Measurements of the Isobaric Specific Heat Capacity and Density for HFO-1234yf in the Liquid State

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The isobaric specific heat capacity and density of the HFO-1234yf (2,3,3,3-tetrafluoropropene, $CH_2{=}CFCF_3$) in the liquid state have been measured in the temperature range from (310 to 360) K at pressures up to 5 MPa. The uncertainties in temperature, pressure, isobaric specific heat capacity, and density measurements were estimated to be less than 5 mK, 3 kPa, 5 %, and 0.2 %, respectively. A sample with purity of 99.99 mol % or greater was used for the measurement. Experimental values for the isobaric specific heat capacity were correlated as a function of pressure along isotherms, and those for density were correlated as functions of pressure and temperature. In addition, the saturated liquid isobaric specific heat capacity and density were obtained from extrapolation of these correlations to the vapor pressure.

Introduction

Regarding the F-gas regulation in Europe, HFO-1234yf (2,3,3,3-tetrafluoropropene, $CH_2{=}CFCF_3$) is expected as an alternative refrigerant to HFC-134a for automobile air conditioners.[1] The authors have investigated the saturation state of HFO-1234yf by measurements of the vapor−liquid coexistence curve, vapor pressure, and surface tension and have presented correlations for vapor pressure and surface tension.[2] In this work, measurements of the isobaric specific heat capacity and density of HFO-1234yf in the liquid state were carried out for the development of reliable thermodynamic property models.

Experimental Section

The apparatus is reported in detail in our previous paper.[3,4] The sample cell is a cylinder with a metal-bellows whose volume can be varied from (33 to 43) cm^3 to measure the density. The stainless-sheathed heater is installed at the lowest position of the sample cell, and four stainless-sheathed platinum-resistance thermometers (100 Ω) are set at different positions in the sample cell to measure the isobaric specific heat capacity. The sample was filled to the inner side of a metal-bellows. The mass of the sample was determined from mass difference of the sample bottle. The mass of the sample bottle was measured by a precision analytical balance with the uncertainty of 1 mg. The sample cell was inserted into the pressure vessel. Nitrogen gas as pressure medium was filled between the sample cell and the pressure vessel. The sample was pressurized through the metal-bellows by pressurizing nitrogen gas, and the sample pressure was kept constant. The pressure of nitrogen gas was measured by a precise digital pressure gauge (model: Paroscientific 43K), and the pressure of the sample was set in consideration of the elastic deformation of the metal-bellows with the uncertainty of 3 kPa. The displacement of the metal-bellows was detected by a linear variable differential transformer. The pressure vessel was immersed in the thermostat with silicone oil to keep the temperature of the pressure vessel constant. The temperature of silicone oil was measured by a 25 Ω standard platinum resistance thermometer (model: Chino R800-2) and precise thermometer bridge (model: Tinsley 5840) with the uncertainty of 5 mK.

The isobaric specific heat capacity was determined using the thermal relaxation method. Its principle has been described in the previous paper.[3,4] When a constant heat flow was supplied to the sample, the record of the temperature change of the sample was obtained as an average value of four thermometers. From the record of the temperature change ΔT as expressed in eq 1, the thermal relaxation time τ and maximum temperature change $\Delta T_{\max}$ were obtained.

$$\Delta T = \Delta T_{\max}[1 - \exp(-t/\tau)] \tag{1}$$

The isobaric specific heat capacity was determined from the following equation

$$c_p = \left(k\frac{EI}{\Delta T_{\max}}\tau - C_a\right)/m \tag{2}$$

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 cell. In advance of this measurement, k and C_a were calibrated. The calibration was conducted by using water, methanol, and HFC-134a in the temperature range from (310 to 360) K and pressures up to 5 MPa. The uncertainty of the measurement for the isobaric specific heat capacity was estimated to be within 5 %.

The density was determined from known mass of sample and volume of the sample cell obtained from the displacement of the sample cell. The values for V were calibrated by using HFC-134a in the temperature range from (310 to 360) K and pressures up to 5 MPa. The uncertainty of the density measurement was estimated to be less than 0.2 %.

The sample of HFO-1234yf was manufactured by Daikin Industries, Ltd. Its purity is more than 99.99 % in mole fraction. No further purification was done on the samples before use.

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Table 1. Experimental Results of the Isobaric Specific Heat Capacity for HFO-1234yf

T	P	c_p
K	MPa	$(\mathrm{kJ\cdot kg^{-1}\cdot K^{-1}})$
310.000	5.00	1.35 ± 0.07
310.000	4.00	1.34 ± 0.07
310.000	3.00	1.42 ± 0.08
310.000	2.00	1.45 ± 0.08
320.000	5.00	1.38 ± 0.07
320.000	4.00	1.41 ± 0.08
320.000	3.00	1.47 ± 0.08
320.000	2.00	1.52 ± 0.08
330.000	5.00	1.43 ± 0.08
330.000	4.00	1.48 ± 0.08
330.000	3.00	1.57 ± 0.08
330.000	2.00	1.63 ± 0.09
340.000	5.00	1.49 ± 0.08
340.000	4.00	1.56 ± 0.08
340.000	3.00	1.64 ± 0.09
340.000	2.00	1.80 ± 0.09
350.000	5.00	1.60 ± 0.08
350.000	4.00	1.72 ± 0.09
350.000	3.00	1.91 ± 0.10
360.000	5.00	1.73 ± 0.09
360.000	4.00	1.95 ± 0.10
360.000	3.00	2.61 ± 0.14

Results and Discussion

Isobaric Specific Heat Capacity. Twenty-two data points of the isobaric specific heat capacity of HFO-1234yf were obtained in the temperature range from (310 to 360) K and pressures up to 5 MPa. The numerical values are listed in Table 1. The pressure dependence along isotherms is shown in Figure 1. The values for the isobaric specific heat capacity are correlated as

$$c_p = \alpha P^{\beta} + \gamma \tag{3}$$

where α, β, and γ are constants. Table 2 summarizes values for α, β, and γ. The calculation by eq 3 is also drawn by a solid line in Figure 1. The deviations of the present results from eq 3 are shown in Figure 2, and they are within 2 %. The saturated liquid isobaric specific heat capacity is obtained by the extrapolation of eq 3 to the vapor pressure. The results are listed in Table 3. The vapor pressure correlation presented in the previous work was used.[2] The saturated liquid isobaric specific heat capacity was correlated as

$$c_{ps}(P) = A + BP_{\mathrm{r}} + \frac{C}{(1 - P_{\mathrm{r}})} \tag{4}$$

where $P_{\mathrm{r}} = P/P_{\mathrm{c}}$; P_{c} is 3.382 MPa of the critical pressure;[2] and A, B, and C are parameters. The numerical values A, B, and C were listed in Table 4. The calculation results with eq 4 are also included in Figure 1. The deviations of the present results from eq 4 are shown in Figure 3, and they are less than 1.5 %.

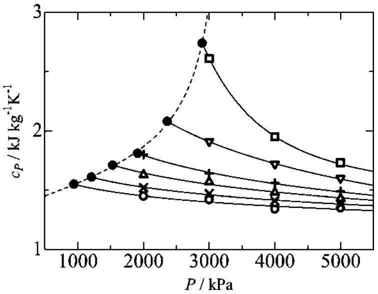

Figure 1. Isobaric specific heat capacity against pressure for HFO-1234yf. ○, present work at 310 K; ×, 320 K; △, 330 K; +, 340 K; ▽, 350 K; □, 360 K; ●, saturated liquid isobaric specific heat capacity of present work; −, isothermal lines by eq 3; - - -, eq 4.

Table 2. Numerical Values of Constants in Equation 3

	α		γ
T/K	$(\mathrm{kJ\cdot kg^{-1}\cdot K^{-1}\cdot KPa^{-1}})$	β	$(\mathrm{kJ\cdot kg^{-1}\cdot K^{-1}})$
310.00	$2.8206\cdot10^{0}$	$-8.7450\cdot10^{-2}$	0
320.00	$3.4072\cdot10^{0}$	$-1.0580\cdot10^{-1}$	0
330.00	$5.0799\cdot10^{0}$	$-1.4836\cdot10^{-1}$	0
340.00	$8.6130\cdot10^{0}$	$-2.0643\cdot10^{-1}$	0
350.00	$3.2786\cdot10^{1}$	$-3.5510\cdot10^{-1}$	0
360.00	$3.0776\cdot10^{10}$	$-3.0000\cdot10^{0}$	$1.4732\cdot10^{0}$

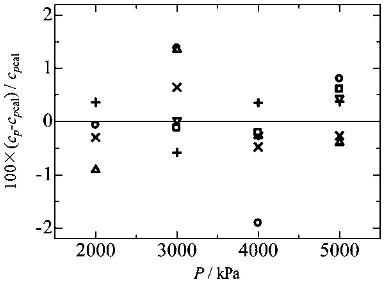

Figure 2. Deviations of the present results of isobaric specific heat capacity from eq 3. ○, present work at 310 K; ×, 320 K; △, 330 K; +, 340 K; ▽, 350 K; □, 360 K.

Table 3. Saturated Liquid Heat Capacity for HFO-1234yf

T	P_{s}	c_{sat}
K	kPa	$(\mathrm{kJ\cdot kg^{-1}\cdot K^{-1}})$
310.00	940	1.55 ± 0.08
320.00	1209	1.61 ± 0.09
330.00	1532	1.71 ± 0.09
340.00	1913	1.81 ± 0.10
350.00	2363	2.08 ± 0.11
360.00	2894	2.74 ± 0.14

Table 4. Numerical Values of Constants in Equation 4

A	B	C
1.1867	0.45491	0.16852

Density. Twenty-three data points of the density of HFO-1234yf were obtained in the temperature range from (310 to 360) K and pressures up to 5 MPa. The values are listed in Table 5 and are plotted on the pressure−density diagram of Figure 4. The densities were correlated as

$$\rho = \sum_{i=0}^{2} a_i P_{\mathrm{r}}^{i} + \frac{\sum_{i=0}^{2} b_i P_{\mathrm{r}}^{i}}{(1 - T_{\mathrm{r}})} + T_{\mathrm{r}} \sum_{i=0}^{2} c_i P_{\mathrm{r}}^{i} \tag{5}$$

where a_i, b_i, and c_i are constants, and $T_{\mathrm{r}} = T/T_{\mathrm{c}}$. Their numerical values were summarized in Table 6. In Figure 4, the calculation results with eq 5 are shown by the solid lines along isotherms. The deviations of the present result from eq 5 are shown in

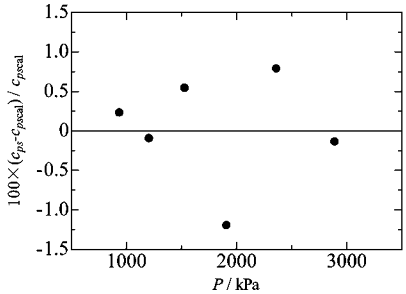

Figure 3. Deviations of the present results of saturated liquid isobaric specific heat capacity from eq 4.

Table 5. Experimental Results of the Compressed Liquid Density for HFO-1234yf

T K	P MPa	ρ $(\mathrm{kg\cdot m^3})$
310.000	5.00	1080.6 ± 1.8
310.000	4.00	1072.8 ± 1.8
310.000	3.00	1065.2 ± 1.7
310.000	2.00	1065.2 ± 1.7
310.000	1.00	1046.5 ± 1.7
320.000	5.00	1044.8 ± 1.7
320.000	4.00	1035.3 ± 1.7
320.000	3.00	1025.1 ± 1.6
320.000	2.00	1013.8 ± 1.6
330.000	5.00	1004.6 ± 1.6
330.000	4.00	992.7 ± 1.5
330.000	3.00	979.2 ± 1.5
330.000	2.00	964.2 ± 1.4
340.000	5.00	961.3 ± 1.4
340.000	4.00	945.3 ± 1.4
340.000	3.00	926.7 ± 1.3
340.000	2.00	903.0 ± 1.3
350.000	5.00	913.1 ± 1.5
350.000	4.00	891.3 ± 1.5
350.000	3.00	861.8 ± 1.4
360.000	5.00	853.9 ± 1.3
360.000	4.00	818.5 ± 1.2
360.000	3.00	751.9 ± 1.1

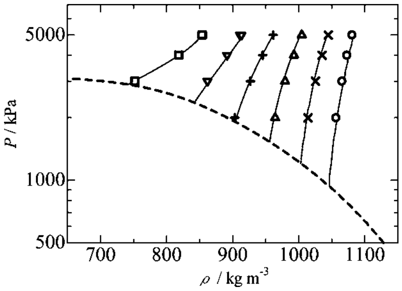

Figure 4. Pressure−density diagram for HFO-1234yf. ○, present work at 310 K; ×, 320 K; △, 330 K; +, 340 K; ▽, 350 K; □, 360 K; ●, saturated liquid isobaric specific heat capacity of present work; −, isothermal lines by eq 3; - - -, eq 4.

Table 6. Numerical Values of Constants in Equation 5

i	a_i	b_i	c_i
0	$1.9639\cdot10^3$	$-1.3619\cdot10^1$	$-1.0017\cdot10^3$
1	$7.7225\cdot10^2$	$1.7641\cdot10^1$	$-9.9358\cdot10^2$
2	$-3.7791\cdot10^2$	$-6.1256\cdot10^0$	$4.8370\cdot10^2$

Figure 5. They are less than 0.4 %. To obtain the saturated liquid density, eq 5 was extrapolated to the vapor pressure. The broken line in Figure 4 shows the saturated liquid densities thus obtained. Comparison of the saturated liquid densities was made with predictions with the correlation developed by Hankinson and Thomson.[5] The result is shown in Figure 6. The saturated liquid densities obtained from extrapolation of eq 5 agree with those from the correlation. The deviations are within 0.4 % except critical region.

Conclusion

Measurements of the isobaric specific heat capacity and density of HFO-1234yf in the liquid state 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 were presented. The isobaric specific heat capacity and density of the saturated liquid were determined by extrapolation of the correlations.

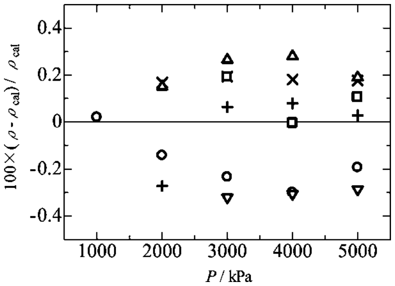

Figure 5. Deviations of the present results of density from eq 5. ○, present work at 310 K; ×, 320 K; △, 330 K; +, 340 K; ▽, 350 K; □, 360 K.

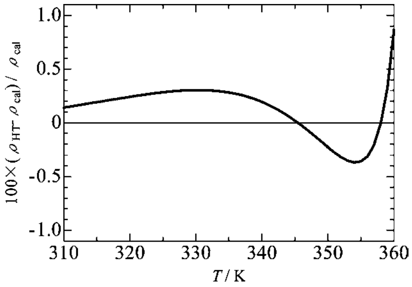

Figure 6. Deviation of the calculation by the Hankinson−Thomson equation from eq 5.

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