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High–Pressure Phase Equilibria Measurements of the Carbon Dioxide + Cycloheptane Binary System

*Sarra Zid^{†,§}, Jean–Patrick Bazile[‡], Jean–Luc Daridon[‡], Jean–Noël Jaubert[^], Jean–Louis Havet^{†,§},
Marie Debacq^{†,§}, and Stéphane Vitu^{†,§*}*

[†] Conservatoire National des Arts et Métiers, 2 rue Conté, 75003 Paris, France

[§] Université Paris–Saclay, INRAE, AgroParisTech, UMR SayFood, 91300 Massy, France

[‡] Université de Pau et des Pays de l’Adour, E2S UPPA, CNRS, TotalEnergies, LFCR UMR5150,
Pau, France

[^] Université de Lorraine, Ecole Nationale Supérieure des Industries Chimiques, Laboratoire
Réactions et Génie des Procédés, 1 rue Grandville, 54000 Nancy, France

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pressure

Abstract:

The phase behavior of the carbon dioxide + cycloheptane binary system for which no literature data are available has been examined at temperatures ranging from (292.6 to 372.8) K. Saturation pressures, ranging from (23.9 to 154.8) bar, were acquired by a synthetic and visual method. In concrete terms, an adjustable volume high-pressure cell was utilized to measure bubble and dew point pressures by visual detection of phase transitions at constant overall composition. A total of 11 different mixtures with mole fractions of carbon dioxide ranging from (0.20 to 0.96) were prepared and a total of 99 experimental points were reported. The experimental results obtained in this work reveal the absence of liquid-liquid immiscibility in the studied temperature range and make it possible to conclude that the vapor-liquid critical line of the binary system is continuous and uninterrupted between the two pure compounds. Experimental data were correlated with the Peng-Robinson equation of state and classical Van der Waals mixing rules with temperature-dependent binary interaction parameters. They were also compared to the PPR78 model, an entirely predictive group contribution method in which the k_{ij} depends on temperature.

1. Introduction

Considering the vast amount of industrially used chemicals, the number of possible mixtures encountered in the different branches of industry is practically unlimited. It is thus unthinkable to measure thermodynamic and transport properties for all the possible industrial mixtures in a wide range of temperature and pressure. Nowadays, in various industrial sectors, several thermodynamic models can be successfully employed to avoid doing systematic and time-consuming experimental measurements.

However, experimental data are still needed for many application areas.^{1,2} Even in the oil and gas sector, high-pressure phase equilibrium data as well as thermodynamic data regarding to uncommon molecules (such as naphthenic components with more than six carbon atoms in ring or with multiple aromatic ring) are welcomed.^{1,3} Due to the important role of carbon dioxide in the chemical, pharmaceutical and petrochemical industries, phase equilibrium data of mixtures containing CO₂ remain crucial.⁴⁻⁸

In our previous works^{3,9}, a lack of data for two kinds of binary systems containing carbon dioxide + a naphthenic compound was noticed; they are CO₂ + branched naphthenes and CO₂ + naphthenes that contains more than 6 carbon atoms in ring (cycloheptane, cyclooctane, etc.). Indeed, the binary systems CO₂ + cyclopentane and CO₂ + cyclohexane were widely investigated in the past and more details about the different studies related to these two systems can be found elsewhere.^{10,11}

No literature data were available for the binary mixture CO₂ + cyclooctane under pressure and we thus recently published³ bubble and dew points for this system. The situation is almost similar for the binary system CO₂ + cycloheptane. Only five solubilities of CO₂ in cycloheptane at atmospheric pressure have been published.¹²

The purpose of this study is to disseminate new VLE measurements for the CO₂ + cycloheptane system under pressure, on the full composition range and therefore to fill in the data gaps concerning such systems. A high–pressure device was employed to measure phase transitions. The experimental data were correlated using the Peng–Robinson equation of state.

This work is the continuation of a series of paper providing missing experimental data with regard to basic binary mixtures ^{13,14} or to more uncommon systems. ^{3,9,15}

2. Experimental section

2.1. Materials

The description of materials used in this work is reported in Table 1. The chemicals were utilized as we received them. Purities given in Table 1 are those provided by the manufacturers.

Table 1. Description and specification of the pure compounds used in this study

compound	linear formula	CAS number	supplier	mass fraction purity ^b
carbon dioxide	CO ₂	124-38-9	Linde	0.99995
cycloheptane	C ₇ H ₁₄	291-64-5	Acros Organics ^a	0.995

^a Thermo Fisher Scientific. ^b information provided by the manufacturers.

2.2. Apparatus and method

The apparatus employed and the experimental strategy were widely described in our previous papers.^{3,13,16} The technique used to perform saturation pressure measurements was a synthetic method, without sampling and analyses. This method is called *synthetic-visual method with variable-volume cell* (SynVisVar) as defined by Dohrn and co-workers.⁴ The main equipment was an adjustable-volume high pressure cell. The device includes a mobile piston and two sapphire windows: one for visual observation of the fluid contained in the cell thanks to an endoscope and the other to light up the interior of the cell. The mixture was continuously mixed by means of a small bar magnet. Internal volume of the cell ranged from 8 to 30 cm³ and the internal temperature was maintained by circulating a coolant distributed through three lines arranged in the cell wall. The mixture temperature enclosed in the cell was measured with an uncertainty of ± 0.1 K using a Pt100 probe inserted in the cell. The pressure was acquired by a Kulite pressure gauge installed

inside the cell to restrict dead volumes. The pressure gauge was calibrated, between 1 and 1000 bar, with an uncertainty better than 0.02%.

In a first step, the device was partly filled with a known quantity of liquid cycloheptane by vacuum extraction. The mass of cycloheptane loaded ($m_{cycloheptane}$) was measured with a precision balance (Ohaus). In a second step, the CO₂ mass (m_{CO_2}) was added under pressure in the cell. To do so, the carbon dioxide was firstly loaded in an aluminum pressure vessel. The vessel was weighed by means of a Metler Toledo high-capacity precision balance. So as CO₂ weighing not to be disturbed by the connecting line, the CO₂ vessel was linked to the cell through a flexible lightweight tubing. This flexible high-pressure capillary does not affect the stability of the balance during the weighing. Moreover, the capillary tube has a small diameter (1/32") and the CO₂ was stored in liquid-vapor equilibrium in the tank in order to keep the pressure constant during CO₂ injection and therefore prevent gas mass changes in the connecting line.

The expanded uncertainties in mass loaded in the apparatus were deemed to be better than 0.005 g for cycloheptane and 0.005 g for CO₂. The composition ($z_{CO_2} = z_1$) of the CO₂ + cycloheptane binary system contained in the cell can be calculated and the standard uncertainty in composition is obtained through the following expression

$$u(z_1) = u(z_{CO_2}) = z_{CO_2}(1 - z_{CO_2}) \sqrt{\left(\frac{u(m_{CO_2})}{m_{CO_2}}\right)^2 + \left(\frac{u(m_{cycloheptane})}{m_{cycloheptane}}\right)^2} \quad (1)$$

Saturation pressures were obtained visually. The phase boundaries were assessed by determining the disappearance conditions of one phase of a two phase equilibrium system.

The experiments were conducted, at constant temperature, by examining the disappearance of the vapor phase for a bubble–point pressure measurement. For a dew point, disappearance of the liquid phase was examined. The principle of the procedure is, in a first step, to reach a two–phase equilibrium by modifying the pressure and, in a second step, to eliminate the last phase formed by slowly inverting the pressure variation. Experiments were replicated to refine the measurements. Bubble pressures and dew pressures were determined with a standard uncertainty of 0.2 bar and 0.4 bar, respectively.^{13,16}

3. Experimental results

For the CO₂ + cycloheptane binary system, 83 bubble points and 16 dew points were acquired, by isoplethic measurements, for 11 different compositions ranging from 0.1996 to 0.9600 CO₂ mole fraction so as to achieve a detailed description of the phase diagram. The obtained data are presented in Table 2 with uncertainties and are partly depicted in Figure 1.

Table 2. Experimental bubble–point and dew–point pressures P , at temperature T , for the CO₂ (1) + cycloheptane (2) binary system at 11 different CO₂ mole fractions z_1 ^{a,b,c,d}

$z_1 = 0.1996 \pm 0.0006$		$z_1 = 0.2999 \pm 0.0006$		$z_1 = 0.3753 \pm 0.0005$		$z_1 = 0.5000 \pm 0.0004$		$z_1 = 0.6002 \pm 0.0003$		$z_1 = 0.7000 \pm 0.0002$	
T/K	P/bar										
293.5	23.9	293.1	32.8	293.9	38.3	293.8	44.0	292.6	46.1	292.7	47.6
302.4	27.3	303.4	37.4	302.6	44.1	302.6	52.0	302.9	56.2	302.7	58.5
311.6	30.5	311.9	42.4	313.4	51.2	311.7	60.6	312.3	66.5	311.6	68.9
321.5	33.9	321.5	47.3	322.7	57.7	321.3	69.5	321.3	76.6	321.2	81.1
331.1	37.6	332.8	52.0	332.3	64.1	330.9	78.5	331.1	88.3	330.8	94.7
341.4	40.7	342.8	57.5	342.2	70.7	341.5	88.4	341.5	100.4	340.9	107.9
349.1	42.9	351.0	62.0	350.5	76.0	350.9	97.3	350.9	111.0	350.8	121.2
358.9	46.5	359.5	66.6	360.4	82.5	361.2	106.4	360.7	122.2	361.4	134.8
371.7	49.9	371.3	72.0	371.7	89.7	372.8	115.5	371.4	132.6	371.7	146.2
$z_1 = 0.8000 \pm 0.0002$		$z_1 = 0.8499 \pm 0.0001$		$z_1 = 0.9000 \pm 0.0001$		$z_1 = 0.9300 \pm 0.0001$		$z_1 = 0.9600 \pm 0.0002$			
T/K	P/bar										
293.3	50.1	293.9	51.1	293.1	51.1	293.7	52.2	293.5	53.5		
304.4	63.3	303.5	62.4	303.1	62.7	302.6	63.4	303.0	65.7		
312.5	73.0	312.6	74.1	312.6	75.6	312.2	76.6	312.0	79.5		
322.5	86.9	322.0	87.4	321.5	89.2	322.5	91.5	321.2	91.1		
332.0	101.0	332.6	103.4	331.4	103.5	331.5	104.0	330.0	100.7		
341.6	115.5	341.4	117.8	341.2	117.2	340.9	115.8	341.3	112.6		
350.6	128.6	351.1	130.9	351.4	130.7	351.4	127.7	351.3	119.0		
360.7	141.7	359.8	141.9	361.2	141.8	361.1	137.3	360.9	122.0		
371.8	154.4	372.4	154.8	370.6	150.0	371.6	143.5	371.6	123.4		

^a Bold data are dew points, the rest are bubble points. ^b Standard uncertainties are $u(T) = 0.1$ K, $u(P) = 0.2$ bar for

bubble points and $u(P) = 0.4$ bar for dew points. ^c Each composition z_1 is reported with its standard uncertainty $u(z_1)$.

^d $z_1 + z_2 = 1$.

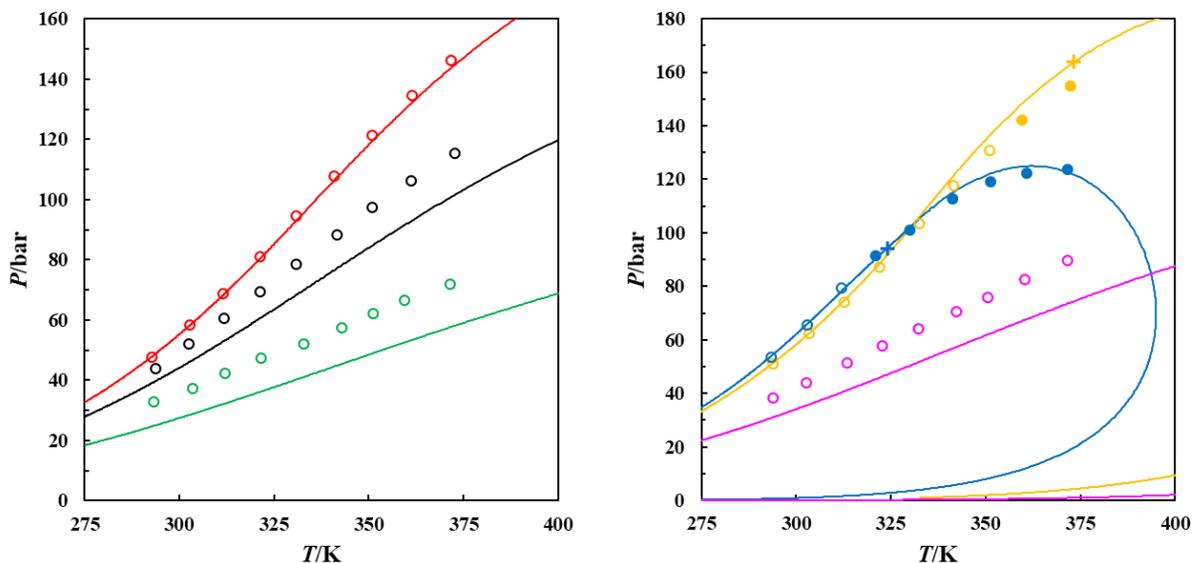


Figure 1. (P , T) phase envelopes of the binary system CO_2 (1) + cycloheptane (2). CO_2 mole fractions are: $z_1 = 0.2999$ (green envelope and green points); $z_1 = 0.5000$ (black envelope and black points); $z_1 = 0.7000$ (red envelope and red points); $z_1 = 0.3753$ (pink envelope and pink points); $z_1 = 0.8499$ (yellow envelope and yellow points); $z_1 = 0.9600$ (blue envelope and blue points). \circ : experimental bubble points measured in this work. \bullet : experimental dew points measured in this work. Solid lines: calculated phase envelopes with the Peng–Robinson equation of state and a temperature–dependent k_{ij} . $+$: calculated mixture critical point.

Measurements were carried out with a particular care for the CO_2 rich mixtures at low temperature, by doing intermediate temperature steps, in order to detect a possible liquid–liquid phase splitting. However, despite all this attention, no liquid–liquid immiscibility was encountered in the investigated temperature range. From the experimental data obtained in this work, it can be concluded that the vapor–liquid critical line of the CO_2 + cycloheptane system is most likely uninterrupted between the pure compounds critical point so that the system is either a type I or a type II binary system in the nomenclature of van Konynenburg and Scott.^{17,18}

To complete the analysis of the system CO_2 + cycloheptane, it is more convenient to represent data in an isothermal (P, x_1, y_1) diagram. However, phase transition measurements were not carried out at exactly the same temperatures for the 11 different mixtures prepared. The isothermal curves (P, x_{CO_2}) thus cannot be graphed directly from the measured data presented in Table 2.

Interpolated values were calculated using second order polynomials to describe the pressure–temperature relationship of the raw experimental data at constant composition, following the reliable method previously described in detail by Schwarz et al.^{6,19–21} The following second order polynomial was used

$$P = AT^2 + BT + C \quad (2)$$

The coefficients of the polynomials (see Table 3) were calculated by fitting the raw experimental data reported in Table 2. These polynomial functions were then employed to generate isothermal data. Fitted coefficients are presented in Table 3 with R^2 values for each composition studied. It is obvious that the functions and the coefficients detailed in Table 3 can be safely used to describe the studied binary system in the strict temperature range of 293.15 to 373.15 K. The (P, x_1, y_1) phase diagrams resulting from these interpolations were displayed in Figure 2 for different isotherms.

Table 3. Coefficients of the P – T polynomial function (P) used to fit the experimental data reported in Table 2 in order to generate isothermal data for the CO₂ (1) + cycloheptane (2) binary system between 293.15 K and 373.15 K^{a,b}

$z_1/\text{mol}\cdot\text{mol}^{-1}$	A/bar·K ⁻²	B/bar·K ⁻¹	C/bar	R ²
0.1996	-5.59793×10^{-04}	0.70530	-134.850	0.9995
0.2999	1.01568×10^{-04}	0.43853	-104.594	0.9992
0.3753	-2.83741×10^{-04}	0.85081	-187.328	1.0000
0.5000	-6.72802×10^{-04}	1.36499	-299.327	0.9998
0.6002	1.02935×10^{-04}	1.05265	-271.631	0.9995
0.7000	4.95344×10^{-04}	0.94864	-273.623	0.9992
0.8000	2.45485×10^{-04}	1.20661	-326.420	0.9986
0.8499	-1.13277×10^{-03}	2.12810	-478.551	0.9976
0.9000	-2.32288×10^{-03}	2.86794	-591.984	0.9982
0.9300	-4.89489×10^{-03}	4.47474	-841.614	0.9982
0.9600	-1.02564×10^{-02}	7.75416	-1340.672	0.9977

^a The polynomial function is $P = AT^2 + BT + C$. ^b Using these coefficients, original experimental data (Table 2) are correlated with AAD of 0.78 bar (0.95%).

4. Modeling and discussion

Initially, the PPR78 model was used to predict the experimental points. This model is today routinely employed²² and is fully described elsewhere.^{23,24} Only most important points of the model are thus recalled below.

For a pure component, the equation of state proposed by Peng and Robinson²⁵ is

$$P = \frac{RT}{v-b_i} - \frac{a_i(T)}{v(v+b_i)+b_i(v-b_i)} \quad (3)$$

And

$$\left\{ \begin{array}{l} R = 8.314472 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ b_i = 0.0777960739 \frac{RT_{c,i}}{P_{c,i}} \\ a_i = 0.457235529 \frac{R^2 T_{c,i}^2}{P_{c,i}} \left[1 + m_i \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2 \\ \text{if } \omega_i \leq 0.491 \quad m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \\ \text{if } \omega_i > 0.491 \quad m_i = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3 \end{array} \right. \quad (4)$$

P is the pressure, R the ideal gas constant, T the temperature, v the molar volume, T_c the critical temperature, P_c the critical pressure and ω the acentric factor.

In the PPR78 model, classical mixing rules are employed

$$\left\{ \begin{array}{l} a = \sum_{i=1}^N \sum_{j=1}^N z_i z_j \sqrt{a_i a_j} (1 - k_{ij}(T)) \\ b = \sum_{i=1}^N z_i b_i \end{array} \right. \quad (5)$$

z_i is the mole fraction of component i in the mixture, N is the number of components in the mixture and $k_{ij}(T)$ is the binary interaction parameter. In the PPR78 model, k_{ij} is temperature-dependent and determined by group contribution:

$$k_{ij}(T) = \frac{-\frac{1}{2} \sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} \cdot \left(\frac{298.15}{T}\right)^{\left(\frac{B_{kl}-1}{A_{kl}}\right)} - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j}\right)^2}{2 \frac{\sqrt{a_i(T) \cdot a_j(T)}}{b_i \cdot b_j}} \quad (6)$$

In eq 6, a_i and b_i are calculated by eq 4, N_g is the number of different groups presents in the mixture and α_{ik} is the fraction of molecule i occupied by group k . A_{kl} and B_{kl} are constant group interaction parameters between group k and group l . The critical properties (T_c and P_c) and the acentric factor (ω) of the two components involved in this work come from the DIPPR database.

In Figure 2, dashed isothermal curves (bubble and dew curves) foreseen by the PPR78 approach are drawn for comparison with interpolated data obtained from the original measurements at six temperatures from 293.15 K to 373.15 K. Figure 2 illustrates that the binary system is qualitatively and to a lesser extent quantitatively predicted accurately by the PPR78 model. With such a model, an average overall deviation on the liquid phase composition of 0.054 and a deviation of 0.030 on the gas phase composition were obtained, respectively. Such deviations are not surprising since (i) no parameters were fitted to represent the experimental data and (ii) this binary system was completely absent from the database used to adjust the interaction parameters of the model (the system CO_2 + cycloheptane is indeed studied for the first time in this paper).

The PPR78 model foresees a type IV phase diagram in the van Konynenburg and Scott nomenclature. The predicted vapor–liquid critical locus is thus interrupted, with the presence of a lower critical end point (at 320.4 K), an upper critical end point (at 324.9 K) and a very narrow liquid–liquid–vapor three–phase line. Such a 3–phase domain was not found experimentally despite a careful examination of the mixture inside the cell in the CO_2 rich region.

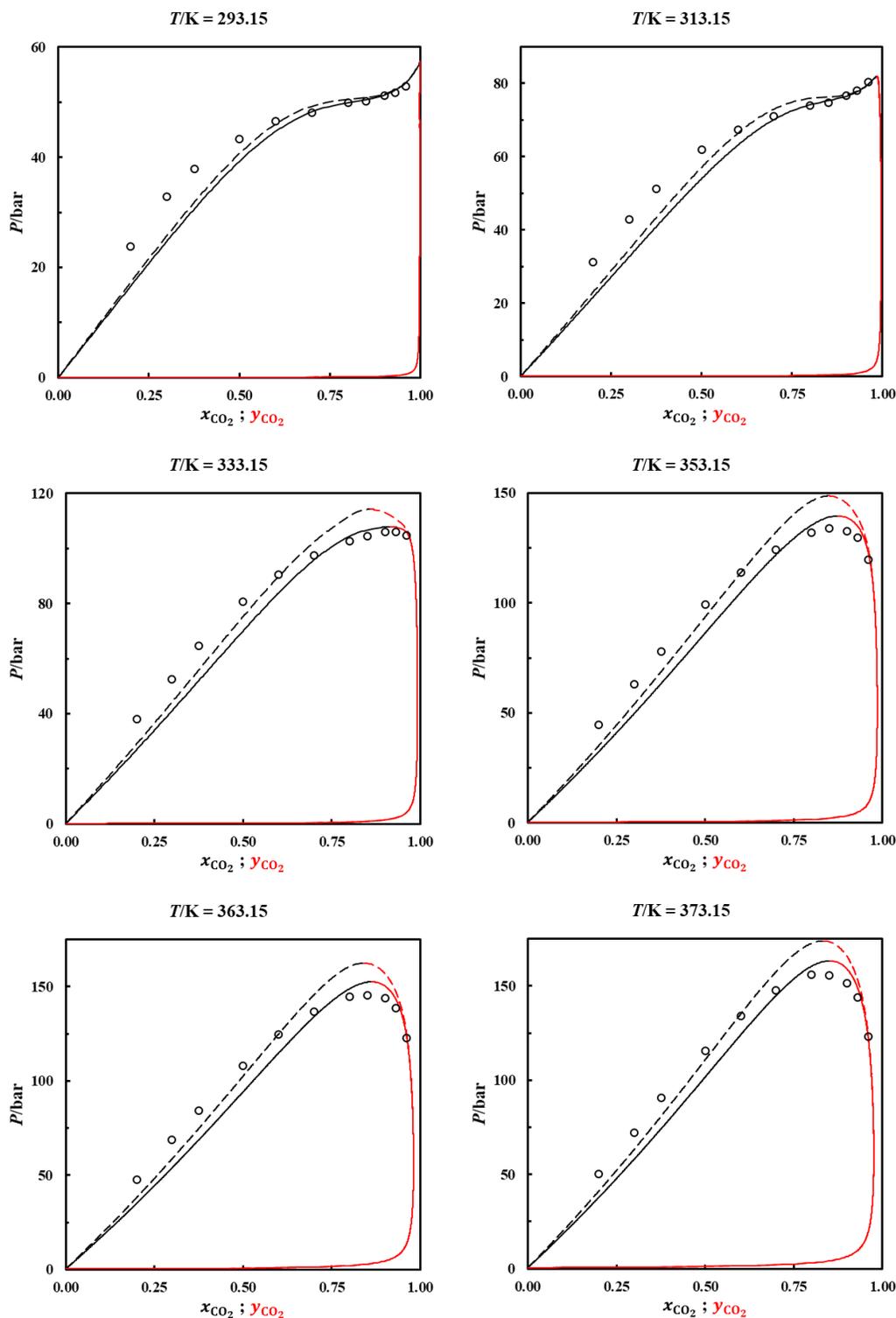


Figure 2. Isothermal phase equilibria of the binary system CO₂ + cycloheptane. ○: interpolated experimental phase transition points. Dashed lines: bubble and dew curves predicted with the PPR78 model. Solid lines: bubble and dew curves calculated with the PR equation of state and a temperature–dependent k_{ij} fitted against interpolated experimental data.

So as to improve the description of the mixture behavior, it was decided to consider each molecule of the binary system as a single group. By doing so, eq 6 becomes

$$k_{ij}(T) = \frac{A_{ij} \cdot \left(\frac{298.15}{T}\right)^{\left(\frac{B_{ij}}{A_{ij}} - 1\right)} - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j}\right)^2}{2 \frac{\sqrt{a_i(T) \cdot a_j(T)}}{b_i \cdot b_j}} \quad (7)$$

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

$A_{12} = 122.1$ MPa and $B_{12} = 281.1$ MPa were found to be the optimal values. Isothermal bubble and dew curves calculated by this method are solid lines in Figure 2. This figure shows that a slightly better representation of the data is obtained in the mixture critical area. By using these adjusted parameters, a continuous vapor–liquid critical locus is now calculated between the two pure compounds, which is in accordance with the experimental observation. The binary interaction parameter is high and slightly decreases with temperature: from 0.1155 at 293.15 K to 0.1007 at 373.15 K, which is in accordance with k_{ij} values reported in the literature for comparable systems.
8,11,14

Finally, Figures 1 and 2 highlight that the Peng–Robinson equation of state is not able to perfectly correlate simultaneously the bubble curve (for low CO₂ compositions) and the critical region. This is a well–documented weakness of cubic equations of state when size-asymmetric systems are correlated. As shown in Figure 2, the PPR78 model (dashed lines) satisfactorily correlates the bubble curve but the prize to pay is an overestimation of the critical pressures. Conversely, the Peng–Robinson equation of state with temperature–dependent k_{ij} fitted against the measured

experimental data better correlates the critical region than the PPR78 prediction but at the expense of less accurate bubble pressures at lower CO₂ mole fractions.

5. Conclusions

The synthetic method was applied to measure new saturation pressures of the CO₂ + cycloheptane binary system between 292.6 K and 372.8 K. To do so, 11 mixtures from (0.20 to 0.96) CO₂ mole fractions were prepared and studied. A total of 83 bubble points and 16 dew points were measured with pressures up to 154.8 bar. Two approaches were employed to model the experimental data: the fully predictive PPR78 model and the equation of state proposed by Peng and Robinson combined with a temperature–dependent binary interaction parameter fitted to experimental data.

This experimental work, and a previous one³ devoted to the binary system CO₂ + cyclooctane, can be used to discuss the phase behavior evolution regarding to the homologous series of CO₂ + naphthenes binary mixtures. Mixtures of CO₂ with cyclopentane and cyclohexane exhibit type I or II phase behavior.^{10,11} From the results reported in this paper, it can be concluded that the binary system CO₂ + cycloheptane also belongs to type I or II since the vapor-liquid critical curve is, highly likely, continuous. Finally, the binary mixture CO₂ + cyclooctane probably exhibits type V phase behavior³ but more experiments are necessary to validate this assumption.

In the future, additional measurements of the system CO₂ + cyclooctane are planned, with small steps in temperature and a particular focus on the CO₂ rich region of the binary diagram to confirm, or not, our supposition. Measurement of the binaries CO₂ + cyclodecane and CO₂ + cyclododecane are also envisaged.

Corresponding Author

* stephane.vitu@lecnam.net

Notes

The authors declare no competing financial interest.

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