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Sarra Zid, Jean-Patrick Bazile, Jean-Luc Daridon, Andrés Piña-Martinez, Jean-Noël Jaubert, et al..
Fluid phase equilibria for the CO₂ + 2,3-dimethylbutane binary system from 291.9 K to 373.1 K.
Journal of Supercritical Fluids, 2022, 179, pp.105387. 10.1016/j.supflu.2021.105387 . hal-03347858

HAL Id: hal-03347858

<https://hal.science/hal-03347858>

Submitted on 21 Sep 2021

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Fluid phase equilibria for the CO₂ + 2,3-dimethylbutane binary system from 291.9 K to 373.1 K

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Abstract

The phase behavior of the CO₂ (1) + 2,3-dimethylbutane (2) binary mixture has been experimentally studied between 293 and 373 K. Saturation pressures, ranging from 14.0 to 112.2 bar, were visually measured using a high-pressure cell at carbon dioxide mole fractions between 0.20 and 0.93.

78 experimental points have been measured: 67 bubble points and 11 dew points. Experimental results reveal that the vapor-liquid critical locus is a continuous curve between the two pure compounds, meaning that the studied binary system exhibits a type I or II phase behavior in the classification scheme of Van Konynenburg and Scott. The experimental data can be very satisfactorily represented by the Peng-Robinson equation of state with mixing rules that embed a temperature-dependent binary interaction parameter.

Keywords

Phase equilibria, High pressure cell, Peng-Robinson equation of state, Supercritical CO₂

1. Introduction

Group contribution concept is a useful tool to estimate pure compounds properties as well as mixture properties and phase equilibria. For example, in the past forty years, various group contribution methods (GCM) were successfully developed to describe vapor-liquid equilibrium (VLE) of multicomponent systems by predicting the activity coefficients in the so-called “ γ - ϕ ” approach or by predicting the binary interaction parameters (k_{ij}) in the “ ϕ - ϕ ” approach.

Let us recall that in group contribution methods, a mixture of components is reduced to a mixture of functional groups. Group interaction parameters are generally fitted on consistent binary VLE data. To obtain reliable results, many phase equilibrium data are needed to adjust the group interaction parameters. Moreover, these data must concern several binary mixtures involving the same elementary groups in the largest temperature/pressure range. Group interaction parameters determined with a limited number of experimental data must be used with great caution.

Even if binary systems are the simplest mixtures, they are still intensively studied because they allow to apprehend fluid phase behaviors and they are needed to build and test thermodynamic models which may subsequently be employed to predict the fluid phase equilibria of more complex mixtures.

With the help of the Dortmund Data Bank (<http://www.ddbst.com/ddb.html>), we noticed that few VLE data were available for binary systems containing CO₂ and a branched alkane. It is thus believed that group interaction parameters between group CO₂ and groups CH and C routinely used in predictive thermodynamic models like PPR78 [1-4], VTPR [5] or UMR-PRU [6] should be refitted over more data in order to guarantee their numerical value.

To support our statement, be aware that the DDB reports VLE data for only seven binary systems consisting of CO₂ + branched alkane: CO₂ + 2-methylpropane [7-13]; + 2,2-dimethylpropane [14-17]; + 2-methylbutane [18-23]; + 3-methylpentane [24]; + 2,5-

dimethylhexane [24]; + 2,2,4-trimethylpentane [24-28]; + 2,6,10,15,19,23-hexamethyltetracosane (squalane) [29-32]. Some of these systems have been only studied in a limited composition range, sometimes without experimental data point in the mixture critical region. For the previously exposed reasons, the aim of this paper is to report VLE measurements on the full composition range for a new binary system consisting of CO₂ + a branched alkane: the binary system CO₂ + 2,3-dimethylbutane.

2. Experimental section

2.1. Materials

The carbon dioxide (CAS 124-28-9) used in this study was purchased from Linde with a mol fraction purity of 0.99995. 2,3-dimethylbutane (C₆H₁₄, CAS 79-29-8) was supplied by Alfa Aesar (Thermo Fisher Scientific) with a mass fraction purity of 0.998. Both components were used without any further treatment.

2.2. Apparatus and procedure

Bubble and dew pressures were measured using a variable volume high-pressure cell with full visibility. The details of this apparatus and the experimental procedure have been described in our previous works [33-36]. The employed experimental technique is based on a synthetic method (Synthetic-visual method with Variable-volume cell, “SynVisVar” according to Dohrn et al. [37]) which avoids sampling and analyses of the phases.

The cell is equipped with a movable piston, two sapphire windows, an optical fiber, an endoscope and a magnetic stirrer. The temperature of the cell is controlled by circulating a thermo-regulated heat-carrier fluid through three lines in the cell wall. The mixture temperature inside the cell is measured with an uncertainty of ± 0.1 K by means of a Pt100 probe. The pressure is measured by a piezoresistive-silicon pressure transducer (Kulite) directly placed inside the cell. This pressure transducer was calibrated, as a function of the temperature, between 0.1 and 100 MPa by means of a primary standard pressure sensor with an uncertainty better than 0.02 % on the full pressure scale.

The mixtures were prepared directly in the cell by adding separately the liquid 2,3-dimethylbutane and the gaseous CO₂. In a first step, vacuum was created in the cell using a vacuum pump. Then, the cell was loaded, by vacuum suck up, with a known quantity of liquid 2,3-dimethylbutane determined with a precision balance (Ohaus). Finally, the carbon dioxide

was added under pressure. The amount of CO₂ charged was obtained by weighing the CO₂ reservoir tank thanks to a high weight / high precision balance (Metler Toledo).

The expended uncertainties in mass introduced in the cell were estimated to be better than 0.005 g for C₆H₁₄ and 0.005 g for CO₂.

Bubble and dew points were determined by a direct visual observation. The phase boundaries were evaluated by determining the disappearance conditions of one phase. The measurements were thus carried out by observing the disappearance of the vapor phase (for a bubble point-pressure measurement) or the liquid phase (for a dew-point pressure measurement) at constant temperature. The method consisted first in observing the formation of a new phase by gradually changing the pressure and then reversing the direction of this variation in a stepwise fashion so as to detect the disappearance of the last phase formed. The procedure was repeated several times by reducing the increment.

By doing so, the standard uncertainty was 0.2 bar for bubble point pressure and 0.4 for dew point pressure.

3. Experimental results

A total of 78 experimental points were measured: 67 bubble points and 11 dew points. The binary system was studied at 9 different compositions ranging from 0.2000 to 0.9300 carbon dioxide mole fraction. The experimentally determined phase transitions are reported in Table 1 and are partially shown, as isopleths, in Fig. 1 with calculated phase envelopes and calculated mixture critical locus.

Table 1. Experimental bubble-point and dew-point pressures and temperatures for the CO₂ + 2,3-dimethylbutane binary mixture at 9 different CO₂ mole fractions as well as the uncertainties

a,b

$x_{CO_2} = 0.2000 \pm 0.0008$		$x_{CO_2} = 0.4002 \pm 0.0006$		$x_{CO_2} = 0.5001 \pm 0.0006$		$x_{CO_2} = 0.6002 \pm 0.0004$		$x_{CO_2} = 0.6999 \pm 0.0003$	
<i>T/K</i>	<i>P/bar</i>								
293.1	14.0	293.1	27.1	293.3	32.5	293.5	37.2	293.4	41.1
303.1	16.4	303.9	32.5	303.4	38.8	303.1	44.3	304.2	50.6
312.7	18.7	313.2	37.4	313.0	45.1	313.0	52.1	312.2	58.0
323.1	21.2	322.9	42.5	322.7	51.7	322.5	60.0	321.0	66.6
333.1	24.5	333.3	48.0	332.6	58.3	332.9	68.5	332.9	78.2
342.9	27.2	342.4	53.2	343.0	65.3	342.8	77.0	340.8	85.8
352.8	29.9	353.3	59.0	352.7	71.8	352.3	84.6	350.9	94.6
362.3	32.5	362.0	63.6	362.0	78.0	362.8	92.3	360.6	102.1
371.6	35.0	372.0	68.9	372.8	84.2	372.0	98.5	372.6	112.2
$x_{CO_2} = 0.8000 \pm 0.0002$		$x_{CO_2} = 0.8500 \pm 0.0003$		$x_{CO_2} = 0.9000 \pm 0.0002$		$x_{CO_2} = 0.9300 \pm 0.0002$			
<i>T/K</i>	<i>P/bar</i>	<i>T/K</i>	<i>P/bar</i>	<i>T/K</i>	<i>P/bar</i>	<i>T/K</i>	<i>P/bar</i>		
291.9	43.3	293.0	46.3	293.1	49.5	293.5	52.6		
302.1	53.4	302.4	56.5	301.9	58.0	303.6	64.8		
311.3	63.4	311.6	66.5	311.2	69.9	312.5	76.2		
320.8	74.3	321.6	78.3	321.3	83.0	321.6	84.5		
331.8	86.7	331.7	91.7	331.3	92.1	330.4	87.9		
341.5	95.9	341.3	98.2	343.1	97.9	340.7	80.8		
352.3	103.7	352.1	103.7	351.7	98.8				
361.1	108.6	361.9	106.2	362.4	93.6				
373.1	112.2	371.6	106.7	372.2	77.0				

^a Bold data are dew points; the rest are bubble points.

^b Standard uncertainties *u* are $u(T) = 0.1$ K and $u(P) = 0.2$ bar for bubble points and $u(P) = 0.4$ bar for dew points.

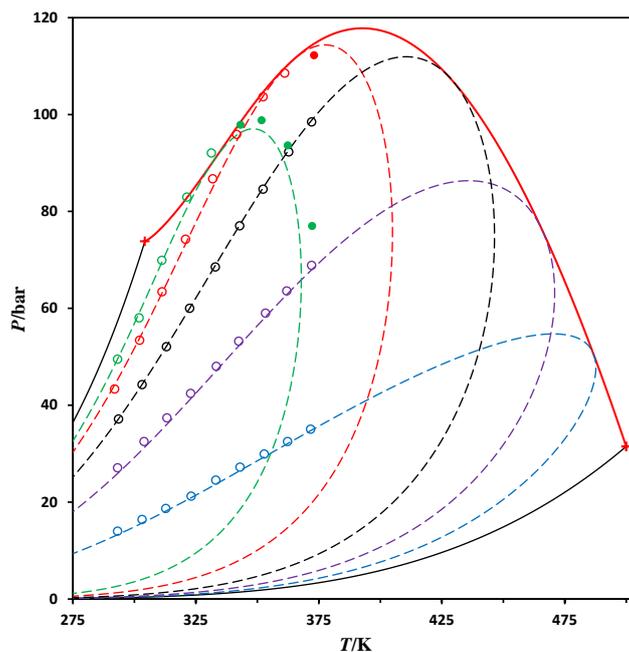


Figure 1. (P, T) phase envelopes of the binary system $\text{CO}_2 + 2,3\text{-dimethylbutane}$. From left to right, CO_2 mole fractions are: $x_{\text{CO}_2} = 0.9000$ (green envelope and green points) ; $x_{\text{CO}_2} = 0.8000$ (red envelope and red points) ; $x_{\text{CO}_2} = 0.6002$ (black envelope and black points) ; $x_{\text{CO}_2} = 0.4002$ (violet envelope and violet points) ; $x_{\text{CO}_2} = 0.2000$ (blue envelope and blue points). o: experimental bubble point. •: experimental dew point. Dashed lines: calculated phase envelopes with the PR equation of state and a temperature-dependent k_{ij} . Black solid lines: vaporization curve of the pure components. Red solid line: calculated mixture critical locus with the PR equation of state and a temperature-dependent k_{ij} .

The experimental data obtained in this study reveal that the binary system $\text{CO}_2 + 2,3\text{-dimethylbutane}$ behaves classically. Indeed, no liquid-liquid immiscibility was observed in the studied temperature range. Moreover, the shape of the phase envelopes for CO_2 rich mixtures (see Fig. 1) allows us to claim that the vapor-liquid critical locus of the binary system is uninterrupted. The studied binary mixture thus belongs to type I or type II systems according to the classification proposed by Van Konynenburg and Scott [38,39].

From the raw isoplethic data measured and reported in Table 1, it was possible to generate isothermal (P , x_{CO_2} or y_{CO_2}) data. Interpolated values at fixed temperatures were reached by smoothing the raw data using fitted polynomials. For nine temperatures ranging from 293.15 K to 373.15 K with a step of 10 K, isothermal (P, x or y) data obtained from the original measurements are given in Table 2 and displayed in Fig. 2.

Table 2. Isothermal (P, x or y) data for the $\text{CO}_2 + 2,3\text{-dimethylbutane}$ binary system at nine different temperatures calculated from the original measurements reported in Table 1.

$T/\text{K} = 293.15$			$T/\text{K} = 303.15$			$T/\text{K} = 313.15$			$T/\text{K} = 323.15$			$T/\text{K} = 333.15$		
P/bar	x_{CO_2}	y_{CO_2}												
14.0	0.2000	-	16.4	0.2000	-	18.7	0.2000	-	21.4	0.2000	-	24.4	0.2000	-
27.1	0.4002	-	32.2	0.4002	-	37.3	0.4002	-	42.6	0.4002	-	48.0	0.4002	-
32.4	0.5001	-	38.6	0.5001	-	45.3	0.5001	-	52.0	0.5001	-	58.7	0.5001	-
36.9	0.6002	-	44.3	0.6002	-	52.2	0.6002	-	60.5	0.6002	-	68.9	0.6002	-
40.9	0.6999	-	49.7	0.6999	-	58.9	0.6999	-	68.6	0.6999	-	78.5	0.6999	-
44.5	0.8000	-	54.5	0.8000	-	65.6	0.8000	-	77.1	0.8000	-	87.9	0.8000	-
46.5	0.8500	-	56.9	0.8500	-	68.7	0.8500	-	80.9	0.8500	-	91.8	0.8500	-
49.6	0.9000	-	59.4	0.9000	-	72.9	0.9000	-	84.8	0.9000	-	93.2	0.9000	-
52.1	0.9300	-	64.3	0.9300	-	76.7	0.9300	-	85.7	-	0.9300	87.3	-	0.9300
$T/\text{K} = 343.15$			$T/\text{K} = 353.15$			$T/\text{K} = 363.15$			$T/\text{K} = 373.15$					
P/bar	x_{CO_2}	y_{CO_2}												
27.3	0.2000	-	30.1	0.2000	-	32.7	0.2000	-	35.6	0.2000	-			
53.5	0.4002	-	59.0	0.4002	-	64.2	0.4002	-	69.5	0.4002	-			
65.4	0.5001	-	72.2	0.5001	-	78.7	0.5001	-	84.4	0.5001	-			
77.2	0.6002	-	85.2	0.6002	-	92.6	0.6002	-	99.2	0.6002	-			
87.9	0.6999	-	96.3	0.6999	-	104.1	0.6999	-	112.7	0.6999	-			
97.2	0.8000	-	104.4	0.8000	-	109.2	0.8000	-	112.2	-	0.8000			
99.9	0.8500	-	104.4	-	0.8500	105.9	-	0.8500	107.2	-	0.8500			
98.0	-	0.9000	98.6	-	0.9000	92.8	-	0.9000	74.6	-	0.9000			
77.1	-	0.9300												

4. Modeling and discussion

4.1. The Peng-Robinson equation of state with temperature-dependent binary interaction parameters

The Peng-Robinson equation of state (PR EOS) [40] was used to represent the experimentally determined bubble and dew points. For a mixture, the PR EOS is

$$P(T, v, z) = \frac{R \cdot T}{v - b_m} - \frac{a_m}{v(v + b_m) + b_m(v - b_m)} \quad (1)$$

Van der Waals mixing rules that embed a temperature-dependent binary interaction parameter ($k_{ij}(T)$) were used in this work to express mixture parameters a_m and b_m as a function of pure compounds parameters a_i and b_i :

$$\begin{cases} b_m = \sum_{i=1}^{NC} z_i b_i \\ a_m = \sum_{i=1}^{NC} \sum_{j=1}^{NC} z_i z_j \sqrt{a_i a_j} (1 - k_{ij}(T)) \end{cases} \quad (2)$$

With:

$$k_{ij}(T) = \frac{A_{ij} \cdot \left(\frac{298.15}{T} \right)^{\left(\frac{B_{ij}-1}{A_{ij}} \right)} - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j} \right)^2}{2 \frac{\sqrt{a_i(T) \cdot a_j(T)}}{b_i \cdot b_j}} \quad (3)$$

Eq. (3) is the expression of the k_{ij} used in the PPR78 model [1-4] in the particular case where each molecule of a binary system is considered as a single group. Results obtained with this equation therefore correspond to the maximum accuracy obtainable with the PPR78 model. Our ambition is to refit in the next few months some group-interaction parameters of the PPR78 model (especially between CO₂ and CH or C group) because it is believed they were determined on a too small number of experimental data. The data acquired in this paper and during measurement campaigns that we are conducting will obviously be used.

Pure-component parameters (a_i and b_i) were classically calculated by:

$$\left\{ \begin{array}{l}
 a_i(T) = a_{c,i} \cdot \alpha_i(T) \\
 \alpha_i(T) = \left[1 + m_i \left(1 - \sqrt{T/T_{c,i}} \right) \right]^2 \\
 m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \\
 a_{c,i} = \Omega_a \cdot \frac{R^2 T_{c,i}^2}{P_{c,i}} \\
 b_i = \Omega_b \cdot \frac{RT_{c,i}}{P_{c,i}} \\
 X = \left[1 + \sqrt[3]{4 - 2\sqrt{2}} + \sqrt[3]{4 + 2\sqrt{2}} \right]^{-1} \approx 0.25308 \\
 \Omega_a = \frac{8 + 40X}{49 - 37X} \approx 0.45724 \\
 \Omega_b = \frac{X}{X + 3} \approx 0.07780
 \end{array} \right. \quad (4)$$

Pure-component properties (experimental critical temperature, $T_{c,i}$, pressure, $P_{c,i}$, and acentric factor, ω_i) used in this study stem from the DIPPR database.

The two parameters A_{ij} and B_{ij} were fitted to experimental data in order to minimize the mean absolute deviations, at specified temperature and pressure, between calculated and experimental liquid phase and gas phase compositions.

The optimal values were found to be: $A_{12} = 127.4$ MPa and $B_{12} = 93.8$ MPa.

These parameters were used to calculate the phase envelopes and the mixture critical locus plotted in Fig. 1 and the isothermal bubble and dew curves drawn in Fig. 2.

4.2. Analysis and discussion

With the adjusted A_{12} and B_{12} parameters, a very good description of the experimental phase behavior of the system was attained. Indeed, an average overall deviation on the liquid phase composition of 0.0087 was obtained whereas a value 0.0095 was reached concerning the average overall deviation on the gas phase composition. It must be indicated that 5 experimental points (4 bubble points and 1 dew point) are located just above the calculated phase diagram, in the vicinity of the mixture critical point (see Fig. 2 at 323.15 K, 333.15 K and 343.15 K). They were thus not considered in the announced deviations.

Fig. 2 clearly shows that the interpolated data, obtained from the original measurements, are well represented by the PR EOS combined with a temperature-dependent k_{ij} even in the mixture critical area. It confirms the good capability of the PR EOS in correlating VLE of mixtures containing CO₂ and hydrocarbons if the binary interaction parameter used is temperature-dependent [4,41-43]. For the binary system CO₂ + 2,3-dimethylbutane, the binary interaction parameter is high and varies significantly with temperature: from 0.1074 at 293.15 K to 0.1507 at 373.15 K, which is in accordance with k_{ij} values found in the literature for such systems [4,17,22,24,44].

Fig. 2 also illustrates that the studied system behaves classically. The mixture has a continuous vapor–liquid critical line connecting the critical points of the pure components without liquid–liquid immiscibility. This observation is not surprising since the 2,3-dimethylbutane is a “light” branched alkane: all the studied binary systems CO₂ + a “light” branched alkane exhibit the same behavior.

At low temperature (see Fig. 2 at 293.15 K and 303.15 K), the bubble and dew curves are increasing between the pure 2,3-dimethylbutane saturation pressure ($x_{\text{CO}_2} = 0$) and the pure CO₂ saturation pressure ($x_{\text{CO}_2} = 1$). It can be noted that the mixture liquid phase does not show important deviation from ideality. When the temperature of the binary system exceeds the pure-

CO₂ critical temperature, a mixture critical phenomenon obviously appears. By increasing the temperature (from 313.15 K to 373.15 K in Fig. 2), the system presents a classical isothermal *tennis-racket shape* phase diagram [39].

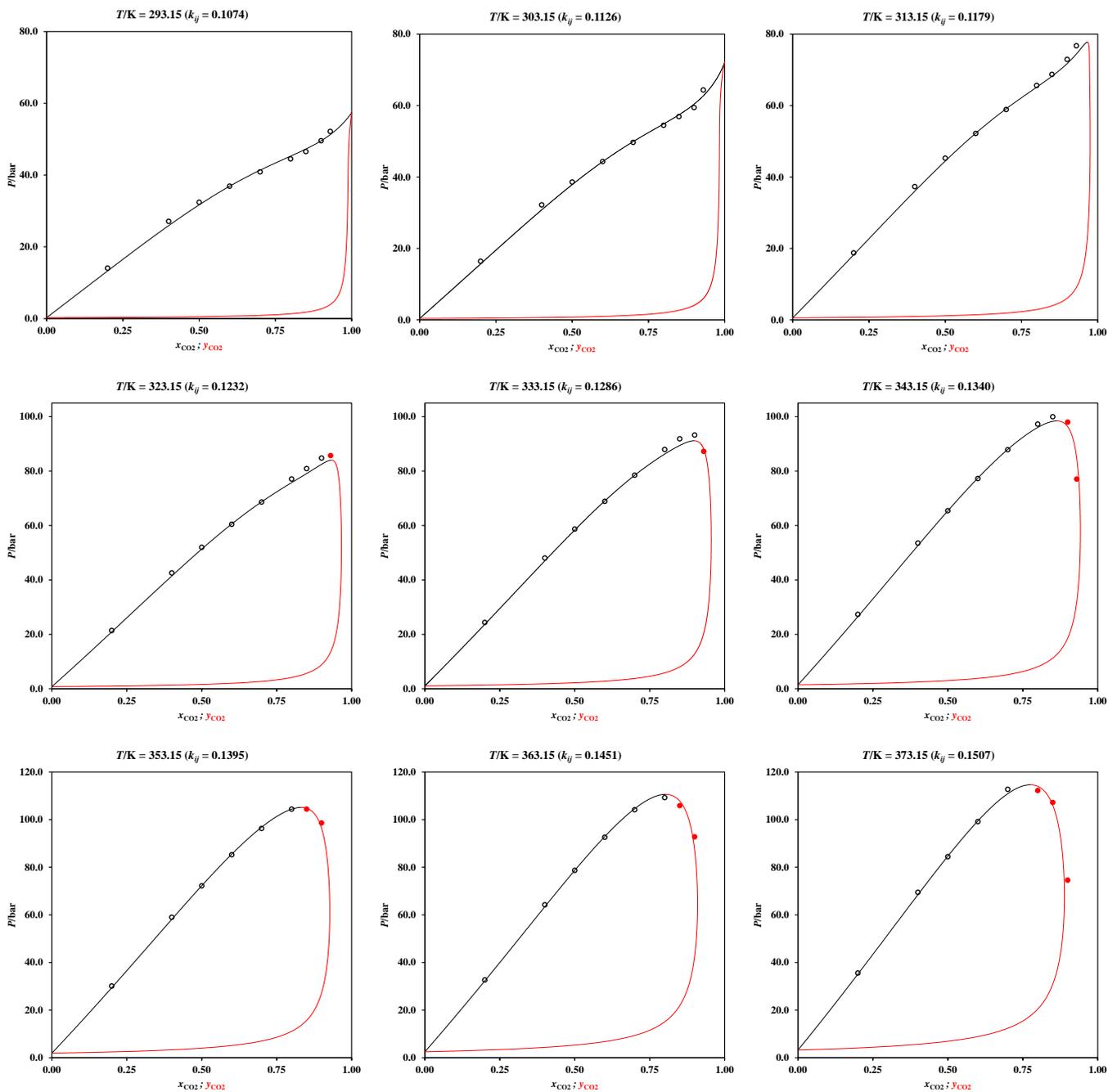


Figure 2. Correlation of the interpolated fluid-phase equilibrium data reported in Table 2 with the PR EOS and temperature-dependent binary interaction parameters. \circ : bubble point. \bullet : dew point.

5. Conclusion

Using a high-pressure variable volume cell, saturation pressures of the CO₂ + 2,3-dimethylbutane binary system were measured at 9 different compositions in the temperature range of 292.9 to 373.1 K. A total of 78 experimental points, ranging from 14.0 to 112.2 bar, were measured. The experimental results were successfully correlated by the PR EOS, by employing a temperature-dependent binary interaction parameter.

The main conclusion of this investigation is that the studied binary system does not exhibit three-phase equilibria (VLLE) in the investigated temperature range and that the vapor-liquid critical locus is undoubtedly a continuous curve between the two pure compounds.

The phase diagram of the binary system CO₂ + 2,3-dimethylbutane is thus very common and may be either a type I or II binary system according to the classification scheme of van Konynenburg and Scott.

List of symbols and acronyms

a = temperature-dependent function of the equation of state

A_{kl}, B_{kl} = constant parameters allowing the calculation of the binary interaction parameters

b = covolume

k_{ij} = binary interaction parameter

m = shape parameter

P = pressure

P_c = critical pressure

R = ideal gas constant

T = temperature

T_c = critical temperature

v = molar volume

x_i, y_i = mole fractions

Greek letters:

ω = acentric factor

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