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Partial Molar Volumes for 1,4-Dioxane + Water

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The densities of 1,4-dioxane + water were measured over the whole composition range at 5, 15, 25, 35, and 45 °C. The apparent and partial molar volumes and partial molar thermal expansions were evaluated for both components. Characteristic extrema were observed in the plots of partial molar quantities against composition for dioxane in the aqueous-rich region and for water in the dioxane-rich region.

Introduction

Dioxane + water is a convenient solvent for the study of electrolyte solutions because of the wide range of dielectric constants covered. Although there are several volumetric studies of this solvent system at 25 °C (*1–8*), little reliable data are available at other temperatures. Furthermore, most of the detailed studies of the partial molar volume for this system have dealt exclusively with dilute aqueous solutions, and little attention has been given to the mixtures in which the mole fraction of water is small.

It is necessary, for a better understanding of nonelectrolyte–water interactions, to investigate the solution properties with sufficient precision and over a sufficiently wide range of compositions at various temperatures. From this point of view we have previously reported the partial molar volumes and thermal expansions for aqueous mixtures of alcohols (*9–11*), ethylene glycol (*12*), and acetonitrile (*13*). The present paper describes the precise density data for the mixtures of water (W) with 1,4-dioxane (D) over the whole composition range at 5, 15, 25, 35, and 45 °C.

Experimental Section

Densities of the solutions were measured relative to densities of the pure 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 ±2 × 10^{-6} g cm^{-3}. Details of the apparatus and procedure have been described earlier (*9, 14*). The temperature of the cells was maintained within ±0.002 °C by using a quartz temperature controller constructed in our laboratory. The densimeter was calibrated at each temperature with water (*15*) and dry air.

1,4-Dioxane was fractionally distilled and stored over molecular sieves (3A). The water content, determined by the Karl-Fischer method, was less than 0.006 wt %. The densities of pure dioxane at five temperatures are listed in Table I along with values from the literature (*16–19*) for comparison. Water was distilled using a quartz still and 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 weighed quantity of a stock solution or a pure component to a known quantity of another component. The measurements over the full mole fraction range were completed by two runs, i.e., one for the aqueous-rich regions starting from pure water and the other for the organic-rich regions starting from pure 1,4-dioxane up to the composition of about 50 wt %.

Results and Discussion

The density differences between solutions and pure solvent at various temperatures are given in Table II for water-rich solutions and in Table III for the dioxane-rich solutions. For a binary solution of components 1 and 2, the apparent molar volume V_{ϕ_2} of component 2 is given by

$$V_{\phi_2} = x_1M_1(\rho_1 - \rho)/x_2\rho_1\rho + M_2/\rho \qquad (1)$$

where x and M are the mole fraction and the molar mass of the components and ρ_1 and ρ are the densities of component 1 and the solution. The apparent molar volumes of dioxane V_{ϕ_D} and of water V_{ϕ_W} in their mixtures are also given in Tables II and III.

Table I. Densities of Pure 1,4-Dioxane

	ρ/(g cm^{-3})	
t/°C	this work	lit.
5	1.050 34[a]	
15	1.039 11	1.039 22,[b] 1.038 24[c]
25	1.027 83	1.028 02,[b] 1.026 93,[c] 1.027 92,[d] 1.027 70[e]
35	1.016 50	1.016 35,[c] 1.016 59,[d] 1.017 04[e]
45	1.005 14	1.005 26,[d] 1.005 31[e]

[a] Supercooling. [b] Reference 16. [c] Reference 17. [d] Reference 18. [e] Reference 19.

For sufficiently dilute solutions the variation of V_{ϕ_2} with molality m can be adequately represented by the following linear equation:

$$V_{\phi_2} = V_{\phi_2}^{\infty} + A_2m \qquad (2)$$

where the infinite dilution value $V_{\phi_2}^{\infty}$ is equal to the limiting partial molar volume V_2^{∞}. The linear relation was found to hold up to about 0.4 and 0.6 mol kg^{-1} for V_{ϕ_D} in water and V_{ϕ_W} in dioxane, respectively, at all temperatures studied.

The parameters of eq 2, determined by the method of weighted least squares, are summarized in Table IV. The values of V_D^{∞} are in good agreement with those from the literature: 78.9 cm^3 mol^{-1} (*4*) at 5 °C and 81.1 (*4*), 80.96 (*5*), 80.94 (*6*), 80.9 (*7*), and 80.99 cm^3 mol^{-1} (*8*) at 25 °C. As far as we know, no precise V_W^{∞} data are available with which the results presented here can be directly compared.

In Table IV are also listed the values of the excess limiting partial molar volume V_2^E, calculated by

$$V_2^E = V_2^{\infty} - V_2^* \qquad (3)$$

where V_2^* is the molar volume of pure component 2. Both values of V_D^E and V_W^E are negative. The negative excess volume seems characteristic of polar nonelectrolyte + water mixtures in general rather than a peculiarity of dioxane solutions. An important feature of the 1,4-dioxane + water system is that the V_W^{∞} value is smaller by only 0.5–0.6 cm^3 mol^{-1} than the V_W^* value and both V_D^E and V_W^E show a minor variation with temperature. These facts are in clear

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Table II. Densities and Apparent Molar Volumes for 1,4-Dioxane (D) + Water (W) in the Aqueous-Rich Regions at 5, 15, 25, 35, and 45 °C

x_D	$10^3(\rho - \rho_W)^a/(\text{g cm}^{-3})$	$V_{\phi_D}/(\text{cm}^3\ \text{mol}^{-1})$	$V_{\phi_W}/(\text{cm}^3\ \text{mol}^{-1})$	x_D	$10^3(\rho - \rho_W)^a/(\text{g cm}^{-3})$	$V_{\phi_D}/(\text{cm}^3\ \text{mol}^{-1})$	$V_{\phi_W}/(\text{cm}^3\ \text{mol}^{-1})$
5 °C							
0.000 568	0.287	78.981	18.013	0.019 80	9.750	78.645	17.910
0.001 089	0.550	78.980	18.010	0.025 09	12.199	78.609	17.880
0.001 528	0.772	78.962	18.008	0.029 65	14.241	78.593	17.854
0.001 938	0.978	78.956	18.006	0.034 61	16.374	78.593	17.826
0.002 428	1.226	78.936	18.004	0.039 31	18.314	78.605	17.800
0.002 952	1.489	78.932	18.001	0.045 05	20.588	78.628	17.768
0.003 573	1.803	78.907	17.998	0.051 54	23.015	78.668	17.732
0.004 051	2.043	78.899	17.995	0.059 83	25.905	78.735	17.688
0.004 598	2.318	78.886	17.993	0.068 62	28.732	78.819	17.643
0.005 100	2.570	78.874	17.990	0.077 29	31.280	78.913	17.599
0.005 628	2.834	78.865	17.987	0.087 29	33.950	79.031	17.552
0.006 308	3.175	78.848	17.984	0.097 99	36.513	79.163	17.503
0.006 847	3.444	78.838	17.981	0.109 89	39.038	79.316	17.452
0.007 496	3.766	78.829	17.977	0.122 34	41.354	79.478	17.402
0.008 309	4.169	78.816	17.973	0.134 93	43.394	79.641	17.354
0.010 18	5.104	78.770	17.963	0.149 25	45.388	79.825	17.304
0.012 93	6.456	78.724	17.948	0.164 58	47.189	80.017	17.254
0.015 72	7.806	78.690	17.933				
15 °C							
0.000 464	0.211	79.960	18.029	0.017 45	7.617	79.839	17.943
0.001 024	0.461	80.033	18.026	0.021 10	9.123	79.820	17.924
0.001 489	0.670	80.022	18.024	0.024 67	10.559	79.809	17.905
0.001 985	0.892	80.022	18.022	0.028 57	12.084	79.806	17.885
0.002 501	1.121	80.025	18.019	0.032 95	13.743	79.809	17.861
0.003 069	1.376	80.008	18.017	0.037 85	15.526	79.822	17.836
0.003 612	1.618	80.001	18.014	0.043 95	17.652	79.845	17.804
0.004 128	1.848	79.991	18.011	0.050 26	19.729	79.880	17.771
0.004 641	2.076	79.984	18.009	0.058 45	22.249	79.937	17.730
0.005 236	2.340	79.975	18.006	0.066 71	24.594	80.006	17.689
0.005 822	2.601	79.961	18.003	0.075 47	26.878	80.089	17.647
0.006 484	2.892	79.956	18.000	0.087 05	29.598	80.207	17.594
0.007 162	3.190	79.949	17.996	0.098 95	32.065	80.337	17.542
0.007 863	3.498	79.940	17.993	0.111 44	34.334	80.470	17.491
0.009 29	4.125	79.918	17.986	0.128 20	36.922	80.673	17.426
0.011 44	5.059	79.891	17.975	0.139 00	38.343	80.798	17.387
0.013 97	6.147	79.866	17.961	0.153 85	40.028	80.968	17.336
25 °C							
0.000 442	0.177	81.097	18.066	0.016 71	6.521	80.886	17.986
0.000 881	0.354	81.061	18.064	0.020 43	7.890	80.873	17.967
0.001 321	0.532	81.038	18.062	0.024 60	9.375	80.870	17.946
0.001 770	0.712	81.031	18.060	0.029 40	11.029	80.875	17.922
0.002 209	0.890	81.008	18.058	0.036 32	13.300	80.894	17.886
0.002 704	1.089	80.999	18.056	0.043 69	15.568	80.928	17.849
0.003 225	1.297	80.996	18.053	0.052 33	18.038	80.983	17.807
0.003 722	1.496	80.988	18.051	0.061 89	20.540	81.056	17.761
0.004 226	1.698	80.979	18.048	0.072 74	23.102	81.150	17.710
0.004 755	1.909	80.971	18.046	0.084 21	25.512	81.260	17.658
0.005 419	2.172	80.967	18.042	0.096 02	27.699	81.380	17.607
0.006 120	2.450	80.958	18.039	0.109 62	29.888	81.524	17.552
0.006 880	2.750	80.950	18.035	0.122 83	31.709	81.666	17.501
0.007 601	3.032	80.947	18.032	0.137 15	33.387	81.821	17.449
0.008 88	3.532	80.936	18.026	0.150 76	34.722	81.968	17.402
0.010 97	4.344	80.915	18.015	0.165 47	35.925	82.125	17.355
0.013 58	5.346	80.898	18.002				
35 °C							
0.000 477	0.175	81.935	18.121	0.016 19	5.685	81.867	18.044
0.000 925	0.337	81.973	18.119	0.020 34	7.048	81.867	18.023
0.001 339	0.489	81.946	18.117	0.026 00	8.830	81.876	17.995
0.001 781	0.649	81.948	18.115	0.031 83	10.580	81.896	17.966
0.002 227	0.811	81.945	18.113	0.040 58	13.041	81.939	17.923
0.002 739	0.996	81.940	18.110	0.049 25	15.282	81.995	17.881
0.003 195	1.162	81.930	18.108	0.058 90	17.562	82.069	17.835
0.003 772	1.370	81.926	18.105	0.069 46	19.809	82.159	17.786
0.004 429	1.607	81.917	18.102	0.081 07	22.003	82.267	17.734
0.005 169	1.872	81.912	18.098	0.093 42	24.044	82.388	17.681
0.005 881	2.127	81.904	18.095	0.107 19	26.001	82.528	17.625
0.006 782	2.445	81.905	18.091	0.121 02	27.664	82.671	17.572
0.007 83	2.818	81.896	18.085	0.134 76	29.050	82.814	17.522
0.010 83	3.864	81.882	18.071	0.149 53	30.283	82.967	17.471
0.012 88	4.569	81.872	18.061	0.164 47	31.290	83.120	17.423
45 °C							
0.000 268	0.089	82.878	18.192	0.000 978	0.322	82.905	18.188
0.000 548	0.181	82.897	18.190	0.001 393	0.459	82.893	18.186

Table II. (Continued)

x_{D}	$10^3(\rho - \rho_{\mathrm{W}})^a/(\mathrm{g\ cm^{-3}})$	$V_{\phi_{\mathrm{D}}}/(\mathrm{cm^3\ mol^{-1}})$	$V_{\phi_{\mathrm{W}}}/(\mathrm{cm^3\ mol^{-1}})$	x_{D}	$10^3(\rho - \rho_{\mathrm{W}})^a/(\mathrm{g\ cm^{-3}})$	$V_{\phi_{\mathrm{D}}}/(\mathrm{cm^3\ mol^{-1}})$	$V_{\phi_{\mathrm{W}}}/(\mathrm{cm^3\ mol^{-1}})$
45 °C							
0.001 747	0.576	82.880	18.185	0.018 10	5.694	82.827	18.104
0.002 123	0.700	82.873	18.183	0.022 89	7.070	82.841	18.080
0.002 636	0.869	82.864	18.180	0.029 04	8.757	82.865	18.050
0.003 042	1.001	82.866	18.178	0.036 50	10.673	82.907	18.013
0.003 550	1.167	82.861	18.176	0.043 03	12.240	82.950	17.981
0.004 025	1.320	82.865	18.174	0.051 88	14.205	83.016	17.939
0.004 528	1.484	82.858	18.171	0.060 87	16.020	83.091	17.897
0.005 164	1.690	82.853	18.168	0.071 42	17.933	83.187	17.849
0.005 867	1.919	82.842	18.165	0.083 17	19.808	83.299	17.798
0.006 824	2.226	82.838	18.160	0.096 06	21.587	83.426	17.744
0.007 760	2.526	82.831	18.155	0.108 87	23.092	83.556	17.692
0.008 88	2.879	82.831	18.150	0.122 11	24.403	83.691	17.642
0.010 84	3.494	82.826	18.140	0.135 01	25.466	83.823	17.595
0.013 92	4.444	82.822	18.125	0.148 32	26.371	83.959	17.549

[a] Densities of pure water are 0.999 964, 0.999 100, 0.997 045, 0.994 032, and 0.990 213 g cm^{-3} at 5, 15, 25, 35, and 45 °C, respectively (*15*).

Table III. Densities and Apparent Molar Volumes for 1,4-Dioxane (D) + Water (W) in the Dioxane-Rich Regions at 5, 15, 25, 35, and 45 °C

x_{W}	$10^3(\rho - \rho_{\mathrm{D}})/(\mathrm{g\ cm^{-3}})$	$V_{\phi_{\mathrm{W}}}/(\mathrm{cm^3\ mol^{-1}})$	$V_{\phi_{\mathrm{D}}}/(\mathrm{cm^3\ mol^{-1}})$	x_{W}	$10^3(\rho - \rho_{\mathrm{D}})/(\mathrm{g\ cm^{-3}})$	$V_{\phi_{\mathrm{W}}}/(\mathrm{cm^3\ mol^{-1}})$	$V_{\phi_{\mathrm{D}}}/(\mathrm{cm^3\ mol^{-1}})$
5 °C							
0.006 444	−0.022	17.423	83.879	0.331 12	2.272	16.749	83.256
0.013 074	−0.036	17.369	83.874	0.363 43	2.578	16.750	83.160
0.019 341	−0.039	17.310	83.869	0.411 20	3.019	16.758	83.005
0.025 438	−0.038	17.268	83.863	0.443 70	3.307	16.768	82.888
0.029 549	−0.037	17.249	83.860	0.483 31	3.633	16.783	82.730
0.034 760	−0.032	17.223	83.854	0.529 65	3.962	16.807	82.522
0.040 353	−0.020	17.190	83.848	0.573 46	4.190	16.835	82.296
0.047 437	−0.003	17.156	83.840	0.615 41	4.282	16.869	82.048
0.054 681	0.021	17.122	83.831	0.658 34	4.161	16.912	81.756
0.062 467	0.050	17.091	83.821	0.695 36	3.790	16.958	81.468
0.069 315	0.080	17.064	83.812	0.727 69	3.154	17.006	81.186
0.079 055	0.127	17.031	83.799	0.759 13	2.131	17.063	80.880
0.090 877	0.193	16.994	83.781	0.789 87	0.583	17.130	80.553
0.098 620	0.240	16.972	83.769	0.814 46	−1.188	17.193	80.270
0.126 93	0.434	16.906	83.722	0.837 97	−3.459	17.262	79.984
0.166 44	0.750	16.840	83.648	0.858 70	−6.052	17.331	79.722
0.211 68	1.149	16.791	83.554	0.877 13	−8.928	17.399	79.483
0.251 42	1.516	16.767	83.464	0.893 31	−11.984	17.465	79.273
0.287 82	1.860	16.754	83.373				
15 °C							
0.009 624	−0.010	17.421	84.784	0.318 84	2.941	16.777	84.203
0.014 899	−0.006	17.369	84.780	0.370 64	3.619	16.777	84.052
0.019 919	0.000	17.337	84.776	0.409 00	4.124	16.784	83.927
0.026 728	0.012	17.301	84.770	0.446 34	4.608	16.796	83.794
0.031 410	0.025	17.274	84.766	0.495 75	5.227	16.819	83.598
0.037 051	0.042	17.247	84.760	0.539 20	5.733	16.844	83.401
0.041 985	0.060	17.224	84.755	0.577 25	6.117	16.872	83.207
0.047 991	0.084	17.200	84.748	0.612 60	6.393	16.903	83.006
0.054 149	0.117	17.168	84.741	0.652 68	6.559	16.945	82.749
0.062 228	0.160	17.138	84.731	0.688 08	6.501	16.990	82.494
0.070 474	0.210	17.108	84.720	0.721 32	6.186	17.041	82.226
0.078 727	0.267	17.078	84.709	0.754 51	5.496	17.101	81.930
0.086 530	0.323	17.053	84.697	0.786 26	4.328	17.169	81.620
0.097 625	0.411	17.020	84.681	0.810 89	2.954	17.232	81.362
0.135 57	0.755	16.932	84.618	0.834 99	1.084	17.301	81.097
0.169 94	1.117	16.874	84.553	0.855 63	−1.035	17.369	80.863
0.204 95	1.516	16.833	84.481	0.873 79	−3.384	17.434	80.653
0.245 09	2.002	16.801	84.391	0.889 89	−5.916	17.496	80.467
0.282 91	2.477	16.785	84.298				
25 °C							
0.006 115	0.002	17.499	85.717	0.090 246	0.491	17.106	85.625
0.012 717	0.012	17.449	85.712	0.132 63	0.938	17.000	85.557
0.019 978	0.031	17.400	85.707	0.170 56	1.410	16.932	85.487
0.025 564	0.050	17.367	85.702	0.217 02	2.057	16.874	85.389
0.032 518	0.079	17.330	85.695	0.267 03	2.809	16.838	85.272
0.037 169	0.099	17.312	85.691	0.308 70	3.472	16.822	85.164
0.043 070	0.132	17.280	85.685	0.345 28	4.069	16.817	85.060
0.047 628	0.158	17.261	85.680	0.385 19	4.736	16.819	84.938
0.053 047	0.193	17.237	85.674	0.424 40	5.398	16.828	84.806
0.059 556	0.237	17.211	85.666	0.461 86	6.033	16.842	84.668
0.066 023	0.284	17.187	85.658	0.508 96	6.821	16.866	84.475
0.073 947	0.346	17.160	85.648	0.548 52	7.455	16.893	84.292
0.080 501	0.401	17.139	85.639	0.587 62	8.028	16.925	84.091

Table III. (Continued)

x_W	$10^3(\rho - \rho_D)/(g\ cm^{-3})$	$V_{\phi W}/(cm^3\ mol^{-1})$	$V_{\phi D}/(cm^3\ mol^{-1})$	x_W	$10^3(\rho - \rho_D)/(g\ cm^{-3})$	$V_{\phi W}/(cm^3\ mol^{-1})$	$V_{\phi D}/(cm^3\ mol^{-1})$
25 °C							
0.628 04	8.526	16.965	83.858	0.792 39	7.422	17.241	82.561
0.666 86	8.854	17.012	83.605	0.823 56	5.844	17.324	82.247
0.698 80	8.950	17.057	83.374	0.848 51	3.954	17.401	81.984
0.731 05	8.803	17.111	83.117	0.869 06	1.856	17.472	81.764
0.762 67	8.317	17.172	82.841	0.886 43	−0.379	17.538	81.578
35 °C							
0.006 520	0.013	17.553	86.672	0.313 33	4.190	16.870	86.104
0.012 342	0.030	17.517	86.668	0.348 64	4.877	16.865	86.002
0.019 136	0.056	17.477	86.663	0.382 13	5.541	16.867	85.898
0.025 417	0.085	17.443	86.658	0.411 51	6.144	16.871	85.800
0.031 898	0.118	17.415	86.652	0.452 98	7.007	16.885	85.650
0.037 277	0.153	17.383	86.647	0.490 93	7.800	16.903	85.499
0.043 578	0.192	17.360	86.641	0.533 05	8.673	16.930	85.314
0.048 168	0.224	17.341	86.636	0.571 41	9.442	16.961	85.126
0.051 903	0.253	17.324	86.632	0.608 72	10.139	16.997	84.924
0.058 445	0.304	17.300	86.624	0.646 53	10.756	17.041	84.696
0.064 642	0.357	17.276	86.617	0.683 82	11.212	17.092	84.445
0.071 798	0.424	17.248	86.608	0.723 19	11.435	17.156	84.149
0.082 436	0.531	17.210	86.593	0.758 41	11.272	17.225	83.857
0.091 789	0.632	17.179	86.580	0.787 93	10.750	17.293	83.591
0.131 65	1.125	17.071	86.516	0.811 71	9.974	17.355	83.364
0.178 94	1.817	16.981	86.427	0.839 28	9.550	17.436	83.088
0.226 84	2.609	16.921	86.323	0.860 78	6.939	17.507	82.868
0.269 41	3.368	16.888	86.220	0.879 84	5.054	17.576	82.671
45 °C							
0.008 593	0.030	17.621	87.651	0.375 51	6.181	16.922	86.892
0.016 649	0.067	17.577	87.645	0.406 40	6.910	16.926	86.788
0.025 406	0.114	17.540	87.639	0.435 39	7.607	16.934	86.685
0.032 843	0.163	17.502	87.632	0.466 10	8.357	16.947	86.568
0.043 258	0.242	17.452	87.622	0.503 67	9.286	16.968	86.413
0.051 421	0.312	17.416	87.613	0.536 48	10.094	16.992	86.265
0.058 855	0.381	17.385	87.605	0.573 54	10.998	17.024	86.083
0.068 668	0.477	17.350	87.594	0.612 96	11.915	17.065	85.868
0.077 166	0.571	17.318	87.582	0.650 53	12.711	17.111	85.641
0.086 120	0.673	17.289	87.570	0.689 80	13.400	17.169	85.377
0.095 487	0.791	17.256	87.557	0.723 27	13.796	17.226	85.128
0.142 43	1.463	17.130	87.479	0.753 43	13.921	17.286	84.885
0.186 50	2.209	17.045	87.392	0.780 24	13.772	17.347	84.652
0.222 00	2.873	16.996	87.314	0.802 11	13.407	17.402	84.451
0.258 56	3.603	16.961	87.226	0.822 17	12.825	17.458	84.258
0.289 22	4.246	16.941	87.146	0.841 30	11.993	17.517	84.070
0.317 90	4.871	16.929	87.067	0.857 14	11.061	17.569	83.910
0.346 49	5.514	16.923	86.982	0.871 59	10.000	17.619	83.760

Table IV. Limiting Partial Molar Volumes V_2^∞, Deviation Constants A_2, and Excess Limiting Partial Molar Volumes V_2^E for 1,4-Dioxane (D) + Water (W)

$t/°C$	$V_D^\infty/(cm^3\ mol^{-1})$	$A_D/(cm^3\ kg\ mol^{-2})$	$V_D^E/(cm^3\ mol^{-1})$	$V_W^\infty/(cm^3\ mol^{-1})$	$A_W/(cm^3\ kg\ mol^{-2})$	$V_W^E/(cm^3\ mol^{-1})$
5	78.98	−0.37	−4.90	17.41	−0.46	−0.60
15	80.05	−0.25	−4.74	17.43	−0.41	−0.60
25	81.03	−0.21	−4.69	17.49	−0.41	−0.57
35	81.95	−0.14	−4.72	17.56	−0.38	−0.56
45	82.89	−0.14	−4.76	17.65	−0.38	−0.54

contrast with the case for monohydric alcohol + water mixtures (*9–11*).

The partial molar volumes V_2 of component 2 were evaluated over the whole composition range by using the relation

$$V_2 = V_{\phi_2} + x_1 x_2 (\partial V_{\phi_2} / \partial x_2) \qquad (4)$$

The results calculated for V_D and for V_W are shown as a function of the mole fraction of dioxane x_D in Figures 1 and 2, respectively. The partial molar thermal expansions, $E_2 = \partial V_2/\partial T$, were also calculated for both components, and the results at 25 °C are illustrated in Figure 3.

At a very low mole fraction of dioxane the $V_D(x_D)$ curve has a small but significant minimum. This minimum is more pronounced and shifts to a higher mole fraction as the temperature is lowered, as is evident from the low-mole-fraction inset of Figure 1. The $E_D(x_D)$ curve passes through a maximum at a mole fraction similar to that of the V_D minimum. The existence of these extrema at a low mole fraction of the nonaqueous component is typical of the most aqueous solutions of monofunctional nonelectrolytes. However, the depth of the extrema for 1,4-dioxane is much smaller compared, for instance, with monohydric alcohol solutions (*9–11*). The present results are similar to those of the aqueous solutions of more hydrophilic solutes such as ethylene glycol (*12*) or acetonitrile (*13*). The concentration dependence of the partial molar volume in aqueous-rich solutions has generally been interpreted in terms of the structural change of water (*20*). At present, however, this theory cannot explain satisfactorily all volumetric properties of aqueous nonelectrolyte solutions, as has been described in some detail earlier (*9*).

Figure 2 shows that a marked minimum is observed in the $V_W(x_D)$ curve at a low mole fraction of water. The V_W

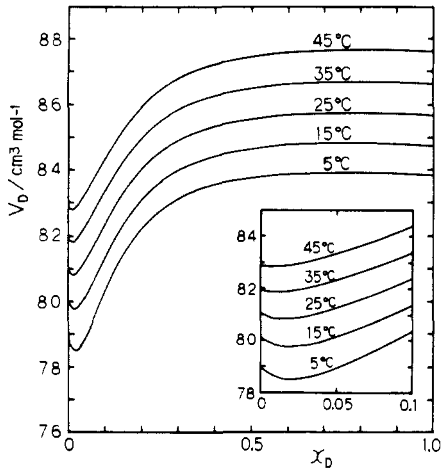

Figure 1. Partial molar volumes of 1,4-dioxane V_D in 1,4-dioxane + water.

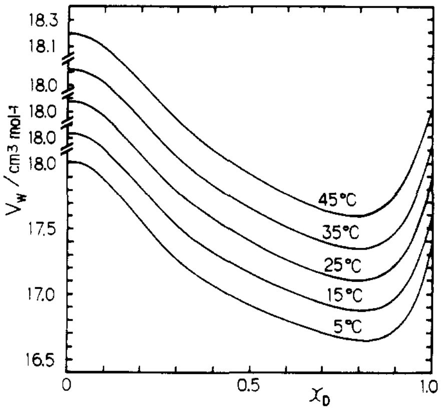

Figure 2. Partial molar volumes of water V_W in 1,4-dioxane + water.

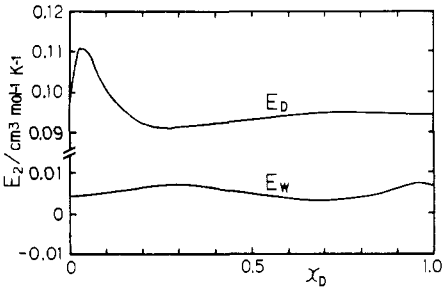

Figure 3. Partial molar thermal expansions of 1,4-dioxane E_D and water E_W in 1,4-dioxane + water at 25 °C.

minimum has already been reported by several researchers (*1–3*), although the concentration at the minimum is considerably different from the present results. We have reported such a V_W minimum in the organic-rich solution for the aqueous mixtures of *tert*-butyl alcohol (*9*), tetrahydrofuran (*21*), and acetonitrile (*13*), but not for the other alcohols or ethylene glycol solutions (*12*).

Although the variation of V_W or E_W with composition in the dioxane-rich regions seems to be moderate compared with the variation of V_D or E_D in the aqueous-rich regions, one should keep in mind that the molar mass of water is about 5 times smaller than that of dioxane. When the molar masses of the individual component differ considerably, it may be adequate to represent specific quantities as a function of volume or weight fraction instead of using the correlation between molar quantities and mole fraction. As shown in Figures 4 and 5, where the partial specific volumes and the partial specific thermal expansions are plotted against the weight fraction of 1,4-dioxane, the extent of the variation of partial specific quantities of water in dioxane is quite comparable to that of dioxane in water. The existence of these extrema may be interpreted in terms of the competitions between solute–solvent and solute–solute hydrogen bondings (*21*).

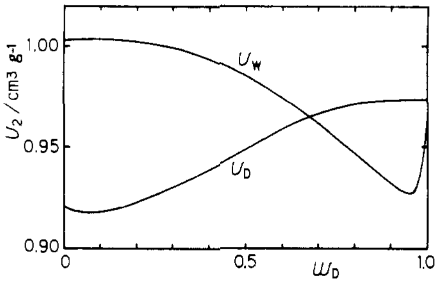

Figure 4. Partial specific volumes of 1,4-dioxane v_D and water v_W in 1,4-dioxane + water as a function of the weight fraction of dioxane at 25 °C.

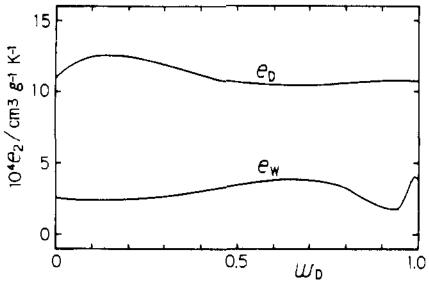

Figure 5. Partial specific thermal expansions of 1,4-dioxane e_D and water e_W in 1,4-dioxane + water as a function of the weight fraction of dioxane at 25 °C.

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