Measurements of the Isobaric Specific Heat Capacity and Density for Dimethyl Ether in the Liquid State

Katsuyuki Tanaka* and Yukihiro Higashi

Department of Mechanical Systems and Design Engineering, Iwaki Meisei University, Iwaki, Fukushima 970-8551, Japan

The isobaric specific heat capacity and density for dimethyl ether were measured in the temperature range from (310 to 360) K at pressures up to 5 MPa in the liquid state. Measurements were conducted by the metal-bellows calorimeter. The uncertainties of isobaric specific heat capacity and density measurements were estimated to be less than 5 % and 0.2 %, respectively. Experimental values for the isobaric specific heat capacity and density were correlated as functions of pressure and temperature. In addition, the saturated liquid isobaric specific heat capacity and saturated liquid density were obtained from extrapolation of these correlations to the vapor pressure.

Introduction

Dimethyl ether is expected to be useful for refrigerants as well as diesel engine fuel and hydrogen transport medium. For effective use of these applications, the reliable thermodynamic property model is required. A fundamental equation of state for dimethyl ether was proposed by Ihmels and Lemmon.[1] However, the experimental thermodynamic property data of the liquid state used in the fit for their equation of state are very limited. As for liquid density, there are a few data by Maass and Boomer,[2] by Outcalt and McLinden,[3] by Ihmels and Lemmon,[1] and by Bobbo et al.[4] Moreover, as for isobaric specific heat capacity, there is only one set of data by Kennedy et al.[5] in the temperature range from (129 to 246) K at saturation state and no data in the liquid state. So the reliable equation for the heat capacities formulated by Wilhoit et al.[6] is limited in the temperature range up to 250 K.

In this work, measurements of the isobaric specific heat capacity and density for dimethyl ether in the liquid state were carried out along six isotherms between (310 and 360) K at an interval of 10 K and pressures up to 5 MPa at an interval of 1 MPa. The saturated liquid isobaric specific heat capacity and saturated liquid density were obtained by extrapolating the data of the liquid state up to the vapor pressure.

Experimental Apparatus

The metal-bellows calorimeter was used to measure the isobaric specific heat capacity, density, and vapor pressure. Its principle and procedure of measurements in detail are reported in our previous paper.[7−11] The sample container is a cylinder with a metal bellows whose volume can be varied from (34 to 44) cm^3. A sample of known mass was loaded into the sample container. Nitrogen gas was filled outside the bellows to compress or expand the sample. The pressure of sample is balanced with that of nitrogen gas.

The metal-bellows calorimeter was immersed in the thermostat with silicone oil to keep the temperature constant with the fluctuation of 3 mK. The temperature was measured by 25 Ω standard platinum resistance thermometer (model: Chino R800-2) and precise thermometer bridge (model: Tinsley 5840) with the uncertainty of 5 mK.

The pressure was measured by a precise digital pressure gauge (model: Paroscientific 43K). The uncertainty of the pressure measurement in the liquid state was estimated to be 3 kPa in consideration of the elastic deformation of the metal bellows. The uncertainty of the vapor-pressure measurement is estimated to be 1 kPa because measurement of the vapor pressure was conducted when the bellows displacement is near zero so as to neglect the elastic deformation of the bellows.

The sample density can be determined from the mass of the sample and the volume of the bellows. The mass of the sample was determined from the mass difference of the sample bottle. The mass of the sample bottle was measured by a precision analytical balance with the uncertainty of 2 mg. The variation of the volume with the bellows displacement was calibrated using 1,1,1,2-tetrafluoroethane (HFC-134a). The uncertainty of the density measurement was estimated to be 0.2 %.

The isobaric specific heat capacity was measured by the thermal relaxation method.[5,11] When a constant heat flow was supplied to the sample, the thermal relaxation time τ and maximum temperature change $\Delta T_{\max}$ were obtained from the record of the temperature change of the sample. The isobaric specific heat capacity c_p was determined from eq 1.

$$c_p = \left(k\frac{EI}{\Delta T_{\max}}\tau - C_a\right)/m \qquad (1)$$

where E is the voltage, I is the electrical current, k is the heater coefficient, m is the mass of the sample, and C_a is the heat capacity of the sample container. The calibration of the apparatus constant was conducted by using water, methanol, and HFC-134a. The uncertainty of the isobaric specific heat capacity measurement was estimated to be within 5 %.

The sample of dimethyl ether was manufactured by Takachiho, Co. Ltd., Japan. Its purity is more than 0.995 in mass fraction. No further purification was done on the samples before use.

Experimental Results and Discussion

Isobaric Specific Heat Capacity. Twenty-two data points of the isobaric specific heat capacity for dimethyl ether in the liquid

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* Corresponding author. Tel.: +81-246-29-7026. Fax: +81-246-29-0577. E-mail: ktanaka@iwakimu.ac.jp.

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Table 1. Experimental Results of the Isobaric Specific Heat Capacity for Dimethyl Ether

T / K	P / MPa	c_p / $\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
310.00	5.00	2.63 ± 0.14
310.00	4.00	2.64 ± 0.14
310.00	3.00	2.65 ± 0.14
310.00	2.00	2.69 ± 0.14
320.00	5.00	2.71 ± 0.14
320.00	4.00	2.71 ± 0.14
320.00	3.00	2.73 ± 0.14
320.00	2.00	2.77 ± 0.14
330.00	5.00	2.76 ± 0.14
330.00	4.00	2.78 ± 0.14
330.00	3.00	2.79 ± 0.14
330.00	2.00	2.85 ± 0.15
340.00	5.00	2.81 ± 0.14
340.00	4.00	2.87 ± 0.15
340.00	3.00	2.93 ± 0.15
340.00	2.00	2.99 ± 0.15
350.00	5.00	2.88 ± 0.15
350.00	4.00	2.98 ± 0.15
350.00	3.00	3.05 ± 0.16
360.00	5.00	2.96 ± 0.15
360.00	4.00	3.15 ± 0.16
360.00	3.00	3.34 ± 0.17

state were obtained in the temperature range from (310 to 360) K and pressures up to 5 MPa. The experimental results are listed in Table 1. The pressure dependence along the isotherms is shown in Figure 1. The values for the isobaric specific heat capacity are correlated as

$$c_p = \alpha + \beta p_r^{0.5} \tag{2}$$

where

$$\alpha = \alpha_1 + \frac{\alpha_2}{(1 - T_r)^2} \tag{3}$$

$$\beta = \beta_1 + \beta_2(1 - T_r) + \frac{\beta_3}{(1 - T_r)} + \frac{\beta_4}{(1 - T_r)^2} \tag{4}$$

$p_r = p/p_c$, and $T_r = T/T_c$. The fundamental functional form of eq 2 is used as the same that by Nakagawa et al.[12,13] and Yomo et al.[14] adopted for the liquid c_p of some refrigerants. Critical pressure p_c and critical temperature T_c are 5.356 MPa and 400.378 K determined by Wu et al.[15] The coefficients in eqs 3 and 4 are listed in Table 2. The calculations by eq 2 are also drawn along isotherms with solid lines in Figure 1. The deviations of the present results from eq 2 are shown in Figure 2. The present results are reproduced with an absolute average deviation of 0.4 % and a maximum deviation of 1.0 %. The present results were compared with a fundamental equation of state by Ihmels and Lemmon.[1] As shown in Figure 3, the deviations from the fundamental equation of state by Ihmels and Lemmon become larger at lower temperature and lower pressure ranges and about 10 % near the saturated vapor pressure. It might be caused by lack of the data for heat capacity in developing the equation of state. The present data complement the existing data and are useful to modify the equation of state.

The saturated liquid isobaric specific heat capacity was obtained by the extrapolation of eq 2 to the vapor pressure. The vapor pressure was also measured between (310 and 360) K at an interval of 10 K. The results are listed in Table 3 and included in Figures 1 and 3 as filled circle plots.

The deviations from the fundamental equation of state by Ihmels and Lemmon were systematically low, and its values were about 10 %. As for the saturated liquid isobaric specific heat capacity, the present data complement the existing data and are useful to modify the equation of state.

Density. Twenty-two data points of the density for dimethyl ether in the liquid state were obtained in the temperature range

Table 2. Coefficients in Equation 2

α_1 / $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$	α_2 / $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$	β_1 / $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$	β_2 / $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$	β_3 / $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$	β_4 / $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$
2.2831	0.023206	1.6991	−3.9175	−0.13586	−0.016311

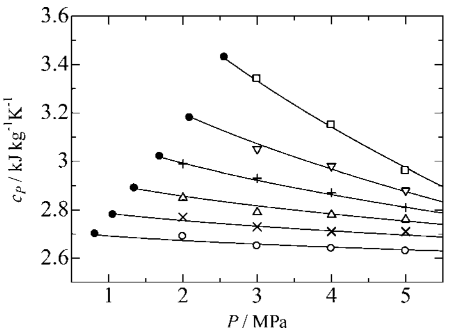

Figure 1. Isobaric specific heat capacity against pressure for dimethyl ether. ○, present work at 310 K; ×, 320 K; △, 330 K; +, 340 K; ▽, 350 K; □, 360 K; ●, saturated liquid isobaric specific heat capacity of present work; —, isothermal lines by eq 2.

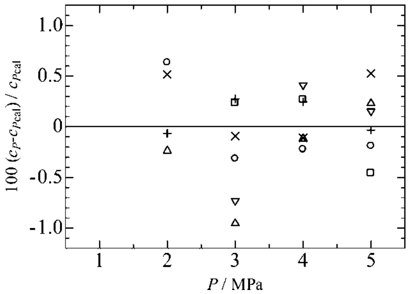

Figure 2. Deviations of the present results of isobaric specific heat capacity from eq 2. ○, present work at 310 K; ×, 320 K; △, 330 K; +, 340 K; ▽, 350 K; □, 360 K.

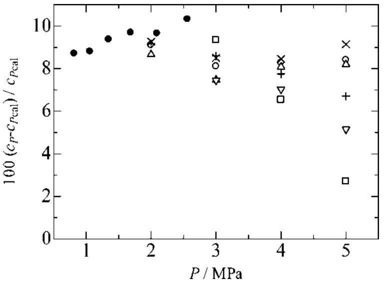

Figure 3. Comparison of the present results with calculations from a fundamental equation of state by Ihmels and Lemmon.[1] ○, present work at 310 K; ×, 320 K; △, 330 K; +, 340 K; ▽, 350 K; □, 360 K; ●, saturated liquid isobaric specific heat capacity of present work.

Table 3. Saturated Liquid Heat Capacity for Dimethyl Ether

T / K	P_sat / MPa	$c_{p\text{sat}}$ / $\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
310.00	0.817	2.70
320.00	1.059	2.78
330.00	1.348	2.89
340.00	1.689	3.02
350.00	2.092	3.18
360.00	2.561	3.43

Table 4. Experimental Results of the Density for Dimethyl Ether

T / K	P / MPa	ρ / kg·m^{-3}
310.00	5.00	650.2 ± 1.1
310.00	4.00	648.0 ± 1.1
310.00	3.00	646.0 ± 1.1
310.00	2.00	643.5 ± 1.1
320.00	5.00	634.3 ± 1.0
320.00	4.00	631.1 ± 1.0
320.00	3.00	628.7 ± 1.0
320.00	2.00	626.0 ± 1.0
330.00	5.00	616.5 ± 1.0
330.00	4.00	613.4 ± 1.0
330.00	3.00	609.8 ± 1.0
330.00	2.00	606.5 ± 1.0
340.00	5.00	597.4 ± 0.9
340.00	4.00	593.6 ± 0.9
340.00	3.00	589.6 ± 0.9
340.00	2.00	585.3 ± 0.9
350.00	5.00	576.7 ± 0.9
350.00	4.00	572.0 ± 0.9
350.00	3.00	566.8 ± 0.8
360.00	5.00	553.5 ± 0.8
360.00	4.00	547.4 ± 0.8
360.00	3.00	540.2 ± 0.8

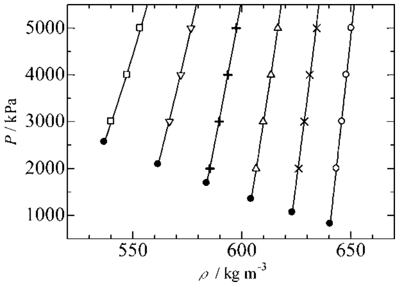

Figure 4. Pressure−density diagram for dimethyl ether. ○, present work at 310 K; ×, 320 K; △, 330 K; +, 340 K; ▽, 350 K; □, 360 K; ●, saturated liquid density; −, isothermal lines by eq 5.

Table 5. Coefficients in Equation 5

a_0	102.2818
a_1	−195.0355
a_2	92.0613
b	0.1367
c	0.5498

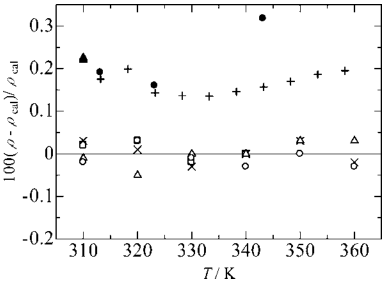

Figure 5. Deviations of the present results of density from eq 5. ○, present work at 5 MPa; △, 4 MPa; ×, 3 MPa; □, 2 MPa; +, Ihmels and Lemmon[1] at 5 MPa; ●, Bobbo et al.[4] at 5 MPa; ▲, Oulcalt and McLinden[3] at (2 to 5) MPa.

Table 6. Saturated Liquid Density for Dimethyl Ether

T / K	P_{sat} / MPa	ρ_{sat} / kg·m^{-3}
310.00	0.817	640.5
320.00	1.059	623.1
330.00	1.348	604.3
340.00	1.689	583.9
350.00	2.092	561.6
360.00	2.561	537.0

from (310 to 360) K and pressures up to 5 MPa. The values are listed in Table 4 and are plotted on the pressure−density diagram of Figure 4. The densities were correlated as

$$\rho = \rho_c \frac{(p_r + a(T_r))^b}{c} \tag{5}$$

where $a(T_r) = \sum_{i=0}^{2} a_i(T_r)^i$ and critical density ρ_c is 272 kg·m^{-3} determined by Wu et al.[15] The functional form in this work is used as the same that by Kayukawa[16,17] adopted for some hydrofluoroethers (HFEs) and hydrocarbons (HCs). Its original function was proposed by Sato.[18] Their numerical values are summarized in Table 5. In Figure 4, the calculation results by eq 5 are shown by the solid lines along isotherms. The deviations of the experimental data with the literature data from eq 5 in the effective pressure and temperature range are shown in Figure 5. The present results are reproduced with an absolute average deviation of 0.02 % and a maximum deviation of 0.05 %. A comparison with the data by Maass and Boomer[2] could not be carried out because their data is in a low temperature range. The data by Outcalt and McLinden[3] at 310 K in the pressure range from (2 to 5) MPa deviate systematically about 0.2 %. The data by Bobbo et al.[4] deviated systematically from (0.2 to 0.3) %. The data by Ihmels and Lemmon[1] also deviated systematically from (0.1 to 0.3) %. However, these data were in good agreement with this work in consideration of the experimental uncertainty and the reproducibility of the correlation.

To obtain the saturated liquid density, eq 5 was extrapolated to the vapor pressure. The filled circle plots in Figure 4 were calculations for the saturated liquid density. The values are listed in Table 6. The present data and literature data by Wu et al.[15,19] were compared with the calculations from the equation of state developed by Ihmels and Lemmon[1] as shown in Figure 6. Although the deviation of the present data from the equation of state is increasing with increasing temperature, the present data have similar behavior to the data by Wu et al.[19]

Conclusion

Measurements of the isobaric specific heat capacity and density for dimethyl ether were carried out in the temperature range from (310 to 360) K and pressures up to 5 MPa. On the basis of the measurements, correlations for the isobaric specific heat capacity and density in the liquid state were formulated. The isobaric specific heat capacity and density of the saturated liquid were also determined by extrapolation of these correlations to vapor pressure measured in this work. The data of the density are good agreement with the literature value. As for the isobaric specific heat capacity, the data were provided in

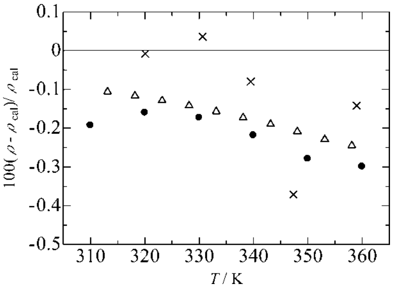

Figure 6. Deviations of the present results and literature data of saturated liquid density from equation of state developed by Ihmels and Lemmon. ●, present work; ×, Wu et al.;[15] △, Wu et al.[19]

the nonexistent temperature and pressure ranges in this work. It is found that it is difficult for the existing equation of state to reproduce the experimental isobaric specific heat capacity data.

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