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Isochoric Heat Capacities of Alkanols and Their Aqueous Mixtures[†]

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Isochoric heat capacities (c_v) of methanol, ethanol, and 1-propanol and binary mixtures of water with each of these alkanols were measured in the temperature range from 280 to 420 K and at pressures up to 30 MPa. The measurements were carried out on liquid-phase samples with a twin-cell type adiabatic calorimeter. Liquid densities were also reported in this work on the basis of the mass of the sample and the volume of the calorimetric cell. The experimental expanded uncertainty (with a coverage factor k = 2) of temperature measurements is ±13 mK, and that of pressure measurements is ±8 kPa. The expanded relative uncertainty for isochoric heat capacity is estimated to be ±2.2% for the liquid-phase measurements, and for density it is ±0.16%. The behavior of c_v is anomolous, indicating that alkanol + water mixtures are strongly associated due to the influence of hydrogen bonds.

Introduction

It is well-known that alkanols and water are highly polar substances that associate by hydrogen bonding in solution. Due to the presence of a strong hydrogen bond, interactions between water and alkanol molecules can lead to anomalous behavior of thermodynamic properties. Measurements of thermodynamic properties are essential to characterize such interactions and to accurately model this behavior.

To develop a reliable equation of state for a fluid, various thermodynamic property measurements of the fluid are required. Among them, isochoric specific heat capacity measurements provide a very useful check for calculations of the second derivative of the pressure with respect to temperature, which is essential information to calculate caloric properties but is challenging to measure accurately.

In the compressed liquid phase, measurements of c_v have been reported for methanol (CH_3OH) and ethanol (C_2H_5OH),[1] for $CH_3OH + H_2O$ mixtures,[2,3] and for $C_2H_5OH + H_2O$ mixtures.[4]

In this paper, the presented measurements were obtained at temperatures from 280 to 420 K and at pressures up to 30 MPa for c_v and pressure−volume−temperature−composition ($pvTx$) properties of the C_1 to C_3 alkanols CH_3OH, C_2H_5OH, and propanol (1-C_3H_7OH) and their aqueous mixtures.

Experimental Section

Materials. High-purity samples of H_2O, CH_3OH, C_2H_5OH, and 1-C_3H_7OH were obtained to prepare the binary mixtures. The H_2O sample was twice-distilled and has a minimum purity of 0.9999 mass fraction. For the CH_3OH samples, the commercial supplier claimed a minimum liquid purity of 0.998 mass fraction. For the C_2H_5OH sample, the commercial supplier claimed a minimum liquid purity of 0.995 volume fraction with less than 0.04 volume fraction of H_2O. The measured moisture content in the sample is 0.008 volume fraction, which was analyzed with a Karl Fischer titrator, which leads to a claim that the actual purity of our C_2H_5OH sample is 0.998 volume fraction. The 1-C_3H_7OH samples have a certified minimum liquid purity of 0.995 volume fraction. The alkanol samples were carefully degassed three or four cycles before they were used. The binary mixtures were prepared by mass, and the resulting mole fraction compositions were calculated by using the molecular masses of the components.

Measurements. The calorimeter used in these experiments, and experimental procedures have been described previously in detail.[1,5] The calorimeter is a twin-cell type whose sample and reference cells ($V_{\text{cell}} = 33\ \text{cm}^3$) and their adiabatic shields are heated by electric power. The cells are surrounded by a high vacuum. During the experiment, the heating power was carefully controlled so that the cell temperature increased uniformly. The reference cell was always evacuated and was heated with a constant current. The temperature of the sample cell tracked that of the reference cell by means of an automatic control system. Temperatures were measured with a platinum resistance thermometer (PRT) on the bottom of each cell and were reported on the ITS-90 scale. Sample pressure measurements were made with a quartz crystal transducer. Densities were calculated from the volume of the calorimeter cell and sample mass. The heater wires are capable of reaching 470 K. The reliability of the apparatus was confirmed by comparing our experimental data for distilled H_2O with a published reliable equation of state (EOS) published by Wagner and Pruss.[6] Since the measured c_v of H_2O coincided with the EOS within ±1%, these test results were considered satisfactory.

For the heat capacity measurement, a precisely determined electrical energy (Q) is applied and the resulting temperature rise ($\Delta T = T_2 - T_1$) is measured. The c_v is obtained from

$$c_v = \left(\frac{\partial U}{\partial T}\right)_V \cong \frac{\alpha(\Delta Q - \Delta Q_0) - W_{PV}}{m\Delta T} \tag{1}$$

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Table 1. Experimental c_v and PvT Properties for the xCH$_3$OH + (1 − x)H$_2$O Mixture

T K	p MPa	ρ g·cm^{-3}	c_v J·g^{-1}·K^{-1}	T K	p MPa	ρ g·cm^{-3}	c_v J·g^{-1}·K^{-1}
			$x = 0.059$				
350.15	13.660	0.9656	3.899	385.15	10.606	0.9372	3.740
355.15	19.904	0.9650	3.864	390.15	17.692	0.9366	3.670
360.15	26.338	0.9644	3.799	395.15	24.873	0.9360	3.620
365.15	5.602	0.9518	3.854	400.15	5.808	0.9190	3.668
370.15	12.205	0.9512	3.780	405.15	13.034	0.9184	3.617
375.15	18.936	0.9506	3.720	410.15	20.328	0.9178	3.581
380.15	25.821	0.9500	3.695	415.15	27.681	0.9173	3.545
			$x = 0.352$				
290.15	6.968	0.9336	3.485	360.15	29.375	0.8961	3.490
295.15	11.962	0.9332	3.498	365.15	15.637	0.8844	3.502
300.15	17.905	0.9327	3.507	370.15	22.394	0.8838	3.471
305.15	23.971	0.9323	3.520	380.15	14.106	0.8698	3.454
310.15	7.400	0.9222	3.552	385.15	20.802	0.8693	3.457
315.15	13.630	0.9218	3.545	390.15	27.539	0.8688	3.432
320.15	19.961	0.9213	3.550	390.15	8.856	0.8567	3.476
325.15	26.388	0.9208	3.557	395.15	15.432	0.8562	3.441
335.15	16.237	0.9090	3.539	400.15	22.041	0.8557	3.420
340.15	22.854	0.9085	3.532	405.15	28.682	0.8552	3.366
345.15	29.545	0.9079	3.510	410.15	17.590	0.8424	3.426
350.15	15.977	0.8971	3.521	415.15	24.082	0.8419	3.383
			$x = 0.502$				
290.15	12.286	0.8838	2.919	350.15	26.146	0.8510	3.205
295.15	18.228	0.8833	2.935	355.15	8.187	0.8349	3.246
300.15	24.362	0.8828	2.973	360.15	13.921	0.8344	3.235
340.15	14.622	0.8520	3.205	365.15	19.649	0.8340	3.244
345.15	20.393	0.8515	3.205	370.15	25.365	0.8335	3.219
			$x = 0.708$				
320.15	7.082	0.8190	2.807	370.15	13.094	0.7859	2.929
325.15	12.187	0.8186	2.801	375.15	17.936	0.7855	2.952
330.15	17.420	0.8182	2.805	380.15	22.827	0.7851	2.953
335.15	22.708	0.8177	2.811	385.15	27.757	0.7847	2.967
340.15	28.044	0.8173	2.826	390.15	11.638	0.7637	3.017
345.15	10.073	0.8072	2.851	395.15	16.251	0.7633	2.983
350.15	15.074	0.8068	2.860	400.15	20.918	0.7629	2.993
355.15	20.145	0.8063	2.883	405.15	25.628	0.7625	2.970
360.15	25.267	0.8059	2.878				

Table 2. Experimental c_v and PvT Properties for the x1-C$_3$H$_7$OH + (1 − x)H$_2$O Mixture

T K	p MPa	ρ g·cm^{-3}	c_v J·g^{-1}·K^{-1}	T K	p MPa	ρ g·cm^{-3}	c_v J·g^{-1}·K^{-1}
			$x = 0.255$				
290.15	10.897	0.8958	3.414	355.15	15.208	0.8521	3.505
295.15	16.682	0.8954	3.407	360.15	21.108	0.8517	3.496
300.15	22.460	0.8949	3.399	365.15	27.010	0.8512	3.497
305.15	28.282	0.8945	3.444	370.15	10.693	0.8366	3.505
310.15	10.047	0.8820	3.455	375.15	16.511	0.8361	3.480
315.15	16.079	0.8815	3.464	380.15	22.403	0.8357	3.455
320.15	22.115	0.8810	3.461	390.15	13.229	0.8201	3.416
325.15	28.173	0.8805	3.460	395.15	18.905	0.8196	3.372
330.15	10.031	0.8673	3.490	400.15	24.635	0.8192	3.358
335.15	15.914	0.8668	3.488	405.15	8.162	0.8009	3.419
340.15	21.805	0.8663	3.491	410.15	13.554	0.8005	3.410
345.15	27.639	0.8659	3.482	415.15	19.000	0.8000	3.370
350.15	9.377	0.8526	3.526	420.15	24.509	0.7996	3.298
			$x = 0.510$				
285.15	9.096	0.8700	2.842	355.15	14.697	0.8205	3.182
290.15	14.544	0.8696	2.869	360.15	20.078	0.8200	3.193
295.15	19.855	0.8691	2.893	365.15	25.522	0.8196	3.187
300.15	25.023	0.8687	2.920	370.15	8.880	0.8022	3.257
310.15	11.470	0.8547	2.974	375.15	14.029	0.8017	3.242
315.15	17.068	0.8543	2.987	380.15	19.230	0.8013	3.229
320.15	22.715	0.8538	3.014	385.15	24.479	0.8009	3.229
325.15	28.417	0.8533	3.027	400.15	17.097	0.7809	3.221
330.15	10.413	0.8386	3.106	405.15	21.945	0.7805	3.188
335.15	15.890	0.8381	3.107	410.15	26.795	0.7801	3.176
340.15	21.427	0.8376	3.128	420.15	13.582	0.7559	3.198
345.15	27.022	0.8372	3.148	425.15	18.164	0.7555	3.207
			$x = 0.738$				
285.15	9.401	0.8385	2.304	345.15	26.709	0.8020	2.726
290.15	14.933	0.8380	2.329	350.15	9.813	0.7840	2.778
295.15	20.482	0.8375	2.372	355.15	14.510	0.7836	2.783
300.15	26.045	0.8371	2.394	360.15	19.248	0.7832	2.809
305.15	8.424	0.8218	2.473	375.15	9.622	0.7600	2.903
310.15	13.658	0.8214	2.504	380.15	14.016	0.7596	2.898
315.15	18.912	0.8209	2.564	400.15	9.277	0.7332	2.985
320.15	24.190	0.8205	2.559	405.15	13.330	0.7329	2.969
325.15	29.499	0.8201	2.588	410.15	17.420	0.7325	3.002
330.15	11.698	0.8033	2.651	415.15	21.545	0.7321	2.964
335.15	16.667	0.8029	2.675	420.15	25.700	0.7318	2.979
340.15	21.672	0.8025	2.708	425.15	29.883	0.7314	2.968
			$x = 1.000$ (1-Propanol)				
315.15	5.217	0.7898	2.180	370.15	26.008	0.7630	2.601
320.15	9.526	0.7894	2.224	375.15	5.118	0.7365	2.704
325.15	13.871	0.7890	2.269	380.15	8.887	0.7361	2.723
330.15	18.193	0.7886	2.308	385.15	12.702	0.7357	2.737
335.15	22.585	0.7881	2.354	390.15	16.562	0.7353	2.733
340.15	27.006	0.7877	2.392	395.15	20.459	0.7350	2.735
345.15	5.478	0.7649	2.485	400.15	24.395	0.7346	2.729
350.15	9.514	0.7645	2.509	405.15	28.362	0.7342	2.714
355.15	13.587	0.7641	2.524	415.15	10.841	0.7015	2.892
360.15	17.670	0.7638	2.585	420.15	14.316	0.7012	2.871
365.15	21.811	0.7634	2.586	430.15	21.353	0.7005	2.863

where U is the internal energy, ΔQ_0 is the electric power difference between the sample cell heater and the reference cell heater when both cells are empty, ΔQ refers to the electric power added during an experiment with a sample in the sample cell and a blank (vacuum) in the reference cell, W_{PV} is the change-of-volume work due to the slight dilation of the cell, α is the coefficient of the available electrical energy supplied to the cell heater,[1,7] and m is the mass of sample in the sample cell.

In the first measurement of each substance, the sample cell was charged with the sample and was cooled to a starting temperature below room temperature. Then, measurements were performed with increasing temperature until the pressure limit (30 MPa) was attained along isochores. At the completion of a run, a portion of the sample in the cell was cryopumped into a lightweight cylinder. The next run was started with a lower density. When the runs were completed, the remaining sample in the cell was discharged and weighted. The sample mass of each run was determined from the sum of the mass increments for that run.

Assessment of Uncertainties. The experimental expanded uncertainty (with a coverage factor $k = 2$) of the absolute temperature measurement is ±13 mK, by considering the calibration report of the PRTs (±2 mK), the temperature distribution on the cell walls, and the accuracy of the instruments. That of the pressure measurement is ±8 kPa, based on the pressure transducer's specifications and the accuracy of the instruments. The estimated expanded uncertainty of density is ±0.16%, from the standard uncertainty of the inner cell volume and the mass measurement. The expanded uncertainty of the sample mole fraction composition is ±0.1%. The expanded uncertainty of c_v is estimated from a combination of the standard uncertainty of the elapsed time required for a 1 K temperature rise (0.65%), that of the change-of-volume work (20%) that contributes 0.3% to the uncertainty in c_v, the experimental standard deviation of α of 0.6%, the uncertainty of the density, and the temperature fluctuation of the adiabatic shields, which contributes $0.4/m$ J·g^{-1}·K^{-1} to the uncertainty in c_v. The resulting expanded uncertainty of c_v is ±2.2% for the liquid-phase measurements of this work.

Results

Measurements with this calorimeter for (CH$_3$OH and C$_2$H$_5$OH)[1] and C$_2$H$_5$OH + H$_2$O mixtures[4] have been reported previously. In this work, new experimental results for c_v and $pvTx$ information are reported at temperatures spaced by 5 K for xCH$_3$OH + (1 − x)H$_2$O mixtures (Table 1) and for x1-C$_3$H$_7$OH + (1 − x)H$_2$O mixtures (Table 2).

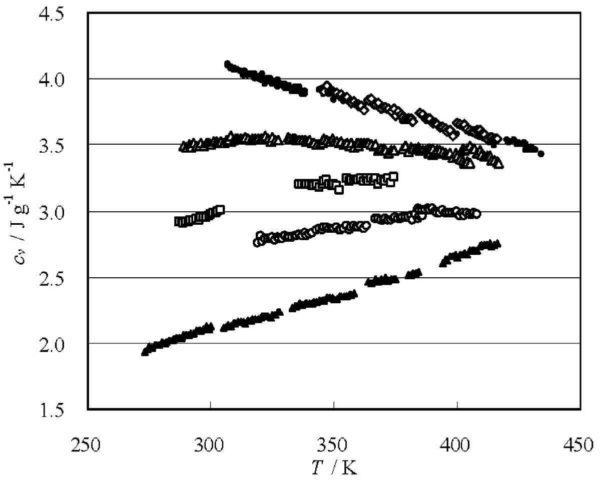

Figure 1. Isochoric heat capacities for $\{x\mathrm{CH_3OH} + (1 - x)\mathrm{H_2O}\}$: ◇, this work ($x = 0.059$); △, this work ($x = 0.352$); □, this work ($x = 0.502$); ○, this work ($x = 0.708$); ▲, Kitajima et al.[1] ($\mathrm{CH_3OH}$); ●, Kitajima et al.[1] ($\mathrm{H_2O}$).

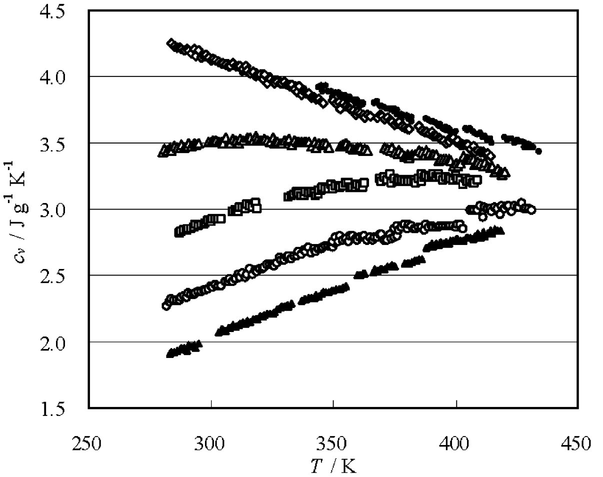

Figure 2. Isochoric heat capacities for $\{x\mathrm{C_2H_5OH} + (1 - x)\mathrm{H_2O}\}$: ◇, Kitajima et al.[4] ($x = 0.104$); △, Kitajima et al.[4] ($x = 0.253$); □, Kitajima et al.[4] ($x = 0.498$); ○, Kitajima et al.[4] ($x = 0.755$); ▲, Kitajima et al.[1] ($\mathrm{C_2H_5OH}$); ●, Kitajima et al.[1] ($\mathrm{H_2O}$).

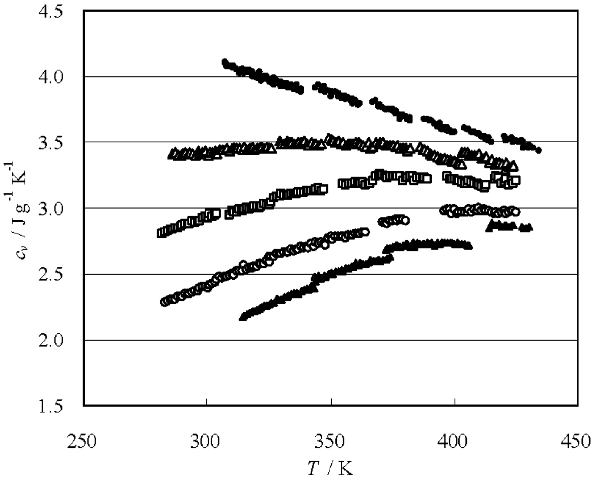

Figure 3. Isochoric heat capacities for $\{x\text{1-}\mathrm{C_3H_7OH} + (1 - x)\mathrm{H_2O}\}$: △, this work ($x = 0.255$); □, this work ($x = 0.510$); ○, this work ($x = 0.738$); ▲, this work (1-$\mathrm{C_3H_7OH}$); ●, Kitajima et al.[1] ($\mathrm{H_2O}$).

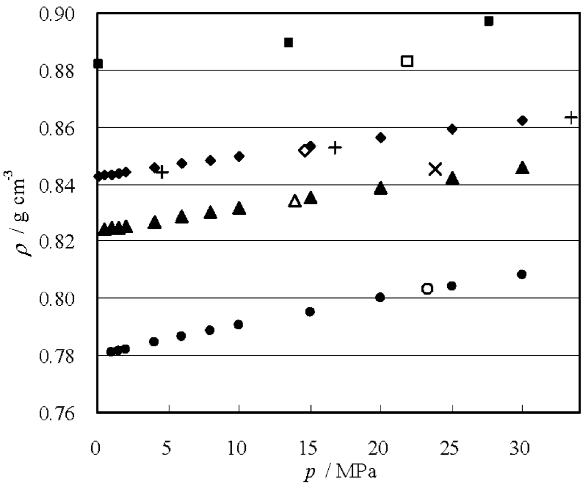

Figure 4. Distribution of densities for $\{x\mathrm{CH_3OH} + (1 - x)\mathrm{H_2O}\}$ on $x \cong 0.5$ at temperatures from 298 K to 400 K: □, this work (298.15 K); ◇, this work (340.15 K); ×, this work (348.15 K); △, this work (360.15 K); ○, this work (400.15 K); ■, Kubota et al.[9] (298.15 K); +, Kubota et al.[9] (348.15K); ◆, Osada et al.[10] (340 K); ▲, Osada et al.[10] (360 K); ●, Osada et al.[10] (400 K).

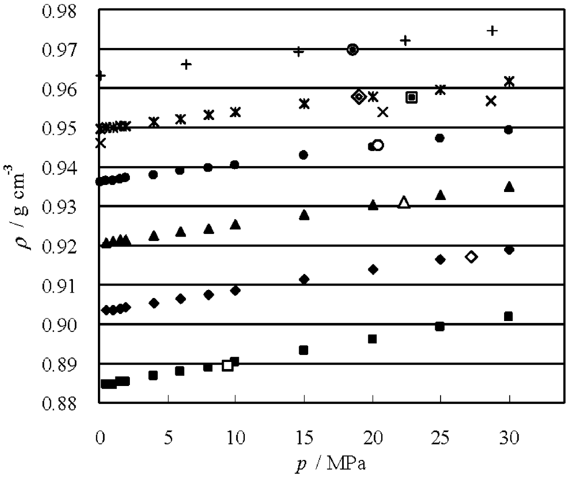

Figure 5. Distribution of densities for $\{x\mathrm{C_2H_5OH} + (1 - x)\mathrm{H_2O}\}$ on $x \cong 0.1$ at temperatures from 298 K to 400 K: ⊙, Kitajima et al.[4] (298.15 K); diamond in a diamond, Kitajima et al.[4] (320.15 K); solid box in an open box, Kitajima et al.[4] (323.15 K); ○, Kitajima et al.[4] (340.15 K); △, Kitajima et al.[4] (360.15 K); ◇, Kitajima et al.[4] (380.15 K); □, Kitajima et al.[4] (400.15 K); ∗, Takiguchi et al.[11] (320 K); ●, Takiguchi et al.[11] (340 K); ◆, Takiguchi et al.[11] (360 K); ▲, Takiguchi et al.[11] (380 K); ■, Takiguchi et al.[11] (400 K); +, Tanaka et al.[12] (298.15 K); ×, Tanaka et al.[12] (323.15 K).

Figures 1−3 show c_v measurements for the alkanol + water mixtures considered, including those data presented in earlier work. Comparison of Figures 1−3 reveals a remarkable similarity in the behavior of the temperature dependence of the heat capacity on the isochores. We find that the slope of these plots $(\partial c_v/\partial T)_\rho$ is positive for each of the alkanols but is negative for water, and changes smoothly from one to the other as the mixture composition is changed. Also, for a given composition, we note that the slope $(\partial c_v/\partial T)_\rho$ is nearly a constant for a given sample composition, which gives the appearance that all heat capacities for a constant composition could be adequately represented with a single line. Because of this behavior, a single composition exists for each binary mixture that exhibits a slope $(\partial c_v/\partial T)_\rho \approx 0$ in the temperature and pressure range of this work. The anomalous temperature dependence for these mixtures indicates that a cancellation of two competing contributions is the probable cause in all three cases. The present measurements of 1-propanol show similar behavior to that of ref 8.

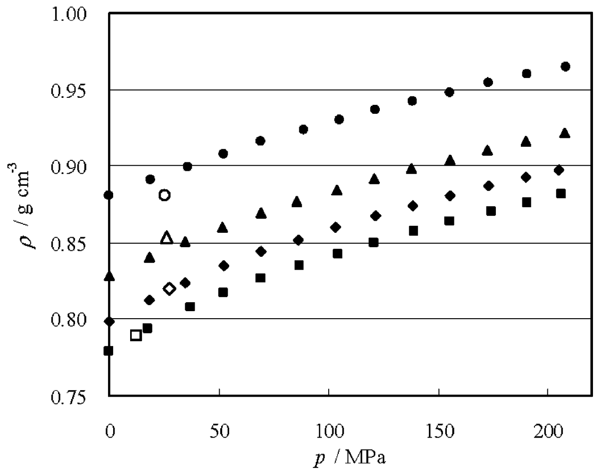

Figure 6. Distribution of densities for $\{x\text{1-C}_3H_7OH + (1 - x)H_2O\}$ at 323.15 K: ○, this work ($x = 0.255$); △, this work ($x = 0.510$); ◇, this work ($x = 0.738$); □, this work (1-C_3H_7OH); ●, Kubota[9] ($x = 0.25$); ◆, Kubota et al.[9] ($x = 0.50$); ▲, Kubota et al.[9] ($x = 0.75$); ■, Kubota et al.[9] (1-C_3H_7OH).

Figures 4 and 5 show comparisons of *pvTx* measurements with published data for the alkanol + water mixtures. Figure 4 shows a $p-\rho$ diagram for the $xCH_3OH + (1 - x)H_2O$ mixtures at a near equimolar composition ($x \cong 0.5$) for temperatures from 298 to 400 K. The present measurements are lower than those of Kubota et al.[9] by about 1.4% but agree well with those of Osada et al.[10] Figure 5 shows a $p-\rho$ diagram for $xC_2H_5OH + (1 - x)H_2O$ mixtures for a composition near $x \cong 0.1$ at temperatures from 298 to 400 K. The present measurements agree with those of Takiguchi et al.[11] and Tanaka et al.[12] within ±0.1%, except for measurements at 323 K. Figure 6 shows a $p-\rho$ diagram for $x\text{1-C}_3H_7OH + (1 - x)H_2O$ mixtures at a temperature of 323 K for propanol and three mixtures. The differences between the present measurements and those of Kubota et al.[9] are typically ±0.1% for 1-C_3H_7OH, +0.17% for $x = 0.738$, +1.0% for $x = 0.510$, and −1.6% for $x = 0.255$.

Acknowledgment

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Supporting Information Available:

Tables showing a full report of all compositions, temperatures, pressures, densities, and heat capacities that were measured with the calorimeter as part of this project. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Kitajima, H.; Kagawa, N.; Tsuruno, S.; Endo, H. Endo Measurement of Isochoric Specific Heat Capacity for Pure Alcohol with Adiabatic Twin-Cell Calorimeter (in Japanese). *Trans. Jpn. Soc. Mech. Eng., Ser. B* **2003**, *69*, 1921−1927.

(2) Abdulagatov, I. M.; Dvoryanchikov, V. I.; Aliev, M. M.; Kamalov, A. N. Isochoric Heat Capacity of a 0.5 Water and 0.5 Methanol Mixture at Subcritical and Supercritical Conditions. In *Steam, Water, and Hydrothermal Systems*: *Physics and Chemistry Meeting the Needs of Industry*; *Proceedings of the 13th International Conference on the Properties of Water and Steam*; Tremaine, P. R., Hill, P. G., Irish, D. E., Balakrishnan, P. V., Eds.; NRC Press: Ottawa, 2000.

(3) Kitajima, H.; Miyamoto, H.; Kagawa, N.; Magee, J. W.; Endo, H.; Tsruno, S.; Watanabe, K. Study on Isochoric Specific Heat Capacities for Liquid Methanol−Water Mixtures. *Proc. Jpn. Symp. Thermophys. Prop.* **2002**, *23*, 184−186.

(4) Kitajima, H.; Kagawa, N.; Endo, H.; Tsuruno, S.; Magee, J. W. Isochoric Heat Capacities of Ethanol−Water Mixtures at Temperatures from 280 K to 420 K and Pressures to 30 MPa. *Trans. Jpn. Soc. Refrig. Air Cond. Eng.* **2003**, *20*, 239−248.

(5) Kuroki, T.; Kagawa, N.; Endo, H.; Tsuruno, S.; Magee, J. W. *J. Chem. Eng. Data* **2001**, *46*, 1101−1106.

(6) Wagner, W.; Pruss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387−535.

(7) Kitajima, H.; Kagawa, N.; Tsuruno, S.; Magee, J. W.; Watanabe, K. Isochoric Heat Capacities of Propane + Isobutane Mixtures at Temperatures from 280 K to 420 K and Pressures to 30 MPa. *Proc. 15th Symp. Thermophys. Prop.* (CD-ROM), Boulder, CO, June 22−27, 2003.

(8) Amirkanov, K. I.; Stepanov, G. V.; Abdulagatov, I. M.; Byoi, O. A. *Isochoric Heat Capacity of Propan-1-ol and Propan-2-ol*; Sychev, V. V., Ed.; Dagestan Scientific Center of the Russian Academy of Sciences: Makhachkla, 1989.

(9) Kubota, H.; Tanaka, Y.; Makita, T. Volumetric Behavior of Pure Alcohols and Their Water Mixtures Under High Pressure. *Int. J. Thermophys.* **1987**, *8*, 47−70.

(10) Osada, O.; Sato, M.; Uematsu, M. Thermodynamic properties of $\{xCH_3OH + (1\text{-}x)H_2O\}$ with $x = (1.0000$ and $0.4993)$ in the temperature range from 320 K to 420 K at pressures up to 200 MPa. *J. Chem. Thermodyn.* **1999**, *31*, 451−464.

(11) Takiguchi, Y.; Osada, O.; Uematsu, M. Thermodynamic properties of {xC2H5OH + (1-x)H2O} in the temperature range from 320 K to 420 K at pressures up to 200 MPa. *J. Chem. Thermodyn.* **1996**, *28*, 1375−1385.

(12) Tanaka, Y.; Yamamoto, T.; Satomi, Y.; Kubota, H.; Makita, T. Specific Volume and Viscosity of Ethnaol-Water Mixtures under High Pressure. *Rev. Phys. Chem. Jpn.* **1997**, *47*, 12−24.

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