288 *J. Chem. Eng. Data* **1988**, *33*, 288-292

Φ_i segment fraction of component *i*

Registry No. Ethanol, 64-17-5; acetonitrile, 75-05-8; chloroform, 67-66-3.

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Excess Volumes for 2-Methyl-2-propanol + Water at 5 K Intervals from 303.15 to 323.15 K

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Excess volumes of mixtures of 2-methyl-2-propanol (x_a) + water (x_w) have been measured at 5 K intervals from 303.15 to 323.15 K by using a dilution dilatometer. The partial molar excess volume of 2-methyl-2-propanol at infinite dilution in water is extremely temperature-dependent, becoming more negative as the temperature increases. The partial molar excess volume of 2-methyl-2-propanol in dilute solutions with water is very concentration-dependent and the dependence reduces as temperature increases. At $x_a = 0.019$, the partial excess volume of 2-methyl-2-propanol is independent of temperature, having a value of −9.83 cm^3 mol^{-1}, while the excess volume is independent of temperature at $x_a = 0.039$, having a value of −0.0376 cm^3 mol^{-1} over the temperature range measured. These unusual observations are explained in terms of the variation of the temperature of maximum density and hydrophobic interaction for dilute 2-methyl-2-propanol solutions.

Introduction

Volumetric properties of mixtures of alcohols with water have been investigated by numerous researchers. The nonideal behavior of these mixtures has been discussed on the basis of MacMillan-Mayer theory (*1*), scaled-particle theory (*2*), and the cosphere-solvation concept of Gurney (*3*, *4*).

2-Methyl-2-propanol is of particular interest since it is completely miscible in water, although other C_4 alcohol isomers are only partially miscible. Kenttamaa and co-workers (*5*) measured the densities of 2-methyl-2-propanol + water with an Oswald pycnometer from 288.15 to 323.15 K and reported the partial molar volumes covering the majority of the mole fraction range. Density measurements of 2-methyl-2-propanol + water were made by Nakanishi et al. (*6*) at 298.15 K with an accuracy of $\pm 1 \times 10^{-5}$ g cm^{-3} and the excess volumes were calculated over the whole composition range.

Frank and Smith (*7*) used a float technique to measure the densities of solution up to the molal concentration of 0.1 (x_a = 0.018) at 273.65, 278.15, 298.15, and 313.15 K with a precision of $\pm 1 \times 10^{-6}$ g cm^{-3}. They discussed various methods of extrapolating density results to obtain the partial molar volume at infinite dilution, V_a^∞, and suggested that, as x_a approaches zero, $(\partial V_a/\partial x_a)$ should approach zero rather than have the temperature-dependent finite slope usually observed. Hvidt et al. (*8*) measured the densities of 2-methyl-2-propanol + water up to x_a = 0.4 between 278.15 and 298.15 K with an accuracy of $\pm 1 \times 10^{-5}$ g cm^{-3}. They argued that the unusual apparent molar volumes at infinite dilution of alcohol were determined not only by an overlapping of hydrophobic cospheres but also by a shift in mobile equilibria between different structures in the water near the nonpolar groups. Jolicoeur et al. (*9*) measured densities of alcohol isomers using a flow densimeter and discussed the effect of alcohols on the structure of water. The variation of nonpolar group size and geometry of alcohols was not conclusively attributed to specific effects in the hydration of the alkyl groups.

Precise measurements of excess volumes over the whole composition range are necessary to understand the nature of interactions between nonpolar groups and water, the so-called hydrophobic solvation. However, there have been no direct measurements of the excess volumes of 2-methyl-2-propanol + water covering the whole composition range. Furthermore, there are insufficient measurements at high alcohol concentrations over a wide temperaure range. Such data are required for custody transfer of 2-methyl-2-propanol.

The curve fitting for excess volume is important to estimate the density of mixtures. Marsh et al. (*10*) have tried to fit their excess volume data of ethanol + water mixtures to the skewed Redlich–Kister function, equation 1, with standard deviations close to experimental error, but they failed. They found that

$$V_m^E/(\text{cm}^3\ \text{mol}^{-1}) = x_a x_w \left(\frac{\sum_{i=0}^{n} a_i(1 - 2x_a)^i}{(1 + q(1 - 2x_a))} \right) \qquad (1)$$

eq 1 does not adequately describe excess volumes of alcohol + water systems due to the steep curvatures in the dilute alcohol region. Davis (*11*) proposed a four-segmented-composition model which has two water-rich regions, a microheterogeneous region, and an alcohol-rich region. The four-segmented-composition model improves the standard deviation in fitting but has discontinuities of its derivatives between segments.

We have measured the excess volumes over the whole composition range at 5 K intervals from 303.15 to 323.15 K and have determined parameters of the switching function whose superiority has been demonstrated in curve fitting excess en-

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Table I. Density of Pure 2-Methyl-2-propanol

	density, g cm^{-3}	
T/K	present work	lit.
303.15	0.775 21	0.775 24,^{a} 0.776 20^b
308.15	0.769 97	0.770 19,^{c} 0.770 90^d
313.15	0.764 69	0.765 03^e
318.15	0.759 37	
323.15	0.754 01	0.754 48^e
328.15	0.748 61	

[a] Reference *21*. [b] Reference *22*. [c] Reference *23*. [d] Reference *24*. [e] Reference *5*.

thalpies for ethanol + water by Ott et al. (*12*).

Experiment

Three liters of 2-methyl-2-propanol sample (Fluka Chemical Co.) was distilled over freshly ignited calcium oxide (to remove water) in a 2-m distillation column packed with stainless steel helices (approximately 80 theoretical plates). It was stored over Linde Type 3A molecular sieve which had been activated at 300 °C under vacuum. All samples were covered by dry nitrogen to exclude atmospheric moisture.

The purities of the samples were determined on a routine basis by gas-liquid chromatography using both a 2-m BP-5 column with a hydrogen flame ionization detector to detect organic impurities and a 2-m Porapak Q column on a Varian 1400 gas chromatography with a thermal conductivity detector to detect water. The purity of 2-methyl-2-propanol was better than 99.97 mol %.

The solubility of air in 2-methyl-2-propanol is high, so unless it is thoroughly degassed, the addition of water causes a "salting out" of the air and hence the formation of a bubble, which ruins a dilatometer run. The alcohol and water were thoroughly degassed by either pumping or boiling, or by the use of a multiple freeze-pump-thaw technique.

The temperature was controlled better than ±2 mK. All temperatures were measured with a standard platinum resistance thermometer which had been calibrated by the National Bureau of Standards adjusted to IPTS 68.

The densities of pure 2-methyl-2-propanol were measured in a single-arm flash pycnometer having a volume of about 40 cm^3 and a 1-mm precision bore tubing marked with a reference line. The accuracy of 2-methyl-2-propanol densities is better than $\pm 1 \times 10^{-5}$ g cm^{-3}. The excess volumes were determined by using a continuous dilution dilatometer described by Stokes et al. (*13*) and Marsh et al. (*10*) with an accuracy of better than ±0.001 cm^3 mol^{-1}.

Results

The densities of pure 2-methyl-2-propanol are given in Table I. Our density values are lower than previous measurements. The freezing point of a purified sample is about 298.87 K. The highest estimated literature freezing point, obtained by extrapolation, is found to be 298.81 K by Simonsen et al. (*14*). An extrapolated value obtained by Ott et al. (*15*) is 298.77 K. The higher freezing point and lower densities indicate that our sample probably had a lower water content than pure samples used previously. Values of $V_m^E/x_a x_w$ are given in Table II and shown in Figures 1 and 2. We estimate that the precision of $V_m^E/x_a x_w$ is better than ±0.2% over most of the composition range. The primary uncertainty in the measurement arises from the calibration of the 1-mm-bore capillary.

Values of $V_m^E/x_a x_w$ for dilute solutions of 2-methyl-2-propanol are plotted in Figure 2. The partial molar excess volumes of 2-methyl-2-propanol up to $x_a = 0.05$ shown in Figure 3 are obtained from $\Delta V/\Delta n_a$ for each individual addition where ΔV is the volume change for the addition of Δn_a moles of 2-methyl-2-propanol. The values are plotted against the mean value of the mole fraction for the addition.

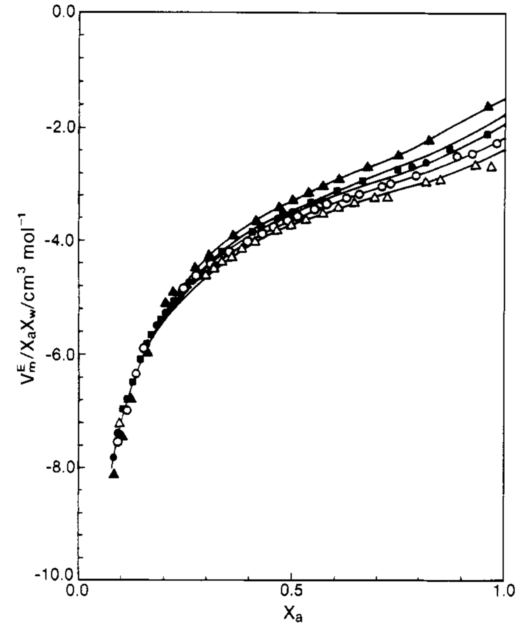

Figure 1. Excess volumes, expressed as $V_m^E/x_a x_w$, for 2-methyl-2-propanol (x_a) + water (x_w) from x_a = 0.1 to x_a = 1.0. Experimental results are given for ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K; ○, 318.15 K; △, 323.15 K.

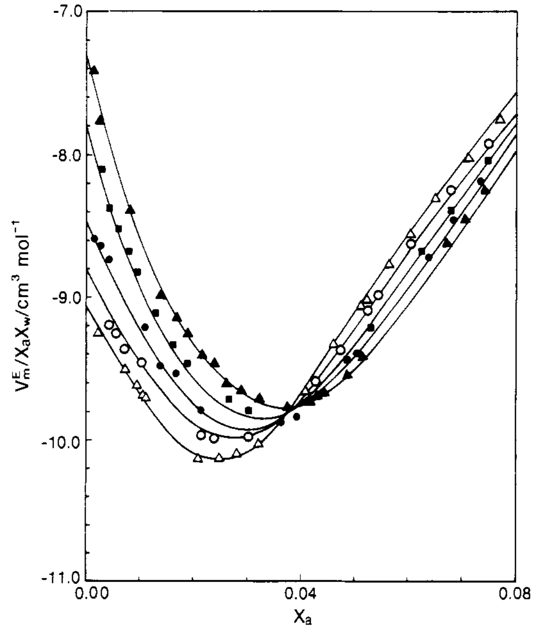

Figure 2. Excess volumes, expressed as $V_m^E/x_a x_w$, for 2-methyl-2-propanol (x_a) + water (x_w) from x_a = 0.0 to x_a = 0.08. Experimental results are given for ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K; ○, 318.15 K; △, 323.15 K.

At $x_a = 0.019 \pm 0.001$ the partial molar excess volume is approximately independent of temperature between 303.15 and 323.15 K, having a value of -9.83 ± 0.01 cm^3 mol^{-1}. The partial molar excess volumes of 2-methyl-2-propanol at infinite dilution in water, V_a^∞, and a partial molar volumes of water at infinite dilution in the alcohol, V_w^∞, are given in Table III. The temperature dependence of the limiting partial properties are plotted in Figures 4-7.

Data Evaluation

Ott et al. (*12*) have investigated the use of an equation containing an exponential switching factor to fit results of the excess enthalpies of ethanol + water. Equation 2, which is similar to their equation, was used to fit the excess volumes

Table II. Excess Volumes of 2-Methyl-2-propanol (x_a) + Water (x_w) as V^E/x_ax_w from 303.15 to 323.15 K

x_z	V^E/x_ax_w/ cm^3 mol^{-1}	x_z	V^E/x_ax_w/ cm^3 mol^{-1}	x_z	V^E/x_ax_w/ cm^3 mol^{-1}
T = 303.15 K					
0.008 07	−7.765	0.043 14	−9.575	0.269 94	−4.497
0.010 48	−8.825	0.057 50	−9.193	0.298 96	−4.280
0.013 82	−8.995	0.061 29	−8.999	0.355 11	−3.932
0.017 20	−9.158	0.067 86	−8.670	0.409 14	−3.662
0.018 98	−9.270	0.071 52	−8.495	0.462 26	−3.436
0.021 74	−9.419	0.075 34	−8.303	0.494 46	−3.300
0.026 21	−9.618	0.080 13	−8.124	0.565 81	−3.044
0.029 00	−9.673	0.096 98	−7.426	0.602 98	−2.930
0.032 09	−9.736	0.116 63	−6.787	0.666 82	−2.688
0.035 06	−9.796	0.151 95	−5.967	0.738 67	−2.498
0.037 83	−9.794	0.201 07	−5.108	0.816 82	−2.217
0.042 01	−9.763	0.222 00	−4.925	0.929 63	−1.830
T = 308.15 K					
0.006 04	−8.521	0.050 76	−9.433	0.233 66	−4.886
0.007 84	−8.685	0.064 39	−8.759	0.258 45	−4.675
0.009 35	−8.839	0.068 87	−8.509	0.298 55	−4.388
0.012 73	−9.127	0.074 09	−8.236	0.370 51	−3.996
0.016 22	−9.346	0.084 64	−7.742	0.420 42	−3.772
0.018 94	−9.485	0.094 07	−7.379	0.472 90	−3.570
0.023 30	−9.663	0.123 30	−6.506	0.538 48	−3.349
0.026 74	−9.739	0.140 50	−6.115	0.598 11	−3.180
0.334 56	−9.812	0.156 63	−5.819	0.657 67	−3.045
0.040 27	−9.767	0.167 34	−5.669	0.739 68	−2.863
0.044 45	−9.658	0.185 99	−5.395	0.865 17	−2.372
0.047 40	−9.548	0.214 08	−5.079	0.963 54	−0.057
T = 313.15 K					
0.002 76	−8.646	0.053 21	−9.239	0.459 19	−3.623
0.004 37	−8.747	0.058 14	−8.979	0.563 92	−3.295
0.006 49	−8.874	0.068 46	−8.437	0.635 47	−3.051
0.008 98	−9.023	0.075 53	−8.098	0.713 04	−2.851
0.010 82	−9.221	0.123 50	−6.507	0.743 58	−2.763
0.016 96	−9.552	0.165 55	−5.642	0.776 30	−2.694
0.021 46	−9.803	0.195 22	−5.263	0.901 14	−2.216
0.035 55	−9.909	0.216 39	−5.043	0.956 17	−2.138
0.039 54	−9.871	0.238 50	−4.832		
0.433 07	−9.727	0.377 46	−3.967		
T = 318.15 K					
0.054 92	−9.267	0.054 55	−9.026	0.571 64	−3.383
0.007 31	−9.374	0.061 02	−8.670	0.620 91	−3.256
0.010 27	−9.471	0.075 95	−7.976	0.648 40	−3.177
0.017 79	−9.960	0.123 30	−6.342	0.704 02	−3.059
0.021 68	−9.977	0.152 97	−5.884	0.722 42	−2.995
0.024 19	−10.004	0.252 76	−4.756	0.784 85	−2.844
0.030 14	−10.003	0.308 31	−4.428	0.812 36	−2.681
0.033 83	−9.925	0.343 25	−4.224	0.848 49	−2.599
0.038 72	−9.799	0.423 89	−3.884	0.882 05	−2.507
0.04314	−9.619	0.481 53	−3.671	0.918 03	−2.433
0.047 54	−9.403	0.506 68	−3.587	0.962 38	−2.162
0.052 55	−9.132	0.545 55	−3.462	0.978 56	−2.268
T = 323.15 K					
0.002 07	−9.258	0.072 09	−7.820	0.459 09	−3.841
0.004 79	−9.328	0.156 77	−5.820	0.524 26	−3.638
0.007 08	−9.514	0.178 93	−5.515	0.562 70	−3.523
0.011 25	−9.734	0.202 41	−5.275	0.562 70	−3.523
0.021 11	−10.159	0.223 73	−5.076	0.600 78	−3.438
0.028 18	−10.130	0.259 90	−4.791	0.637 58	−3.354
0.032 05	−10.055	0.286 11	−4.617	0.720 19	−3.245
0.041 06	−9.692	0.301 37	−4.525	0.811 42	−2.982
0.051 88	−9.105	0.326 03	−4.397	0.842 21	−2.961
0.057 09	−8.815	0.346 60	−4.292	0.927 53	−2.691
0.060 76	−8.612	0.373 81	−4.167		
0.066 02	−8.357	0.402 89	−4.047		

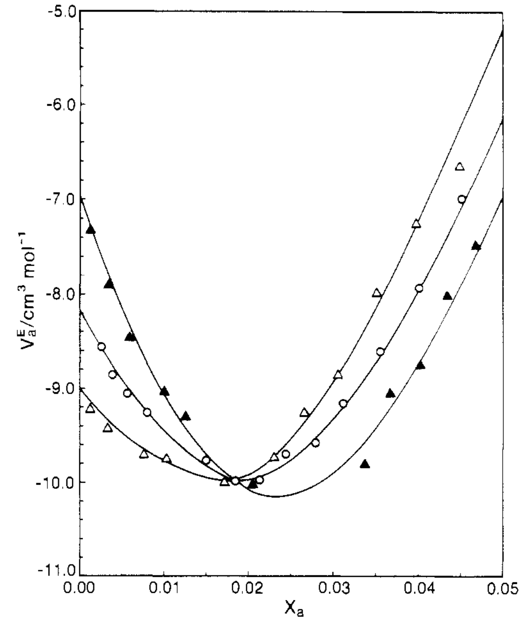

Figure 3. Variation of the partial molar excess volume of 2-methyl-2-propanol with concentration for 2-methyl-2-propanol (x_a) + water (x_w). Experimental results are given for ▲, 303.15 K; ●, 313.15 K; △, 323.15 K.

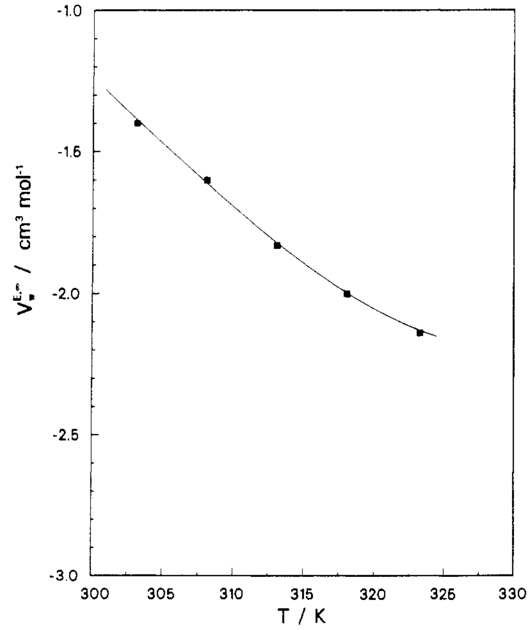

Figure 4. Variation of the partial molar excess volume of water at infinite dilution in 2-methyl-2-propanol, $V_w^{E,\infty}$, with temperature.

Table III. Partial Molar Excess Volumes and Partial Molar Volumes for 2-Methyl-2-propanol (x_a) + Water (x_w) at Infinite Dilution

T/K	$V_w^{E,\infty}$/ cm^3 mol^{-1}	V_w^{∞}/ cm^3 mol^{-1}	$V_a^{E,\infty}$/ cm^3 mol^{-1}	V_a^{∞}/ cm^3 mol^{-1}
303.15	−1.400	16.694	−7.09	88.522
308.15	−1.601	16.523	−7.70	88.555
313.15	−1.832	16.326	−8.27	88.652
318.15	−2.000	16.193	−8.72	88.876
323.15	−2.140	16.094	−9.11	89.207

with a nonlinear curve-fitting program, which minimizes the deviations using a Marquart algorithm (*16*).

$$V_m^E/(\text{cm}^3\ \text{mol}^{-1}) = x_ax_w[e^{-\alpha x_a}(\sum_{i=0}^{k} b_i(1-2x_a)^i) + (1-e^{-\alpha x_a})\sum_{i=0}^{m} c_i(1-2x_a)^i] \quad (2)$$

We have chosen $k = 1$ and $m = 3$. Values of parameters in the switching function are listed in Table IV.

In eq 2, the exponential serves as a switching function to change the coefficients in the Redlich–Kister equation from a set which fits the results at low alcohol mole fraction to a set which is valid over the remainder of the composition range. The smaller standard deviations given in Table IV as compared to

Table IV. Parameters of the Switching Function for 2-Methyl-2-propanol (x_a) + Water (x_w)

T/K	α	b_0	b_1	c_0	c_1	c_2	c_3	σ/cm^3 mol^{-1}
303.15	29.816	−134.64	128.15	−3.276	−1.900	−1.032	−1.137	0.0018
308.15	32.417	−131.14	124.29	−3.476	−1.579	−1.154	−1.421	0.0019
318.15	29.805	−107.19	98.51	−3.605	−1.618	−0.967	−0.882	0.0017
323.15	31.723	−107.44	98.34	−3.712	−1.447	−1.080	−1.046	0.0014

Table V. Parameters of the Skewed Redlich–Kister Function for 2-Methyl-2-propanol (x_a) + Water (x_w)

T/K	a_0	a_1	a_2	a_3	a_4	a_5	q	σ/cm^3 mol
303.15	−3.293	0.2857	0.6894	−0.9320	−0.8155	−0.4128	−0.64	0.0122
308.15	−3.481	0.4654	0.0165	0.1417	0.155	−1.9730	−0.61	0.0097
313.15	−3.482	0.2153	0.2220	0.0651	−0.6157	−1.8838	−0.58	0.0088
318.15	−3.614	0.1660	0.1881	0.5073	−0.8550	−2.1557	−0.52	0.0075
323.15	−3.721	0.1982	−0.1247	1.0247	−0.5647	−2.9571	−0.49	0.0066

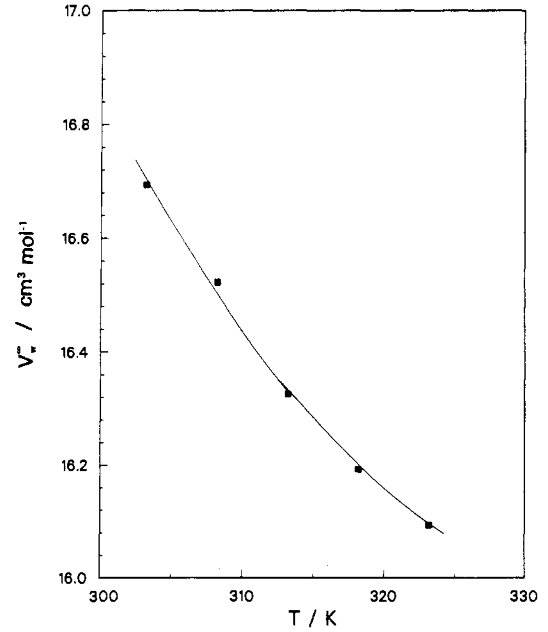

Figure 5. Variation of the partial molar volume of water at infinite dilution in 2-methyl-2-propanol, V_a^∞, with temperature.

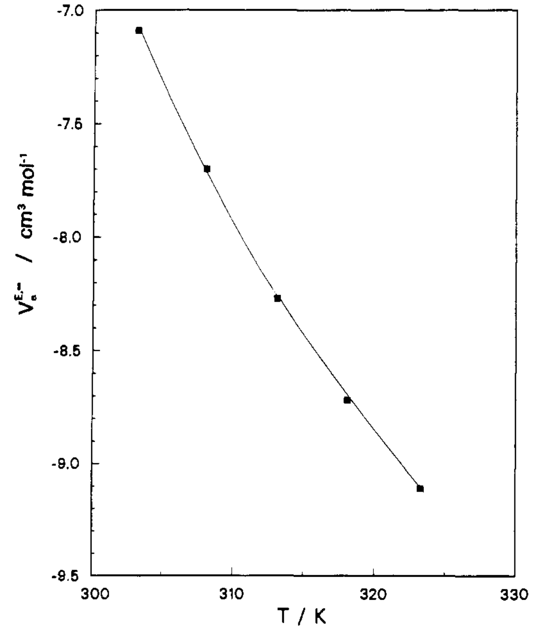

Figure 6. Variation of the partial molar excess volume of 2-methyl-2-propanol at infinite dilution in water, $V_a^{E,\infty}$, with temperature.

those in Table V show the superiority of eq 2 over eq 1 in fitting V_m^E at 303.15, 308.15, 313.15, 318.15, and 323.15 K for the 2-methyl-2-propanol + water system.

Discussion

Excess volumes calculated from the density results of Kenttamaa et al. (*5*) at 313.15 and 323.15 K are about 0.009 cm^3 mol^{-1} less negative than our data in the water-rich region. However, above x_a = 0.05 the agreement with our data is generally within 0.001 cm^3 mol^{-1}. Their value for the limiting partial molar excess volumes of 2-methyl-2-propanol are about 2.3 cm^3 mol^{-1} more positive than our results. These differences can be ascribed to impurities in 2-methyl-2-propanol and their extrapolation method. Their values for densities of 2-methyl-2-propanol at 313.15 and 323.15 K are 0.764 99 and 0.754 48 g cm^{-3}, respectively, which are 0.05% greater than the present results of 0.764 69 and 0.754 01 g cm^{-3}. The higher densities indicate that the alcohol used for their measurements might contain more than 0.03 mol % water.

Values of excess volumes obtained from the apparent molal volumes of Visser et al. (*17*) at 313.15 K agree with our results within the combined experimental error. Their value for the partial molar volume of 88.63 cm^3 mol^{-1} for 2-methyl-2-propanol at infinite dilution in water at 313.15 K is slightly lower than our value of 88.65 cm^3 mol^{-1}. This difference between the estimates may be ascribed to well-known problems involved in the extrapolation of the experimental data to zero concentration. The strong concentration dependence in the water-rich region and the scattering of values of apparent molal volumes of x_a approaching zero complicate the extrapolation.

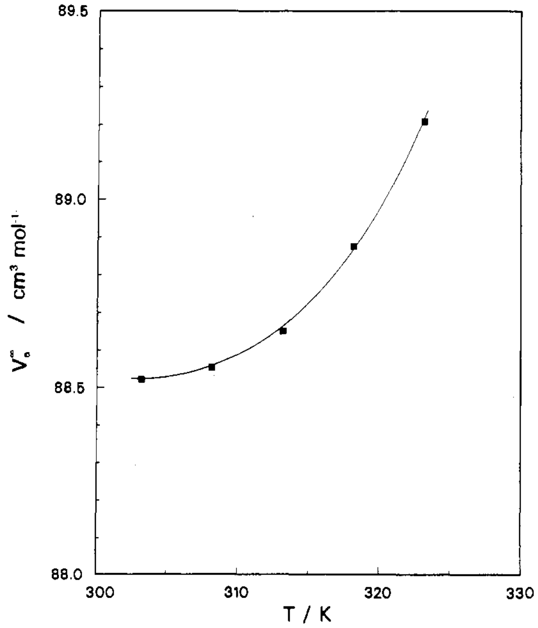

Figure 7. Variation of the partial molar volume of 2-methyl-2-propanol at infinite dilution in water, V_a^∞, with temperature.

Franks and Watson (*18*) have related the change in the temperature of maximum density, $\Delta\theta$, to the variation of the excess volume with temperature $(\partial V_m^E/\partial T)_P$ by

$$\Delta\theta = \Delta\theta_i + \Delta\theta_s = \frac{x_a \alpha_a V_a^0(273.15\ \mathrm{K})}{2\alpha_w V_w^0(277.13\ \mathrm{K})} - \frac{(\partial V_m^E/\partial T)_P}{2\alpha_w x_w V_w(277.13\ \mathrm{K})} \qquad (3)$$

where $V_a^0(273.15\ \mathrm{K})$ is the extrapolated molar volume of the alcohol at 273.15 K, $V_w^0(277.15\ \mathrm{K})$ is the molar volume of pure water at the temperature of maximum density, and α_a and α_w are coefficients of thermal expansion of alcohol and water. $\Delta\theta_i$ and $\Delta\theta_s$ are temperatures of maximum density due to the ideal mixing and structural change, respectively. The maximum of $\Delta\theta_s$ occurs at $x_a = x_a^*$ as pointed by Armitage et al. (*19*).

$$\left(\frac{\partial \Delta\theta_s}{\partial x_a}\right)_{x_a = x_a^*} = -\frac{\partial(\partial(V_m^E/x_w)/\partial x_a)_{x_a=x_a^*}}{\partial T} = 0 \qquad (4)$$

hence

$$(\partial V_a^E/\partial T)_{x_a = x_a^*} = 0 \qquad (5)$$

Figure 3 shows that the partial molar excess volume of 2-methyl-2-propanol at low values of x_a, V_a^E, is strongly temperature-dependent, becoming more negative as the temperature increases. At $x_a^* = 0.019$, the partial molar excess volume of 2-methyl-2-propanol is independent of temperature, having a value of -9.83 cm^3 mol^{-1}. The excess volume is independent of temperature at $x_a^{**} = 0.039$ as shown in Figure 2 with -0.0376 cm^3 mol^{-1}. The mole fraction of alcohol where $(\partial V_a^E/\partial T) = 0$ is half the mole fraction of alcohol at which $(\partial V_m^E/\partial T) = 0$. This would indicate that $\Delta\theta_s$ has a quadratic relationship to x_a. Above $x_a = 0.039$, the partial molar volume and excess volume increase with increase in temperature.

The pairwise interaction of alkyl groups of alcohol at infinite dilution is observed from the apparent molar volume model suggested by Franks (*20*). The apparent molar volume at infinite dilution of alcohol, V_{app}, is related to the pair (v_{xx}) and triple (v_{xxx}) interaction coefficients between nonpolar groups in the solute molecule.

$$V_{\mathrm{app}} - V_a^\infty = (V_a^0 + V_a^E) - V_a^\infty = v_{xx} x_a + v_{xxx} x_a^2 + \ldots \qquad (6)$$

V_a^0 is the pure molar volume of 2-methyl-2-propanol. Negative slopes of V_a^E at infinite dilution indicate that pairwise interactions of v_{xx} contribute to decreasing the excess and partial excess volumes for aqueous alcohol solutions. The pairwise interaction decreases in magnitude with rising temperature and approaches zero at 323.15 K. The decrease of partial excess volume of alcohol with increasing molar concentration of alcohol in the dilute region is ascribed to the solute–solute interaction.

Nakanishi et al. (*25*) and Tanaka et al. (*26*) have recently published molecular dynamics simulations on an infinite dilute and a 3 mol % 2-methyl-2-propanol solution in water. They observe a large negative molar excess volume of the alcohol. From a study of the partial radial distribution functions of each of the species they conclude that the water structure is promoted and the alcohol molecule occupies the cavity of the water structure. This result in a very large negative excess volume which is partly compensated by a small volume increase of water around 2-methyl-2-propanol due to hydrophobic hydration effect. In addition to hydrophobic hydration at finite concentrations, the hydrophobic interaction leads to the overlapping of the hydration sphere and thus a further decrease in the excess volume at the dilute alcohol region. They could conclude nothing about more concentrated solutions.

Registry No. 2-Methyl-2-propanol, 75-65-0.

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