Measurements of the Vapor-liquid Coexistence Curve and Determination of the Critical Parameters for Refrigerant 13B1*

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Measurements of the vapor-liquid coexistence curve in the critical region for Refrigerant 13B1 (CBrF_3) were made by visual observation of the disappearance of the meniscus at the vapor-liquid interface within an optical cell. Twenty-two saturated densities for temperatures between 332 and 340 K were obtained in the range of densities 376 to 1108 kg/m^3 . The experimental uncertainties in temperature and density measurements were estimated within ± 10 mK and ± 0.5 %, respectively. Based upon the results along the coexistence curve, the critical temperature T_c , the critical density ρ_c and the critical pressure P_c for R 13B1 were determined to be 340.08 K, 764 kg/m^3 and 3.956 MPa, respectively, in consideration of the disappearing meniscus level as well as the intensity of the critical opalescence. In addition, the critical exponent β was determined to be 0.340 and the correlation of the vapor-liquid coexistence curve for R 13B1 was established.

Key Words : Thermophysical Properties, Bromotrifluoromethane, Vapor-liquid Coexistence Curve, Critical Point, Critical Parameters, Critical Exponent

1. Introduction

The critical parameters of temperature, density and pressure are of essential importance for formulating an equation of state and for predicting various thermodynamic properties with an aid of the principle of corresponding states as well as for understanding the thermodynamic state surface of fluids. The thermodynamic behaviors of fluids near the critical point, however, are too complicated to determine the critical parameters easily. Only limited informations about the critical parameters of fluids with high accuracy are available.

Using the apparatus designed by Okazaki et al.⁽¹⁾ to determine the critical parameters by a relatively simple procedure but with high accuracy, measurements of the vapor-liquid coexistence curve in the critical region for bromotrifluoromethane (R 13B1 : CBrF_3), which is expected to be a working fluid for refrigeration, heat pump and organic Rankine cycle systems, were made by visual observation of the meniscus disappearance at the vapor-liquid interface. On the basis of these results, the critical parameters of R 13B1 were determined. In addition, the correlation of the vapor-liquid coexistence curve which is

applicable in a wide density range is established.

2. Experimental Apparatus and Procedures

2.1 Principle of measurement

In the present study, the meniscus disappearance at the vapor-liquid interface was directly observed to determine the vapor-liquid coexistence curve in the critical region and the critical parameters. Three kinds of phase transitions in an optical cell with constant volume can be recognized on account of a difference in the sample density. Suppose the sample of a certain density, which is smaller than the critical density, is confined in the cell. In this case the meniscus locates below the center level of the cell in the two-phase region where the saturated vapor and saturated liquid coexist, and descends gradually with increasing temperature. Finally the vapor occupies the cell completely at the dew point and the meniscus disappears at the bottom of the cell. When the density is larger than the critical density, the meniscus locates above the center level of the cell in the two-phase region. With increasing temperature, the meniscus ascends gradually until the liquid occupies the cell completely at the bubble point and disappears at the top of the cell. In case of the critical density, the meniscus level remains almost unchanged at the middle of the cell even with increasing temperature. And then the vapor-liquid interface becomes indistinguishable and finally disappears at the critical point where the dew- and bubble-point curves meet. At this state the critical opalescence which is a very important phenomenon to determine the critical parameters is intense.

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On the basis of these visual observations, the saturation temperature along the vapor-liquid coexistence curve in the critical region can be measured as the meniscus disappearing temperature. And then the critical parameters can be determined by considering the meniscus disappearing level as well as the intensity of the critical opalescence.

2.2 Experimental apparatus

A schematic setup of the experimental apparatus used is shown in Fig. 1. The main portion of the apparatus is composed of an optical cell A, an expansion vessel B and a supplying vessel C. The meniscus behavior of the sample in the optical cell is observed through two sapphire windows (15 mm in thickness). The expansion vessel is used to change the sample density in the optical cell and the supplying vessel for supplying the sample to the optical cell. These three cylindrical vessels made of 304 stainless steel are connected to each other by three high pressure valves, i.e., V_1 , V_2 and V_3 . A rocking mechanism is provided in this apparatus to carry out the measurements not only of pure substances but also of mixtures. Three vessels are set on the rocking frame, which is designed to generate a rocking motion to 10 cycles per minute, in order to keep homogeneity of the sample density and composition in charging or expansion of the sample.

The main portion of the apparatus is installed in a thermostated bath D (600 x 600 x 650 mm in inner dimensions) with two flat glass windows (150 mm in vertical and 250 mm in horizontal). Owing to the light of a 10 W fluorescent lamp coming through the optical cell from the window on one side of the thermostated bath, the meniscus behavior and the critical opalescence can be directly observed from the window on the other side. The bath is equipped with five independent electric heaters E (1 kW x 1,

750 W x 2, 500 W x 2) in two side walls which are not equipped with windows and in the bottom of the bath. A heat transfer medium F is heated by supplying the electric power to the heaters. In the selection of the heat transfer medium, high thermal stability, low viscosity and transparency were considered. Thermal stability and viscosity are required to control the temperature in the thermostated bath, while transparency is essential to detect a delicate change in colors and intensities of the critical opalescence. In the present study, water was used as a heat transfer medium and was circulated by a stirrer G to minimize the temperature distribution in the thermostated bath.

The temperature measurements were conducted with a 25 Ω platinum resistance thermometer H (Chino:Model R800-1) on IPTS-68 with an aid of a Mueller-type bridge (Shimadzu:type BD-100). The thermometer was mounted in the vicinity of the optical cell at the same level in the thermostated bath. Since the sample temperature was not measured directly, full care was taken to confirm thermodynamic equilibrium between the sample and the thermostated bath fluid during the experiments. The increasing rate of temperature in the bath was 180 to 200 mK/min for temperatures up to about 2 K below the saturation temperature, and was gradually reduced to 1 to 5 mK/min with approaching to the saturation temperature. When the temperature became close enough to the saturation temperature, the bath fluid temperature was kept constant within a fluctuation of ± 5 mK for about 30 min., and the behavior of the meniscus was carefully observed. Then the bath fluid temperature was increased again by a few mK, and kept constant. Repeating this procedure until the meniscus disappears completely, the saturation temperature was determined as the temperature when the vapor-liquid interface disappeared. In the case of the density being near the critical point, especially, the bath temperature was kept constant for about one or two hours and the meniscus behavior was observed with particular care. The possible uncertainty in the temperature measurements is estimated within ± 10 mK, including the fluctuation of temperature controlled which is within ± 5 mK, the precision of the thermometer used which is within ± 1 mK, and an individual difference with respect to the determination of the meniscus disappearance temperature.

2.3 Experimental procedure

The present measurements were carried out by the constant-volume method coupled with expansion procedures to change the sample density. After the sample whose mass was m was prepared in the supplying vessel, the three vessels, i.e., the optical cell A (15.067 ± 0.005 and 15.126 ± 0.005 cm³ in inner volume^{*1}), the expansion vessel B (7.355 ± 0.005 cm³) and the supplying vessel C (77.052 ± 0.005 cm³), were assembled and immersed into the thermostated bath D as shown in Fig. 1. The inner volume of the three vessels, including the tubing and the valves, was

- A : Optical cell
- B : Expansion vessel
- C : Supplying vessel
- D : Thermostated bath
- E : Electric heater
- F : Heat transfer medium
- G : Stirrer
- H : Platinum resistance thermometer
- V_1, V_2, V_3 : High pressure valves

Fig. 1 Experimental setup

calibrated by filling water with known density values under the room temperature condition. Evacuating the optical cell and the expansion vessel to a vacuum of around 0.5 mPa, the sample in the supplying vessel was transferred into the optical cell and the expansion vessel. We call this process of transferring the sample from the supplying vessel "principal expansion". After the first principal expansion, the sample density, $\rho(1,0)$, was obtained in the optical cell. The initial mass filling the supplying vessel divided by the overall inner volumes of three vessels is taken as the sample density, $\rho(1,0)$.

After completing the measurement for the density $\rho(1,0)$, the valve V_2 leading to the vacuum pump was opened to discharge the sample from the expansion vessel and to evacuate the expansion vessel, while the other two valves V_1 and V_3 were closed. Then the sample within the optical cell was expanded only into the expansion vessel and thus a new density $\rho(1,1)$ of the sample was established within the system including the optical cell and the expansion vessel. We call this secondary expansion process "subsequent expansion". The value of the density, $\rho(1,1)$, can be calculated by the initial mass filling the supplying vessel and the overall inner volumes of the three vessels.

By combining these two expansion procedures, i.e., principal and subsequent expansions, almost infinite measurements may be performed by a single filling of the sample into the supplying vessel as far as the theory is concerned. After completing the principal expansion N_p times and the subsequent expansion N_s times, the density of the sample $\rho(N_p, N_s)$ can be expressed by the equation

$$\rho(N_p, N_s) = \frac{m V_A^{N_p} V_C^{N_s}}{(V_A + V_B + V_C)^{N_p} (V_A + V_B)^{N_s}}, \quad (1)$$

where N_p is an arbitrary integer starting from unity and N_s from zero.

Although we can perform a considerable number of measurements by a single filling of the sample by this method, it is unavoidable that the experimental uncertainty with respect to the measured density becomes larger in proportion to the total number of expansion procedures. Hence, in the present study, we have always limited the expansion procedures until $N_p \leq 3$ as well as $N_s \leq 2$ corresponding to each single principal expansion so as to maintain the uncertainty of the measured density within $\pm 0.5\%$. The thermal expansion of the inner volume containing the sample amounts to about 0.43 % of the inner volume at the highest temperature of the present study. This temperature effect was corrected using the available information about the linear thermal expansion coefficient for the 304 stainless steel⁽²⁾. The pressure deforma-

tion was calculated by the theoretical stress analysis under the condition of 5 MPa and 383 K which is higher than the critical condition. The result was much less than 1/27 of the effect due to the thermal expansion. Therefore we concluded that pressure effect was negligible.

3. Measurements of the Vapor-liquid Coexistence Curve

The experimental results of the meniscus disappearing temperature for the sample density of R 13B1 in the critical region are given in Table 1. The sample purity of R 13B1 used in the present study is shown in Table 2. Twenty-two measurements have been made for densities between 376.5 and 1108.0 kg/m³ corresponding to temperatures between 332.02 and 340.08 K. The uncertainty in temperature measurements is estimated within ± 10 mK. The uncertainty in density measurements is estimated by applying the propagation of error to Eq. (1) as follows: within $\pm 0.08\%$ for the densities of 559.4, 768.2, 908.6, 975.5, 1024.2 and 1108.0 kg/m³ corresponding to $\rho(1,0)$, within $\pm 0.27\%$ for the densities of 376.5, 516.9, 611.3, 656.3 and 745.3 kg/m³ corresponding to $\rho(1,1)$, within $\pm 0.47\%$ for the densities of 411.4, 441.7 and 501.5 kg/m³ corresponding to $\rho(1,2)$, within $\pm 0.16\%$ for the densities of 594.7, 703.4, 755.1, 793.2 and 857.5 kg/m³ corresponding to $\rho(2,0)$, within $\pm 0.36\%$ for the densities of 400.2 and 473.3 kg/m³ corresponding to $\rho(2,1)$, and within $\pm 0.24\%$ for the density of 544.5 kg/m³ corresponding to $\rho(3,0)$, respectively.

The meniscus for 12 densities between 376.5 and 656.3 kg/m³ descended with increasing temperature and disappeared at the bottom of the optical cell, whereas that for four densities between 908.6 and 1108.0 kg/m³ ascended with increasing temperature and disappeared at the top of the optical cell. The meniscus for the densities of 703.4 and 745.3 kg/m³ descended with increasing temperature but

Table 1 Experimental results for R 13B1

T (K)	ρ (kg/m ³)	T (K)	ρ (kg/m ³)
332.016	376.5	339.917	656.3*
333.401	400.2	340.019	703.4*
333.924	411.4	340.082	745.3*
335.284	441.7	340.076	755.1*
336.543	473.3	340.084	768.2*
337.510	501.5	340.079	793.2*
337.950	516.9	340.008	857.5*
338.722	544.5	339.573	908.6
338.964	559.4	338.655	975.5
339.451	594.7	337.680	1024.2
339.605	611.3	334.920	1108.0

*) Values with an asterisk were measured with observing the critical opalescence.

*1 The optical cell was disassembled twice before and during the experiment in order to clear the inside. Since its inner volume was calibrated whenever it was reassembled, we report here two values of the inner volume of the optical cell.

Fig. 2 Coexistence curve for R 13B1 in the critical region

Table 2 Sample purity

R 13 B1	99.965 wt%
R 22	0.013 wt%
R 23	0.005 wt%
R 13	0.004 wt%
unknown	0.013 wt%

disappeared prior to reaching the bottom of the optical cell, whereas that for the densities of 793.2 and 857.5 kg/m³ ascended with increasing temperature but disappeared prior to reaching the top of the optical cell.³ For the densities of 755.1 and 768.2 kg/m³, the meniscus level remained unchanged with increasing temperature, then became indistinguishable and finally disappeared.

When the sample density is equivalent to the critical density, the critical opalescence being a light scattering in the vicinity of the critical point is observed most intensely and uniformly above and below the vapor-liquid interface corresponding to the vapor phase and to the liquid phase, respectively. However, when the sample density is different from the critical density, a difference in the intensity of the critical opalescence between the vapor phase and the liquid phase is recognized. In the present study, the critical opalescence was observed in seven measurements for the densities between 656.3 and 857.5 kg/m³ marked in Fig. 2 with a black circle. At three densities of 656.3, 703.4 and 745.3 kg/m³ the critical opalescence in the liquid phase was observed more intensely than that in the vapor phase, whereas at two densities of 793.2 and 857.5 kg/m³ the critical opalescence in the vapor phase was observed more intensely than that in the liquid phase. At two densities of 755.1 and 768.2 kg/m³ no difference in the intensity of the critical opalescence was observed between the two phases.

As shown in Fig. 2, no measurements have been made in the density range below 1145 kg/m³ including the vicinity of the critical point. The present results are

the first measurements done to make clear the shape of the vapor-liquid coexistence curve for R 13B1 in the critical region. The meniscus disappearing temperatures in four measurements around the critical density between 745.3 and 793.2 kg/m³ agree within the uncertainty of the measured temperature. This shows that the shape of the vapor-liquid coexistence curve is flat on T - ρ plane in the very vicinity of the critical point. The saturated vapor line calculated from the equations of state by Rombusch⁽³⁾ and by Perel'shtein and Aleshin⁽⁴⁾ and the saturated liquid line calculated from the correlations for the saturated liquid density proposed by Rombusch⁽³⁾ and by Perel'shtein and Aleshin⁽⁴⁾ are also shown in Fig. 2. With respect to the saturated liquid density, the correlation by Rombusch is in good agreement with the present data. With respect to the saturated vapor density, the equation of state by Perel'shtein and Aleshin is in good agreement with present data.

4. Determination of the Critical Parameters and the Critical Exponent β

4.1 Determination of the critical parameters

The critical parameters of R 13B1 have been determined on the basis of the present results along the vapor-liquid coexistence curve given in Table 1. With respect to the determination of the critical density ρ_c , we first determined, as described in Section 2.1, whether respective results corresponded to saturated vapor or to saturated liquid in consideration of the meniscus disappearing level and the intensity of the critical opalescence. As a result of this procedure, it was found that the critical density of R 13B1 is between 755.1 and 768.2 kg/m³. For the density of 755.1 kg/m³, the meniscus disappeared as it descended slightly from the center level of the optical cell to a little lower level with increasing temperature. The critical opalescence at the liquid phase was observed more intensely than that at the vapor phase. The meniscus reappearing level with decreasing temperature came between the center and the bottom of the optical cell. For the density of 768.2 kg/m³, the meniscus disappeared as it ascended very slightly from the center level of the optical cell to a little lower level with increasing temperature. The critical opalescence at the liquid phase was observed as intensely as that at the vapor phase. The meniscus reappearing level with decreasing temperature was the center of the optical cell. On the basis of these observations, we considered that the density of 768.2 kg/m³ was closer to the critical density than that of 755.1 kg/m³. Hence in consideration of the uncertainty of the measured density, we have determined the critical density of R 13B1 as

$$\rho_c = 764 \pm 3 [\text{kg/m}^3], \dots \dots \dots (2)$$

Table 3 Reported values of the critical parameters for R 13B1

Investigator(s)	T_c (K)	ρ_c (kg/m ³)	P_c (MPa)	Sample purity	Method*
Eiseman, Jr. ⁽⁶⁾	340.05	750	4.34	—	6
du Pont ⁽⁷⁾	340.15	744.8	3.964	—	—
Rombusch ⁽³⁾	340.15	744.8	3.9846	—	5
Perel'shtein et al. ⁽⁴⁾	340.05	717.3	3.9577	99.99%	3, 4
Rathjen et al. ⁽⁸⁾	340.185±0.015	745	4.063	99.98%	2, 5
Present work	340.08±0.01	764±3	3.956±0.002	99.965%	1, 3, 6

*) 1. Disappearance of the meniscus, 2. Reappearance of the meniscus,
3. Extrapolation of vapor pressure correlation, 4. Law of rectilinear diameter,
5. The selected value, 6. Other method.

The critical temperature T_c can be determined as the saturation temperature (strictly speaking, the meniscus disappearing temperature in the present study) corresponding to the critical density. The meniscus disappearing temperature in four measurements around the critical density in the density range between 745.3 and 793.2 kg/m³ agree within the uncertainty of the measured temperature ±10 mK. Therefore, considering the flat shape of the vapor-liquid coexistence curve in the very vicinity of the critical point on T - ρ plane, we have graphically determined the critical temperature from the data in Table 1 as

$$T_c = 340.08 \pm 0.01 [\text{K}], \dots \dots \dots (3)$$

Since we did not measure the sample pressure directly for the purpose of preventing the thermodynamic stability of the sample from being disturbed, the critical pressure P_c was determined by extrapolating the most reliable vapor-pressure correlation to the critical temperature. As for the vapor-pressure correlation of R 13B1, we adopted the one given by Suzuki ⁽⁵⁾, because the sample purity of R 13B1 used in his experiment was the same as that of our sample and his correlation reproduced his experimental results with an average pressure-deviation of 0.02 %. The critical pressure was determined as 3.956₀ MPa by extrapolation Suzuki's vapor-pressure correlation to the critical temperature determined as 340.08 K. In consideration of the uncertainty of the critical temperature determined and that of vapor-pressure correlation used, we have determined the critical pressure of R 13B1 as

$$P_c = 3.956 \pm 0.002 [\text{MPa}], \dots \dots \dots (4)$$

Information about the critical parameters of R 13B1 is summarized in Table 3. Although the critical parameters of R 13B1 have been reported by five investigations, no experimental information except that on given by du Pont ⁽⁷⁾ and Rathjen and Straub ⁽⁸⁾ is available. The critical temperature determined in the present study is not in good agreement with other reported values within the uncertainties claimed by each investigation. The present T_c value is higher than those Eiseman, Jr. ⁽⁶⁾ and of Perel'shtein and Aleshin ⁽⁴⁾ by 30 mK,

whereas it is lower than that of du Pont ⁽⁷⁾ and of Rombusch ⁽⁸⁾ by 70 mK and of Rathjen and Straub ⁽⁸⁾ by 105 mK. The present ρ_c value is larger than other five values reported. For the density of 745.3 kg/m³ which is close to the critical density proposed by the previous investigators, meniscus was observed below the center level of the optical cell when the sample temperature was lower by 20 K than the meniscus disappearing temperature. The meniscus descended with increasing temperature and disappeared prior to reaching the bottom of the optical cell. It was confirmed that this density was smaller than the critical density. The present P_c value is in good agreement with that determined by Perel'shtein and Aleshin. As for the value reported by Rathjen and Straub, we fear that there may exist some mistakes in the conversion of units for P_c values of R 13B1, R 12, R 22, etc., in their report.

4.2 Determination of the critical exponent β

The critical exponent β is important to correlate the vapor-liquid coexistence curve in the critical region and it can be defined by the power law representation as

$$|(\rho - \rho_c)/\rho_c| = B|(T - T_c)/T_c|^\beta, \dots \dots \dots (5)$$

where ρ , T , ρ_c , T_c and B denote density, temperature, critical density, critical temperature and adjustable parameter, respectively. Applying least-squares fitting to Eq. (5) based on 18 available data in the range of reduced temperature differences $1.8 \times 10^{-4} < |(T - T_c)/T_c| < 2.4 \times 10^{-2}$, we have determined the values of β and B as 0.340 and 1.821, respectively. Four measurements around the critical point were excluded from input data for least-squares fitting, because the temperature in those measurements was very close to the critical temperatures. The values of β and B are in good agreement with those reported by Rathjen and Straub ⁽⁸⁾, i.e., $\beta = 0.3414$ and $B = 1.90725$. The authors' research group reported previously the critical exponent β for other refrigerants, i.e., 0.345 for R 116 ⁽⁹⁾, 0.347 for R 23 ⁽¹⁰⁾, 0.337 for R 12 ⁽¹¹⁾ and 0.348 for R 22 ⁽¹¹⁾. All of these values are a little greater than 1/3 and theoretical results due to scaling law, i.e., 0.325 ⁽¹²⁾.

5. Formulation of the Correlation of the Vapor-liquid Coexistence Curve

Recently the saturated vapor density and the saturated liquid density are expressed as a function of temperature in a single expression⁽¹³⁾. The expression for the vapor-liquid coexistence curve is generally given as follows:

$$\rho = \rho^{\pm}(T), \dots\dots\dots (6)$$

where the positive sign in the superscript indicates the saturated liquid and the negative sign the saturated vapor. Based on the present results in addition to the experimental data evaluated to be reliable, the vapor-liquid coexistence curve of R 13B1 was correlated by a process of extending the applicable range of temperatures from the critical temperature to the lower temperature. We intend to generalize the vapor-liquid coexistence curve correlation so as to suit the power law near the critical point, to make the functional form as simple as possible and to make it applicable to many different fluids.

The law of rectilinear diameter and the power law are well known as the simplest representation of the vapor-liquid coexistence curve, in other words, the relations between temperature and density of the saturated liquid, ρ^+ , and the saturated vapor, ρ^- . These laws are represented by any one of the following expressions.

$$(\rho^+ + \rho^-)/2\rho_c = 1 + D_1|\Delta T^*|, \dots\dots\dots (7)$$

$$(\rho^+ - \rho^-)/2\rho_c = B_0|\Delta T^*|^{\beta}, \dots\dots\dots (8)$$

Here ΔT^* indicates the reduced temperature difference $(T - T_c)/T_c$. B in Eq. (5) is equivalent to B_0 in Eq. (8). By combining Eqs. (7) and (8), the following expression can be derived

$$(\Delta\rho^*)^{\alpha} = D_1|\Delta T^*| \pm B_0|\Delta T^*|^{\beta}, \dots\dots\dots (9)$$

where $\Delta\rho^*$ indicates the reduced density difference $(\rho - \rho_c)/\rho_c$. The densities of saturated liquid and vapor are conveniently expressed by the same equation⁽¹⁴⁾ given in Eq. (9). It is known, however, that the law of rectilinear diameter is not applicable near the critical point even if that is applicable in the range far from the critical point⁽¹⁵⁾. We should be careful in combining the law of rectilinear diameter and the power law which is applicable near the critical point.

Thus we discussed the following two representations by Wegner expansion for the coexistence curve⁽¹²⁾, which is considered the representation for the expansions of the law of rectilinear diameter and of the power law.

$$(\rho^+ + \rho^-)/2\rho_c = 1 + D_0|\Delta T^*|^{1-\alpha} + D_1|\Delta T^*| + D_2|\Delta T^*|^{1-\alpha+d_1} + \dots, \dots\dots\dots (10)$$

$$(\rho^+ - \rho^-)/2\rho_c = B_0|\Delta T^*|^{\beta} + B_1|\Delta T^*|^{\beta+d_1} + \dots, \dots\dots\dots (11)$$

As a result of trial and error, we adopted the simplest functional form obtained by the first two terms in Eq. (10) and the first term in Eq. (11).

$$(\Delta\rho^*)^{\alpha} = D_0|\Delta T^*|^{1-\alpha} \pm B_0|\Delta T^*|^{\beta}, \dots\dots\dots (12)$$

Here α indicates the critical exponent for the heat capacity at constant volume which becomes infinite at the critical point and is defined by the equation

$$C_v = A^*|\Delta T^*|^{-\alpha}, \dots\dots\dots (13)$$

The critical exponent α can not be determined from the present results. We adopted 0.1085 for α which is the value selected from the results of several theoretical analyses by Levelt Sengers and Sengers⁽¹²⁾.

With respect to the coefficient B and the critical exponent β in Eq. (12), the values determined in Section 4.2 were adopted. Using 30 input data composed of 18 present data, which were used for the determination of β , and 12 data for the saturated liquid density by du Pont⁽⁷⁾ in the temperature range between 173 and 333 K, the coefficient D_0 in Eq. (12) was determined by least squares fitting. Seven data on the saturated liquid density were reported by Geller and Nikul'shin⁽¹⁶⁾ in the temperature range between 203 and 263 K. We excluded their data from the input data on the correlation since their data showed a difference tendency from those of the present results and of du Pont.

The correlation of the vapor-liquid coexistence curve of R 13B1 has been determined in the present study as follows,

$$(\Delta\rho^*)^{\alpha} = 0.7612|\Delta T^*|^{0.8915} \pm 1.821|\Delta T^*|^{0.340}, \dots\dots\dots (14)$$

Figure 3 shows the results calculated from Eq. (14) on T - ρ plane with the data of the present work, of du Pont and of Geller and Nikul'shin. In order to check the behavior of the saturated vapor densities, the results calculated from the equation of state by Perel'shtein and Aleshin⁽⁴⁾ are also shown for every 10 K in the temperature range between 143 and 323 K.

The average deviation and the systematic deviation, which is the average value of density deviations, of the 18 present data used as the input data on the correlation are 1.66 and -1.45 %, respectively. Fifteen present data except three data for temperatures from 332.016 to 332.924 K are in agreement with Eq. (14) within ± 2 %. The average deviation and the systematic deviation of 12 du Pont's data are 0.14 and -0.05 %, respectively. Ten data in the temperature range below 323.15 K are in good agreement with Eq. (14) within ± 0.2 %. With respect to Geller and Nikul'shin's data excluded from the input data, the density deviation becomes greater with increasing temperature and that at 263.15 K, which is the highest temperature of their data is -1.84 %.

The saturated liquid density can be calculated by Eq. (14) with high accuracy as mentioned above. However Eq. (14) does not satisfactorily reproduce the saturated

Fig. 3 Coexistence curve for R 13B1

vapor density, though it shows generally an acceptable behavior on T - ρ plane as shown in Fig. 3. The difference between the results calculated from Eq. (14) and those from the equation of state by Perel'shtein and Aleshin exceeds -10 %. The reason is not only due to the lack of the experimental data below 330 K, which resulted in correlating Eq. (14) without input data of the saturated vapor density covering the temperature range below 330 K, but also due to the unsuitability of the functional form of Eq. (14) for the saturated vapor density. In the midst of the process of reaching this correlation, we found the term of $|\Delta T^*|^{1-\alpha+\Delta 1}$ in Eq. (10) effective to represent the saturated vapor density but not for the saturated liquid density. Although it is necessary to add some terms to Eq. (14) in order to represent both the saturated liquid density and the saturated vapor density with high accuracy, the published data on R 13B1 are too much limited not only qualitatively but also quantitatively.

6. Conclusion

In the present study, we measured the vapor-liquid coexistence curve of R 13B1 in the critical region for the first time and made clear its shape on T - ρ plane. On the basis of present data near the critical point, we newly determined the critical parameters of R 13B1 with high accuracy and compared them with previous values reported. In addition, applying the Wegner expansion, we correlated the vapor-liquid coexistence curve including the critical region. Although the correlation given in Eq. (14) is not accurate enough to calculate the saturated vapor density, the saturated liquid density can be calculated by Eq. (14) with high accuracy.

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