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Critical Parameters for 2-Methylpropane (R600a)

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Measurements of the vapor−liquid coexistence curve near the critical point for 2-methylpropane (isobutane; R600a) were carried out in the reduced temperature range of $0.957 < T/T_c < 1$ and in the reduced density range of $0.40 < \rho/\rho_c < 1.70$, and the critical temperature T_c and critical density ρ_c were determined. The critical pressure P_c was calculated by extrapolating reliable vapor−pressure data in the vicinity of the critical point. The critical parameters determined are $T_c = (407.795 \pm 0.010)$ K, $\rho_c = (229 \pm 2)$ kg·m^{-3}, $V_c = (253.8 \pm 2.2)$ cm^3·mol^{-1}, and $P_c = (3628.2 \pm 1.4)$ kPa. In addition, the critical exponent β along the coexistence curve is discussed.

Introduction

Because of their low ozone-depletion potentials and low global warming potentials, hydrocarbons are being considered as CFC, HCFC, and HFC alternatives. Most of commercial house refrigerators in Japan are adopting 2-methylpropane (isobutane; R600a) as an environmentally acceptable refrigerant. The critical parameters (i.e., critical temperature T_c, critical density ρ_c, and critical pressure P_c) are important not only for understanding the thermodynamic state surface but also for making correlations. However, the critical parameters of 2-methylpropane determined from direct measurements are limited except for three older reports by Seibert and Burrell,[1] by Harand,[2] and by Gilliland and Scheeline.[3] Levelt Sengers et al.[4] determined the critical temperature and critical density for 2-methylpropane by the observation of the meniscus disappearance. Their reported values are $T_c = 407.84 \pm 0.02$ K (IPTS-68), $\rho_c = 225.5 \pm 2$ kg·m^{-3}. The critical pressure of 2-methylpropane, $P_c = 3629.0$ kPa, was determined from fit to *PVT* data. The sample purity of 2-methylpropane they used was 99.98 mol %.

In the present paper, the saturated densities along the vapor−liquid coexistence curve near the critical point have been measured by visual observation of the meniscus disappearance. On the basis of the present results, the critical parameters for 2-methylpropane have been determined with high accuracy. In addition, the critical exponent β along the coexistence curve is also discussed.

Experimental Section

Chemicals. The sample of pure 2-methylpropane was furnished by Takachiho Chemical Industrial Co. Ltd., Japan. The manufacturer stated that the sample purity of 2-methylpropane was better than 99.99 %. This sample was used without further purification.

Apparatus for the Vapor−Liquid Coexistence Curve Measurement. The measurements of the vapor−liquid coexistence curve near the critical point was made by the observation of the meniscus disappearance. The apparatus has been described in detail the previous papers.[5,6] The main portion of the apparatus was composed of an optical cell, an expansion vessel, and a supply vessel. The optical cell was the main vessel in which the change of the meniscus behavior of the sample mixture was observed. The cylindrical body of this optical cell was made of 304 stainless steel (50 mm long, (16 to18) mm i.d., and 12 cm^3 volume) with two Pyrex windows (15 mm thick). The inner shape of this optical cell was barrel-shaped in order to make it easier to observe the meniscus disappearance. The expansion vessel and supply vessel were used to change the sample density in the optical cell without a new sample charge.

The apparatus was installed in a thermostated silicone oil bath. The bath temperature was kept constant within a temperature fluctuation of ± 5 mK. Temperature measurement was made with a 25 Ω standard platinum resistance thermometer calibrated against ITS-90 with the aid of a thermometer bridge (Automatic Systems Laboratories, F17A). The thermometer was mounted in the vicinity of the optical cell. The uncertainty of temperature measurements was estimated to be within ± 10 mK. The sample density was calculated from the sample mass and the inner volumes of the pressure vessels. The uncertainty of the sample density was estimated to be within ± (0.3 to 0.6) kg·m^{-3}.

Results and Discussions

Measurements of the Vapor−Liquid Coexistence Curve near the Critical Point. The vapor−liquid coexistence curve near the critical point for 2-methylpropane was measured by the observation of the meniscus disappearance. The experimental data of saturated liquid and vapor densities are summarized in Table 1. Twelve data of saturated vapor densities, nine data of saturated liquid densities, and one datum in the close vicinity of the critical point, which was undistinguishable as to whether of was saturated liquid or saturated vapor, were obtained in the temperature range from 390.397 K to the critical temperature and in the density range between (90.6 and 388.9) kg·m^{-3}. The uncertainty of each density measurement is different because an expansion procedure was introduced to change the sample density. The uncertainty of the density measurements is given in Table 1.

Figure 1 shows the vapor−liquid coexistence curve near the critical point for 2-methylpropane on the temperature−density plane. No other experimental data along the coexistence curve near the critical point can be found. The calculation results with

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Table 1. Experimental Saturated Densities near the Critical Point for 2-Methylpropane[a]

T/K	ρ/kg·m^{-3}	$\Delta\rho$/kg·m^{-3}	T/K	ρ/kg·m^{-3}	$\Delta\rho$/kg·m^{-3}
390.397	388.9	0.3	407.788	219.3*	0.6
397.488	358.7	0.3	407.757	202.3*	0.5
400.692	341.9	0.3	407.653	192.9*	0.5
402.344	330.3	0.3	407.214	179.1	0.1
405.220	308.1	0.5	407.029	173.9	0.6
406.706	289.4	0.2	406.169	160.4	0.6
406.958	284.3	0.4	404.542	142.0	0.2
407.516	271.0*	0.4	398.815	114.2	0.5
407.751	244.3*	0.6	394.977	101.1	0.3
407.795	229.4*	0.3	393.732	98.2	0.5
407.791	225.4*	0.5	391.403	90.6	0.5

[a] Critical opalescence was observed at the data point with an asterisk.

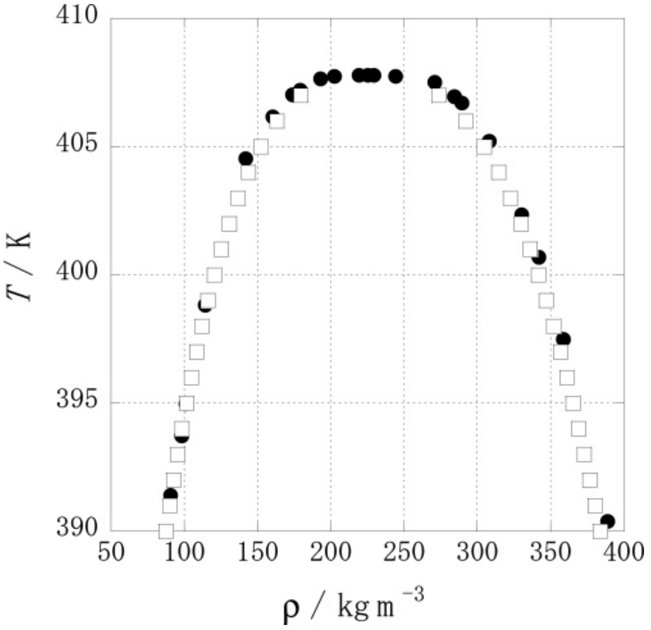

Figure 1. Vapor−liquid coexistence curve near the critical point for 2-methylpropane: ●, present work, □, REFPROP 7.0.

the interval of 1 K by REFPROP 7.0[7] are also plotted in this figure. To calculate the saturated liquid and vapor densities for 2-methylpropane, REFPROP 7.0 had adopted the equation of states developed by Miyamaoto and Watanabe.[8] With respect to the saturated vapor density, the present data are in good agreement with the REFPROP calculation. On the other hand, the saturated-liquid density values of the present work are systematically greater than the REFPROP values.

Critical Temperature and Critical Density for 2-Methylpropane. The critical opalescence was observed at seven data marked with asterisk in Table 1 in the density range from (192.9 to 271.0) kg·m^{-3}. The meniscus at the density of 219.3 kg·m^{-3} was located at the center level in the optical cell when the temperature was room temperature. With increase in temperature, the meniscus level gradually descended but disappeared prior to reaching the bottom of the optical cell. At this density, the intensity of the critical opalescence in the liquid phase was observed to be stronger than that in the vapor phase. This density was considered to be at a condition that was lower than the critical density.

The meniscus at the density of 244.3 kg·m^{-3} was located at the center level in the optical cell when the temperature was room temperature. With increase in temperature, the meniscus level gradually ascended but disappeared prior to reaching the top of the optical cell. At this density, the intensity of the critical opalescence in the vapor phase was observed to be stronger than that in the liquid phase. This density was considered to be at a condition that was higher than the critical density.

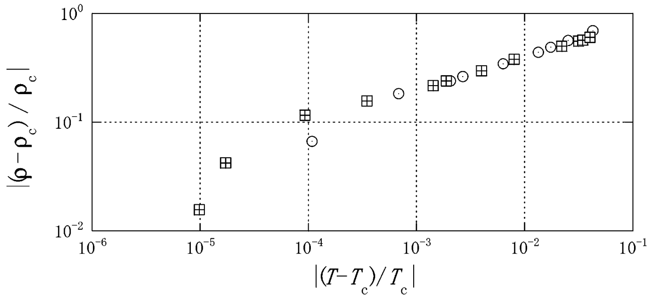

Figure 2. Temperature dependence of the reduced density difference: ○, saturated liquid; □, saturated vapor.

The meniscus at the densities of (225.4 and 229.4) kg·m^{-3} were located at the center level in the optical cell when the temperature was the room temperature. The meniscus level was unchanged at the center in the optical cell with increasing temperature and finally disappeared at the center level. Moreover the meniscus reappearance level was located at the center level. It was observed that, at the density of 229.4 kg·m^{-3}, the intensity of the critical opalescence in the vapor phase was almost same as that in the liquid phase. But at the density of 225.4 kg·m^{-3}, the intensity of the critical opalescence in the liquid phase was observed to be just stronger than that in the vapor phase. Therefore, the density of 229.4 kg·m^{-3} was considered to be very close to the critical density, but the density of 225.4 kg·m^{-3} was slightly toward the saturated vapor density value.

On the basis of these observations of meniscus disappearance, the critical temperature T_c and the critical density ρ_c for 2-methylpropane were experimentally determined as:

$$T_c = (407.795 \pm 0.010)\ \mathrm{K} \tag{1}$$

$$\rho_c = (229 \pm 2)\ \mathrm{kg{\cdot}m^{-3}} \tag{2}$$

The critical molar volume V_c was converted from the critical density using the molar mass of 2-methylpropane,[9] $M = 58.1222$ g·mol^{-1}:

$$V_c = (253.8 \pm 2.2)\ \mathrm{cm^3{\cdot}mol^{-1}} \tag{3}$$

Critical Pressure for 2-Methylpropane. The critical pressure P_c could be determined indirectly with this experimental apparatus. The critical pressure was calculated by the extrapolation from the vapor-pressure correlation with the aid of T_c value given in eq 1. The scaled vapor−pressure correlation proposed by Levelt Sengers et al.[4] was used because of its high reliability and high reproducibility in the vicinity of the critical point.

With respect to the vapor−pressure correlation by Levelt Sengers et al., their critical temperature T_c value of 407.84 K (IPTS-68) was determined by direct measurements. Since their T_c value is slightly higher than the present T_c value in eq 1, the present critical pressure was calculated by substituting the present T_c value in their vapor-pressure correlation. The critical pressure for 2-methylpropane was determined as 3628.2 kPa. The uncertainty of the critical pressure depends on the uncertainty of the critical temperature and the accuracy of the vapor−pressure correlation. Taking into consideration of these factors, the critical pressure for 2-methylpropane was estimated finally as follows:

$$P_c = (3628.2 \pm 1.4)\ \mathrm{kPa} \tag{4}$$

The critical temperature reported by Levelt Sengers et al., $T_c = 407.84 \pm 0.02$ K seems to be greater than the present critical temperature 0.045 K. It should be noted that their paper was published in 1983. At that time, the temperature scale was used not ITS-90 but IPTS-68. Converted the temperature value from IPTS-68 to ITS-90, the T_c value by Levelt Sengers et al. changes to (407.807 ± 0.020) K. This new T_c value is in good agreement with the present T_c value, (407.795 ± 0.010) K within the experimental uncertainty.

Critical Exponent β**.** The critical exponent β along the coexistence curve can be determined on the basis of the power law representations:

$$(\rho - \rho_c)/\rho_c = B|\Delta T^*|^{\beta} \qquad (5)$$

where $\Delta T^* = (T - T_c)/T_c$ is the reduced temperature difference. Coefficient B and exponent β stand for the critical amplitude and the critical exponent along the coexistence curve, respectively.

The relation between $\log|(\rho - \rho_c)/\rho_c|$ and $\log|\Delta T^*|$ in eq 5 was drawn in Figure 2. The power law representation by eq 5 suggests that the experimental results may be fitted by a straight line with a gradient equivalent to the critical exponent β. Twenty saturated-density data except two data (i.e., 407.795 K and 407.791 K) in the close vicinity of the critical point were used to determine B and β by a least-squares fit. Using all of 20 data, the values of B and β and in eq 5 were obtained as $B = 1.85 \pm 0.14$ and $\beta = 0.330 \pm 0.012$. As for the critical exponent β, the present result is in agreement with the theoretical value of 0.325.

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