International Journal of Thermophysics, Vol. 5, No. 2, 1984

Determination of the Vapor–Liquid Coexistence Curve and the Critical Parameters for Refrigerant 502[1]

Y. Higashi,[2] M. Uematsu,[2] and K. Watanabe[2]

Received February 8, 1984

The vapor–liquid coexistence curve for refrigerant 502 (R 502) near the critical point has been determined by visual observation of the disappearance of the meniscus. Twenty-six saturated densities between 262 and 899 $\text{kg} \cdot \text{m}^{-3}$ have been obtained within an experimental error in temperature and density of ±10 mK and ±0.5%, respectively. Using these results along the vapor–liquid coexistence curve, the critical parameters, i.e., the critical temperature $T_c = 355.37 \pm 0.01$ K and the critical density $\rho_c = 555 \pm 3$ $\text{kg} \cdot \text{m}^{-3}$, have been determined based on the disappearance of the meniscus level as well as on the intensity of the critical opalescence. A critical pressure $P_c = 4.070 \pm 0.002$ MPa has been calculated from the existing vapor-pressure correlation using the present T_c value. In addition, the critical exponent β along the coexistence curve and the law of rectilinear diameter near the critical point are discussed.

KEY WORDS: critical exponent; critical parameter; critical point; law of rectilinear diameter; refrigerant 502 (R 502); vapor–liquid coexistence curve.

1. INTRODUCTION

The critical parameters of temperature, density, and pressure are of essential importance not only for understanding the thermodynamic state surface of fluids, but also for predicting various thermodynamic properties with the aid of the principle of corresponding states. Here we discuss the critical parameters of refrigerant 502 (R 502) in accord with the vapor–

---

[1] Paper presented at the Japan–United States Joint Seminar on Thermophysical Properties, October 24–26, 1983, Tokyo, Japan.

[2] Department of Mechanical Engineering, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223, Japan.

0195-928X/84/0600-0117$03.50/0

liquid coexistence curve in the region near the critical point, for which very few results have been reported up to now.

Refrigerant 502 is expected to be a prospective working fluid for advanced heat pump systems; it is assigned to a minimum-boiling azeotrope of 48.8 wt % R 22 ($CHClF_2$: chlorodifluoromethane) + 51.2 wt % R 115 (C_2ClF_5: chloropentafluoroethane). We have measured the compressibility and vapor pressure of this substance in the range of temperatures 273–383 K and of pressures 0.12–12.3 MPa [1]. This paper reports measurements of the vapor–liquid coexistence curve for R 502 in the density range 262.4–898.6 $kg \cdot m^{-3}$ based on visual observation of the disappearance of the meniscus at the vapor–liquid interface. The critical parameters are also reported.

2. EXPERIMENTAL

The vapor–liquid phase transition for a given mass of sample fluid can be observed using an optical cell with constant volume as shown schematically in Fig. 1. Suppose that a certain density ρ_A smaller than the critical density is realized in the cell. The meniscus at a state A_1 at temperature T_1 descends gradually through A_2 with increasing temperature. The meniscus then disappears at the bottom of the cell at A_s, where the vapor occupies the cell completely. The temperature corresponding to this state A_s is the saturation temperature for ρ_A. For a different density ρ_B larger than the critical density the meniscus ascends gradually with increasing temperature from a state B_1 through B_2 to B_s where the saturated liquid state is observed at the saturation temperature. In the case of the critical density

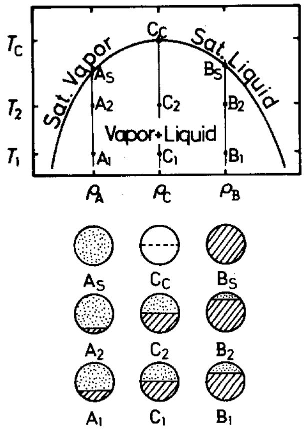

Fig. 1. Meniscus behavior of the coexisting fluid.

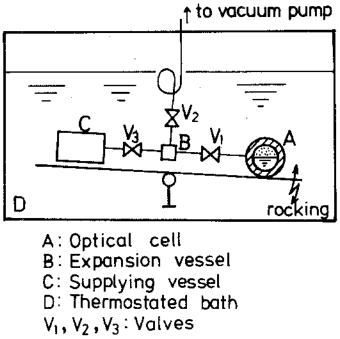

Fig. 2. Experimental setup.

ρ_C, however, the meniscus level is kept almost unchanged at the central level of the cell, as shown with C_1 and C_2, even with increasing temperature. The vapor–liquid interface becomes indistinguishable and finally disappears at a state C_c where critical opalescence is observed intensely. The temperature at this state is determined as the critical temperature. Careful visual observation yields the vapor–liquid coexistence curve, and the critical temperature and density are directly determined by analyzing the data based on disappearance of the meniscus level as well as on the intensity of the critical opalescence.

The experimental apparatus used is shown in Fig. 2; details are described in previous publications [2, 3]. For the purpose of measuring saturation temperatures successively for a series of densities along the coexistence curve, we used an expansion technique in the meniscus observation. The optical cell was connected with an expansion vessel to repeat the expansion procedures from the optical cell to the expansion vessel after the measurement of a saturation temperature. Another vessel, called a supplying vessel, was connected with both the optical cell and the expansion vessel, which allowed the sample in the supplying vessel to be supplied to the optical cell after completion of a single series of expansion procedures. Careful attention was paid to the expansion procedure in order not to change the sample composition and also to homogenize the sample density after the expansion procedure.

The optical cell was a cylindrical vessel made of 304 stainless steel (50 mm long, 19 mm in inner diameter, 15 cm^3 in inner volume) with two synthetic sapphire windows (15 mm in thickness). The inner volume of the cell was calibrated to be 15.126 ± 0.005 cm^3 by filling water with known density values under room-temperature conditions. The expansion vessel and the supplying vessel were also cylindrical and made of 304 stainless steel. Their inner volumes were 7.355 ± 0.005 and 77.052 ± 0.005 cm^3, respectively.

After the sample, which was weighed on a precision chemical balance (Chyo: C_2-3000), was prepared in the supplying vessel, these three vessels were assembled and immersed in a thermostated bath where liquid paraffin oil was used as a heat transfer medium. When the optical cell and the expansion vessel were evacuated under vacuum to around 0.5 mPa, the sample in the supplying vessel was then expanded into the system of the optical cell and the expansion vessel. After the valves between vessels were closed, the behavior of the meniscus in the optical cell was carefully observed with increasing temperature and the saturation temperature was determined as the temperature when the vapor–liquid interface disappeared. Then the experiment was continued by expansion procedures.

The density of the sample in the optical cell can be calculated from the mass of the sample and the inner volumes of the three vessels used. Although we can obtain a considerable quantity of data by a single filling of the sample with the expansion procedures, it is unavoidable that the experimental error with respect to the measured density becomes large in proportion to the total number of expansion procedures. Hence, in the present study, we restricted the expansion procedures to eight times so as to maintain the error of the measured density within $\pm 0.5\%$.

The temperature measurements were conducted with a 25-Ω platinum resistance thermometer (Chino: Model R800-1) calibrated with a precision of 5 mK against IPTS-68 at the National Research Laboratory of Metrology, Ibaraki, Japan, with the 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 attention was paid to establish thermodynamic equilibrium between the sample in the optical cell and the thermostated bath fluid during the experiments. The bath temperature was kept constant within the fluctuation of ± 3 mK. The uncertainty in the temperature measurement is mainly due to such factors as the precision of the thermometer used, the fluctuation of the controlled temperature, and individual differences with respect to the temperature determination of the disappearing meniscus. We estimated it within the uncertainty of ± 10 mK.

The composition of the sample of R 502 used in the present study was analyzed to be 49.02 wt % R 22 and 50.97 wt % R 115 by gas chromatography.

3. RESULTS AND DISCUSSION

3.1. Vapor–Liquid Coexistence Curve

The experimental temperature–density data along the vapor–liquid coexistence curve of R 502 are given in Table I. Twenty-six measurements

Table I. Experimental Results for R 502[a]

T (K)	ρ ($\mathrm{kg \cdot m^{-3}}$)
345.97_2	262.4 ± 1.4
347.67_1	279.5 ± 1.5
348.57_9	293.6 ± 1.6
349.18_2	301.9 ± 1.3
350.23_6	321.6 ± 1.4
351.44_1	338.9 ± 1.6
352.63_3	361.0 ± 1.7
353.02_1	371.2 ± 1.0
353.96_4	406.6 ± 1.9
354.67_5	436.3 ± 1.5
354.88_3	448.5 ± 1.0
354.99_8	467.8 ± 1.6
355.14_1	477.8 ± 1.1
355.29_3	503.5 ± 1.4*
355.37_6	536.5 ± 1.4*
355.36_5	551.6 ± 0.4*
355.37_0	563.5 ± 1.5*
355.33_2	579.3 ± 0.9*
355.28_2	604.3 ± 1.6*
355.26_2	617.2 ± 0.9*
355.05_8	648.4 ± 1.0*
354.49_7	695.3 ± 1.0
353.15_4	748.5 ± 0.6
351.34_9	797.5 ± 0.6
349.25_2	837.8 ± 0.7
345.00_1	898.6 ± 0.7

[a] The critical opalescence was observed when the values with an asterisk were measured.

have been made for densities 262.4–898.6 $\mathrm{kg \cdot m^{-3}}$ corresponding to temperatures between 345.00 and 355.38 K. The uncertainty in density of each measurement is also shown in Table I.

The meniscus for 14 densities between 262.4 and 503.5 $\mathrm{kg \cdot m^{-3}}$ descended with increasing temperature and disappeared at the bottom of the optical cell, whereas that for seven densities between 617.2 and 898.6 $\mathrm{kg \cdot m^{-3}}$ ascended with increasing temperature and disappeared at the top of the optical cell. The meniscus for the density of 536.5 $\mathrm{kg \cdot m^{-3}}$ descended with increasing temperature but disappeared prior to reaching the bottom of the optical cell, whereas that for the densities of 579.3 and 604.3 $\mathrm{kg \cdot m^{-3}}$ ascended with increasing temperature but disappeared prior to reaching the top of the optical cell. In the case of the densities of 551.6 and 563.5 $\mathrm{kg \cdot m^{-3}}$, the meniscus level was unchanged at the center of the

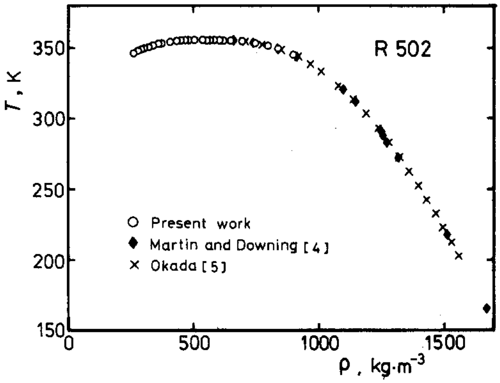

Fig. 3. Coexistence curve for R 502.

optical cell with increasing temperature, then became indistinguishable and finally disappeared.

The present results along the vapor–liquid coexistence curve are shown in Fig. 3 on the temperature–density plane. Only two other investigations along the coexistence curve are available, and are also depicted in Fig. 3. One is by Martin and Downing [4], who measured 13 saturated liquid densities between 660.8 and 1666 $\mathrm{kg \cdot m^{-3}}$ in the temperature range 165.48–354.86 K. The other measurements were by Okada [5] for 20 saturated liquid densities between 708.6 and 1559 $\mathrm{kg \cdot m^{-3}}$ and covered the temperature range 203.12–354.15 K. No investigation for the saturated vapor density has been reported according to our survey. Although R 502 is an azeotropic mixture, we found that the shape of the coexistence curve was almost similar to that for a pure substance.

3.2. Critical Parameters

The critical opalescence was observed at eight measurements for densities between 503.5 and 648.4 $\mathrm{kg \cdot m^{-3}}$, which are indicated with an asterisk in Table I. For lower densities of 503.5 and 536.5 $\mathrm{kg \cdot m^{-3}}$, the critical opalescence at the liquid phase was observed more intensely than that at the vapor phase, whereas the critical opalescence at the vapor phase for the higher four densities between 579.3 and 648.4 $\mathrm{kg \cdot m^{-3}}$ was observed more intensely. For the densities of 551.6 and 563.5 $\mathrm{kg \cdot m^{-3}}$, the critical opalescence was observed most intensely in eight measurements and that at the vapor phase was observed as intensely as that at the liquid phase. No significant difference between R 502 and the other pure refrigerants studied previously by the authors, i.e., R 23 [2], R 12 [3], R 22 [3],

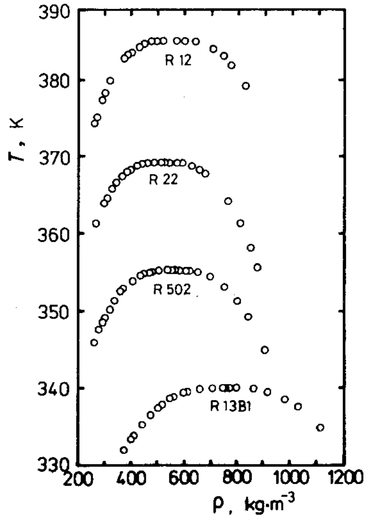

Fig. 4. Coexistence curve for several refrigerants.

and R 13B1 [6], was observed as far as the meniscus disappearance and the intensity of the critical opalescence were concerned. Figure 4 shows the vapor–liquid coexistence curves for different refrigerants [3, 6], including R 502, plotted on a single temperature–density plane. Since each difference of the critical temperature is about 15 K, these coexistence curves show similar trends in the critical region.

As the result of meniscus observations, it was found that the critical density of R 502 is between 551.6 and 563.5 $\mathrm{kg \cdot m^{-3}}$. Careful examination showed that the meniscus at 551.6 $\mathrm{kg \cdot m^{-3}}$ disappeared as descending very slightly with increasing temperature and appeared again at the central level of the optical cell with decreasing temperature. For the density of 563.5 $\mathrm{kg \cdot m^{-3}}$, the meniscus disappeared as ascending slightly with increasing temperature and appeared again at a little lower level than the center of the optical cell with decreasing temperature. On the basis of these two observations, we considered that the density of 551.6 $\mathrm{kg \cdot m^{-3}}$ was closer to the critical density than the density of 563.5 $\mathrm{kg \cdot m^{-3}}$, and hence we determined the critical density of R 502 as

$$\rho_c = 555 \pm 3 \ \mathrm{kg \cdot m^{-3}}$$

The critical temperature can be determined as the saturation temperature corresponding to the critical density. For densities of 551.6 and 563.5

$\text{kg} \cdot \text{m}^{-3}$, the saturation temperatures are 355.365 and 355.370 K, respectively, the difference of which is half the uncertainty of the temperature measurement. Considering the flatness of the coexistence curve in the vicinity of the critical point, we determined the critical temperature of R 502 as

$$T_c = 355.37 \pm 0.01 \text{ K}$$

The saturation temperature for the density of 536.5 $\text{kg} \cdot \text{m}^{-3}$, which is smaller than the critical density, is higher than T_c by 6 mK, although this difference is within the uncertainty of the present temperature measurements.

The critical pressure of R 502 was calculated as

$$P_c = 4.070 \pm 0.002 \text{ MPa}$$

by our vapor-pressure correlation [1] with the present value of T_c. The quoted uncertainty of the critical pressure was estimated as resulting from the uncertainty of the critical temperature and that of the vapor-pressure correlation used.

Information about the critical parameters of R 502 is summarized in Table II. The values from du Pont appeared in a nonscientific publication [7] and their detailed background has not been reported. Löffler [8] determined $T_c = 355.85 \pm 0.5$ K directly by the visual observation of the meniscus behavior and he obtained $P_c = 4.12 \pm 0.025$ MPa as well as $\rho_c = 560 \pm 4$ $\text{kg} \cdot \text{m}^{-3}$ from his own vapor-pressure and saturated liquid volume correlations, respectively. It is noted, however, that there exists a minor inconsistency in the number of figures between the values of T_c and P_c and those for the uncertainties reported by Löffler. Martin and Downing [4] determined $T_c = 355.31$ K as an average temperature of the reappearance and disappearance of the meniscus at the central level of the glass test tube. They obtained $P_c = 4.0748$ MPa by extrapolating their vapor-pressure correlation to their measured T_c and $\rho_c = 561$ $\text{kg} \cdot \text{m}^{-3}$ from the law of rectilinear diameter. Unfortunately, they did not report the uncertainties with respect to the critical parameters. The data by Wakamatsu [9], on the other hand, did not include the critical density value, although $T_c = 354.969 \pm 0.015$ K and $P_c = 4.140$ MPa were given.

The present T_c value is lower than that of Löffler by 480 mK, whereas it is higher than that of Martin and Downing by 60 mK. In consideration of the uncertainty of P_c due to that of the T_c determination, the present P_c value is in good agreement with that by Martin and Downing. As for ρ_c, the present result is in good agreement with values by Löffler and by Martin and Downing within a deviation of 1%.

Table II. Reported Values of the Critical Parameters of R 502

Reference	T_c (K)	ρ_c ($kg \cdot m^{-3}$)	P_c (MPa)	Sample composition
du Pont [7]	355.35	559	—	—
Löffler [8]	355.85 ± 0.5	560±4	4.12 ± 0.025	48.8 wt % R 22 + 51.2 wt % R 115
Martin and Downing [4]	355.31	561	4.0748	48.8 wt % R 22 + 51.2 wt % R 115
Wakamatsu [9]	354.969 ± 0.015	—	4.140	48.8 wt % R 22 + 51.2 wt % R 115
Present work	355.37 ± 0.01	555±3	4.070 ± 0.002	49.0 wt % R 22 + 51.0 wt % R 115

3.3. Critical Exponent β along the Coexistence Curve

The critical exponent β along the coexistence curve can be determined on the basis of the power law representation

$$(\rho' - \rho'')/2\rho_c = B|(T - T_c)/T_c|^\beta \tag{1}$$

where B stands for an adjustable parameter, and ρ' and ρ'' indicate the saturated liquid and vapor density, respectively. In order to determine the critical exponent β with an aid of Eq. (1), ρ' and ρ'' values at the same temperatures along the coexistence curve are required. However, we did not measure ρ' and ρ'' at the same temperatures. Therefore we correlated the temperature dependences of ρ' and ρ'' independently in the region of interest near the critical point based upon the present measurements. The correlations thus obtained through applying the Wegner expansion [10] are

$$\begin{aligned}\rho'/\rho_c = {} & 1 - 4849.83|\Delta T^*|^{0.8915} + 3368.68|\Delta T^*| \\ & - 944.573|\Delta T^*|^{1.3915} - 1.05698|\Delta T^*|^{0.325} \\ & + 2164.31|\Delta T^*|^{0.825}\end{aligned} \tag{2}$$

$$\begin{aligned}\rho''/\rho_c = {} & 1 - 76.1895|\Delta T^*|^{0.8915} + 120.710|\Delta T^*| \\ & - 88.1378|\Delta T^*|^{1.3915} - 1.24010|\Delta T^*|^{0.325} \\ & + 4.19643|\Delta T^*|^{0.825}\end{aligned} \tag{3}$$

where $\Delta T^* = (T - T_c)/T_c$. The values of T_c and ρ_c used in Eqs. (2) and (3) are 355.37 K and 555 $\text{kg} \cdot \text{m}^{-3}$, respectively, which were determined in the present study. Equation (2) reproduces nine data for the saturated liquid density in the temperature range 345.001–355.332 K with an average deviation of 0.31% and a maximum deviation of 1.04%. Equation (3) reproduces 14 data for the saturated vapor density in the temperature range 345.972–355.293 K with an average deviation of 0.55% and a maximum deviation of 1.17%.

For the present analysis of the critical exponent β, we excluded three data points that fell within the estimated uncertainty of T_c, i.e., those corresponding to the temperatures 355.376, 355.365, and 355.370 K given in Table I. For the purpose of obtaining ρ'' values at the temperatures that correspond to the measured ρ' values, Eq. (3) was used. Conversely, Eq. (2)

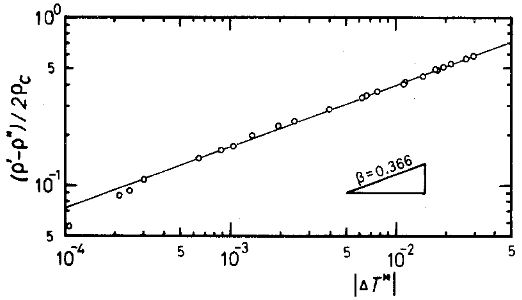

Fig. 5. Temperature dependence of the difference in coexisting densities.

was used to obtain the equivalent ρ' values at the respective temperatures where ρ'' was measured. Thus the relation between $\log[(\rho' - \rho'')/2\rho_c]$ and $\log|(T - T_c)/T_c|$ was as shown in Fig. 5. The power law representation by Eq. (1) suggests that the experimental results may be fitted by a straight line with a gradient equivalent to the critical exponent β in such a plot as Fig. 5. In the present study, we found linearity for the range of the reduced temperature $|\Delta T^*| > 3 \times 10^{-4}$ and the values of β and B were obtained as $\beta = 0.366$ and $B = 2.144$ as a result of least squares fitting.

In our previous studies [3, 6], the values of β and B for several refrigerants had been determined by using the expression

$$|(\rho - \rho_c)/\rho_c| = B|(T - T_c)/T_c|^{\beta} \tag{4}$$

Thus we reported $\beta = 0.337$ with $B = 1.872$ for R 12 (CCl_2F_2: dichlorodifluoromethane) [3], $\beta = 0.348$ with $B = 1.996$ for R 22 [3], and $\beta = 0.340$ with $B = 1.821$ for R 13B1 ($CBrF_3$: bromotrifluoromethane) [6], respectively. Although the present method of analysis of the critical exponent β is different from the previous one, the present results for R 502 are greater than those obtained with respect to other refrigerants. It is also noteworthy that all of the values we obtained are also greater than the theoretical values due to renormalization group theory and Ising model series expansions, i.e., 0.325 and 0.312, respectively [10].

3.4. Law of Rectilinear Diameter

Traditionally the critical density has been determined by the law of rectilinear diameter. Our previous analysis of the rectilinear diameter near the critical point of R 116 (C_2F_6: hexafluoroethane) [11] and some addi-

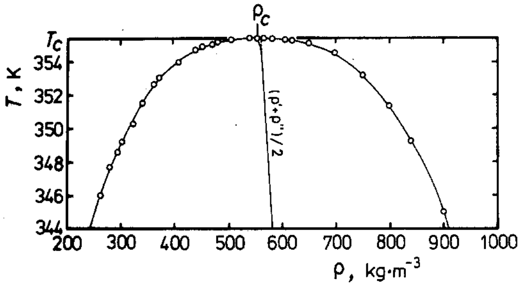

Fig. 6. Present results in the critical region.

tional investigations [12] supported the observation that it was not straight all the way to the critical point, but bent slightly toward smaller densities in the vicinity of the critical point.

Figure 6 was prepared from the present experimental data with the aid of Eqs. (2) and (3), and it again shows that the directly determined critical density ρ_c becomes smaller by ~1% than the value along the extrapolated broken line according to the rectilinear diameter. Similar but more detailed comparison is given in Fig. 7, where the relation between temperature and the averaged coexisting densities, i.e., $(\rho' + \rho'')/2$, is plotted. Thus we can conclude that the evaluation of the critical density from the law of rectilinear diameter is not a reliable method, especially when a satisfactory quantity of measured data with reasonable quality are available along the coexistence curve in the critical region.

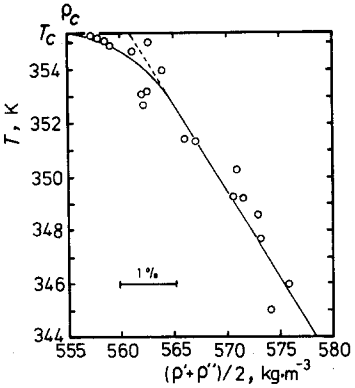

Fig. 7. Temperature dependence of the averaged coexisting densities.

ACKNOWLEDGMENTS

The authors are greatly indebted to Mitsui Fluorochemicals Co., Tokyo, Japan, for kindly furnishing the sample, and also to the National Research Laboratory of Metrology, Ibaraki, Japan, for the calibration of the thermometer. The assistance of Toru Okano, who made elaborate observations with the present authors, is greatly appreciated. The present work was partially supported by a grant from Amano Institute of Technology, Hamamatsu, Japan.

REFERENCES

1. T. Kimura, M. Uematsu, and K. Watanabe, *J. Chem. Eng. Data* **26**:109 (1981).
2. S. Okazaki, Y. Higashi, Y. Takaishi, M. Uematsu, and K. Watanabe, *Rev. Sci. Instrum.* **54**:21 (1983).
3. Y. Higashi, S. Okazaki, Y. Takaishi, M. Uematsu, and K. Watanabe, *J. Chem. Eng. Data* **29**:31 (1984).
4. J. J. Martin and R. C. Downing, *ASHRAE Trans.* **76**:129 (1970).
5. M. Okada, Ph.D. Thesis, Keio University, Yokohama, Japan (1984).
6. Y. Higashi, M. Uematsu, and K. Watanabe, submitted to *Nippon Kikaigakkai Ronbunshu B-Hen*.
7. E. I. du Pont de Nemours & Co., Bulletin T-502 (1963).
8. H. J. Löffler, *Kältetechnik* **19**:201 (1967).
9. N. Wakamatsu, M.S. Thesis, Department of Industrial Chemistry, Tokyo Metropolitan University, Tokyo, Japan (1976).
10. J. M. H. Levelt Sengers and J. V. Sengers, in *Perspectives in Statistical Physics*, H. J. Raveché, ed. (North-Holland, Amsterdam, 1981), Chap. 14.
11. K. Saikawa, J. Kijima, M. Uematsu, and K. Watanabe, *J. Chem. Eng. Data* **24**:165 (1979).
12. M. Ley-Koo and M. S. Green, *Phys. Rev. A* **23**:2650 (1981).