

Coexistence curve of perfluoromethylcyclohexane+carbon tetrachloride near the critical point in composition-pressure and composition-temperature space

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Coexistence curves in volume fraction-temperature (ϕ - T) space and in volume fraction-pressure (ϕ - p) space have been measured for the binary system perfluoromethylcyclohexane+carbon tetrachloride in the temperature range $T_c - T < 0.8$ K and in the pressure range $p - p_c < 3.2$ MPa near the critical point (T_c, p_c, ϕ_c). The observed coexistence curves were expressed by the simple scaling relation $\phi^+ - \phi^- = B_T(T_c - T)^{\beta_T}$ in ϕ - T space and by $\phi^+ - \phi^- = B_p(p - p_c)^{\beta_p}$ in ϕ - p space. The exponent was determined as $\beta_T = 0.326 \pm 0.001$ and $\beta_p = 0.330 \pm 0.006$, which agree with each other and with the theoretical value $\beta = 0.327$ for the Ising model. The observed coefficients give $(B_p/B_T)^{1/\beta} = 0.42 \pm 0.02$ K/MPa, which may be compared with the slope $(dT/dp)_c = 0.38$ K/MPa of the p - T critical line in light of a thermodynamic argument. This means that the pressure range is converted into the temperature range with the slope $(dT/dp)_c$ as a scale factor. © 1998 American Institute of Physics. [S0021-9606(98)50222-X]

I. INTRODUCTION

Liquid-liquid phase equilibrium of binary systems is given in the three-dimensional space of temperature T , pressure p , and composition ϕ . In most experimental studies phase-equilibrium and cloud-point measurements have been made at the atmospheric pressure or vapor pressure of the systems. Pressure dependence of phase-equilibrium properties has been studied by measuring p - T cloud-point curves at constant composition. Observed isopleths have been used to construct coexistence curves at elevated pressures.¹⁻³ The critical behavior of coexistence curves has been investigated exclusively at the atmospheric pressure, because compositions in two coexisting phases are difficult to determine accurately at high pressures. Moreover, since at usual thermodynamic conditions the critical exponent β_p for a coexistence curve in ϕ - p space is not expected to differ from the exponent β_T in ϕ - T space, the equality of $\beta_p = \beta_T$ has been out of the scope of an experimental verification. In p - T - ϕ space, the coexistence surface exhibits characteristic behavior near the critical double point, tricritical point, and quadruple critical point.⁴⁻⁸

In this work we have measured the coexistence curves of the system perfluoromethylcyclohexane (C_7F_{14}) + carbon tetrachloride (CCl_4) in the pressure range $p - p_c < 3.2$ MPa and in the temperature range $T_c - T < 0.8$ K near the critical point (T_c, p_c, ϕ_c). The primary aim of this experiment is to determine β_p directly by a phase-equilibrium measurement, and to compare it with β_T . In view of a phenomenological study of coexistence curves,^{9,10} the equality $\beta_p = \beta_T$ should be subjected to an experimental verification. The quantitative comparison of the coexistence curves in ϕ - T and ϕ - p spaces

required a scale factor which relates the pressure distance $p - p_c$ to the temperature distance $T_c - T$. According to a classical thermodynamic argument, we compared the observed coexistence curves in ϕ - T and ϕ - p spaces with the slope $(dT/dp)_c$ of the p - T critical line as a scale factor. The present experimental range of $p - p_c$ was found to be comparable with that of $T_c - T$ by the transformation. Both the observed coexistence curves did not deviate from a simple scaling relation and confirmed the equality $\beta_p = \beta_T$.

II. EXPERIMENT

Reagent grade C_7F_{14} and CCl_4 were obtained from Aldrich Chemical Co. Ltd. and Wako Pure Chemical Ind. Ltd., respectively. These solvents were twice distilled after being passed through fine silica gel. No impurities were detected by gas chromatography measurements. The binary system has an upper critical point at atmosphere near room temperature and the slope of the critical line $(dT/dp)_c$ is positive. Thus we can determine the coexistence curves in ϕ - T and ϕ - p space for the critical point by increasing pressure and by decreasing temperature, respectively. The coexistence curves were measured by a differential refractometer, details of which are described elsewhere.¹¹ For the measurement of a pressure-induced coexistence curve, the differential cell was sealed with mercury to transmit pressure directly to the solution. The air was carefully removed out from the differential cell. Then the cell was put into a pressure vessel, which was made of a stainless steel block and had two parallel windows of poly(methyl methacrylate) to pass a laser beam. Pressure was supplied from a nitrogen gas cylinder to the pressure vessel and measured by a pressure gauge (P21E, Transmetrics) with a digital multimeter. The pressure vessel

TABLE I. Coexistence curve data in ϕ - T space and ϕ - p space. $T_c - T$, and $p - p_c$ are the temperature and pressure differences from the critical ones. ϕ^+ and ϕ^- indicate the volume fractions of perfluoromethylcyclohexane in concentrated phase and dilute phase, respectively.

$T_c - T$	ϕ^+	ϕ^-	$p - p_c$	ϕ^+	ϕ^-
0.014	0.4855	0.4233	0.07	0.4936	0.4158
0.019	0.4894	0.4203	0.10	0.4977	0.4110
0.024	0.4917	0.4172	0.11	0.5016	0.4092
0.031	0.4954	0.4138	0.15	0.5075	0.4037
0.038	0.4984	0.4104	0.31	0.5185	0.3923
0.053	0.5040	0.4068	0.54	0.5337	0.3791
0.071	0.5093	0.4023	0.93	0.5504	0.3640
0.123	0.5181	0.3900	1.49	0.5663	0.3501
0.163	0.5255	0.3850	2.17	0.5827	0.3358
0.301	0.5402	0.3695	3.13	0.5958	0.3211
0.427	0.5522	0.3603			
0.578	0.5615	0.3500			
0.702	0.5697	0.3443			

was immersed in a water bath, the temperature of which was regulated to ± 0.003 K. The pressure was controlled within a precision of ± 0.01 MPa. The volume fraction ϕ of C_7F_{14} was determined with a precision better than ± 0.0002 . To determine the critical volume fraction, ϕ_c , several solutions of $C_7F_{14} + CCl_4$ with different volume fractions in the range 0.4–0.5 were prepared and the coexistence curve for each solution was measured very near the cloud point at atmospheric pressure. The obtained curves agreed with each other in ϕ - T diagram and the mid-point between two coexisting phases yielded a straight line. We determined the critical volume fraction as $\phi_c = 0.454$ from the diameter and cloud points. We used the solution of this composition for the measurements of the coexistence curves in ϕ - T and ϕ - p spaces. The solution was ascertained to give rise to two coexisting phases of the same volume just below the cloud point temperature.

At first we measured a coexistence curve at atmospheric pressure and determined the critical temperature as 28.626 °C. Then a coexistence curve was measured, varying pressure at the critical temperature. (Thus, the critical pressure p_c is atmosphere.) This was made by quenching the solution into the two-phase region by a sudden increase in pressure from the atmospheric pressure. After a two-phase equilibrium was achieved, the volume fraction of each phase was measured. Usually, the two-phase equilibrium was reached less than 2 h after setting the temperature and pressure. For the same system Thompson and Rice¹² obtained $T_c = 28.626$ °C and the critical mole fraction 0.285, which yields $\phi_c = 0.447$ with the densities 1.774 g/cm³ for C_7F_{14} and 1.575 g/cm³ for CCl_4 . The values of T_c and ϕ_c obtained in this study agree closely with those by Thompson and Rice, who determined the coexistence curve by a density method with a glass bob. The data are summarized in Table I.

III. RESULTS AND DISCUSSION

Figure 1 shows double logarithmic plots of volume fraction differences $\Delta\phi (= \phi^+ - \phi^-)$ versus temperature differ-

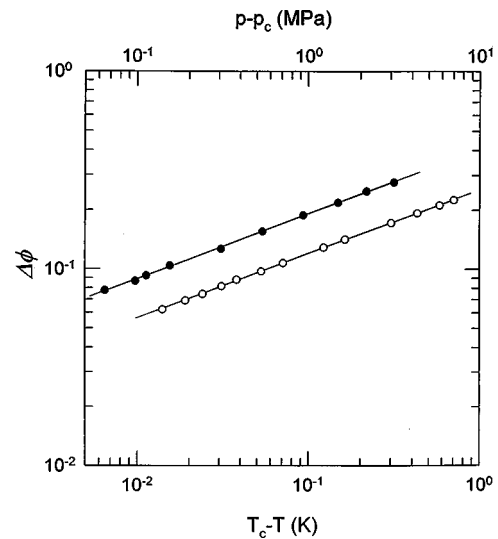


FIG. 1. Double logarithmic plots of volume fraction differences versus temperature distance (O) and pressure distance (●) from the critical point.

ence $T_c - T$ (O) and pressure difference $p - p_c$ (●). Each plot is represented by a straight line and fitted to the simple scaling form

$$\phi^+ - \phi^- = B_T (T_c - T)^{\beta_T} \quad (1)$$

in ϕ - T space and

$$\phi^+ - \phi^- = B_p (p - p_c)^{\beta_p} \quad (2)$$

in ϕ - p space. Here, ϕ^+ and ϕ^- indicate the volume fractions of C_7F_{14} in two coexisting phases. The data were analyzed by a nonlinear least squares method indicating no systematic deviations from simple scaling. Thus we obtained $\beta_T = 0.326 \pm 0.001$, $\beta_p = 0.330 \pm 0.006$ and $B_T = 0.253 \pm 0.001$, $B_p = 0.190 \pm 0.001$ in the whole experimental ranges of $(T_c - T) < 0.8$ K and $(p - p_c) < 3.2$ MPa. The errors are the standard deviations. The values of β_T and β_p agree with each other within the errors and with the theoretical value $\beta = 0.327$ for the three-dimensional Ising model.¹³

To compare the coexistence curves in ϕ - T and ϕ - p spaces, it is necessary to transform the pressure distance ($p - p_c$) to the temperature distance ($T_c - T$). A conceivable scale factor is the slope $(dT/dp)_c$ of the p - T critical line and the relation $(B_p/B_T)^{1/\beta} = (dT/dp)_c$ is suggested. This relation is just derived by the classical theory. The critical conditions for molar free energy g as a function of T , p , and mole fraction x for composition variable of binary mixtures are given by $g_{2x}^c = g_{3x}^c = 0$ and $g_{4x} > 0$, where g_{nx}^c ($n = 2, 3, 4$) denotes the derivative $(\partial^n g / \partial x^n)_{T,p}$ at fixed T and p , and the superscript c indicates the critical state. g may be expanded in a Taylor series in $\delta x = x - x_c$, $\delta T = T - T_c$, and $\delta p = p - p_c$ about the critical point (x_c, T_c, p_c) . The leading terms are given by¹⁴

$$g = g^c + g_x^c(\delta x) - s^c(\delta T) + v^c(\delta p) - s_x^c(\delta x)(\delta T) + v_x^c(\delta x)(\delta p) - (1/2)s_{2x}^c(\delta x)^2(\delta T) + (1/2)v_{2x}^c(\delta x)^2(\delta p) + (1/24)g_{4x}^c(\delta x)^4 + \dots, \quad (3)$$

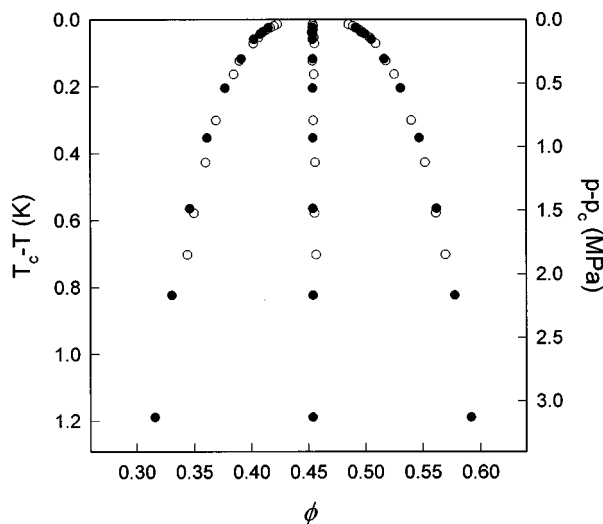


FIG. 2. Coexistence curve for the system perfluoromethylcyclohexane in carbon tetrachloride in ϕ - T space at constant pressure (\circ) and ϕ - p space at constant temperature (\bullet). The pressure scale at the right ordinate is converted into the temperature scale at the left ordinate when scaled by $(dT/dp)_c(p-p_c)$.

where s and v are the molar entropy and volume, respectively, and the suffix has the same meaning as in g_{nx}^c . The mole fractions $\delta x'$ and $\delta x''$ in the two coexisting phases are derived with the phase equilibrium conditions of $g_{x'} = g_{x''}$ and $g' - (\delta x')g_{x'} = g'' - (\delta x'')g_{x''}$ due to the chemical potential equality. The conditions give $\delta x' = -\delta x'' = (1/2)(x^+ - x^-)$ and

$$(1/6)g_{4x}^c(\delta x')^2 = s_{2x}^c(\delta T) - v_{2x}^c(\delta p). \quad (4)$$

Thus we obtain the coefficients corresponding to those in Eqs. (1) and (2) as $B_T = 2(-6s_{2x}^c/g_{4x}^c)^\beta$ and $B_p = 2(-6v_{2x}^c/g_{4x}^c)^\beta$ and the ratio $B_p/B_T = (v_{2x}^c/s_{2x}^c)^\beta$ with $\beta = 1/2$. Here, it should be recalled that the slope of the p - T critical line is given by $(dT/dp)_c = v_{2x}^c/s_{2x}^c$. The observed

values of B_p and B_T give $(B_p/B_T)^{1/\beta} = 0.42 \pm 0.02$ K/MPa, which is in fairly good agreement with the slope $(dT/dp)_c = 0.38$.^{12,15} In the present experiment the temperature range is comparable with the pressure range scaled by $(dT/dp)_c$. A straight critical line and pressure independence of B_T may give the relation $(B_p/B_T)^{1/\beta} = (dT/dp)_c$. The above relation between $(B_p/B_T)^{1/\beta}$ and $(dT/dp)_c$ seems to indicate a subtle behavior of the coexistence surface near the critical point. Figure 2 gives the observed coexistence curves in ϕ - p space (\bullet) and ϕ - T space (\circ) with the scaled pressure. The pressure scale at the right ordinate can be converted into the temperature scale at the left when scaled as $(dT/dp)_c(p-p_c)$. Two coexistence curves agree closely with each other. It is interesting to measure coexistence curves beyond the range of simple scaling to compare the deviations from simple scaling in ϕ - p and ϕ - T spaces.

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