0.849 883		25.60	0.0345	0.852 698	26.91	27.38	0.1071	0.858 569	27.49	28.06
0.0070	0.850 456	26.13	26.52	0.0578	0.854 586	27.15	27.71	0.1380	0.861 049	27.61	28.15
0.0204	0.851 552	26.69	27.06	0.0767	0.856 114	27.32	27.88				
$x = 0.917$											
$t = 15.00$ °C											
0.0000	0.809 558		19.15	0.0261	0.811 720	20.55	21.10	0.0810	0.816 227	21.18	21.66
0.0066	0.810 110	19.84	20.31	0.0388	0.812 761	20.81	21.84	0.1027	0.818 002	21.27	21.67
0.0146	0.810 767	20.40	20.74	0.0555	0.814 138	20.99	21.53				
$t = 25.00$ °C											
0.0000	0.800 480		15.07	0.0214	0.802 286	16.63	17.29	0.0680	0.806 190	17.47	18.18
0.0048	0.800 890	15.97	16.28	0.0362	0.803 528	17.01	17.72	0.0680	0.806 190	17.47	18.18
0.0097	0.801 306	16.16	16.70	0.0496	0.804 653	17.23	17.97				
$t = 35.00$ °C											
0.0000	0.791 280		12.23	0.0223	0.793 181	14.17	14.96	0.0584	0.796 226	15.03	16.03
0.0052	0.791 724	13.27	13.70	0.0293	0.793 772	14.37	15.26	0.1314	0.802 333	15.83	16.71
0.0141	0.792 486	13.78	14.51	0.0364	0.794 375	14.58	15.50				
$t = 45.00$ °C											
0.0000	0.781 959		9.88	0.0267	0.784 245	12.37	13.42	0.0548	0.786 616	13.21	14.50
0.0072	0.782 576	11.23	11.90	0.0356	0.784 996	12.67	13.84	0.0694	0.787 841	13.52	14.87
0.0142	0.783 180	11.80	12.61	0.0452	0.785 809	12.98	14.20				
$x = 1.000$											
$t = 15.00$ °C											
0.0000	0.795 906		15.97	0.0207	0.797 634	17.43	17.95	0.0505	0.800 110	17.91	18.50
0.0042	0.796 263	16.64	17.03	0.0272	0.798 181	17.54	18.14	0.0606	0.800 949	18.01	18.58
0.0157	0.797 221	17.30	17.77	0.0438	0.799 561	17.85	18.43				
$t = 25.00$ °C											
0.0000	0.786 498		11.13	0.0232	0.788 487	13.00	13.74	0.0557	0.791 239	13.69	14.57
0.0047	0.786 907	11.99	12.48	0.0314	0.789 181	13.23	14.03	0.0639	0.791 927	13.81	14.68
0.0140	0.787 700	12.70	13.28	0.0473	0.790 527	13.57	14.42				
$t = 35.00$ °C											
0.0000	0.777 040		7.78	0.0246	0.779 164	10.12	11.05	0.0814	0.783 999	11.40	12.59
0.0050	0.777 478	8.84	9.44	0.0427	0.780 716	10.66	11.77	0.1083	0.786 279	11.73	12.89
0.0131	0.778 176	9.57	10.31	0.0610	0.782 269	11.08	12.24				
$t = 45.00$ °C											
0.0000	0.767 460		5.03	0.0287	0.769 949	8.00	9.27	0.0717	0.773 611	9.33	10.90
0.0088	0.768 231	6.83	7.61	0.0402	0.770 927	8.46	9.85	0.0895	0.775 116	9.68	11.29
0.0178	0.769 008	7.42	8.52	0.0532	0.772 044	8.86	10.36				

Table 3. Partial Molal Volumes of the Electrolytes at Infinite Dilution V_B^∞ in x Methanol + $(1 - x)$ Water

	V_B^∞/(cm^3·mol^{-1})					
t/°C	$x = 0.000$	$x = 0.129$	$x = 0.307$	$x = 0.571$	$x = 0.917$	$x = 1.000$
NaBr						
15.00	23.04[a]	22.75 ± 0.05	22.44 ± 0.06	19.74 ± 0.07	9.48 ± 0.13	6.65 ± 0.10
25.00	23.54[a]	22.98 ± 0.07	22.24 ± 0.06	18.64 ± 0.07	5.55 ± 0.10	1.54 ± 0.08, 2.7[b]
35.00	24.44[a]	23.28 ± 0.04	22.34 ± 0.08	17.78 ± 0.07	2.77 ± 0.06	−2.14 ± 0.08
45.00	25.12[a]	23.83 ± 0.03	22.63 ± 0.04	17.48 ± 0.13	0.27 ± 0.13	−5.35 ± 0.12
KBr						
15.00	32.65[a]	32.98 ± 0.07	32.75 ± 0.01	29.36 ± 0.01	19.15 ± 0.11	15.97 ± 0.23
25.00	33.73[a]	33.52 ± 0.04	32.67 ± 0.06	27.69 ± 0.08	15.07 ± 0.14	11.13 ± 0.21, 11.0[c]
35.00	34.48[a]	34.08 ± 0.07	32.58 ± 0.09	26.56 ± 0.08	12.23 ± 0.11	7.78 ± 0.17
45.00	35.04[a]	34.46 ± 0.01	32.59 ± 0.08	25.60 ± 0.09	9.88 ± 0.15	5.03 ± 0.11

[a] Reference 7. [b] Reference 2. [c] Reference 3.

6, *7*, *11*). The mean value of A_v was calculated from the observed A_v on the solutions of sodium chloride (*9*), potassium chloride (*9*), sodium bromide, potassium bromide, sodium iodide (*10*), and potassium iodide (*10*).

In these tables, the maximum errors for $V_{B\varphi}^\infty$, A_v, and b_v were also listed, respectively. Each value of the error for $V_{B\varphi}^\infty$ or b_v is correlated to two factors: (i) ±1 count in the reading of the densimeter, (ii) ±0.1 mg of mass of the electrolyte. The error listed in the tables is the root of the sum of squares of the two errors on $V_{B\varphi}^\infty$ or on b_v. The errors shown in Table 4 are the standard deviations. In Table 3, the observed V_B^∞ for each electrolyte in pure methanol at 25 °C is consistent with that taken from the literature within experimental error. However, the abso-

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

	$A_v/(\mathrm{cm^3{\cdot}kg^{1/2}{\cdot}mol^{-3/2}})$					
t/°C	$x = 0.000$	$x = 0.129$	$x = 0.307$	$x = 0.571$	$x = 0.917$	$x = 1.000$
15.00	1.7150[a]	2.1 ± 0.82	3.2 ± 1.31	6.2 ± 2.51	10.9 ± 4.54	12.1 ± 5.21
25.00	1.8743[a]	2.4 ± 0.90	3.5 ± 0.99	7.0 ± 1.57	12.9 ± 2.35	14.5 ± 2.52
35.00	2.0547[a]	2.6 ± 0.43	3.8 ± 1.14	7.7 ± 1.74	15.0 ± 2.45	17.1 ± 2.37
45.00	2.2601[a]	2.9 ± 0.55	4.2 ± 1.31	8.2 ± 1.69	17.4 ± 2.63	20.3 ± 2.52
25.00	1.861[b]	2.275[b]	3.475[b]	6.989[b]	13.792[b]	14.457[b] 9.61[c] 14.00[d]

[a] Reference 1. [b] Reference 6. [c] Reference 11. [d] Reference 4.

Table 5. Apparent Molal Volume Concentration Dependence Constants b_v in x Methanol + $(1 - x)$ Water

	$b_v/(\mathrm{cm^3{\cdot}kg{\cdot}mol^{-2}})$					
t/°C	$X = 0.000$	$X = 0.129$	$X = 0.307$	$X = 0.571$	$X = 0.917$	$X = 1.000$
			NaBr			
15.00	0.095[a]	−0.1 ± 0.2	−1.8 ± 0.3	−5.2 ± 0.3	−10.0 ± 1.5	−12.3 ± 1.4
25.00	−0.196[a]	−0.7 ± 0.3	−2.5 ± 0.3	−5.5 ± 0.7	−10.5 ± 1.8	−11.6 ± 0.5, −4.2[b]
35.00	−0.421[a]	−1.3 ± 0.1	−2.8 ± 0.8	−6.3 ± 0.4	−10.8 ± 0.4	−11.7 ± 0.1
45.00	−0.640[a]	−1.7 ± 0.1	−3.5 ± 0.3	−6.4 ± 1.7	−9.7 ± 1.0	−11.6 ± 1.7
			KBr			
15.00	0.180[a]	−0.3 ± 0.4	−2.6 ± 0.1	−6.8 ± 0.1	−13.3 ± 1.5	−15.4 ± 5.2
25.00	−0.072[a]	−0.6 ± 0.2	−3.0 ± 0.3	−7.3 ± 1.2	−14.2 ± 2.2	−15.3 ± 4.4, −3.2[b]
35.00	−0.265[a]	−1.0 ± 0.6	−3.1 ± 0.9	−7.4 ± 0.8	−14.0 ± 1.4	−15.5 ± 2.3
45.00	−0.397[a]	−1.2 ± 0.1	−3.1 ± 0.4	−7.2 ± 0.9	−13.5 ± 2.9	−15.8 ± 1.7

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

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	$X = 0.000$	$X = 0.129$	$X = 0.307$	$X = 0.571$	$X = 0.917$	$X = 1.000$
			NaBr			
15.00	0.058	0.011 ± 0.004	−0.030 ± 0.005	−0.137 ± 0.003	−0.411 ± 0.007	−0.540 ± 0.006
25.00	0.067	0.027 ± 0.003	−0.005 ± 0.004	−0.097 ± 0.006	−0.340 ± 0.008	−0.445 ± 0.007
35.00	0.076	0.044 ± 0.003	0.019 ± 0.003	−0.057 ± 0.008	−0.268 ± 0.009	−0.349 ± 0.008
45.00	0.085	0.060 ± 0.002	0.043 ± 0.002	−0.016 ± 0.011	−0.197 ± 0.010	−0.254 ± 0.009
			KBr			
15.00	0.118	0.062 ± 0.009	−0.013 ± 0.007	−0.177 ± 0.002	−0.436 ± 0.005	−0.519 ± 0.019
25.00	0.092	0.054 ± 0.005	−0.008 ± 0.001	−0.142 ± 0.002	−0.350 ± 0.008	−0.414 ± 0.015
35.00	0.066	0.046 ± 0.001	−0.003 ± 0.004	−0.106 ± 0.006	−0.263 ± 0.011	−0.309 ± 0.010
45.00	0.040	0.038 ± 0.003	−0.001 ± 0.010	−0.070 ± 0.010	−0.176 ± 0.014	−0.204 ± 0.008

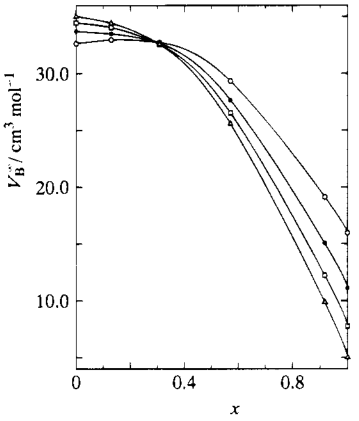

Figure 1. Partial molal volumes of sodium bromide at infinite dilution in x methanol + $(1 - x)$ water at various temperatures: ○, 15 °C; □, 25 °C; ◇, 35 °C; △, 45 °C.

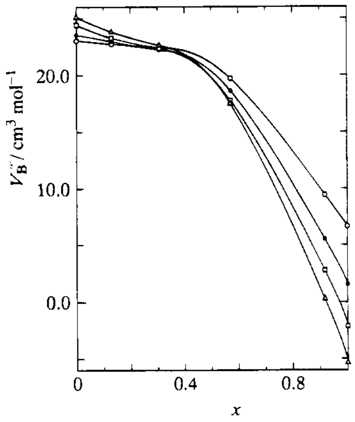

Figure 2. Partial molal volumes of potassium bromide at infinite dilution in x methanol + $(1 - x)$ water at various temperatures: ○, 15 °C; □, 25 °C; ◇, 35 °C; △, 45 °C.

lute value of the observed b_v in Table 5 is larger than that taken from the literature. In Figures 1 and 2, V_B^∞ values for sodium bromide and potassium bromide were plotted against x at various temperatures, respectively. For lithium chloride, sodium chloride, and potassium chloride V_B^∞ values in the mixtures were determined previously (*9*). In Figure 3, V_B^∞ values at 25 °C were plotted against x for each electrolyte solution.

In a previous paper (*9*), it has been shown that A_v for lithium chloride solution is smaller than that for sodium chloride or potassium chloride solution and that the evaluated A_v for sodium chloride solution is identical to that for potassium chloride solution within experimental error. In the present work, the A_v values for sodium bromide and potassium bromide solution are identical to each other within experimental error. Moreover, the A_v values for all the measured electrolyte solutions are identical except that for lithium chloride solution (*9*).

Partial molal thermal expansions of the electrolytes $(\partial V_B^\infty/\partial T)_p$ are given in Table 6. In the table, the maximum

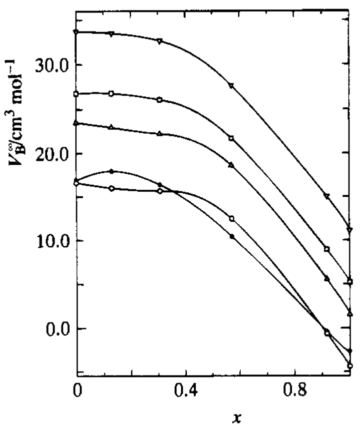

Figure 3. Partial molal volumes of electrolytes at infinite dilution in x methanol + $(1 - x)$ water at 25 °C: △, NaBr; ▽, KBr; ●, LiCl (*9*); ○, NaCl (*9*); □, KCl (*9*).

errors which are caused by the maximum errors in Table 3 are shown. In Tables 3 and 6, both V_B^∞ and the thermal expansion decrease with an increase in temperature or an increase in methanol concentration.

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