higher temperatures and higher propane concentration. The dependence of k_{12} on temperature can be seen in Figure 3.

Registry No. Eicosane, 112-95-8; propane, 74-98-6.

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Partial Molar Volumes for Acetonitrile + Water

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The densities of acetonitrile + 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 expansibilities were evaluated for both components as a function of mole fraction. In the aqueous-rich region, the partial molar volume of acetonitrile increases abruptly with the mole fraction. Only a small minimum of the partial molar volume was observed at very dilute solutions at lower temperatures, although a marked maximum was recognized in the partial molar expansibility curve. The partial molar volume of water vs composition curve, on the other hand, passes through a pronounced minimum in the organic-rich region, that is, in contrast with most alcohols + water.

Introduction

The present work is part of a systematic study on the volumetric behavior of aqueous organic mixtures. There have been reliable partial molar volume data for many nonelectrolytes in dilute aqueous solutions at 25 °C. However, relatively little data are available at other temperatures, and little attention has been given to the aqueous mixtures in which the mole fraction of water is small.

It is well known that the partial molar quantities vs composition curves have a characteristic minimum or maximum in the water-rich region for a number of aqueous solutions, typically alcohols + water (*1*). Previously we have reported that a pronounced minimum is also observed for the partial molar volume of water in organic regions for tetrahydrofuran (*2*) or *tert*-butyl alcohol (*3*) solutions, but not for the other alcohol solutions (*2*, *4–7*). A similar minimum has been reported for acetonitrile solutions at 25 °C by Armitage et al. (*8*) and de Visser et al. (*9*). This paper describes the more precise density data for water (W) + acetonitrile (A) at various temperatures.

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). Details of the apparatus and procedure have been described elsewhere (*3*, *10*). 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 (*11*) and dry air.

The acetonitrile was fractionally distilled and stored over molecular sieves 3A. The water content, determined by the Karl-Fischer method, was less then 0.002 wt %. The water was distilled using a quartz still and degassed before using. All solutions were prepared by successive addition of a stock solution or a pure component to a known quantity of another component up to about 50 wt %. The addition was carried out by weight in a mixing chamber connected to the density measuring cell with a Teflon tube and a flow pump.

Results and Discussion

The density differences between solution and pure water ($\rho - \rho_W$) are summarized in Table I.

For the 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.

For dilute solutions the variation of V_{ϕ_2} with molality m can be fitted with a linear equation:

$$V_{\phi_2} = V_2^{\infty} + A_2m \qquad (2)$$

where V_2^{∞} is the limiting partial molar volume. The linear relation was found to hold up to about 0.5 and 1.2 mol kg^{-1} for V_{ϕ_A} in water and V_{ϕ_W} in acetonitrile, respectively, at all temperatures studied. The parameters of eq 2, determined by the method of weighted least squares, are summarized in Table II. In general the limiting partial molar volumes are in good agreement with those from the literature. In the table are also reported 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 the pure solute. Both values of V_A^E and V_W^E are negative as well as those for aqueous solutions of polar nonelectrolytes. The characteristic feature of acetonitrile + water is that the deviation constants A_A and

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Table I. Densities and Partial Molar Volumes for Acetonitrile (A) + Water (W) at 5, 15, 25, 35, and 45 °C

x_A	$10^3(\rho - \rho_w)$/(g cm^{-3})	V_A/(cm^3 mol^{-1})	V_w/(cm^3 mol^{-1})	x_A	$10^3(\rho - \rho_w)$/(g cm^{-3})	V_A/(cm^3 mol^{-1})	V_w/(cm^3 mol^{-1})
			At 5 °C				
0	0[a]	45.52[b]	18.01	0.295 138	-90.443	50.87	17.40
0.000 454	-0.113	45.53	18.01	0.298 825	-91.446	50.86	17.40
0.000 885	-0.220	45.53	18.01	0.318 208	-96.569	50.92	17.38
0.001 360	-0.338	45.50	18.01	0.344 751	-103.260	50.97	17.35
0.001 750	-0.433	45.48	18.01	0.378 671	-111.332	51.03	17.32
0.002 191	-0.539	45.44	18.01	0.412 980	-118.970	51.08	17.29
0.002 629	-0.648	45.47	18.01	0.451 887	-127.067	51.13	17.25
0.003 085	-0.757	45.46	18.01	0.491 260	-134.716	51.19	17.20
0.003 511	-0.861	45.43	18.01	0.528 430	-141.485	51.23	17.15
0.004 028	-0.984	45.43	18.01	0.567 835	-148.243	51.28	17.09
0.004 557	-1.111	45.42	18.01	0.606 326	-154.475	51.33	17.02
0.005 209	-1.269	45.43	18.01	0.632 899	-158.588	51.36	16.97
0.005 729	-1.391	45.42	18.01	0.662 294	-162.972	51.39	16.92
0.006 382	-1.547	45.40	18.01	0.692 861	-167.344	51.41	16.86
0.006 955	-1.684	45.41	18.01	0.723 330	-171.537	51.44	16.81
0.007 542	-1.821	45.40	18.01	0.755 449	-175.775	51.45	16.76
0.008 177	-1.971	45.40	18.01	0.787 675	-179.852	51.47	16.72
0.008 925	-2.148	45.43	18.01	0.817 912	-183.512	51.47	16.69
0.010 296	-2.474	45.45	18.01	0.850 888	-187.329	51.47	16.68
0.012 138	-2.908	45.47	18.01	0.878 975	-190.431	51.47	16.69
0.015 220	-3.639	45.51	18.01	0.898 947	-192.563	51.47	16.72
0.018 725	-4.467	45.56	18.01	0.919 663	-194.684	51.46	16.78
0.023 281	-5.551	45.66	18.01	0.940 176	-196.709	51.45	16.88
0.034 117	-8.194	45.99	18.00	0.952 618	-197.876	51.45	16.94
0.047 968	-11.804	46.56	17.97	0.957 139	-198.299	51.45	16.94
0.063 701	-16.303	47.29	17.93	0.961 147	-198.669	51.45	16.95
0.079 762	-21.292	48.00	17.88	0.965 315	-199.049	51.45	16.99
0.097 230	-27.062	48.66	17.82	0.969 413	-199.420	51.45	17.02
0.121 927	-35.553	49.37	17.73	0.973 507	-199.785	51.45	17.05
0.143 602	-43.060	49.81	17.66	0.977 807	-200.164	51.45	17.09
0.169 698	-52.028	50.19	17.59	0.981 909	-200.521	51.45	17.12
0.194 276	-60.220	50.43	17.54	0.986 488	-200.915	51.45	17.15
0.222 442	-69.214	50.62	17.49	0.911 104	-201.306	51.44	17.19
0.248 083	-77.057	50.75	17.45	0.995 657	-201.687	51.44	17.27
0.271 062	-83.743	50.81	17.42	1.0	-202.041[c]	51.44	17.31[b]
0.274 455	-84.719	50.82	17.42				
			At 15 °C				
0	0[a]	46.45[b]	18.03	0.279 148	-92.780	51.46	17.49
0.000 325	-0.096	46.44	18.03	0.299 883	-98.675	51.52	17.46
0.000 725	-0.215	46.47	18.03	0.299 940	-98.645	51.54	17.45
0.001 107	-0.329	46.48	18.03	0.324 564	-105.316	51.61	17.42
0.001 549	-0.459	46.45	18.03	0.353 811	-112.808	51.67	17.39
0.001 970	-0.584	46.44	18.03	0.383 313	-119.949	51.73	17.35
0.002 440	-0.722	46.44	18.03	0.419 526	-128.188	51.79	17.31
0.002 879	-0.851	46.43	18.03	0.459 457	-136.669	51.86	17.26
0.003 442	-1.016	46.43	18.03	0.500 942	-144.869	51.92	17.21
0.003 958	-1.168	46.42	18.03	0.546 074	-153.188	51.98	17.14
0.004 505	-1.327	46.41	18.03	0.580 971	-159.222	52.02	17.09
0.005 019	-1.475	46.40	18.03	0.609 829	-163.980	52.05	17.04
0.005 548	-1.629	46.41	18.03	0.641 107	-168.913	52.08	16.98
0.006 142	-1.802	46.43	18.03	0.667 448	-172.909	52.11	16.93
0.006 771	-1.984	46.42	18.03	0.694 102	-176.819	52.13	16.89
0.007 394	-2.164	46.43	18.03	0.722 213	-180.770	52.15	16.84
0.008 042	-2.352	46.45	18.03	0.748 456	-184.332	52.16	16.81
0.008 686	-2.538	46.47	18.03	0.777 664	-188.140	52.17	16.78
0.010 125	-2.959	46.52	18.03	0.805 344	-191.606	52.18	16.75
0.012 086	-3.532	46.56	18.03	0.836 595	-195.357	52.18	16.74
0.014 718	-4.301	46.60	18.02	0.861 410	-198.213	52.18	16.75
0.017 490	-5.111	46.66	18.02	0.886 631	-200.993	52.17	16.79
0.022 575	-6.604	46.78	18.02	0.915 285	-204.003	52.16	16.91
0.029 714	-8.728	47.00	18.02	0.935 084	-205.981	52.15	17.02
0.040 032	-11.889	47.38	18.00	0.953 522	-207.718	52.14	17.11
0.049 733	-14.970	47.77	17.98	0.957 845	-208.121	52.15	17.08
0.060 757	-18.608	48.22	17.96	0.961 722	-208.480	52.15	17.10
0.078 641	-24.798	48.90	17.91	0.965 558	-208.830	52.14	17.13
0.099 062	-32.159	49.55	17.85	0.969 347	-209.173	52.14	17.17
0.121 018	-40.209	50.10	17.78	0.973 919	-209.581	52.14	17.20
0.413 488	-48.405	50.50	17.72	0.978 648	-209.998	52.14	17.24
0.168 514	-57.342	50.83	17.66	0.983 256	-210.398	52.14	17.27
0.193 371	-65.929	51.06	17.61	0.987 285	-210.745	52.14	17.30
0.217 797	-74.030	51.23	17.56	0.991 449	-211.098	52.14	17.35
0.240 327	-81.190	51.35	17.52	0.995 490	-211.436	52.14	17.43
0.271 019	-90.460	51.46	17.49	1.0	-211.803[c]	52.14	17.48[b]

Table I (Continued)

x_A	$10^3(\rho - \rho_w)$/ (g cm^{-3})	V_A/ (cm^3 mol^{-1})	V_w/ (cm^3 mol^{-1})	x_A	$10^3(\rho - \rho_w)$/ (g cm^{-3})	V_A/ (cm^3 mol^{-1})	V_w/ (cm^3 mol^{-1})
			At 25 °C				
0	0[a]	47.33[b]	18.06	0.277 757	−98.332	52.18	17.54
0.000 470	−0.161	47.38	18.06	0.294 267	−103.163	52.22	17.52
0.000 857	−0.293	47.32	18.06	0.302 513	−105.512	52.25	17.51
0.001 284	−0.436	47.29	18.06	0.317 190	−109.607	52.29	17.49
0.001 653	−0.561	47.30	18.06	0.325 764	−111.944	52.31	17.48
0.002 029	−0.688	47.33	18.06	0.343 382	−116.622	52.35	17.46
0.002 495	−0.845	47.33	18.06	0.371 407	−123.744	52.42	17.42
0.002 987	−1.011	47.32	18.06	0.401 766	−131.045	52.48	17.38
0.003 496	−1.182	47.32	18.06	0.434 665	−138.507	52.54	17.34
0.004 001	−1.351	47.31	18.06	0.466 069	−145.226	52.59	17.30
0.004 459	−1.504	47.31	18.06	0.501 782	−152.438	52.65	17.25
0.005 009	−1.688	47.31	18.06	0.542 374	−160.132	52.71	17.18
0.005 545	−1.865	47.32	18.06	0.589 419	−168.454	52.76	17.11
0.006 075	−2.042	47.34	18.06	0.622 122	−173.893	52.80	17.05
0.006 660	−2.240	47.36	18.06	0.647 901	−178.006	52.83	17.01
0.007 186	−2.414	47.36	18.06	0.672 716	−181.822	52.85	16.97
0.007 790	−2.615	47.35	18.06	0.699 836	−185.841	52.87	16.92
0.008 392	−2.816	47.40	18.06	0.726 012	−189.575	52.88	16.89
0.010 093	−3.389	47.45	18.06	0.754 046	−193.420	52.89	16.85
0.011 645	−3.908	47.49	18.06	0.783 240	−197.268	52.90	16.82
0.013 280	−4.458	47.52	18.06	0.811 877	−200.882	52.91	16.81
0.015 317	−5.146	47.57	18.06	0.842 676	−204.597	52.90	16.82
0.017 322	−5.815	47.60	18.06	0.870 351	−207.778	52.90	16.85
0.019 441	−6.530	47.66	18.06	0.898 363	−210.842	52.89	16.91
0.021 777	−7.319	47.74	18.06	0.921 232	−213.220	52.88	17.00
0.025 484	−8.583	47.87	18.05	0.940 710	−215.159	52.87	17.11
0.029 551	−9.981	48.01	18.05	0.952 920	−216.323	52.87	17.18
0.034 121	−11.563	48.18	18.05	0.957 238	−216.729	52.87	17.19
0.048 473	−16.672	48.71	18.02	0.961 368	−217.113	52.87	17.23
0.063 692	−22.280	49.26	17.99	0.966 038	−217.543	52.87	17.27
0.080 375	−28.610	49.83	17.95	0.969 877	−217.890	52.86	17.30
0.100 183	−36.263	50.38	17.89	0.974 152	−218.274	52.86	17.33
0.122 106	−44.746	50.86	17.83	0.978 543	−218.663	52.86	17.36
0.145 510	−53.659	51.24	17.78	0.982 485	−219.009	52.86	17.39
0.171 291	−63.182	51.54	17.72	0.987 339	−219.429	52.86	17.44
0.197 124	−72.352	51.77	17.67	0.911 799	−219.811	52.86	17.50
0.224 662	−81.680	51.95	17.62	0.995 787	−220.145	52.86	17.57
0.249 388	−89.647	52.07	17.58	0	−220.493[c]	52.86	17.58[b]
			At 35 °C				
0	0[a]	48.16[b]	18.12	0.363 737	−127.858	53.15	17.50
0.000 475	−0.180	48.25	18.12	0.394 798	−135.626	53.22	17.46
0.000 833	−0.316	48.20	18.12	0.430 302	−143.962	53.30	17.41
0.001 257	−0.474	48.15	18.12	0.466 414	−151.918	53.36	17.35
0.001 684	−0.633	48.13	18.12	0.500 821	−159.041	53.42	17.30
0.002 086	−0.786	48.18	18.12	0.538 533	−166.387	53.47	17.24
0.002 449	−0.920	48.17	18.12	0.573 206	−172.761	53.52	17.19
0.002 987	−1.121	48.14	18.12	0.603 106	−177.980	53.55	17.13
0.003 468	−1.300	48.16	18.12	0.635 907	−183.444	53.58	17.08
0.003 976	−1.489	48.17	18.12	0.658 723	−187.093	53.61	17.04
0.004 555	−1.705	48.17	18.12	0.683 529	−190.922	53.62	17.00
0.005 133	−1.919	48.18	18.12	0.709 572	−194.794	53.64	16.96
0.005 631	−2.104	48.19	18.12	0.737 578	−198.799	53.65	16.93
0.006 148	−2.297	48.21	18.12	0.764 552	−202.499	53.66	16.90
0.006 752	−2.521	48.23	18.12	0.791 990	−206.115	53.67	16.89
0.007 335	−2.738	48.24	18.12	0.818 451	−209.456	53.67	16.89
0.007 979	−2.979	48.27	18.12	0.846 077	−212.796	53.66	16.91
0.008 663	−3.232	48.34	18.12	0.871 756	−215.759	53.65	16.96
0.019 051	−7.168	48.67	18.11	0.899 027	−218.754	53.64	17.05
0.032 125	−12.173	49.10	18.10	0.921 525	−221.097	53.63	17.14
0.049 140	−18.852	49.68	18.08	0.940 579	−222.996	53.62	17.25
0.064 199	−24.899	50.19	18.05	0.951 926	−224.083	53.62	17.32
0.083 233	−32.653	50.76	18.00	0.956 685	−224.533	53.62	17.35
0.101 956	−40.311	51.23	17.96	0.960 685	−224.905	53.62	17.38
0.126 130	−50.083	51.69	17.90	0.964 607	−225.267	53.62	17.41
0.153 187	−60.721	52.07	17.83	0.968 654	−225.635	53.62	17.44
0.177 957	−70.079	52.33	17.78	0.973 002	−226.027	53.61	17.48
0.203 135	−79.188	52.53	17.74	0.977 666	−226.442	53.61	17.52
0.234 710	−90.012	52.71	17.68	0.981 674	−226.793	53.61	17.56
0.261 503	−98.673	52.82	17.64	0.986 428	−227.206	53.61	17.60
0.289 506	−107.249	52.92	17.61	0.990 978	−227.595	53.61	17.65
0.299 083	−110.126	52.96	17.59	0.995 491	−227.975	53.61	17.71
0.326 274	−117.856	53.05	17.55	1.0	−228.349[c]	53.61	17.74[b]

Table I (Continued)

x_A	$10^3(\rho - \rho_w)$/(g cm^{-3})	V_A/(cm^3 mol^{-1})	V_w/(cm^3 mol^{-1})	x_A	$10^3(\rho - \rho_w)$/(g cm^{-3})	V_A/(cm^3 mol^{-1})	V_w/(cm^3 mol^{-1})
			At 45 °C				
0	0[a]	49.06[b]	18.19	0.320 908	−121.484	53.80	17.64
0.000 287	−0.119	49.13	18.19	0.348 497	−129.178	53.89	17.59
0.000 538	−0.224	49.16	18.19	0.383 230	−138.306	53.98	17.54
0.000 878	−0.366	49.10	18.19	0.417 773	−146.805	54.06	17.49
0.001 141	−0.473	49.04	18.19	0.453 529	−155.049	54.13	17.43
0.001 478	−0.611	49.01	18.19	0.486 513	−162.202	54.19	17.38
0.001 858	−0.768	49.07	18.19	0.524 342	−169.928	54.25	17.32
0.002 236	−0.924	49.06	18.19	0.561 987	−177.144	54.30	17.25
0.002 647	−1.094	49.05	18.19	0.592 151	−182.619	54.34	17.20
0.003 040	−1.251	49.02	18.19	0.616 139	−186.799	54.37	17.16
0.003 494	−1.438	49.04	18.19	0.642 787	−191.259	54.39	17.12
0.004 011	−1.650	49.09	18.19	0.669 817	−195.600	54.41	17.08
0.004 453	−1.832	49.09	18.19	0.695 855	−199.615	54.43	17.04
0.004 934	−2.027	49.11	18.19	0.724 846	−203.913	54.44	17.01
0.005 540	−2.276	49.13	18.19	0.753 925	−208.029	54.45	16.99
0.006 126	−2.520	49.14	18.19	0.783 358	−212.014	54.45	16.98
0.006 681	−2.745	49.12	18.19	0.811 350	−215.619	54.45	16.99
0.007 348	−3.013	49.07	18.19	0.835 244	−218.577	54.45	17.01
0.008 047	−3.300	49.12	18.19	0.860 826	−221.608	54.44	17.05
0.008 686	−3.555	49.15	18.19	0.880 726	−223.866	54.43	17.10
0.009 805	−4.015	49.26	18.19	0.900 875	−226.068	54.42	17.18
0.017 757	−7.307	49.55	18.18	0.920 104	−228.082	54.41	17.25
0.032 204	−13.363	50.05	18.17	0.936 561	−229.737	54.41	17.33
0.047 730	−19.962	50.57	18.15	0.951 643	−231.207	54.40	17.44
0.062 917	−26.490	51.05	18.12	0.955 622	−231.583	54.40	17.48
0.085 446	−36.228	51.67	18.07	0.959 838	−231.978	54.40	17.52
0.107 933	−45.837	52.15	18.02	0.964 065	−232.369	54.40	17.55
0.131 772	−55.794	52.55	17.97	0.968 466	−232.772	54.40	17.59
0.153 570	−64.623	52.83	17.92	0.972 163	−233.106	54.39	17.62
0.179 794	−74.792	53.08	17.87	0.976 474	−233.492	54.39	17.67
0.208 813	−85.502	53.30	17.81	0.980 669	−233.862	54.39	17.71
0.237 705	−95.572	53.47	17.77	0.985 265	−234.262	54.39	17.74
0.265 150	−104.609	53.57	17.73	0.989 879	−234.659	54.39	17.77
0.291 120	−112.659	53.61	17.72	0.994 745	−235.073	54.39	17.83
0.292 314	−113.052	53.71	17.68	1.0	−235.510[c]	54.39	17.90[b]

[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 (*11*). [b] Extrapolated values by using eq 2. [c] Literature values of ρ_A/(g cm^{-3}): at 5 °C, 0.797 81 (*12*); at 15 °C, 0.787 20 (*12*), 0.787 139 (*13*); at 25 °C, 0.776 45 (*12*), 0.776 549 (*13*), 0.775 298 (*14*), 0.776 68 (*15*); at 35 °C, 0.765 78 (*12*), 0.765 846 (*13*), 0.765 75 (*16*), 0.765 87 (*17*).

Table II. Limiting Partial Molar Volumes of Acetonitrile and Water

t/°C	V_A^{∞}[a]/(cm^3 mol^{-1})	A_A/(cm^3 kg mol^{-2})	V_A^E/(cm^3 mol^{-1})	V_w^{∞}[b]/(cm^3 mol^{-1})	A_w/(cm^3 kg mol^{-2})	V_w^E/(cm^3 mol^{-1})
5	45.52	−0.15	−5.93	17.31	−0.19	−0.70
15	46.45	−0.04	−5.69	17.48	−0.21	−0.55
25	47.33	0.01	−5.53	17.58	−0.19	−0.49
35	48.16	0.08	−5.46	17.74	−0.19	−0.38
45	49.06	0.06	−5.33	17.90	−0.19	−0.29

[a] Literature values of V_A^{∞}/(cm^3 mol^{-1}): at 5 °C, 44.84 (*12*); at 15 °C, 46.04 (*12*); at 25 °C, 47.21 (*12*), 47.40 (*9, 13*), 47.416 (*18*), 47.06 (*19*). [b] Literature values of V_w^{∞}/(cm^3 mol^{-1}): at 5 °C, 17.61 (*12*); at 15 °C, 17.72 (*12*); at 25 °C, 17.47 (*9*), 17.78 (*12*).

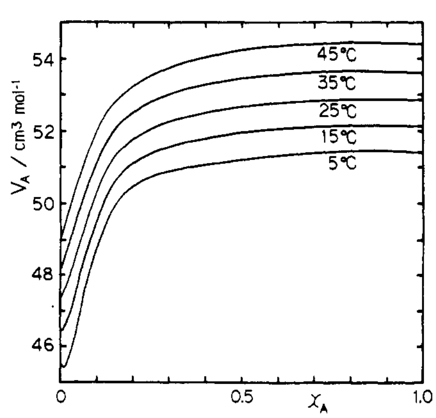

Figure 1. Partial molar volumes of acetonitrile in acetonitrile + water.

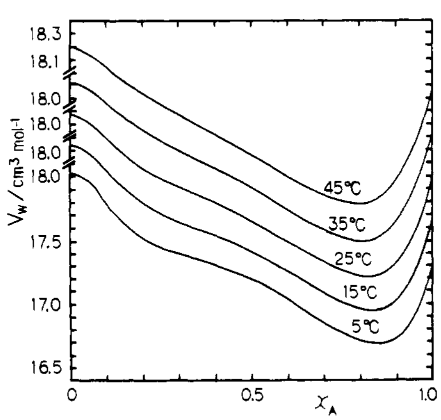

Figure 2. Partial molar volumes of water in acetonitrile + water.

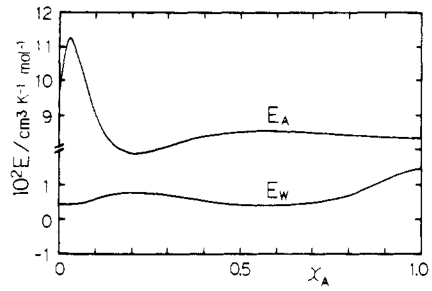

Figure 3. Partial molar expansibilities of acetonitrile and water at 25 °C.

A_W and excess limiting partial molar volumes of acetonitrile V_A^E show only a minor variation with temperature. These facts are in clear contrast with the case for mixtures of water with monohydric alcohols (*3*, *5*, *6*), but are similar to ethylene glycol + water (*7*).

The partial molar volumes were evaluated over the whole composition range by using the relation

$$V_2 = V_{\phi_2} + x_1x_2(\partial V_{\phi_2}/\partial x_2) \qquad (4)$$

The results for V_A and V_W are listed in Table I and are shown in Figures 1 and 2, respectively. The partial molar expansibilities, $E_2 = \partial V_2/\partial T$, were also calculated for both components, and the results at 25 °C are illustrated in Figure 3. It is well known that for many aqueous solutions the $V_2(x_2)$ and $E_2(x_2)$ curves have a characteristic minimum and maximum, respectively, in the water-rich region, and these extrema are more pronounced and shift to a higher mole fraction of solute 2 as the temperature decreases (*1*). In the acetonitrile solutions, a slight minimum appears in the $V_A(x_A)$ curve only at lower temperatures as can be seen from Figure 1 and Table II (where A_A is negative). On the other hand, Figure 3 reveals a distinct maximum in the $E_A(x_A)$ curve; this maximum is more pronounced as the temperature is lowered, in a manner similar to that of aqueous alcohol solutions (*3*).

The most striking characteristic of acetonitrile + water is the appearance of a large minimum in the $V_W(x_A)$ curve in the organic-rich region as shown in Figure 2. As can been seen from Table I, the $V_A(x_A)$ isotherm in Figure 1 passes through a broad maximum at the composition of the V_W minimum according to the Gibbs–Duhem relation. Similar results have been reported by Armitage et al. (*8*) and de Visser et al. (*9*). Such a minimum has also been observed in tetrahydrofuran (*2*) or in *tert*-butyl alcohol solution (*3*), but not in the other alcohol solutions (*4*–*7*). For the acetonitrile solution, however, the V_W minimum is less pronounced and shifts to a lower mole fraction of water with the decrease in temperature, in contrast with the V_W minimum for the *tert*-butyl alcohol solution or the V_2 minimum in the water-rich region discussed above. Figure 4 illustrates a comparison of the present results with those for two solvent systems reported previously, i.e., isopropyl alcohol (*5*) and ethylene glycol (*7*) as a typical example of the more hydrophobic solvent and a mixture exhibiting only a minor departure from ideality, respectively. Thus, the partial molar volume behavior of water differs significantly for different solvents, although molecular aspects of this behavior remain poorly understood.

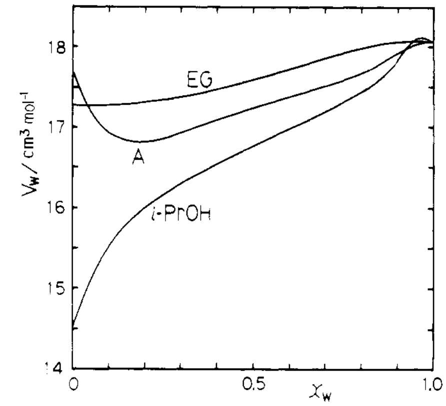

Figure 4. Partial molar volumes of water in acetonitrile (A), ethylene glycol (EG), and isopropyl alcohol (*i*-PrOH) at 25 °C.

Registry No. Acetonitrile, 75-05-8.

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