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 \((T_c, p_c, \phi_c)\). The observed coexistence curves were expressed by the simple scaling relation

\[
\phi^+ - \phi^- = B_p(T_c - T)^{\beta_p} \quad \text{in} \quad \phi - T \quad \text{space and by} \quad \phi^+ - \phi^- = B_p(p - p_c)^{\beta_p} \quad \text{in} \quad \phi - p \quad \text{space.}
\]

The exponent \( \beta_p \) was determined \( \beta_p = 0.326 \pm 0.001 \) and \( \beta_p = 0.330 \pm 0.006 \), which agree with each other and with the theoretical value \( \beta_p = 0.327 \) for the Ising model. The observed coefficients give \( B_p/\beta_p^{1/\beta} = 0.42 \pm 0.02 \) 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 \( \phi \). 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 isotherms 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 \( \beta_p \) for a coexistence curve in \( \phi - p \) space is not expected to differ from the exponent \( \beta_T \) in \( \phi - T \) space, the equality of \( \beta_p = \beta_T \) has been out of the scope of an experimental verification. In \( p - T - \phi \) 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\(_7\)F\(_{14}\)) + 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 \((T_c, p_c, \phi_c)\). The primary aim of this experiment is to determine \( \beta_p \) directly by a phase-equilibrium measurement, and to compare it with \( \beta_T \). 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 \( \phi - T \) and \( \phi - p \) 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 \( \phi - T \) and \( \phi - p \) 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\(_7\)F\(_{14}\) 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 \( \phi - T \) and \( \phi - p \) 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 \( \phi-T \) space and \( \phi-p \) space. \( T_c-T \), and \( p-p_c \), are the temperature and pressure differences from the critical ones. \( \phi^+ \) and \( \phi^- \) indicate the volume fractions of perfluoromethylenechlohexane in concentrated phase and dilute phase, respectively.

<table>
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<tr>
<th>( T_c-T )</th>
<th>( \phi^+ )</th>
<th>( \phi^- )</th>
<th>( p-p_c )</th>
<th>( \phi^+ )</th>
<th>( \phi^- )</th>
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<td>0.07</td>
<td>0.4936</td>
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</table>

III. RESULTS AND DISCUSSION

Figure 1 shows double logarithmic plots of volume fraction differences \( \Delta \phi(=\phi^+-\phi^-) \) versus temperature difference \( T_c-T(\circ) \) and pressure difference \( p-p_c(\bullet) \). Each plot is represented by a straight line and fitted to the simple scaling form

\[ \phi^+ - \phi^- = B_T(T_c-T)^{\beta_T} \]

in \( \phi-T \) space and

\[ \phi^+ - \phi^- = B_p(p-p_c)^{\beta_p} \]

in \( \phi-p \) space. Here, \( \phi^+ \) and \( \phi^- \) indicate the volume fractions of C\(_7\)F\(_{14}\) in two coexisting phases. The data were analyzed by a nonlinear least squares method indicating no systematic deviations from simple scaling. Thus we obtained \( B_T = 0.326 \pm 0.001 \), \( \beta_T = 0.330 \pm 0.006 \) and \( B_p = 0.253 \pm 0.001 \), \( B_p = 0.190 \pm 0.001 \) in the whole experimental ranges of \( (T_c-T) < 0.8 \text{ K} \) and \( (p-p_c) < 3.2 \text{ MPa} \). The errors are the standard deviations. The values of \( \beta_T \) and \( \beta_p \) 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 \( \phi-T \) and \( \phi-p \) spaces, it is necessary to transform the pressure distance \( (p-p_c) \) to the temperature distance \( (T_c-T) \). A conceivably scale factor is the slope \( (dT/dp)_c \) of the \( p-T \) critical line and the relation \( (B_p/B_T)^{1/\beta_p} = (dT/dp)_c \) 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 \( (d^ng/dx^n)_T,p \) 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 by

\[ g = g^c + g_{2x}^c(\delta x) - s^c(\delta T) + v^c(\delta p) - s_{1x}^c(\delta x)^2(\delta T) \]
\[ + (1/2)v_{2x}^c(\delta x)^2(\delta p) + (1/24)g_{4x}^c(\delta x)^4 + \cdots, \]

FIG. 1. Double logarithmic plots of volume fraction differences versus temperature distance (○) and pressure difference (●) from the critical point.
FIG. 2. Coexistence curve for the system perfluoromethylcyclohexane in carbon tetrachloride in \( \phi - T \) space at constant pressure (○) and \( \phi - p \) space at constant temperature (●). 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 \( g_{nx}^e \). The mole fractions \( \delta x^e \) and \( \delta x^n \) in the two coexisting phases are derived with the phase equilibrium conditions of \( g_{x}^e = g_{x}^o \) and \( g^e - \delta x^e = g^o - \delta x^o \) due to the chemical potential equality. The conditions give \( \delta x^e = - \delta x^n = (1/2)(x^e - x^n) \) and

\[
(1/6)g_{x}^e (\delta x^e)^2 = s_{2x}^e (\delta T) - v_{2x}^e (\delta p).
\]

(4)

Thus we obtain the coefficients corresponding to those in Eqs. (1) and (2) as \( B_T = 2(-6s_{2x}^e/g_{x}^e)\beta \) and \( B_p = 2(-6v_{2x}^e/g_{x}^e)\beta \) 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 \( (dT/dp)_c = 0.38^{12,15} \). The pressure scale at the right ordinate 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 \( \phi - p \) space (●) and \( \phi - T \) space (○) 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 \( \phi - p \) and \( \phi - T \) spaces.