

Specific Heat Capacity at Constant Volume for Water, Methanol and their Mixtures at
Temperatures from 300 to 400 K and Pressures to 20 MPa

Takahiro Kuroki, Noboru Kagawa^{*}, Harumi Endo, Seizou Tsuruno,
and Joseph W. Magee^a

National Defense Academy, Yokosuka 239-0811, Japan

*To whom correspondence should be addressed.

(e-mail: kagawa@cc.nda.ac.jp, FAX: +81-468-44-5900)

^a Permanent address: Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, Colorado 80303-3328, U.S.A.

Abstract

Specific heat capacities at constant volume (c_v) of water, methanol and their mixtures were measured with a new adiabatic calorimeter. Temperatures ranged from 300 K to 400 K, and pressures ranged to 20 MPa. Densities were determined at the initial and final end points during each calorimetric experiment. The calorimeter is a twin-cell type whose sample and reference cells (33 cm³) and their 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 temperature by means an automatic control system. Automated sample pressure measurements were made with a crystal quartz transducer. The expanded relative uncertainty for c_v is estimated to be 1% for liquid phase measurements, and for density it is about 0.2%.

Introduction

In order to develop a reliable equation of state for a fluid, various thermodynamic property measurements of the fluid are required. Among them, isochoric 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 develop an accurate equation but is quite a challenge to measure accurately. Applying molecular theory, vibrational and orientational modes of molecules can account for the thermodynamic properties of a substance. When heating a substance, the increasing vibrational energy stored in molecules makes a strong contribution to the heat capacity. On the other hand, changes of molecular structure with temperature can also affect the magnitude of the heat capacity contribution which is dominated by orientational energy.

Hydrogen bonding of water (H_2O) is certain to introduce the effect of the molecular energy to the heat capacity. In fact, interactions between water and methanol (CH_3OH) molecules show anomalous thermodynamic properties due to the presence of strong hydrogen bonding.¹ There is considerable recent interest in studies of H_2O and $\text{H}_2\text{O} + \text{CH}_3\text{OH}$ mixtures in the supercritical and high density regions; for example, PVT_x properties,^{2,3} densities,⁴ excess molar heat capacity and excess molar enthalpies.⁵⁻⁷ However, published information on the isochoric heat capacity of the mixtures is very limited. Abdulagatov et al.⁸ measured the isochoric heat capacity of a 50 mass % $\text{H}_2\text{O}+50$ mass % CH_3OH mixture and their pure components in the temperature range from 435 to 645 K using a high-temperature adiabatic calorimeter.⁸

To measure heat capacity of fluids, various methods have been proposed.⁹ The most accurate methods are the adiabatic methods. In principle, heat exchange between the calorimeter and the surroundings does not occur in an adiabatic system; thus, the energy applied to the sample cell would be precisely the desired quantity to calculate the heat flow and heat capacity. In any actual instrument, however, the ideal adiabatic situation is very difficult to realize due to heat leakage by thermal conduction, convection, and thermal radiation. If heat leakage is considerable, it may be important to evaluate the amount of the

heat leakage accurately to correct the measured values. A small heat leakage is self-correcting if we use the twin calorimeter method in which there are two identical vessels (cells). One cell contains the sample to be measured and in the other is either a reference fluid or it may be empty. A novel twin-cell adiabatic calorimeter was developed^{10,11} in the NIST labs and was successfully used for measurements on H₂O and H₂O + NH₃ mixtures.^{11,12} In a recent development, a new twin-cell adiabatic calorimeter¹³ was built in Japan which traces its roots to the design of the NIST calorimeter, but features numerous improvements such as a smaller footprint and greater simplicity.

In this paper, heat capacities of H₂O, CH₃OH, and their mixtures are presented which were measured for liquid regions from 280 to 400 K with the new twin-cell adiabatic calorimeter. From the volume of the calorimeter cell and sample mass measurements, densities are calculated.

Experimental Section

Materials. High-purity samples of H₂O and CH₃OH were obtained to prepare the mixtures. The H₂O sample was twice-distilled and has a minimum purity of 0.9999 mass fraction. For the CH₃OH sample, the commercial supplier claimed a minimum liquid purity of 0.998 mass fraction with 0.001 mass fraction H₂O and 0.0005 mass fraction C₂H₇OH. The two mixtures of this study, shown in Table 1, were prepared in the calorimeter cell. A quantity of each pure component was filled into its own lightweight cylinder (75 cm³) and was accurately weighted with a 0.1 mg uncertainty. Each component of the mixture was introduced into the cell from its cylinder and then the cell was cooled below 278 K with a mini-cooler. The remaining mass in each cylinder was weighed and the composition of the sample in the cell was calculated from the masses charged to the cell. To ensure complete homogenization, the sample cell temperature was cyclically increased until the sample pressure reached the limit of 20 MPa. This process was repeated twice before the first measurement was started.

Measurements. A twin-cell adiabatic calorimeter,¹³ shown in Figure 1, was used for these measurements. A type-304 stainless steel spherical cell of 33 cm³ capacity was designed

for this apparatus. It has a maximum permissible pressure of 60 MPa at 800 K. A pair of these cells was made from stainless steel stock by spinning in a lathe to machine hemispheres within $\pm 5 \mu\text{m}$ tolerances, which were then welded together. On the bottom of each cell was brazed a type-304 stainless steel block with a hole drilled to accept a platinum resistance thermometer (PRT). Absolute temperatures are measured with the PRT's and are reported on the ITS-90. Sheath heaters, specially insulated and are capable of reaching 900 K in vacuum, were prepared for this apparatus. A 2 ohm heater was wound around each sphere with a pitch of about 5 mm. Small strips were attached to the cell surface to hold the heater wires in place.

A 6.4 mm outer diameter (OD) type-316 stainless steel tube was welded into a hole in the top of each sphere. A 1.735 mm inner diameter capillary, through which sample may be introduced to the cell, was welded into the 6.4 mm OD tube. A pair of type-K thermocouples sealed in a stainless steel sheath were brazed on each cell surface to read the temperature difference between each cell and its associated adiabatic shield, also made from type-304 stainless steel. Each cell was jacketed in a cylindrical adiabatic shield whose temperature is maintained by a 3 ohm sheath heater for the sides and a 0.8 ohm one for the top to keep it in equilibrium with the cell temperature. To control the temperature, two type-K thermocouples were brazed on each adiabatic shield side and one was brazed to each shield top. A pressure transducer using a precision quartz crystal resonator, attached to the charging manifold, provides pressure measurements to 68 MPa. Adiabatic conditions are ensured by each thermal radiation shield and by maintaining a high vacuum (approximately 1×10^{-4} Pa) in the vacuum vessel which surrounds both cell/adiabatic shield assemblies.

Each of the six heaters (cell, shield side, and shield top for each set) in the calorimeter is driven by a direct current power supply system. Two 4-channel 16-bit A/D converters control it. The entire instrument is connected to a personal computer (486DX) via an IEEE-488 standard interface bus. The computer has several functions of temperature control and data acquisition with an aid of a graphical programming language and a

specially developed program. The measurement and temperature-control tasks are executed every 30 seconds. During this time interval, the cell temperature would increase about 35 mK. The temperature difference between the cells is maintained within ± 3 mK during a measurement. Also, the system controls temperature differences between the cells and shield sides, and between the cells and shield tops within ± 10 mK.

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 isochoric specific heat capacity is obtained from

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

where U is the internal energy, ΔQ_0 is the energy difference between the sample cell, $Q_{0,\text{sam}}$ and reference cell, $Q_{0,\text{ref}}$ when the cells are empty, ΔQ refers to the energy 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, 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 upper pressure limit of 20 MPa was attained. 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 weighed. The sample mass of each run was determined from the sum of the mass increments for that run.

Uncertainties. The claimed uncertainty of the absolute temperature measurement is ± 10 mK, by considering the calibration report of the PRTs (± 2 mK), temperature distribution in the cell, and systematic accuracy of the instruments. Uncertainty of the temperature rise is ± 1.4 mK. Uncertainty of the pressure measurement is ± 7 kPa, based on the pressure transducer's specifications. The uncertainty of the change-of-volume work, which was

calculated¹⁴ with eq 2 below, may be determined from the experimental *PVT* data because the derivative of the pressure with respect to temperature can be estimated from the measured temperature rise and pressure difference.

$$W_{PV} = \left(T_2 \left(\frac{\partial P}{\partial T} \right)_{V_2} - \frac{1}{2} \Delta P \right) \Delta V \quad (2)$$

From the fluctuation of the experimental data, the estimated uncertainty of the change-of-volume work is $\pm 2\%$, which contributes $\pm 0.08\%$ to the uncertainty of specific heat capacity.

The energy applied to the cells is the product of the power (voltage \times current) and the time interval to heat from T_1 to T_2 . The measurements of the electrical quantities are exceptionally accurate and have an estimated uncertainty of $\pm 0.02\%$. A function of temperature was fitted to the energy difference ΔQ_0 applied to the empty cells; the observed fluctuation is less than $\pm 2.5 \text{ J}\cdot\text{K}^{-1}$ which leads to an uncertainty of $\pm 0.5\%$ in the specific heat capacity. The expanded uncertainty of specific heat capacity is estimated to be $\pm 1\%$ by combining the various sources of experimental uncertainty.

Blank tests. The empty calorimeter function was determined from heating the evacuated cells. Heating experiments covering a temperature range from 280 to 400 K were repeated before each series. The energy data in unit of Joules are shown in Figure 2. An equation in the temperature was fit to the data; most data agreed with eq 3 within $\pm 0.25 \text{ J}$.

$$\Delta Q_0 = 8.6260 \times 10^{-4} T - 0.070299 \quad (3)$$

Heat Capacity and Density Results

The isochoric specific heat capacity data, c_v of each run (start and end points, and every 5 K) are shown in Table 2. The densities ρ were calculated from the measured sample mass and the calibrated cell volume at the measured temperatures and the pressures. As shown in eq 4, the calibrated cell volume, V_{cell} in cm^3 is obtained from the coefficient of thermal expansion of stainless steel and an empirical coefficient related to pressure-dependence of the volume.

$$V_{cell} = \{0.0015287(T - 273.15) + 33.132\}(1 + 4.3322 \times 10^{-5} P) \quad (4)$$

A portion of the sample mass resides in the noxious volume which consists of the combined volumes of the connecting tubing, the charging valve orifice, and the pressure transducer. In total, the noxious volume is approximately 3% of the cell volume. The amount of the sample mass in the noxious volume is calculated from an assumed temperature profile of this volume and from densities calculated with an equation of state¹⁵ or, when appropriate, with correlations based on measured PVT_x properties from this apparatus.

Figure 3 shows the deviations of experimental densities of H₂O from those calculated with IAPWS-97.¹⁵ Deviations from this international reference equation of state were not greater than 0.1%. Figure 4 shows a comparison of measured c_v for H₂O with the equation of state. The deviations of c_v are within ± 3 %. While 3 % is a reasonable deviation, we would expect deviations to improve if this series were repeated, since the series depicted in Figure 4 had some problems with temperature excursions of the adiabatic shields.

Figure 5 shows the c_v data of H₂O, CH₃OH, and their mixtures. It shows an interesting behavior of the thermodynamic surfaces of the fluids. The liquid heat capacities are not strong functions of temperature in this region. A shallow minimum is not observed in the temperature range for these fluids.

Acknowledgements

The authors gratefully acknowledge Katsumasa Araoka and his group of PIC, Toshiba Corporation for his design and their construction of the twin-cell adiabatic calorimeter. We also thank Hidehiko Ichikawa of Sanyo Electric Software Co., Ltd. for his technical assistance.

Literature Cited

(1) D'Arrigo, G.; Paparelli, A. Anomalous Ultrasonic Absorption in Alkoxyethanols

Aqueous Solutions near their Critical and Melting Points. *J. Chem. Phys.*, **1989**, *91*(4), 2587-2593.

- (2) Kubota, H.; Tanaka, Y.; Makita, T., Volumetric Behavior of Pure Alcohols and their Water Mixtures under High Pressures. *Int. J. Thermophys.*, **1987**, *8*, 47-70.
- (3) Osada, O.; Sato, M.; Uematsu, M. Thermodynamic Properties of $\{x\text{CH}_3\text{OH}+(1-x)\text{H}_2\text{O}\}$ with $x=(1.000$ 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.
- (4) Xiao, C.; Bianchi, H.; Tremaine, P. R. Excess Molar Volume and Densities of (Methanol+Water) at Temperatures between 323 and 573 K and at Pressures of 7 MPa and 13.5 MPa. *J. Chem. Thermodyn.*, **1997**, *29*, 261-286.
- (5) Lama, R. F.; Lu, B. C.-Y. Excess Thermodynamic Properties of Aqueous Alcohol Solutions. *J. Chem. Eng. Data*, **1965**, *10*, 216-219.
- (6) Benson, G. C.; D'Arcy, P. J. Excess Isobaric Heat Capacities of Water-n-Alcohol Mixtures. *J. Chem. Eng. Data*, **1982**, *27*, 439-442.
- (7) Simonson, J. M.; Bradley, D. J.; Busey, R. H. Excess Molar Enthalpies and the Thermodynamics of (Methanol+Water) to 573 K and 40 MPa. *J. Chem. Thermodyn.*, **1987**, *19*, 479-492.
- (8) 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. To appear 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*; Eds. P. R. Tremaine, P. G. Hill, D. E. Irish and P. V. Balakrishnan; NRC Press: Ottawa, 2000.
- (9) Hemminger, W.; Hohne, G. *Calorimetry –Fundamentals and Practice*; Verlag Chemie: Weinheim, 1984.

- (10) Magee, J. W. High-Temperature Adiabatic Calorimeter for Constant-Volume Heat Capacity Measurements of Compressed Gases and Liquids. *Proc. 9th Symp. on Energy Eng, Sciences*, Argonne Natl. Lab., **1991**.
- (11) Magee, J. W.; Blanco, J. C.; Deal, R. J. High-Temperature Adiabatic Calorimeter for Constant-Volume Heat Capacity of Compressed Gases and Liquids. *J. Res. Natl. Inst. Stand. Technol.*, **1998**, *103*, 63-75.
- (12) Magee, J. W.; Kagawa, N. Specific Heat Capacity at Constant Volume for $\{x\text{NH}_3+(1-x)\text{H}_2\text{O}\}$ at Temperatures from 300 to 520 K and Pressures to 20 MPa. *J. Chem. Eng. Data*, **1999**, *43*, 1082-1090.
- (13) Kuroki, T.; Kagawa, N.; Araoka, K; Endo; H.; Tsuruno, S. Specific Heat Capacity Measurement of Fluids with an Adiabatic Calorimeter. *Proc. 20 Japan Symp. Thermophys. Props.*; Tokyo, 1999, pp. 456-460 .
- (14) Goodwin, R. D.; Weber, L. A. Specific Heats C_v of Fluid Oxygen from the Triple Point to 300 K at Pressures to 350 Atmospheres. *J. Res. Natl. Bur. Stand.*, **1969**, *73A*, 15-24.
- (15) *IAPWS Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam*; 1997, pp.1-48.

Table 1. Mass Fraction w , and Mole Fraction x of $\{x\text{H}_2\text{O}+(1-x)\text{CH}_3\text{OH}\}$ Mixtures Used in this Study

w	x
0.19010	0.29452
0.64858	0.76649

Table 2. Experimental Densities and Heat Capacities for H_2O , CH_3OH , $0.3\text{H}_2\text{O}+0.7\text{CH}_3\text{OH}$, and $0.8\text{H}_2\text{O}+0.2\text{CH}_3\text{OH}$

T_1 / K	P / MPa	$\rho / \text{kg}\cdot\text{m}^{-3}$	$c_v / \text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
H_2O			
293.161	0.094*	992.58	4.193
298.171	0.119*	992.35	4.007
303.168	0.163*	992.13	4.128
308.160	0.274*	991.91	4.229
314.160	1.168*	991.60	4.114
318.161	3.524	991.30	4.114
323.186	7.498	990.88	4.039
328.162	11.911	990.43	4.031
333.170	16.711	989.97	3.923
336.181	19.741	989.68	3.822
343.176	0.162*	973.75	3.879
347.171	0.348*	973.58	3.838
353.173	4.082	973.13	3.942
358.173	9.925	972.63	3.829
363.156	16.068	972.11	3.706
366.158	19.865	971.79	3.531
368.164	0.107*	932.55	3.736
373.169	0.124*	932.35	3.777

378.168	0.141*	932.15	3.785
382.155	0.156*	932.00	3.756
389.151	0.186*	931.72	3.630
CH ₃ OH			
286.172	1.924*	797.83	2.630
288.163	3.711	797.67	2.552
293.161	8.032	797.31	2.607
298.182	12.170	796.96	2.710
303.188	16.310	796.61	2.725
307.151	19.571	796.34	2.727
308.169	1.870	778.51	
313.162	5.585	778.15	2.798
318.152	9.583	777.80	2.808
323.166	13.629	777.46	2.849
328.167	17.689	777.11	2.882
330.180	19.332	776.98	2.853
308.395	1.298*	778.53	
313.150	4.643	778.21	
318.183	8.908	777.84	2.823
323.157	13.066	777.49	2.865
328.165	17.206	777.14	2.861
331.154	19.669	776.94	2.912
333.171	0.347*	761.80	2.861
338.181	4.088	761.44	2.959
343.182	7.849	761.10	3.026
348.176	11.609	760.76	3.038
353.161	15.373	760.43	3.076
358.170	19.160	760.11	3.086

359.154	19.910	760.04	3.069
373.168	1.625*	715.00	3.390
378.155	4.765	714.83	3.268
383.153	8.031	714.53	3.293
388.153	11.342	714.24	
0.3H ₂ O+0.7CH ₃ OH			
283.170	4.351	879.33	
288.160	9.812	878.80	2.965
293.152	15.385	878.19	2.900
298.187	20.969	877.56	3.095
301.156	7.062	863.98	3.180
303.167	9.207	863.73	3.161
308.163	14.491	863.10	3.114
313.179	19.802	862.44	3.135
315.187	21.932	862.16	3.109
330.161	2.334	834.23	
333.162	5.223	833.98	3.200
338.176	10.067	833.50	3.264
343.179	14.907	832.99	3.233
348.165	19.778	832.44	3.317
353.155	4.760	819.70	3.322
359.171	10.336	819.16	3.432
363.155	14.061	818.78	3.261
368.175	18.760	818.26	3.312
369.165	19.697	818.16	3.299
369.530	4.434	804.52	
373.179	7.623	804.23	3.444
378.176	12.125	803.79	3.453

383.176	16.647	803.32	3.408
386.153	19.313	803.02	3.437
0.8H ₂ O+0.2CH ₃ OH			
382.168	12.992	888.05	3.556
388.159	20.921	884.59	3.537

*Pressure has a larger uncertainty than 7 kPa.

Figure Captions

Figure 1. Twin-cell adiabatic calorimeter.

Figure 2. Measured ΔQ_0 of the apparatus.

Figure 3. Deviations of measured densities for H₂O from calculations with IAPWS-IF97.¹⁵

Figure 4. Deviations of measured c_v for H₂O from calculations with IAPWS-IF97.¹⁵

Figure 5. Measurements of c_v for H₂O, CH₃OH, 0.3H₂O+0.7CH₃OH, and 0.8H₂O+0.2CH₃OH.







