International Journal of Thermophysics, Vol. 17, No. 2, 1996

Volumetric Properties of Mixtures of 1,4-Dioxane and Water at High Pressures

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Received July 10, 1995

Densities of aqueous of 1,4-dioxane have been measured at temperatures from 298 to 348 K and at pressures up to 40 MPa by a vibrating-tube method. Molar volumes obtained with an estimated uncertainty of ±0.2% are correlated with pressure by the Tait equation within the experimental uncertainty. Pressure and composition dependences of the excess molar volume, partial molar volume, and isothermal compressibility are determined and they are compared with those of other aqueous solutions.

KEY WORDS: aqueous solutions; compressibility; density; dioxane; high pressure; partial molar volume.

1. INTRODUCTION

Aqueous solutions of nonpolar substances exhibit anomalous temperature, pressure, and composition dependences in their thermophysical properties and they are in general explained on the basis of two concepts, hydrophobic hydration and hydrophobic interaction [1–3]. Similar anomalous behaviours of the aqueous solutions of alcohols are also qualitatively interpreted in term of the same concepts because of the existence of hydrophobic groups in the alcohol molecules [4, 5]. In our recent publications [6, 7], we have reported measurements of the density and viscosity of aqueous solutions of three fluoroalcohols, 2, 2, 2-trifluoroethanol, 2, 2, 3, 3-tetrafluoropropanol, and 2, 2, 3, 3, 3-pentafluoropropanol; their

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temperature, pressure, and composition dependences were discussed in comparison with those of the aqueous solutions of corresponding hydrocarbon alcohols. Specifically, the excess molar volumes of fluoroalcohol mixtures are found to be negative over most of the composition range and those absolute values are smaller than those for hydrocarbon alcohol mixtures. The partial molar volumes of fluoroalcohols were compared with the Raman spectrum frequency shift of the C–H stretching bands of fluoroalcohols upon dilution by water [8] and similar composition dependences were observed between these properties. It was also found that there exists a significant similarity between the compostion dependences of the viscosity and the nuclear magnetic resonance (NMR) spectroscopic data [8]. These results seem to stand by the above concepts, but the accumulation of accurate experimental data is still required to explicate the anomalies on thermophysical properties for aqueous solutions.

In the present work, the density of the aqueous solutions of 1,4-dioxane has been measured by a vibrating-tube method at temperatures from 298 to 323 K and at pressures up to 40 MPa. The estimated uncertainties of the densities obtained are ±0.1% for pure components and ±0.2% for mixtures, respectively.

2. EXPERIMENTS

Measurements were performed with a high-pressure vibrating-tube densitometer, Paar DMA512, whose pressure limit is 40 MPa. Some supplementary measurements were performed at 298 K and at atmospheric pressure with a more precise vibrating-tube densitometer, DMA602, to examine the existence of a tiny minimum in the partial molar volume of 1,4-dioxane at a very dilute concentration. Details of these densitometers have been described elsewhere [6, 9]. In this study, the density was obtained on a relative basis and the instrument constants of each densitometer have been calibrated against the recommended density values of pure water [10] and pure heavy water [11] over the entire range of measurements. Each densitometer cell is jacketed and maintained isothermally at ±10 mK by circulating water. Temperature and pressure are measured with a precise thermistor (Technol Seven E640) to within ±10 mK and a digitized Bourdon gauge (Heise 901B) to within ±0.2 MPa, respectively. 1,4-Dioxane and pure heavy water with a guaranteed purity better than 99.0 and 99.75%, respectively were obtained from Wako Pure Chemical Industries, Ltd. Before preparing the sample mixtures, 1,4-dioxane was stored over 4-Å molecular sieves for more than 48h to remove water and the pure water was used after degassing. Judging from the precision of instruments, the purity of samples, and the reproducibility of measurements, we estimate the uncertainties of the densities obtained to be within ±0.1% for the pure components. For the mixtures the uncertainty increases to ±0.2% because of the additional uncertainties arising from the gravimetric preparation procedure.

3. RESULTS AND DISCUSSION

3.1. Pressure Dependence of Molar Volume

The densities of pure 1,4-dioxane obtained with Paar DMA512 are presented in Table I. The measurements were performed at nominal pressures spaced 3 MPa apart from 0.1 to 39.5 MPa. If bubbles remain in the vibrating-tube owing to imperfect filling of the sample liquid, the period of vibration indicates a much higher value than expected. Therefore, some supplementary measurements were carried out at pressures lower than 3 MPa to confirm that the vibrating tube is completely filled with the sample liquid. As shown in Table I, the density at a given temperature increases monotonically with increasing pressure and no indication of density jump owing to the remaining of bubbles was observed. The measurements for the 1,4-dioxane and water mixture were performed at the same pressures as for the pure component, and the same pressure dependence as shown in Fig. 1 is observed.

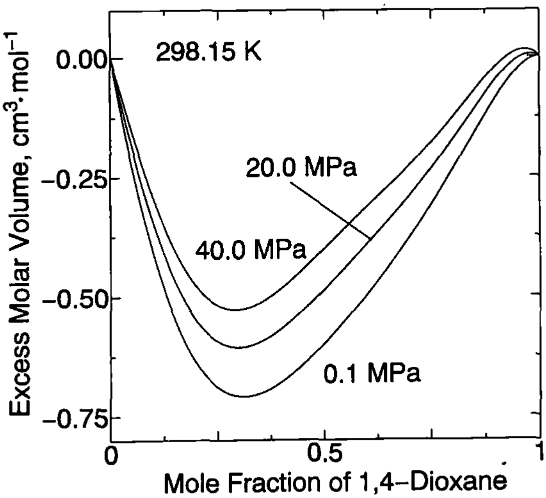

Fig. 1. Excess molar volume of 1,4-dioxane and water mixture at 298 K and at various pressures.

Table I. Experimental Densities of Pure 1,4-Dioxane

	ρ (kg·m^{-3})		
P (MPa)	298.15 K	323.15 K	348.15 K
0.10	1027.79	999.55	969.82
0.30	1027.93	999.72	970.07
0.60	1028.05	999.93	970.42
1.00	1028.35	1000.26	970.87
3.00	1029.85	1002.00	973.02
6.00	1032.11	1004.56	976.13
9.00	1034.34	1007.06	979.12
12.00	1036.44	1009.52	982.02
15.00	1038.57	1011.85	984.81
18.00	1040.54	1014.21	987.49
21.00	1042.61	1016.50	990.12
24.00	1044.61	1018.77	992.66
27.00	1046.58	1021.01	995.13
30.00	1048.52	1023.21	997.59
33.00	1050.44	1025.35	999.95
36.00	1052.32	1027.47	1002.29
39.50	1054.47	1029.89	1004.93

In the previous works on a series of the aqueous solutions of primary hydrocarbon alcohols [12] and of fluoroalcohols [6], the pressure dependence of the volumetric properties were discussed in terms of the following Tait equation:

$$V_P = V_0\left(1 - C\ln\frac{B+P}{B+P_0}\right) \tag{1}$$

Here V_p and V_0 are the molar volumes in cm^3·mol^{-1} at pressure P and at atmospheric pressure P_0 in MPa. To avoid the inferences concering the derivative properties due to a different correlation equation, the Tait equation is adopted again in the present investigation. The coefficients of Eq. (1) determined by least-squares fitting are given in Tables II–IV together with the average and maximum deviations. In the fitting procedure, V_0 was also determined as a fitting parameter of Eq. (1) as well as B and C. The deviation for an individual mixture is sufficiently within the uncertainty of the measurements and the experimental densities are found to be satisfactorily represented by the Tait equation as well as the aqueous solutions of primary hydrocarbon alcohols and of fluoroalcohols.

To interpolate the molar volume against the composition, correlation of empirical coefficients V_0, B, and C in Eq. (1) with the mole fraction of

Table II. Coefficients in Eq. (1) for 1,4-Dioxane and Water Mixtures at 298.15 K

				Dev. (%)		Dev. (%)[a]	
x_d	V_0 ($cm^3 \cdot mol^{-1}$)	B (MPa)	C	Max.	Ave.	Max.	Ave.
0.00915	18.6518	353.4504	0.15617	0.001	0.001	0.055	0.029
0.01998	19.3289	425.8088	0.18205	0.003	0.001	0.037	0.020
0.02996	19.9576	387.0478	0.16368	0.002	0.001	0.035	0.019
0.06029	21.8732	323.9400	0.13478	0.002	0.001	0.017	0.007
0.10092	24.4695	277.6437	0.11641	0.002	0.001	0.032	0.020
0.15006	27.6635	266.3035	0.11567	0.003	0.001	0.021	0.013
0.19979	30.9422	275.4071	0.12479	0.004	0.001	0.027	0.013
0.29982	37.6434	209.0816	0.10478	0.004	0.001	0.025	0.012
0.39955	44.4242	185.9207	0.10179	0.002	0.001	0.009	0.008
0.49945	51.2509	159.0095	0.09379	0.003	0.001	0.024	0.019
0.59971	58.1409	142.1792	0.09009	0.003	0.001	0.031	0.018
0.69940	65.0082	126.2586	0.08464	0.005	0.001	0.019	0.010
0.80148	72.0634	132.4273	0.09205	0.003	0.001	0.006	0.004
0.89702	78.6641	119.4205	0.08672	0.001	0.001	0.006	0.004
1.0	85.7234	129.6731	0.09567	0.006	0.003	0.039	0.022

[a] Deviation from the smoothed Tait equation.

Table III. Coefficients in Eq. (1) for 1,4-Dioxane and Water Mixtures at 323.15 K

				Dev. (%)		Dev. (%)[a]	
x_d	V_0 ($cm^3 \cdot mol^{-1}$)	B (MPa)	C	Max.	Ave.	Max.	Ave.
0.00915	18.8333	502.1157	0.21526	0.002	0.001	0.031	0.016
0.01998	19.5423	481.1440	0.20591	0.004	0.001	0.040	0.026
0.02996	20.1919	650.9188	0.27380	0.004	0.001	0.024	0.017
0.06029	22.1820	375.0088	0.16236	0.003	0.001	0.034	0.015
0.10092	24.8747	355.7149	0.15794	0.002	0.001	0.021	0.017
0.15006	28.1839	379.9181	0.17733	0.005	0.002	0.024	0.012
0.19979	31.5678	270.7401	0.13592	0.004	0.002	0.020	0.010
0.29982	38.4954	180.6808	0.10409	0.003	0.001	0.022	0.014
0.39955	45.4895	185.0019	0.11560	0.003	0.002	0.010	0.007
0.49945	52.5454	139.3432	0.09628	0.003	0.001	0.019	0.012
0.59971	59.6516	153.4375	0.11049	0.004	0.002	0.015	0.010
0.69940	66.7582	123.4691	0.09632	0.005	0.002	0.020	0.009
0.80148	74.0497	119.6438	0.09783	0.003	0.001	0.016	0.006
0.89702	80.8743	111.8995	0.09548	0.006	0.002	0.015	0.007
1.0	88.1423	113.8002	0.09926	0.004	0.002	0.033	0.018

[a] Deviation from the smoothed Tait equation.

Table IV. Coefficients in Eq. (1) for 1,4-Dioxane and Water Mixtures at 348.15 K

				Dev. (%)		Dev. (%)[a]	
x_d	V_0 ($cm^3 \cdot mol^{-1}$)	B (MPa)	C	Max.	Ave.	Max.	Ave.
0.00915	19.1064	272.1245	0.12501	0.002	0.001	0.051	0.027
0.01998	19.8400	305.9716	0.14053	0.004	0.002	0.055	0.031
0.02996	20.5120	351.2967	0.16015	0.003	0.002	0.031	0.018
0.06029	22.5746	243.4261	0.11528	0.003	0.001	0.026	0.011
0.10092	25.3627	205.2540	0.10273	0.002	0.001	0.035	0.029
0.15006	28.7924	195.8013	0.10541	0.004	0.002	0.023	0.011
0.19979	32.2955	175.8551	0.10186	0.005	0.003	0.029	0.013
0.29982	39.4472	119.5393	0.08078	0.003	0.001	0.030	0.010
0.39955	46.6942	114.1655	0.08623	0.004	0.002	0.032	0.026
0.49945	53.9733	96.3825	0.08002	0.003	0.001	0.036	0.033
0.59971	61.3665	91.8961	0.08271	0.003	0.002	0.026	0.011
0.69940	68.7198	87.6953	0.08448	0.003	0.002	0.044	0.017
0.80148	72.2624	78.0442	0.07990	0.003	0.001	0.017	0.008
0.89702	83.3085	80.6963	0.08502	0.005	0.002	0.018	0.008
1.0	90.8361	66.2528	0.07472	0.005	0.003	0.045	0.018

[a] Deviation from the smoothed Tait equation.

1,4-dioxane, x_d was attempted as follows. First, the parameter V_0 in Tables II–IV was correlated with x_d by the following equations:

$$V_0 = x_d V_{0,d} + (1 - x_d) V_{0,H_2O} + V_0^E \tag{2}$$

$$V_0^E = x_d(1 - x_d) \sum_{i=1}^{5} a_i (1 - 2x_d)^{i-1} \tag{3}$$

Here V_0 and V_0^E are the molar volume and the excess molar volume in $cm^3 \cdot mol^{-1}$ at atmospheric pressure and the subscripts d and H_2O refer to pure 1,4-dioxane and pure water, respectively. The coefficients a_i of Eq. (3) are given in Table V together with the molar volumes of pure components $V_{0,d}$ and V_{0,H_2O}. Since the parameter C in Tables II–IV was found to be difficult to be correlated with x_d by a single equation, the following two correlation equations were used according to the concentration of mixture. In the mole fraction range of 1,4-dioxane larger than 0.03, the following equation was employed:

$$C = c_1 \exp(c_2 x_d^{c_3}) \qquad (x_d \geqslant 0.03) \tag{4}$$

Table V. Coefficients in Eqs. (2) and (3)

	Temperature (K)		
	298.15	323.15	348.15
$V_{0,\mathrm{d}}$ ($\mathrm{cm^3 \cdot mol^{-1}}$)	85.7234	88.1423	90.8361
$V_{0,\mathrm{H_2O}}$ ($\mathrm{cm^3 \cdot mol^{-1}}$)	18.0684	18.2331	18.4798
a_1	−2.39762	−2.41065	−2.51364
a_2	−1.86734	−1.81854	−2.06767
a_3	−1.39347	−1.14365	−0.66649
a_4	−0.68648	−0.88790	−0.42947
a_5	1.25061	1.33003	0.68834
Ave. dev. (%)	0.014	0.010	0.015
Max. dev. (%)	0.055	0.025	0.053

In the lower contentration range, between 0 and 0.03, the following simple polynomial equation was used:

$$C = C_{\mathrm{H_2O}} + \sum_{i=1}^{3} c_i^* x_{\mathrm{d}}^i \qquad (0 \leqslant x_{\mathrm{d}} < 0.03) \tag{5}$$

Here $C_{\mathrm{H_2O}}$ is the parameter for pure water, which is determined to represent the density values recommended by Kestin and Sengers [10]. The coefficients c_i and c_i^* were determined by least-squares fitting while taking account of the continuity of these equations. The composition dependence of the parameter B, which was redetermined with the smoothed values of V_0 and C calculated with Eqs. (2)–(5), was found to be difficult to be represented by a single equation, and therefore correlation equations similar to thoese used for determining the parameter C were adopted as follows:

$$B = b_1 \exp(b_2 x_{\mathrm{d}}^{b_3}) \qquad (x_{\mathrm{d}} \geqslant 0.03) \tag{6}$$

$$B = B_{\mathrm{H_2O}} + \sum_{i=1}^{3} b_i^* x_{\mathrm{d}}^i \qquad (0 \leqslant x_{\mathrm{d}} < 0.03) \tag{7}$$

Here $B_{\mathrm{H_2O}}$ is the parameter for pure water, which is determined simultaneously with $C_{\mathrm{H_2O}}$ mentioned above. The continuity of Eqs. (6) and (7) was again taken into account in determining the coefficients b_i and b_i^*. The coefficients of Eqs. (4) to (7) are given in Table VI. The average and maximum deviations of molar volume by the Tait equation with the smoothed parameters V_0, C, and B in Eqs. (2) to (7) are tabulated in the

Table VI. Coefficients in Eqs. (4) to (7)

	Temperature (K)				Temperature (K)		
	298.15	323.15	348.15		298.15	323.15	348.15
			$0.03 \leqslant x_d \leqslant 1.0$				
b_1	760.6003	135373.1069	2624.2830	c_1	0.0461563	0.0629329	0.06688136
b_2	−1.881455	−7.148979	−3.627496	c_2	0.645606	0.4084208	0.1659723
b_3	0.2960173	0.0796297	0.1589192	c_3	−0.187800	−0.3499176	−0.4467541
			$0 \leqslant x_d < 0.03$				
B_{H_2O}	323.1040	317.0865	290.8844	C_{H_2O}	0.1463000	0.1401447	0.1327405
b_1^*	10277.3473	23454.68	3718.0286	c_1^*	2.528773	7.834683	0.0323181
b_2^*	−374446.62	−306873.7	−1621.05	c_2^*	−78.88660	−7.32207	107.53083
b_3^*	3563357	−5094175	−2680519	c_3^*	351.8322	−4264.39	−3051.011

seventh and eighth columns in Tables II–IV. Compared to the Tait equation with the original parameters in the same table, the deviations become about 10 times larger on the average but are still sufficiently within the stated experimental uncertainties of ±0.2%.

The density of pure 1,4-dioxane obtained at 298 K and at atmospheric pressure agrees with the literature values, i.e., 0.004 and 0.013% lower than those of Sakurai [13] and Inglese et al. [14], and 0.009 and 0.084% higher than those of Rao and Reddy [15] and Papanastasiou et al. [16], respectively. For mixtures, the present results at 298 K and at atmospheric pressure agree with those of Sakurai [13] within 0.06% in the entire range of composition. No reference data at high pressure are available.

3.2. Composition Dependences of Volumetric Properties

To obtain the basic information which is important to examine solute–solvent and solute–solute interaction, the composition dependences of some volumetric properties were determined at various pressures in terms of the smoothed parameters of the Tait equation given in Tables V and VI. The excess molar volume obtained at 298 K is shown in Fig. 1. As is evident from this figure, the excess molar volume is negative over most of the composition range and the isobar shifts to the positive direction with increasing pressure. But the curvatures of the isobars are convex at higher concentrations of 1,4-dioxane and the isobars at 20 and 40 MPa show slightly positive values of excess molar volume at the very high composition range. The excess molar volumes at 323 and 348 K show the same tendency as those at 298 K and the inversion to the positive value at higher pressure and at higher concentration is more definite than at 298 K. The similar S-shaped curves of excess molar volume and the pressure dependence have been reported in the previous work for the aqueous solutions of some fluoroalcohols. [6]. Gotze and Schneider have measured the excess molar volumes of some binary aqueous nonelectrolyte mixtures at high pressures, up to 250 MPa [17], and reported a similar S-shaped curve for acetonitrile and water mixtures. They also reported the inversion of the excess molar volume from a negative to a positive value with increasing pressure for two aqueous solutions of acetonitrile and pyridine.

The partial molar volumes of 1,4-dioxane, $\tilde{V}_d$, and of water, $\tilde{V}_{H_2O}$, defined by the following equations, are roughly determined over the whole composition range by use of the smoothed parameters of the Tait equation:

$$\tilde{V}_d = V + (1 - x_d)\left(\frac{\partial V}{\partial x_d}\right)_{T,P} \tag{8}$$

$$\tilde{V}_{H_2O} = V - x_d\left(\frac{\partial V}{\partial x_d}\right)_{T,P} \tag{9}$$

Results for the partial molar volume of 1,4-dioxane at 298 K are shown in Fig. 2. One of the interesting peculiarities in this figure is the existence of broad maxima around 0.85 mole fraction, which corresponds to the rather deep minima of the partial molar volume of water, $\tilde{V}_{H_2O}$, according to the Gibbs–Duhem relation. The concentration at which these extrema are observed shifts slightly to a lower concentration of 1,4-dioxane as the pressure increases. In a series of investigations by Sakurai [18–20], similar extrema were also reported in the solute-rich region for the some other aqueous solutions, such as t-butyl alcohol, acetonitrile, and ethylene glycol. The pressure dependence of the infinite dilution value of the partial molar volume of water, $\tilde{V}^{\infty}_{H_2O}$, occasionally becomes the object of discussion. Although an accurate determination of $\tilde{V}^{\infty}_{H_2O}$ from the present experimental data is impossible because of the rough mole fraction intervals in the higher concentration range, we have made a rough estimate of it by using the smoothed parameters of the Tait equation. A ratio of $\tilde{V}^{\infty}_{H_2O}$ at 40 MPa to that at atmospheric pressure is 1.03 ± 0.01, independent of the temperature, and a definite increase in $\tilde{V}^{\infty}_{H_2O}$ with increasing pressure was observed. This paradoxical pressure dependence of $\tilde{V}^{\infty}_{H_2O}$ has been observed not only for the present mixture but also for some other mixtures [21], i.e., aqueous solutions of ethanol, acetic acid, acetone, and pyridine. For ethanol and water mixtures, Hamann [21] recently gave a qualitative description of this unusual pressure dependence based on the electrostatic theory of

Kirkwood [22]. This theory suggests that the positive value of the pressure coefficient of $\tilde{V}^{\infty}_{H_2O}$ is due to the positive trend of the electrostrictive part of the partial molar volume, $\tilde{V}^{el}_{H_2O}$, with increasing pressure. According to Hamann, in fact, $\tilde{V}^{el}_{H_2O}$ in ethanol changes from -2.93 to $-1.95 cm^3 \cdot mol^{-1}$ as the pressure increases from 0.1 to 50.7 MPa. This positive trend with increasing pressure seems to indicate the validity of this theory. But the application of this theory requires accurate experimental data for the dielectic constant at high pressures and we have not tried to apply this theory to the present 1,4-dioxane and water mixture.

For some kinds of aqueous solutions, the partial molar volume indicates another peculiar behavior in the water-rich region. For aqueous solutions of hydrocarbon alcohols, for intance, it is well-known that there exist sharp minima in the partial molar volume of alcohol at dilute alcohol concentration and these minima occur at lower mole fractions and become deeper according to the alkyl chain length of alcohol. For 1,4-dioxane and water mixtures no minimum is observed in Fig. 2. But the minima may be very shallow and very accurate measurements as a function of the composition and a careful correlation are required to examine the existence of the minima. Therefore, we have collected additional density data in the mole fraction range of 1,4-dioxane lower than 0.12899 using a more precise vibrating-tube densitometer, DMA602. Those additional measurements were performed only at 298 K and at atmospheric pressure. The densities obtained are given in Table VII and the excess molar volumes are

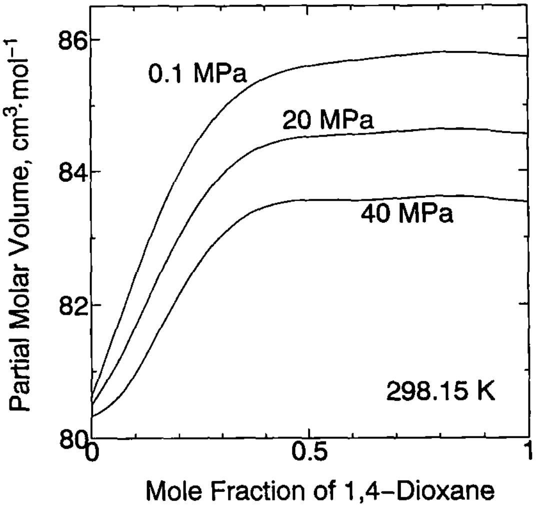

Fig. 2. Partial molar volume of 1,4-dioxane at 298 K and at various pressures.

Table VII. Density and Excess Molar Volume at 298.15 K and at Atmospheric Pressure

x_d	ρ_0 ($kg \cdot m^{-3}$)	V_0^E ($cm^3 \cdot mol^{-1}$)
0.00099	997.40	−0.003822
0.00207	997.85	−0.009189
0.00326	998.36	−0.015536
0.00385	998.58	−0.017985
0.00399	998.66	−0.019204
0.00548	999.19	−0.025177
0.00596	999.37	−0.027169
0.00677	999.69	−0.031115
0.00816	1000.28	−0.038697
0.00888	1000.58	−0.042656
0.01003	1000.92	−0.046192
0.01278	1002.03	−0.060650
0.01657	1003.44	−0.078830
0.02010	1004.79	−0.097014
0.02321	1005.80	−0.110145
0.02625	1006.81	−0.123703
0.03026	1008.34	−0.146148
0.03491	1009.92	−0.169328
0.03975	1011.45	−0.191969
0.04514	1013.01	−0.215443
0.05035	1014.51	−0.238910
0.06045	1017.21	−0.282749
0.07037	1019.60	−0.323100
0.08027	1021.82	−0.362794
0.09002	1023.66	−0.396464
0.09998	1025.43	−0.430417
0.12899	1029.57	−0.516353

correlated satisfactorily with the mole fraction by the following simple polynomial equation:

$$V^E = \sum_{i=1}^{5} a_i x_d^i \qquad (10)$$

$$a_1 = -4.544424$$

$$a_2 = -18.84243$$

$$a_3 = 400.7441$$

$$a_4 = -2442.434$$

$$a_5 = 5584.867$$

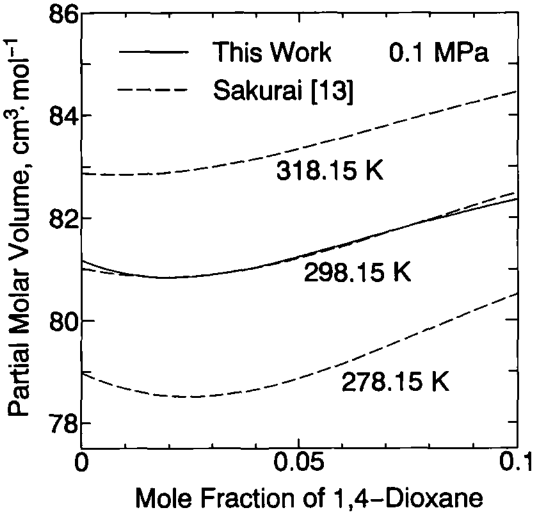

Fig. 3. Partial molar volume of 1,4-dioxane in the lower concentration range.

The partial molar volume of 1,4-dioxane, which is precisely redetermined by Eq. (10), is illustrated in Fig. 3 together with the reliable referenced data of Sakurai [13]. The agreement with the reference is excellent and the existence of the minimum is confirmed. Sakurai stated that the aqueous solutions of more hydrophilic solutes such as ethylene glycol or acetonitrile and the small minimum observed in the present work might occur for the same reason. The infinite dilution value of the partial molar volume of 1,4-dioxane, $\tilde{V}^{\infty}_{H_2O}$, determined by Eq. (10) is 81.1791cm^3 · mol^{-1}, which is also in good agreement with the references, i.e., only 0.17, 0.27, and 0.29% higher than those of Sakurai [13], Cabani et al. [23], and Kiyohara et al. [24], respectively.

The isothermal compressibilities of the present mixtures, β_T, in MPa^{-1} defined by the following equation are also determined in terms of the smoothed parameters of the Tait equation:

$$\beta_T = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \left(1 - C\ln\frac{B+P}{B+0.1}\right)^{-1}\frac{C}{B+P} \qquad (11)$$

The results at 298 K are given in Fig. 4. The isothermal compressibility at a given pressure increases with the mole fraction of 1,4-dioxane, but the distinct minima are observed at low concentrations, around 0.05 mole fraction. The depth of these minima becomes smaller and the concentration where the minima are observed gradually shifts to a higher concentration

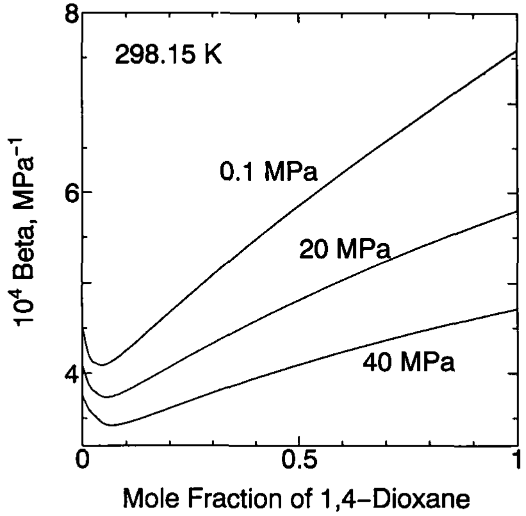

Fig. 4. Isothermal compressibilities of 1,4-dioxane and water mixtures at 298 K as a function of the mole fraction of 1,4-dioxane.

with increasing pressure. Similar results are obtained at 323 and 348 K. It is also found that the isothermal compressibility increases and the depth of the minimum becomes smaller as the temperature increases. A similar minimum behavior has been observed for a series of aqueous solutions of primary hydrocarbon alcohols and fluoroalcohols in previous work [6, 12].

4. CONCLUSION

New experimental density data have been presented for aqueous solutions of 1,4-dioxane. The measurements were performed at temperatures from 298 to 323 K and at pressures up to 40 MPa with two vibrating-tube densitometers. Molar volumes obtained for the present mixtures were correlated with the pressure by the Tait equation within an experimental uncertainty of $\pm 0.2\%$ and the excess molar volumes, partial molar volumes, and isothermal compressibilities of sample mixtures were determined based on this correlating equation. It is found that the infinite dilution value of the partial molar volume of water increases slightly with increasing pressure. At 298 K the existence of a very shallow minimum in the partial molar volume of 1,4-dioxane is also confirmed. The isothermal compressibility of the present mixture indicates the distinct minima at low concentrations as in the cases of the aqueous solution of hydrocarbon alcohols.

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