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Partial Molar Volumes of Uni-univalent Electrolytes in Methanol + Water. 1. Lithium Chloride, Sodium Chloride, and Potassium Chloride

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

Introduction

Methanol + water is a popular mixed solvent and has been extensively studied (*1*). There have been few studies which concern the volumetrics of the interaction between the mixture and an electrolyte.

Partial molar volumes and partial molar thermal expansivities give us useful information concerning the interactions in such mixtures.

Densities were measured for methanol + water and those solutions with lithium chloride, sodium chloride, and potassium chloride at 15, 25, 35, and 45 °C. The partial molar volumes and thermal expansivities of these electrolytes were determined.

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 believed to be $\pm 2 \times 10^{-6}$ g·cm^{-3}. Details of the apparatus and procedure have been described previously (*2*). 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 (*3*) and dry air.

Reagent grade lithium chloride was obtained from Kanto Chemical Co., Inc. Suprapur sodium chloride and potassium chloride 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 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. The mixture was degassed before use, to prevent the formation of bubbles in the density-measuring cell during an experiment. All solutions were prepared by successive addition of a known mass of an electrolyte to a known mass of the mixture. Observed densities of the solvents at various temperatures are given in Table 1. In the table, densities of water are taken from the literature (*3*).

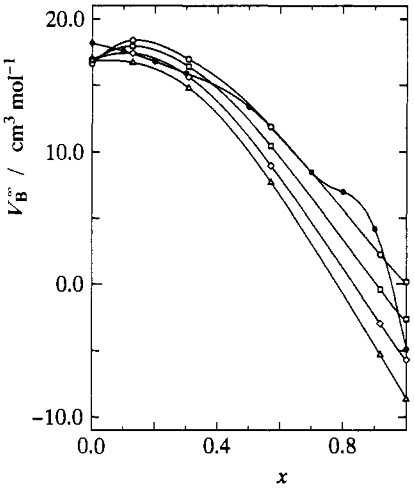

Figure 1. Partial molar volumes of lithium chloride at infinite dilution in x methanol + $(1 - x)$ water at various temperatures: ○, 15 °C; □, 25 °C; ◇, 35 °C; △, 45 °C; ●, 25 °C, ref 8.

Results and Discussion

Observed densities ρ of the solutions of lithium chloride, sodium chloride, and potassium chloride at various temper-

Table 1. Densities of x Methanol + $(1 - x)$ Water, ρ_0, at Various Temperatures

	ρ_0/(g·cm^{-3})						
t/°C	x = 0.000	x = 0.129	x = 0.307	x = 0.571	x = 0.917	x = 1.000	
15.00	0.999 101^a	0.966 975	0.929 678	0.874 663	0.809 600	0.795 899	0.795 825^b
25.00	0.997 047^a	0.963 106	0.923 290	0.866 564	0.800 472	0.786 494	0.786 434^b
35.00	0.994 035^a	0.958 609	0.916 739	0.858 446	0.791 287	0.777 031	0.776 990^b
45.00	0.990 216^a	0.953 383	0.909 505	0.849 904	0.781 960	0.767 472	0.767 411^b

^{a} Reference 3. ^{b} Reference 4.

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

m/(mol·kg)	ρ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})	m/(mol·kg)	ρ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})	m/(mol·kg)	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	0.966 976		18.42	0.1750	0.971 034	18.96	19.25	0.6839	0.982 321	19.53	20.12
0.0164	0.967 363	18.54	18.67	0.2852	0.973 528	19.14	19.49	1.0417	0.989 925	19.81	20.55
0.0406	0.967 930	18.65	18.81	0.4621	0.977 480	19.32	19.80				
$t = 25.00$ °C											
0.0000	0.963 105		17.97	0.0912	0.965 269	18.41	18.63	0.5902	0.976 629	19.05	19.55
0.0070	0.963 274	18.09	18.16	0.2140	0.968 124	18.64	18.96	0.8382	0.982 076	19.24	19.82
0.0319	0.963 869	18.21	18.37	0.3711	0.971 714	18.84	19.25				
$t = 35.00$ °C											
0.0000	0.958 609		17.44	0.0775	0.960 485	17.84	18.09	0.7178	0.975 262	18.65	19.17
0.0070	0.958 781	17.61	17.65	0.1803	0.962 923	18.11	18.40	1.1236	0.984 233	18.90	19.49
0.0396	0.959 573	17.71	17.91	0.3556	0.967 016	18.34	18.73				
$t = 45.00$ °C											
0.0000	0.953 384		16.73	0.2120	0.958 570	17.46	17.85	0.9077	0.974 705	18.22	18.91
0.0168	0.953 803	16.91	17.05	0.4053	0.963 153	17.77	18.24	1.3126	0.983 665	18.50	19.28
0.0669	0.955 044	17.11	17.37	0.6014	0.967 714	17.98	18.54				
$x = 0.307$											
$t = 15.00$ °C											
0.0000	0.929 677		16.99	0.0653	0.931 272	17.34	17.56	0.3671	0.938 422	17.87	18.26
0.0082	0.929 880	17.02	17.19	0.1532	0.933 381	17.57	17.84	0.4825	0.941 108	17.97	18.43
0.0304	0.930 422	17.27	17.38	0.2461	0.935 586	17.71	18.05	0.6612	0.945 203	18.13	18.65
$t = 25.00$ °C											
0.0000	0.923 290		16.42	0.1044	0.925 868	16.91	17.20	0.5742	0.936 998	17.65	18.27
0.0184	0.923 749	16.61	16.75	0.1905	0.927 952	17.12	17.48	0.7981	0.942 126	17.87	18.61
0.0600	0.924 779	16.77	17.01	0.3815	0.932 496	17.44	17.92	1.1751	0.950 528	18.19	19.09
$t = 35.00$ °C											
0.0000	0.916 740		15.64	0.0642	0.918 363	16.12	16.38	0.3205	0.924 634	16.79	17.42
0.0065	0.916 905	15.78	15.86	0.1280	0.919 949	16.34	16.71	0.4424	0.927 532	17.01	17.78
0.0266	0.917 416	15.95	16.10	0.2169	0.922 133	16.56	17.07	0.6630	0.932 662	17.37	18.36
$t = 45.00$ °C											
0.0000	0.909 504		14.81	0.0792	0.911 547	15.41	15.72	0.3976	0.919 453	16.19	16.91
0.0095	0.909 754	15.06	15.12	0.1615	0.913 629	15.67	16.12	0.4984	0.921 884	16.36	17.17
0.0382	0.910 495	15.26	15.44	0.2817	0.916 617	15.97	16.56				
$x = 0.571$											
$t = 15.00$ °C											
0.0000	0.874 662		11.92	0.1414	0.878 484	13.08	13.67	0.3398	0.883 660	13.72	14.64
0.0184	0.875 174	12.13	12.55	0.2041	0.880 131	13.36	14.03	0.4700	0.886 965	14.05	15.12
0.0675	0.876 509	12.69	13.13	0.2627	0.881 667	13.51	14.31				
$t = 25.00$ °C											
0.0000	0.866 564		10.47	0.1187	0.869 881	11.67	12.20	0.3976	0.877 413	12.43	13.17
0.0338	0.867 524	11.10	11.47	0.1859	0.871 716	11.95	12.54	0.5069	0.880 304	12.62	13.37
0.0662	0.868 430	11.35	11.82	0.2933	0.874 623	12.22	12.91				
$t = 35.00$ °C											
0.0000	0.858 446		8.99	0.0654	0.860 339	10.06	10.60	0.2933	0.866 680	11.18	12.18
0.0068	0.858 647	9.40	9.53	0.1154	0.861 757	10.43	11.09	0.4646	0.871 294	11.69	12.87
0.0247	0.859 168	9.65	10.00	0.1791	0.863 539	10.75	11.56				
$t = 45.00$ °C											
0.0000	0.849 905		7.73	0.0704	0.851 983	9.00	9.63	0.3612	0.860 153	10.47	11.70
0.0163	0.850 391	8.37	8.67	0.1649	0.854 688	9.65	10.54	0.4913	0.863 684	10.87	12.24
0.0355	0.850 962	8.63	9.10	0.2498	0.857 072	10.06	11.11				
$x = 0.917$											
$t = 15.00$ °C											
0.0000	0.809 600		2.26	0.1699	0.814 876	4.97	6.14	0.4117	0.822 043	6.16	7.66
0.0191	0.810 212	3.38	3.72	0.2215	0.816 427	5.29	6.57	0.5611	0.826 365	6.64	8.22
0.1206	0.813 374	4.59	5.63	0.2937	0.818 574	5.69	7.06				
$t = 25.00$ °C											
0.0000	0.800 472		−0.40	0.0828	0.803 180	1.89	2.92	0.2979	0.809 902	3.52	5.08
0.0114	0.800 857	0.14	0.94	0.1403	0.805 006	2.52	3.73	0.4132	0.813 400	4.06	5.69
0.0326	0.801 558	0.94	1.79	0.2194	0.807 479	3.10	4.51				
$t = 35.00$ °C											
0.0000	0.791 278		−2.96	0.0808	0.794 003	−0.31	0.85	0.3528	0.802 673	1.96	3.92
0.0142	0.791 770	−1.92	−1.25	0.1440	0.796 070	0.43	1.91	0.4794	0.806 566	2.59	4.66
0.0381	0.792 584	−1.24	−0.24	0.2520	0.799 514	1.35	3.13				
$t = 45.00$ °C											
0.0000	0.781 959		−5.32	0.0759	0.784 589	−2.44	−1.10	0.3394	0.793 171	0.19	2.38
0.0152	0.782 504	−4.28	−3.30	0.1123	0.785 809	−1.84	−0.32	0.4942	0.798 016	1.05	3.39
0.0379	0.783 291	−3.26	−2.23	0.1860	0.788 238	−0.99	0.83				

Table 2 (Continued)

m/(mol·kg)	ρ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})	m/(mol·kg)	ρ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})	m/(mol·kg)	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	0.795 898		0.17	0.0630	0.797 935	2.22	3.17	0.2246	0.802 940	3.76	5.20
0.0081	0.796 167	1.01	1.34	0.0922	0.798 856	2.66	3.71	0.3126	0.805 597	4.25	5.81
0.0309	0.796 909	1.63	2.35	0.1595	0.800 951	3.26	4.59				
t = 25.00 °C											
0.0000	0.786 493		−2.65	0.0589	0.788 476	−0.50	0.57	0.3071	0.796 373	1.88	3.74
0.0091	0.786 809	−1.88	−1.30	0.1197	0.790 454	0.39	1.74	0.3945	0.799 057	2.38	4.34
0.0270	0.787 414	−1.14	−0.40	0.1861	0.792 577	1.06	2.62				
t = 35.00 °C											
0.0000	0.777 031		−5.71	0.1021	0.780 542	−2.36	−0.82	0.3620	0.788 941	0.07	2.31
0.0162	0.777 605	−4.25	−3.60	0.1372	0.781 703	−1.82	−0.17	0.4975	0.793 172	0.80	3.17
0.0393	0.778 407	−3.48	−2.51	0.2043	0.783 901	−1.12	0.79	0.6396	0.797 544	1.40	3.83
0.0637	0.779 244	−2.96	−1.73	0.2662	0.785 909	−0.66	1.48	0.7376	0.800 527	1.75	4.18
t = 45.00 °C											
0.0000	0.767 473		−8.67	0.0923	0.770 747	−4.97	−3.24	0.3736	0.780 058	−1.93	0.69
0.0092	0.767 811	−7.47	−6.79	0.1805	0.773 734	−3.62	−1.50	0.4831	0.783 544	−1.22	1.49
0.0277	0.768 479	−6.57	−5.50	0.2494	0.776 015	−2.89	−0.56				

Table 3. Densities of Solutions ρ, Apparent Molar Volumes $V_{B\varphi}$, and Partial Molar Volumes V_B for NaCl in x Methanol + (x − 1) Water

m/(mol·kg)	ρ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})	m/(mol·kg)	ρ/(g·cm^{-3})	$V_{B\varphi}$/(cm^3·mol^{-1})	V_B/(cm^3·mol^{-1})	m/(mol·kg)	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	0.966 974		15.50	0.0698	0.969 865	16.13	16.43	0.3682	0.981 872	16.91	17.59
0.0114	0.967 452	15.69	15.88	0.1476	0.973 037	16.41	16.84	0.5885	0.990 500	17.27	18.12
0.0275	0.968 122	15.87	16.09	0.2271	0.976 246	16.61	17.16				
t = 25.00 °C											
0.0000	0.963 106		16.01	0.1408	0.968 812	16.90	17.31	0.5629	0.985 346	17.68	18.42
0.0148	0.963 715	16.28	16.46	0.2292	0.972 333	17.13	17.64	0.8496	0.996 250	18.01	18.85
0.0451	0.964 955	16.50	16.77	0.3825	0.978 359	17.42	18.05				
t = 35.00 °C											
0.0000	0.958 610		16.29	0.0623	0.961 127	16.93	17.28	0.4852	0.977 635	17.94	18.59
0.0086	0.958 961	16.53	16.68	0.1549	0.964 805	17.32	17.76	0.7471	0.987 568	18.23	18.94
0.0276	0.959 732	16.73	16.97	0.2771	0.969 601	17.61	18.16				
t = 45.00 °C											
0.0000	0.953 384		16.36	0.0535	0.955 533	17.06	17.39	0.4501	0.970 900	18.15	18.85
0.0053	0.953 598	16.59	16.70	0.1098	0.957 763	17.34	17.79	0.7250	0.981 229	18.50	19.26
0.0218	0.954 264	16.83	17.04	0.2692	0.963 975	17.81	18.42				
x = 0.307											
t = 15.00 °C											
0.0000	0.929 679		15.65	0.0406	0.931 308	16.38	16.70	0.1943	0.937 339	17.09	17.71
0.0078	0.929 994	15.98	16.13	0.0724	0.932 572	16.58	17.01	0.2973	0.941 311	17.37	18.08
0.0250	0.930 685	16.18	16.49	0.0939	0.933 419	16.67	17.17				
t = 25.00 °C											
0.0000	0.923 289		15.68	0.0686	0.926 013	16.71	17.18	0.2554	0.933 217	17.51	18.26
0.0076	0.923 595	15.96	16.22	0.1149	0.927 819	16.98	17.56	0.3695	0.937 535	17.80	18.63
0.0370	0.924 766	16.44	16.82	0.1816	0.930 394	17.27	17.95				
t = 35.00 °C											
0.0000	0.916 739		15.31	0.0642	0.919 291	16.43	16.96	0.1636	0.923 147	17.02	17.73
0.0126	0.917 248	15.85	16.10	0.0823	0.919 997	16.59	17.15	0.2624	0.926 922	17.38	18.18
0.0359	0.918 172	16.21	16.59	0.1095	0.921 054	16.76	17.38	0.4185	0.932 801	17.77	18.63
t = 45.00 °C											
0.0000	0.909 506		14.80	0.0701	0.912 293	16.13	16.73	0.2812	0.920 410	17.16	18.04
0.0065	0.909 770	15.29	15.46	0.1475	0.915 302	16.65	17.40	0.4273	0.925 903	17.54	18.44
0.0279	0.910 627	15.65	16.09	0.2196	0.918 067	16.97	17.80				
x = 0.571											
t = 15.00 °C											
0.0000	0.874 663		13.31	0.0498	0.876 650	14.65	15.28	0.2193	0.883 186	15.87	16.90
0.0058	0.874 898	13.79	14.04	0.1006	0.878 633	15.18	15.97	0.2835	0.885 609	16.15	17.23
0.0237	0.875 615	14.23	14.72	0.1643	0.881 086	15.59	16.54				
t = 25.00 °C											
0.0000	0.866 565		12.50	0.0994	0.870 500	14.64	15.53	0.2932	0.877 903	15.74	16.84
0.0164	0.867 231	13.46	13.90	0.1474	0.872 357	15.01	16.00	0.3686	0.880 735	15.99	17.09
0.0604	0.868 975	14.22	14.98	0.2071	0.874 642	15.35	16.42				

Table 3 (Continued)

m/ (mol·kg)	ρ/ (g·cm^{-3})	$V_{B\varphi}$/ (cm^3·mol^{-1})	V_B/ (cm^3·mol^{-1})	m/ (mol·kg)	ρ/ (g·cm^{-3})	$V_{B\varphi}$/ (cm^3·mol^{-1})	V_B/ (cm^3·mol^{-1})	m/ (mol·kg)	ρ/ (g·cm^{-3})	$V_{B\varphi}$/ (cm^3·mol^{-1})	V_B/ (cm^3·mol^{-1})
t = 35.00 °C											
0.0000	0.858 445		11.56	0.0797	0.861 642	13.64	14.57	0.2937	0.869 883	15.05	16.20
0.0147	0.859 047	12.50	13.01	0.1349	0.863 793	14.20	15.22	0.3730	0.872 877	15.33	16.45
0.0371	0.859 948	13.10	13.75	0.2177	0.866 984	14.71	15.84				
t = 45.00 °C											
0.0000	0.849 903		10.47	0.0776	0.853 042	12.75	13.70	0.3047	0.861 861	14.24	15.41
0.0050	0.850 112	10.92	11.43	0.1336	0.855 248	13.31	14.40	0.3979	0.865 406	14.56	15.64
0.0251	0.850 934	11.82	12.49	0.2393	0.859 344	13.99	15.15				
x = 0.917											
t = 15.00 °C											
0.0000	0.809 601		1.57	0.0668	0.812 565	4.43	5.67	0.2071	0.818 565	6.07	7.65
0.0177	0.810 400	3.18	3.89	0.1117	0.814 508	5.13	6.55	0.2607	0.820 823	6.43	8.03
0.0370	0.811 257	3.81	4.78	0.1600	0.816 573	5.66	7.20				
t = 25.00 °C											
0.0000	0.800 471		−0.64	0.0555	0.802 982	2.41	3.68	0.1234	0.805 965	3.53	5.18
0.0149	0.801 158	0.91	1.81	0.0794	0.804 037	2.90	4.33	0.1702	0.807 984	4.10	5.80
0.0304	0.801 862	1.65	2.72	0.1005	0.804 965	3.23	4.78				
t = 35.00 °C											
0.0000	0.791 277		−2.61	0.0469	0.793 435	0.33	1.66	0.1802	0.799 320	2.55	4.50
0.0085	0.791 676	−1.35	−0.63	0.0853	0.795 155	1.23	2.83	0.2407	0.801 931	3.13	5.15
0.0229	0.792 344	−0.50	0.51	0.1118	0.796 330	1.68	3.42				
t = 45.00 °C											
0.0000	0.781 960		−4.69	0.0601	0.784 738	−0.88	0.73	0.1898	0.790 482	1.31	3.52
0.0137	0.782 613	−2.98	−1.84	0.1009	0.786 570	0.05	1.94	0.2411	0.792 701	1.86	4.09
0.0324	0.783 478	−1.87	−0.51	0.1493	0.788 712	0.80	2.92				
x = 1.000											
t = 15.00 °C											
0.0000	0.795 900		−1.64	0.0374	0.797 620	0.81	1.90	0.1295	0.801 719	2.48	4.09
0.0122	0.796 471	−0.24	0.52	0.0504	0.798 205	1.16	2.37	0.1921	0.804 450	3.14	4.84
0.0260	0.797 103	0.41	1.39	0.0912	0.800 028	1.96	3.42				
t = 25.00 °C											
0.0000	0.786 494		−4.38	0.0674	0.789 628	−0.83	0.69	0.1426	0.793 012	0.43	2.23
0.0237	0.787 613	−2.07	−1.10	0.0958	0.790 910	−0.23	1.40				
0.0450	0.788 603	−1.38	−0.06	0.1169	0.791 862	0.08	1.81				
t = 35.00 °C											
0.0000	0.777 030		−7.13	0.0420	0.779 037	−3.90	−2.41	0.0986	0.781 654	−2.40	−0.48
0.0087	0.777 456	−5.56	−4.80	0.0585	0.779 804	−3.34	−1.71	0.1252	0.782 865	−1.96	0.12
0.0251	0.778 239	−4.55	−3.35	0.0777	0.780 696	−2.84	−1.06	0.1696	0.784 865	−1.29	0.90
t = 45.00 °C											
0.0000	0.767 472		−9.90	0.0580	0.770 268	−5.70	−3.82	0.1592	0.774 944	−3.50	−1.01
0.0139	0.768 158	−7.71	−6.65	0.0781	0.771 210	−5.03	−3.04	0.2041	0.776 973	−2.84	−0.29
0.0426	0.769 542	−6.24	−4.55	0.1120	0.772 779	−4.29	−2.04				

Table 4. Densities of Solutions ρ, Apparent Molar Volumes $V_{B\varphi}$, and Partial Molar Volumes V_B for KCl in x Methanol + $(1 - x)$ Water

m/ (mol·kg)	ρ/ (g·cm^{-3})	$V_{B\varphi}$/ (cm^3·mol^{-1})	V_B/ (cm^3·mol^{-1})	m/ (mol·kg)	ρ/ (g·cm^{-3})	$V_{B\varphi}$/ (cm^3·mol^{-1})	V_B/ (cm^3·mol^{-1})	m/ (mol·kg)	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	0.966 975		25.91	0.0757	0.970 546	26.54	26.87	0.2676	0.979 388	27.14	27.80
0.0118	0.967 538	26.17	26.28	0.1285	0.973 007	26.74	27.18	0.3798	0.984 448	27.40	28.20
0.0397	0.968 857	26.37	26.59	0.1930	0.975 979	26.94	27.49				
t = 25.00 °C											
0.0000	0.963 107		26.82	0.0694	0.966 315	27.46	27.77	0.2490	0.974 441	27.99	28.55
0.0106	0.963 600	27.07	27.20	0.1271	0.968 951	27.67	28.08	0.3229	0.977 732	28.15	28.77
0.0366	0.964 806	27.29	27.51	0.1873	0.971 672	27.85	28.33				
t = 35.00 °C											
0.0000	0.958 608		26.89	0.0859	0.962 554	27.67	28.05	0.3118	0.972 662	28.31	28.93
0.0091	0.959 035	27.12	27.29	0.1452	0.965 236	27.90	28.36	0.4249	0.977 619	28.51	29.20
0.0411	0.960 506	27.44	27.71	0.2271	0.968 909	28.12	28.68				
t = 45.00 °C											
0.0000	0.953 383		26.51	0.0685	0.956 544	27.31	27.65	0.2669	0.965 486	27.94	28.52
0.0125	0.953 965	26.89	27.03	0.1256	0.959 146	27.54	28.00	0.3644	0.969 807	28.12	28.76
0.0323	0.954 884	27.07	27.32	0.1880	0.961 964	27.73	28.27				
x = 0.307											
t = 15.00 °C											
0.0000	0.929 678		25.97	0.0670	0.932 759	26.88	27.32	0.1689	0.937 355	27.38	28.01
0.0119	0.930 231	26.41	26.57	0.0923	0.933 907	27.03	27.53	0.2249	0.939 847	27.57	28.28
0.0372	0.931 396	26.68	27.00	0.1302	0.935 618	27.23	27.79				

Table 4 (Continued)

m/ (mol·kg)	ρ/ (g·cm^{-3})	$V_{B\varphi}$/ (cm^3·mol^{-1})	V_B/ (cm^3·mol^{-1})	m/ (mol·kg)	ρ/ (g·cm^{-3})	$V_{B\varphi}$/ (cm^3·mol^{-1})	V_B/ (cm^3·mol^{-1})	m/ (mol·kg)	ρ/ (g·cm^{-3})	$V_{B\varphi}$/ (cm^3·mol^{-1})	V_B/ (cm^3·mol^{-1})
t = 25.00 °C											
0.0000	0.923 291		26.10	0.0506	0.925 607	27.00	27.43	0.2030	0.932 406	27.79	28.52
0.0109	0.923 795	26.54	26.75	0.0902	0.927 389	27.29	27.82	0.2930	0.936 347	28.07	28.88
0.0290	0.924 624	26.78	27.13	0.1444	0.929 815	27.55	28.20				
t = 35.00 °C											
0.0000	0.916 738		25.51	0.0354	0.918 374	26.39	26.79	0.1173	0.922 078	27.02	27.69
0.0081	0.917 114	26.02	26.15	0.0577	0.919 390	26.60	27.11	0.1616	0.924 052	27.25	27.99
0.0197	0.917 653	26.14	26.49	0.0859	0.920 665	26.83	27.42				
t = 45.00 °C											
0.0000	0.909 505		24.72	0.0410	0.911 408	25.78	26.28	0.1280	0.915 363	26.49	27.26
0.0104	0.909 991	25.31	25.54	0.0639	0.912 457	26.01	26.62	0.1757	0.917 497	26.75	27.60
0.0220	0.910 532	25.53	25.89	0.0930	0.913 781	26.27	26.95				
x = 0.571											
t = 15 °C											
0.0000	0.874 664		22.79	0.0278	0.875 965	23.91	24.43	0.0731	0.878 053	24.54	25.30
0.0066	0.874 975	23.39	23.63	0.0458	0.876 799	24.20	24.84	0.0919	0.878 909	24.71	25.55
0.0166	0.875 443	23.68	24.09	0.0600	0.877 454	24.38	25.10				
t = 25.00 °C											
0.0000	0.866 563		21.74	0.0297	0.867 968	22.99	23.58	0.0755	0.870 095	23.65	24.48
0.0062	0.866 862	22.33	22.63	0.0427	0.868 578	23.23	23.90	0.0985	0.871 151	23.88	24.79
0.0167	0.867 358	22.70	23.15	0.0544	0.869 122	23.40	24.13				
x = 0.571											
t = 35.00 °C											
0.0000	0.858 447		20.58	0.0267	0.859 729	21.70	22.26	0.0796	0.862 213	22.50	23.41
0.0061	0.858 743	21.17	21.40	0.0416	0.860 432	21.97	22.66	0.1123	0.863 733	22.84	23.90
0.0138	0.859 110	21.44	21.80	0.0608	0.861 336	22.27	23.07				
t = 45.00 °C											
0.0000	0.849 904		18.83	0.0320	0.851 459	20.39	21.08	0.0655	0.853 058	20.94	21.86
0.0109	0.850 440	19.81	20.22	0.0415	0.851 914	20.56	21.34	0.0782	0.853 661	21.12	22.08
0.0225	0.851 003	20.12	20.76	0.0542	0.852 523	20.80	21.64				
x = 0.917											
t = 15.00 °C											
0.0000	0.809 599		11.37	0.0109	0.810 170	12.67	13.24	0.0345	0.811 377	13.50	14.49
0.0014	0.809 674	11.41	12.07	0.0186	0.810 566	13.02	13.75	0.0587	0.812 598	14.09	15.26
0.0091	0.810 074	12.46	13.08	0.0261	0.810 948	13.29	14.13				
t = 25.00 °C											
0.0000	0.800 473		8.94	0.0251	0.801 794	11.02	11.93	0.0497	0.803 064	11.73	12.94
0.0070	0.800 844	10.06	10.61	0.0320	0.802 150	11.28	12.26	0.0653	0.803 861	12.07	13.40
0.0185	0.801 449	10.67	11.55	0.0384	0.802 483	11.39	12.53				
t = 35.00 °C											
0.0000	0.791 276		6.82	0.0206	0.792 380	8.62	9.55	0.0453	0.793 679	9.51	10.84
0.0036	0.791 474	7.77	7.98	0.0269	0.792 718	8.84	9.93	0.0577	0.794 322	9.85	11.34
0.0147	0.792 068	8.40	9.13	0.0346	0.793 116	9.23	10.34				
t = 45.00 °C											
0.0000	0.781 961		4.57	0.0217	0.783 137	6.70	7.72	0.0488	0.784 575	7.72	9.21
0.0055	0.782 260	5.73	6.18	0.0285	0.783 498	6.98	8.16	0.0595	0.785 134	8.01	9.66
0.0129	0.782 662	6.18	7.01	0.0371	0.783 956	7.30	8.64				
x = 1.000											
t = 15.00 °C											
0.0000	0.795 899		7.59	0.0152	0.796 713	9.19	9.97	0.0339	0.797 695	9.94	10.98
0.0064	0.796 244	8.61	9.18	0.0215	0.797 047	9.51	10.37	0.0419	0.798 115	10.16	11.29
0.0104	0.796 458	9.01	9.59	0.0279	0.797 380	9.72	10.70				
t = 25.00 °C											
0.0000	0.786 495		5.22	0.0241	0.787 793	7.48	8.49	0.0479	0.789 055	8.28	9.61
0.0076	0.786 910	6.54	7.16	0.0301	0.788 114	7.70	8.83	0.0584	0.789 609	8.55	9.97
0.0149	0.787 300	7.01	7.86	0.0390	0.788 587	8.01	9.25				
t = 35.00 °C											
0.0000	0.777 032		2.88	0.0204	0.778 149	5.20	6.30	0.0450	0.779 470	6.23	7.69
0.0045	0.777 280	4.11	4.58	0.0283	0.778 573	5.59	6.83	0.0530	0.779 893	6.47	8.02
0.0121	0.777 700	4.73	5.58	0.0366	0.779 019	5.95	7.29				
t = 45.00 °C											
0.0000	0.767 471		0.51	0.0220	0.768 691	3.22	4.47	0.0471	0.770 048	4.31	6.00
0.0048	0.767 743	1.89	2.48	0.0268	0.768 949	3.47	4.83	0.0624	0.770 863	4.82	6.65
0.0147	0.768 289	2.76	3.82	0.0396	0.769 642	4.08	5.61				

Table 5. Partial Molar Volumes of the Electrolytes at Infinite Dilution, V_B^∞, in x Methanol + $(1 - x)$ Water

	$V_B^\infty/(cm^3\ mol^{-1})$					
$t/°C$	x = 0.000	x = 0.129	x = 0.307	x = 0.571	x = 0.917	x = 1.000
LiCl						
15.00	16.63[a]	18.42	16.99	11.92	2.26	0.17
25.00	16.91[a]	17.97	16.42	10.47	−0.40	−2.65, −3.8[b]
35.00	16.95[a]	17.44	15.64	8.99	−2.96	−5.71
45.00	16.88[a]	16.73	14.81	7.73	−5.32	−8.67
$(\delta V)_{max}(cm^3\ mol^{-1})$		±0.05	±0.07	±0.10	±0.18	±0.20
NaCl						
15.00	15.58[a]	15.50	15.64	13.31	1.57	−1.64
25.00	16.62[a]	16.01	15.68	12.50	−0.64	−4.38, −3.3[b]
35.00	17.28[a]	16.29	15.31	11.56	−2.61	−7.13
45.00	17.59[a]	16.36	14.80	10.48	−4.69	−9.90
$(\delta V)_{max}/(cm^3\ mol^{-1})$		±0.03	±0.05	±0.10	±0.23	±0.25
KCl						
15.00	25.19[a]	25.91	25.97	22.79	11.37	7.59
25.00	26.81[a]	26.82	26.10	21.74	8.94	5.22, 7.3[b]
35.00	27.32[a]	26.89	25.51	20.58	6.82	2.88
45.00	27.51[a]	26.51	24.72	18.83	4.57	0.51
$(\delta V)_{max}/(cm^3\ mol^{-1})$		±0.02	±0.04	±0.11	±0.27	±0.30

[a] Reference 5. [b] Reference 6.

Table 6. Apparent Molar Volume Concentration Dependence Constants A_v in x Methanol + $(1 - x)$ Water

	$A_v/(cm^3\ kg^{1/2}\ mol^{-3/2})$					
$t/°C$	x = 0.000	x = 0.129	x = 0.307	x = 0.571	x = 0.917	x = 1.000
LiCl						
15.00	1.7150[a]	1.3	1.5	3.1	7.5	9.0
25.00	1.8743[a]	1.5	1.6	3.9	8.8	9.7
35.00	2.0547[a]	1.6	1.8	4.5	10.1	11.7
45.00	2.2601[a]	1.7	2.1	5.1	11.5	13.6
NaCl						
15.00	1.7150[a]	2.4	3.4	6.6	12.3	14.9
25.00	1.8743[a]	2.0	4.6	7.3	14.7	16.0
35.00	2.0547[a]	2.6	4.7	8.6	15.2	18.6
45.00	2.2601[a]	3.0	6.6	8.8	17.5	19.0
KCl						
15.00	1.7150[a]	2.2	4.2	7.2	13.3	13.3
25.00	1.8743[a]	3.0	4.0	8.5	14.1	15.8
35.00	2.0547[a]	3.1	5.1	7.1	12.9	16.8
45.00	2.2601[a]	3.5	5.4	10.2	14.8	20.8
$(\delta A)_{max}/(cm^3\ kg^{1/2}\ mol^{-3/2})$		±0.8	±1.2	±2.5	±4.8	±5.0

[a] Reference 7.

Table 7. Apparent Molar 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
LiCl						
15.00	−0.27[a]	0.1	−0.2	0.0	−2.2	−3.1
25.00	−0.36[a]	−0.1	0.0	−1.3	−2.9	−2.8
35.00	−0.39[a]	−0.3	0.4	−0.7	−2.9	−3.5
45.00	−0.40[a]	−0.2	0.1	−0.8	−3.4	−4.2
NaCl						
15.00	0.369[a]	−0.1	−1.1	−2.4	−6.4	−7.2
25.00	0.048[a]	−0.4	−1.3	−3.5	−7.7	−8.6
35.00	−0.127[a]	−0.7	−1.8	−4.0	−7.1	−8.6
45.00	−0.250[a]	−0.9	−2.2	−4.8	−8.6	−9.5
KCl						
15.00	0.453[a]	0.3	−0.8	−2.8	−6.4	−7.3
25.00	0.173[a]	−0.3	−1.2	−3.3	−7.3	−8.3
35.00	−0.029[a]	−0.6	−1.5	−1.2	−1.0	−9.2
45.00	−0.007[a]	−1.0	−1.9	−4.7	−2.6	−10.4
$(\delta b)_{max}/(cm^3\ kg\ mol^{-2})$		±0.3	±0.7	±1.5	±2.7	±3.0

[a] Reference 5.

atures are given in Tables 2–4, respectively, where x is the mole fraction of methanol in the mixed solvent and m is the molality of the electrolyte. The apparent molar volumes of the electrolyte $V_{B\varphi}$ were evaluated as follows:

$$V_{B\varphi} = 1000(\rho_0 - \rho)/m\rho\rho_0 + M_B/\rho \qquad (1)$$

where ρ_0 is the density of the solvent and M_B is the molecular weight of the electrolyte.

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

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

At infinite dilution, the apparent molar volume $V_{B\varphi}^\infty$ is equal to the partial molar volume V_B^∞. The value of the partial molar volume at infinite dilution V_B^∞ and the coefficients in eq 2, A_v and b_v, obtained are given in Tables 5–7, respectively. In these tables, δV, δA, and δb are the maximum errors for $V_{B\varphi}^\infty$, A_v, and b_v, respectively. Each value of the

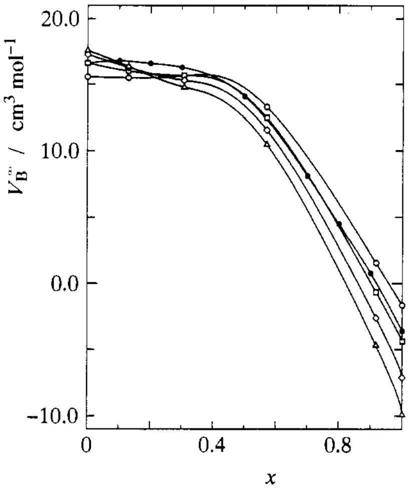

Figure 2. Partial molar volumes of sodium chloride at infinite dilution in x methanol + $(1 - x)$ water at various temperatures: ○, 15 °C; □, 25 °C; ◇, 35 °C; △, 45 °C; ●, 25 °C, ref 8.

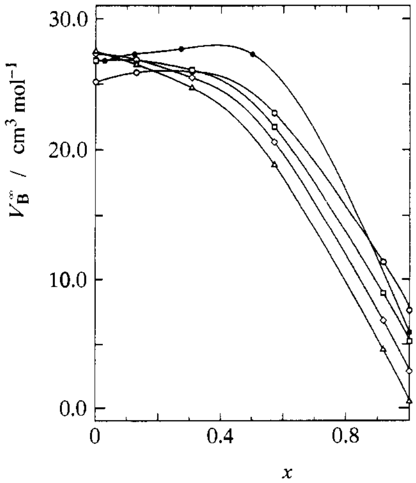

Figure 3. Partial molar volumes of potassium chloride at infinite dilution in x methanol + $(1 - x)$ water at various temperatures: ○, 15 °C; □, 25 °C; ◇, 35 °C; △, 45 °C; ●, 25 °C, ref 8.

Table 8. Partial Molar Thermal Expansivities of the Electrolytes in x Methanol + $(1 - x)$ Water

	$(\partial V^{\infty}_{B\varphi}/\partial T)/(\mathrm{cm^3\ mol^{-1}\ K^{-1}})$					
t/°C	x = 0.000	x = 0.129	x = 0.307	x = 0.571	x = 0.917	x = 1.000
			LiCl			
15.00	0.034	−0.036	−0.054	−0.155	−0.276	−0.286
25.00	0.017	−0.050	−0.067	−0.145	−0.260	−0.292
35.00	−0.001	−0.063	−0.080	−0.136	−0.245	−0.299
45.00	−0.018	−0.076	−0.093	−0.126	−0.230	−0.305
			NaCl			
15.00	0.122	0.062	0.012	−0.074	−0.217	−0.273
25.00	0.085	0.040	−0.015	−0.088	−0.211	−0.275
35.00	0.049	0.017	−0.043	−0.101	−0.204	−0.276
45.00	0.012	−0.005	−0.070	−0.115	−0.197	−0.277
			KCl			
15.00	0.182	0.115	0.025	−0.078	−0.239	−0.236
25.00	0.110	0.051	−0.021	−0.113	−0.230	−0.236
35.00	0.039	−0.014	−0.067	−0.148	−0.221	−0.236
45.00	−0.033	−0.078	−0.112	−0.183	−0.212	−0.236
$(\delta\partial V/\partial T)_{\max}$/ $(\mathrm{cm^3\ mol^{-1}\ K^{-1}})$		±0.05	±0.07	±0.10	±0.15	±0.18

error is correlated to two factors: (i) ±1 count in the reading of the densimeter; (ii) ±0.1 mg in the mass of the electrolyte. Both give us a maximum value when measuring the lowest concentration of each electrolyte solution. Each maximumerror listed in the tables is the root of the sum of the squares of the two errors. In Tables 6 and 7, the errors were nearly constant for changes of the electrolyte or for variation of the temperatures. In Figures 1–3, V^{∞}_{B} was plotted against x at various temperatures. In the figures the evaluated V^{∞}_{B} is compared with the V^{∞}_{B} taken from the literature (*8*). For sodium chloride solutions of the mixtures and lithium chloride or potassium chloride solutions of pure methanol, the evaluated V^{∞}_{B} was equal to V^{∞}_{B} from the literature in experimental error. In spite of the careful measurements, the differences between V^{∞}_{B} evaluated and V^{∞}_{B} from the literature in the mixture were observed. The value of partial molar volumes V_B for each electrolyte in Tables 2–4 were calculated using eq 3.

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

In Debye–Hückel theory, A_v depends on the pressure dependency of permittivity and depends on the isothermal compressibility of the solvent, and it should be identical for all electrolytes. In Table 6, A_v in pure water was taken from the literature (*7*). At each temperature, A_v for sodium chloride is identical to A_v for potassium chloride in experimental error. In the case of lithium chloride, the evaluated A_v is smaller than that for sodium chloride or potassium chloride. It seems to be reasonable that this tendency comes from an imperfect dissociation caused by the strong interaction between lithium ions and chloride ions in the solution.

The partial molar expansion of the electrolytes, $\partial V^{\infty}_{B}/\partial T$, is given in Table 8. In Tables 5 and 8, both V^{∞}_{B} and the thermal expansion decrease with rising temperature or increasing methanol concentration. These tendencies suggest that the bulky liquid structure of the solvents is weakened by addition of methanol or by elevation of the temperature. The electrostriction around ions, although the electrostrictive force is nearly constant, relatively increases with addition of methanol to the solvents or with rising temperature.

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