

# Vapor–liquid equilibrium measurements of the binary mixtures CO<sub>2</sub> + acetone and CO<sub>2</sub> + pentanones

Chieh-Ming Hsieh<sup>\*,a</sup> and Jadran Vrabec<sup>b</sup>

<sup>a</sup>Department of Chemical and Materials Engineering, National Central University, Jhongli,  
Taiwan

<sup>b</sup>Thermodynamics and Energy Technology, University of Paderborn, Paderborn, Germany

## Abstract

Vapor–liquid equilibrium (VLE) data of the binary mixtures carbon dioxide (CO<sub>2</sub>) + acetone and CO<sub>2</sub> + pentanones (i.e. all C<sub>5</sub>-ketones, which are 3-methyl-2-butanone, 2-pentanone, and 3-pentanone) are measured at 313.15 K, 333.15 K, and 353.15 K up to a pressure of 11.8 MPa using a high pressure view cell technique based on the synthetic method. The VLE measurement results of CO<sub>2</sub> + acetone are compared to the available experimental data from the literature in order to validate the employed experimental apparatus. In case of binary CO<sub>2</sub> + pentanone mixtures, only for CO<sub>2</sub> + 3-methyl-2-butanone and CO<sub>2</sub> + 2-pentanone at 313.15 K experimental data are available in the literature. The present measurements thus complete the literature database for binary VLE of CO<sub>2</sub> + pentanones. All present data are compared to the results from the Peng–Robinson equation of state (PR EOS) with the van der Waals one-fluid mixing rule and from the combination of the PR EOS with the UNIQUAC model through the Huron–Vidal mixing rule.

**Keywords:** Peng–Robinson equation of state, phase equilibrium, experiment, carbon dioxide, ketones

\*Corresponding author. Email [hsiehcm@ncu.edu.tw](mailto:hsiehcm@ncu.edu.tw). Tel: +886-3-4227151#34220

## 1. Introduction

Carbon dioxide ( $\text{CO}_2$ ) is a popular solvent in industrial applications because it is nontoxic, nonflammable, and inexpensive and has a moderate critical temperature and critical pressure. Supercritical carbon dioxide ( $\text{ScCO}_2$ ) is widely used in industry, such as for extraction of natural flavors, decaffeination of coffee beans, or as a solvent in polymer synthesis processes [1-8]. Sometimes cosolvents are necessary either to increase the solubility of the solute in  $\text{ScCO}_2$  or to modify the properties of  $\text{ScCO}_2$ . Thermodynamic properties, in particular vapor-liquid equilibrium (VLE) data, for mixtures of  $\text{ScCO}_2$  and cosolvents are important for designing and optimizing processes containing these mixtures [9, 10]. E.g., operating conditions during crystallization processes that employ supercritical anti-solvents strongly affect the size distribution and the mean size of particles [7, 11, 12].

The most reliable way to obtain thermodynamic properties and fluid phase equilibrium data is by experiments. These data are necessary to evaluate the accuracy of thermodynamic models. Several publications have focused on VLE of  $\text{ScCO}_2$  + low molecular weight cosolvents because they are good candidates for the extraction of drugs and food ingredients [5, 13-15]. The most popular cosolvents for  $\text{ScCO}_2$  are low molecular weight alcohols because they can greatly increase the solubility of polar solutes in  $\text{ScCO}_2$  [1, 6, 13, 14, 16]. The phase behavior of  $\text{ScCO}_2$  + alcohols was systematically investigated by several research groups [17-22]. Compared with alcohols, relatively few data were measured for other types of solvents, such as ketones or ethers, which are potential cosolvents for  $\text{ScCO}_2$  in some applications [5]. E.g., the solubility of pharmaceutical compounds in  $\text{ScCO}_2$  + acetone was extensively studied by experimental measurements [12, 13], thermodynamic models [23, 24], and

molecular simulation [25]. It was found that acetone may be a good cosolvent candidate in processes for recovering nondegraded triglycerides from used frying oil and in the extraction of cocoa butter [26, 27]. Acetone is the most popular ketone cosolvent for  $\text{ScCO}_2$  applications. The main reason may be that acetone is a very popular solvent in general. Another possible reason may be that insufficient information (such as experimental data) is available for other ketones.

In this study, the isothermal VLE of  $\text{CO}_2$  + ketones at 313.15 K, 333.15 K, and 353.15 K were systematically investigated by experiments using a high pressure view cell technique based on the synthetic method. There are numerous measured data available for  $\text{CO}_2$  + acetone (the only  $\text{C}_3$ -ketone) and  $\text{CO}_2$  + 2-butanone (the only  $\text{C}_4$ -ketone) [28], but there are very few experimental data in the literature for binary mixtures  $\text{CO}_2$  + pentanones ( $\text{C}_5$ -ketones). Only for  $\text{CO}_2$  + 3-methyl-2-butanone and  $\text{CO}_2$  + 2-pentanone at 313.15 K data were reported. The first step in this work was to measure VLE for the binary mixture  $\text{CO}_2$  + acetone at three temperatures to validate the measurements of the employed experimental apparatus on the basis of data from the literature. Next, VLE of binary mixtures  $\text{CO}_2$  + pentanones (3-methyl-2-pentanone, 2-pentanone, and 3-pentanone) were measured at 313.15 K, 333.15 K, and 353.15 K and also compared with the available experimental data from the literature. The present measurements thus complete the literature database of binary VLE for  $\text{CO}_2$  + ketones up to pentanones. Furthermore, all present data were compared to the results from the Peng–Robinson equation of state (PR EOS) [29] with the van der Waals one-fluid mixing rule and from the combination of the PR EOS with the UNIQUAC model [30] through the Huron–Vidal mixing rule [31].

## 2. Materials and methods

### 2.1. Materials

Acetone (purity  $\geq 99.9\%$ , CAS No.: 67-64-1), 3-methyl-2-butanone (purity 99%, CAS No.: 563-80-4), 2-pentanone (purity 99.5%, CAS No.: 107-87-9), and 3-pentanone (purity 99%, CAS No.: 96-22-0) were purchased from Sigma-Aldrich, Germany. Carbon dioxide (volume fraction 99.995%) was supplied by Air Liquide, Germany. All chemicals were used without further purification.

### 2.2. Experimental apparatus and procedure

Figure 1 shows the apparatus for experimentation in this study. This setup was used for VLE measurements in prior work [17, 32]. The only modification made for this study was that the surrounding climate chamber was removed because all ketones included in this study are liquid at ambient temperature. All pressure transducers (P1 and P2, model Super THE, Honeywell test & measurement with measuring ranges 6.8 MPa and 20 MPa and an uncertainty of  $\pm 0.05\%$  of their full measuring ranges), platinum resistance thermometers (Pt1 to Pt4, with a basic resistance of  $100\ \Omega$  and an uncertainty of  $\pm 0.04\ \text{K}$ ), and spindle presses A and B were calibrated. Briefly summarized, the measurement procedure was as following:

1. Liquid  $\text{CO}_2$  from the gas cylinder was loaded into the calibrated spindle press A which was cooled down by ice water to about  $275\ \text{K}$ .
2. Liquid ketone was filled into the calibrated spindle press B from the reservoir.
3. The high pressure view cell was filled with the desired quantity of ketone from spindle press B and heated up to the measuring temperature.
4. Liquid  $\text{CO}_2$  from spindle press A was slowly loaded into the view cell until it was

observed that the CO<sub>2</sub> + ketone mixture was in a homogenous liquid state. The mixing process was accelerated by a magnetic stirrer in the view cell.

5. The mixture in the view cell was maintained in its homogeneous liquid state for at least 20 minutes.
6. Spindle press A was operated to decrease the pressure in the view cell in very small steps. This expansion was terminated at the saturated liquid state, i.e. when the first tiny vapor bubbles appeared in the view cell.
7. Temperature and vapor pressure of the mixture were measured with the thermometers Pt1 and Pt2 and the pressure transducer P2. The mole fraction of CO<sub>2</sub> ( $x_{\text{CO}_2}$ ) was obtained straightforwardly by the procedure described in previous work [17, 32]. The error analysis in terms of  $x_{\text{CO}_2}$  was taken from Ref. [33] and is briefly summarized in the Supplementary Material.

### 3. Thermodynamic models

Two approaches, both based on the PR EOS [29], were used to correlate the experimental data of the four binary mixtures studied in this work. The PR EOS describes the relation between temperature  $T$ , pressure  $P$ , and molar volume  $v$  of a fluid

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+v(v-b)}, \quad (1)$$

where  $R$  is the gas constant. For a pure fluid, the substance-specific parameters, i.e. the energy parameter  $a$  and covolume parameter  $b$ , were determined from the critical temperature  $T_c$ , the critical pressure  $P_c$ , and the acentric factor  $\omega$  by

$$a(T) = 0.457235 \frac{R^2 T_c^2}{P_c} \left[ 1 + \kappa \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right]^2, \quad (2)$$

$$b = 0.077796 \frac{RT_c}{P_c}, \quad (3)$$

where  $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$ . The required pure substance properties for all relevant substances are summarized in Table 1.

In the case of mixtures, the energy parameter  $a$  and the covolume parameter  $b$  are not only a function of temperature and pure substance properties, but also a function of mole fraction. Therefore, a mixing rule must be used to consider the concentration effects on these two parameters. In this study, two mixing rules were assessed: the van der Waals one-fluid mixing rule and the Huron-Vidal mixing rule [31].

### 3.1. Van der Waals one-fluid mixing rule

The van der Waals one-fluid mixing rule is the simplest mixing rule. It assumes that a mixture is a pseudo one-fluid composed of all substances in the mixture and its energy and covolume parameters are given by

$$a(T, \underline{x}) = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \sqrt{a_i(T) a_j(T)} (1 - k_{ij}), \quad (4)$$

$$b(\underline{x}) = \sum_{i=1}^n x_i b_i, \quad (5)$$

where  $k_{ij}$  is an adjustable binary interaction parameter between species  $i$  and  $j$ ,  $n$  the number of components in the mixture, and  $x_i$  the mole fraction of component  $i$ .  $k_{ij}$  is set to be zero in prediction mode or obtained from correlation to experimental data in correlation mode. Values for the binary interaction parameter  $k_{ij}$  in correlation mode were obtained from the regression of experimental VLE data generated in this study and are summarized in Table 2. These two models are denoted as PR+VDW and

PR+VDW<sub>kij</sub> in the following. The results are discussed in section 4.

### 3.2. Huron-Vidal mixing rule

The Huron-Vidal mixing rule is based on the excess Gibbs free energy  $G^{ex}$  as supplied by additional models. It also specifies the covolume parameter  $b$  with Eq. (5).

The expression for the energy parameter  $a$  is

$$\frac{a(T, \underline{x})}{b(\underline{x})} = \sum_{i=1}^n x_i \frac{a_i(T)}{b_i} + \frac{G^{ex}}{C_{HV}}, \quad (6)$$

where  $C_{HV}$  is an equation of state dependent constant, i.e.  $C_{HV} = \frac{1}{2\sqrt{2}} \ln\left(\frac{2+\sqrt{2}}{2-\sqrt{2}}\right)$  in

case of the PR EOS.  $G^{ex}$  is the excess Gibbs free energy determined from an activity coefficient model,  $G^{ex} = RT \sum_i x_i \ln \gamma_i$ . In this study, the UNIQUAC model [30] was used for this task

$$\ln \gamma_i = \ln \gamma_i^{comb} + \ln \gamma_i^{res}. \quad (7)$$

The Staverman–Guggenheim combinatorial term [34, 35] was taken to consider molecular size and shape effects

$$\ln \gamma_i^{comb} = 1 - \frac{r_i}{\sum_j x_j r_j} + \ln \frac{r_i}{\sum_j x_j r_j} - \frac{z}{2} q_i \left[ 1 - \frac{r_i}{q_i} \frac{\sum_j x_j q_j}{\sum_j x_j r_j} + \ln \frac{r_i}{q_i} \frac{\sum_j x_j q_j}{\sum_j x_j r_j} \right]. \quad (8)$$

The expression for the residual term is

$$\ln \gamma_i^{res} = q_i \left[ 1 - \ln \frac{\sum_j x_j q_j \tau_{ji}}{\sum_j x_j q_j} - \sum_j \frac{x_j q_j \tau_{ij}}{\sum_k x_k q_k \tau_{kj}} \right], \quad (9)$$

where  $z = 10$  is the coordination number.  $r_i$  and  $q_i$  are relative van der Waals volume and surface area of substance  $i$ , respectively. In this study, the values of these two parameters were either taken from the literature [30] or determined from the UNIFAC group contribution method [36].  $\tau_{ij} = \exp(-\Delta u_{ij}/RT)$  is an empirical parameter and  $\Delta u_{ij}$

is the binary interaction parameter between components  $i$  and  $j$ . The values for the binary interaction parameter  $\Delta u_{ij}$  were obtained from a regression to experimental VLE data generated in this study and are summarized in Table 2. This approach is denoted as PR+HV+UNIQUAC in the following.

## 4. Results and discussion

### 4.1 VLE measurements of CO<sub>2</sub> + acetone

The aim of measuring VLE of the binary mixture CO<sub>2</sub> + acetone was to validate the employed experimental apparatus and operation procedure. This is the simplest system of binary mixtures CO<sub>2</sub> + ketones and there are several sets of experimental data available in the literature at 313.15 K [37-46], 333.15 K [42, 47-49], and 353.15 K [47-49]. VLE data of this system were measured here at these three temperatures in a pressure range from 4 MPa to 10 MPa with respect to the saturated liquid line. The measurement results are summarized in Table 3 and are compared with the available experimental data from the literature in Fig. 2. As illustrated there, the relationship between the mole fraction of CO<sub>2</sub> ( $x_{\text{CO}_2}$ ) and the vapor pressure is almost linear at all temperatures, except for the critical region. The solubility of CO<sub>2</sub> in acetone is decreased with rising temperature. At 313.15 K, the present measurement results are consistent with those of Katayama et al. [41], Adrian and Maurer [42], Chiu et al. [43], and Stievano and Elvassore [43], but are slightly lower than the data of Aida et al. [46] and are slightly higher than those of Day et al. [37, 40]. Nevertheless, the experimental data from eight different sources, including our measurements, do not deviate too much from each other (the maximum deviation is about 0.4 MPa at  $x_{\text{CO}_2} \approx 0.52$  mol/mol). At 333.15 K and 353.15 K, the present measurement results are also in

good agreement with those of Sato et al. [47], Aida et al. [46], and Wu et al. [49]. However, the experimental data reported by Han et al. [48] are obviously lower than those measured by other investigators.

## 4.2 VLE measurements of CO<sub>2</sub> + pentanones

The VLE measurement results of the three binary mixtures CO<sub>2</sub> + pentanones at 313.15 K, 333.15 K, and 353.15 K are summarized in Table 3. They are compared with other experimental data, if available in the literature, for CO<sub>2</sub> + 3-methyl-2-butanone in Fig. 3, for CO<sub>2</sub> + 2-pentanone in Fig. 4, and for CO<sub>2</sub> + 3-pentanone in Fig. 5. The temperature dependence of CO<sub>2</sub> solubility in pentanones and the relationship between  $x_{\text{CO}_2}$  and the vapor pressure for these three binary mixtures are qualitatively the same as in case of CO<sub>2</sub> + acetone.

As shown in Figs. 3 to 5, only the binary mixtures CO<sub>2</sub> + 3-methyl-2-butanone and CO<sub>2</sub> + 2-pentanone at 313.15 K were investigated by Aida et al. [46]. No other experimental data are available in the literature for these two binary mixtures at 333.15 K and 353.15 K nor for the binary mixture CO<sub>2</sub> + 3-pentanone at any temperature. Therefore, our measurements enrich the literature database for binary VLE of CO<sub>2</sub> + pentanones significantly. The present measurement results of the binary mixture CO<sub>2</sub> + 3-methyl-2-butanone at 313.15 K are in good agreement with those of Aida et al. (Fig. 3). However, the present vapor pressure data of the binary mixture CO<sub>2</sub> + 2-pentanone are slightly higher than those of Aida et al. [46] (Fig. 4), especially around  $x_{\text{CO}_2} = 0.3 \sim 0.7$  mol/mol. A possible explanation is that the purity of 2-pentanone in the measurements of Aida et al. [46] was insufficient (in Ref. [46], > 95% was reported). Such impurities (up to 5% in 2-pentanone [46]), which are usually heavy components, will typically lead to a lower vapor pressure. Therefore,

we believe that the present measurements are more reliable because 2-pentanone with a high purity of 99.5% was used here. Furthermore, several data points were randomly chosen and measured again to check for reproducibility.

### 4.3 VLE data correlation with thermodynamic models

The VLE data were correlated with two different approaches, PR+VDW $k_{ij}$  (only one binary interaction parameter  $k_{ij}$  per binary mixture in the van der Waals one-fluid mixing rule) and PR+HV+UNIQUAC (two binary interaction parameters  $\Delta u_{ij}$  and  $\Delta u_{ji}$  per binary mixture are necessary). Except for experimental data reported by Han et al. [48] for CO<sub>2</sub> + acetone and by Aida et al. [46] for CO<sub>2</sub> + 2-pentanone, all available experimental VLE data, including the present measuring results, were considered in the correlations. The correlated values of all binary interaction parameters are summarized in Table 2.

As shown in Figs. 2 to 5, the correlation results of PR+HV+UNIQUAC (solid lines) for the four binary mixtures considered in this study are in very good agreement with the experiments, including the temperature dependence. The predictions by PR+VDW (dashed lines) always underestimate the vapor pressure at a given  $x_{\text{CO}_2}$  for these four binary mixtures. These deviations of PR+VDW from experiments were eliminated by introducing one binary interaction parameter  $k_{ij}$  per binary mixture, leading to the PR+VDW $k_{ij}$  model. The results of PR+VDW are illustrated in Figs. 2 to 5, but not those of PR+VDW $k_{ij}$ , because they are very similar to those of PR+HV+UNIQUAC.

Overall, the correlation of VLE data for CO<sub>2</sub> + acetone and CO<sub>2</sub> + pentanones with PR+VDW $k_{ij}$  and PR+HV+UNIQUAC was investigated in this study. Both approaches have a similar accuracy in correlating experimental VLE data for the

considered mixtures. The correlated binary interaction parameters as given in Table 2 can be used in further applications.

#### 4.4 Comparing VLE data of four binary mixtures at 333.15 K

The present results from experiment and correlation of all four binary mixtures at 333.15 K are compared in Fig. 6. In addition to the  $P$ - $x_{\text{CO}_2}$  phase diagram (top), a deviation plot (bottom) is shown. The correlation results of the  $\text{CO}_2$  + acetone mixture were used as the baseline to better distinguish these four systems, where  $\Delta P(x_{\text{CO}_2}) = P(x_{\text{CO}_2}) - P_{\text{CO}_2+\text{acetone}}^{\text{correlation}}(x_{\text{CO}_2})$  at the same mole fraction  $x_{\text{CO}_2}$ . The vapor pressure deviations between measurements and correlation for the  $\text{CO}_2$  + acetone binary mixture are always positive ( $\Delta P \approx 0.15$  MPa) because the correlation was done using all available experimental VLE data. At  $x_{\text{CO}_2} = 0$  mol/mol, the vapor pressure of pure acetone is higher than that of all pentanones. In the  $x_{\text{CO}_2} < 0.4$  mol/mol range, the correlation line shows that the vapor pressure of the three  $\text{CO}_2$  + pentanone mixtures is higher than that of  $\text{CO}_2$  + acetone above a certain mole fraction  $x_{\text{CO}_2}$ . The tendency of vapor pressure of these four binary mixtures at  $x_{\text{CO}_2} = 0.4$  mol/mol is  $P(\text{CO}_2 + 3\text{-pentanone}) \approx P(\text{CO}_2 + 2\text{-pentanone}) > P(\text{CO}_2 + 3\text{-methyl-2-butanone}) \approx P(\text{CO}_2 + \text{acetone})$ . In the  $0.4 < x_{\text{CO}_2} / \text{mol/mol} < 0.85$  range, it can be seen from the present measurements that the tendency of the vapor pressure of these four binary mixtures at the same  $x_{\text{CO}_2}$  is  $P(\text{CO}_2 + 3\text{-pentanone}) > P(\text{CO}_2 + 2\text{-pentanone}) > P(\text{CO}_2 + 3\text{-methyl-2-butanone}) \approx P(\text{CO}_2 + \text{acetone})$ . It can be seen from both measurements and correlations that the vapor pressure of the three  $\text{CO}_2$  + pentanone mixtures is very similar in the critical region ( $x_{\text{CO}_2} > 0.85$  mol/mol). According to the correlation results, the  $\Delta P$  of the three  $\text{CO}_2$  + pentanone mixtures goes up again in the critical region because the  $\text{CO}_2$  + acetone mixture reaches the critical point slightly earlier

with increasing mole fraction  $x_{\text{CO}_2}$ . Overall, the VLE phase boundaries of these four binary mixtures are slightly different and the maximum difference between the vapor pressure at the same mole fraction  $x_{\text{CO}_2}$  is only about 0.4 MPa.

## 5. Conclusions

Experimental VLE data for the binary mixtures  $\text{CO}_2$  + acetone and  $\text{CO}_2$  + pentanones were generated with a high pressure view cell technique based on the synthetic method at 313.15 K, 333.15 K, and 353.15 K up to a pressure of 11.8 MPa. First, the measurements of  $\text{CO}_2$  + acetone were used as a case study for the validation of the employed experimental setup and operation procedure. A comparison of the present measurement results with the experimental data in the literature shows that the present data are in very good agreement with most data from the literature, but not all experimental data sets are consistent with each other. Second, experimental VLE data for three binary mixtures  $\text{CO}_2$  + pentanones (3-methyl-2-butanone, 2-pentanone, and 3-pentanone) were measured. Among these three binary mixtures,  $\text{CO}_2$  + 3-methyl-2-butanone and  $\text{CO}_2$  + 2-pentanone were investigated only at 313.15 K in the past. The mixture  $\text{CO}_2$  + 3-pentanone was not measured before. The present measurements thus broaden the database on VLE data of  $\text{CO}_2$  + pentanones. Finally, all data were compared to the results from the Peng–Robinson equation of state (PR EOS) with the van der Waals one-fluid mixing rule and from the combination of the PR EOS with the UNIQUAC model through the Huron–Vidal mixing rule. Both approaches may correlate these experimental data well. The present experimental measurements and thermodynamic models can be used for the design of processes using  $\text{CO}_2$  + acetone and  $\text{CO}_2$  + pentanones.

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## **Appendix A. Supplementary Material**

The Supplementary Material provides a briefly summary of error analysis in terms of  $x_{\text{CO}_2}$  and can be found online.

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**Table 1. Pure substance parameters of the Peng-Robinson EOS and the UNIQUAC model**

Substance	$T_c/K$	$P_c/MPa$	$\omega$	$q$	$r$
carbon dioxide	304.2 [50]	7.382 [51]	0.225 [51]	1.40 [30]	1.30 [30]
acetone	508.1 [52]	4.7 [52]	0.3065 <sup>a</sup>	2.34 [30]	2.57 [30]
2-pentanone	561.08 [52]	3.694 [52]	0.3433 <sup>a</sup>	4.147 <sup>b</sup>	3.6023 <sup>b</sup>
3-pentanone	560.9 [53]	3.74 [53]	0.3448 <sup>a</sup>	4.3839 <sup>b</sup>	3.6023 <sup>b</sup>
3-methyl-2-butanone	553.4 [53]	3.85 [53]	0.3208 <sup>a</sup>	4.147 <sup>b</sup>	3.6023 <sup>b</sup>

*a*,  $\omega$  were estimated by using experimental vapor pressure data from the DIPPR database [54] if they were not available in literature.

*b*,  $r$  and  $q$  were determined from the UNIFAC group contribution method [36].

**Table 2. Binary parameters of the van der Waals one-fluid mixing rule ( $k_{ij}$ ) and the UNIQUAC model ( $\Delta u_{ij}$ ,  $\Delta u_{ji}$ ) adjusted in the present work**

Mixture	$k_{ij}$ (-)	$\Delta u_{ij}$ (J/mol)	$\Delta u_{ji}$ (J/mol)
CO <sub>2</sub> + acetone	0.00515	-1740.17	2788.26
CO <sub>2</sub> + 3-methyl-2-butanone	0.0196	-1826.81	3333.82
CO <sub>2</sub> + 2-pentanone	0.0306	-1836.42	2812.16
CO <sub>2</sub> + 3-pentanone	0.0357	-2271.16	4128.10

**Table 3. Experimental vapor–liquid equilibrium data along the saturated liquid line of CO<sub>2</sub> + ketone mixtures generated in this work<sup>a</sup>**

<b>CO<sub>2</sub> + acetone</b>					
<b><i>T</i> = 353.15 K</b>		<b><i>T</i> = 333.15 K</b>		<b><i>T</i> = 313.15 K</b>	
<b><i>P</i></b>	<b><i>x</i><sub>CO2</sub></b>	<b><i>P</i></b>	<b><i>x</i><sub>CO2</sub></b>	<b><i>P</i></b>	<b><i>x</i><sub>CO2</sub></b>
<b>(MPa)</b>	<b>(mol/mol)</b>	<b>(MPa)</b>	<b>(mol/mol)</b>	<b>(MPa)</b>	<b>(mol/mol)</b>
10.53	0.794 (4)	8.80	0.823 (5)	6.67	0.843 (5)
9.73	0.729 (4)	7.98	0.756 (4)	6.04	0.778 (5)
8.60	0.648 (4)	7.04	0.675 (4)	5.36	0.699 (4)
7.16	0.552 (3)	5.90	0.582 (3)	4.55	0.612 (4)
6.20	0.485 (3)	5.13	0.516 (3)	4.06	0.551 (4)
<b>CO<sub>2</sub> + 3-methyl-2-butanone</b>					
<b><i>T</i> = 353.15 K</b>		<b><i>T</i> = 333.15 K</b>		<b><i>T</i> = 313.15 K</b>	
<b><i>P</i></b>	<b><i>x</i><sub>CO2</sub></b>	<b><i>P</i></b>	<b><i>x</i><sub>CO2</sub></b>	<b><i>P</i></b>	<b><i>x</i><sub>CO2</sub></b>
<b>(MPa)</b>	<b>(mol/mol)</b>	<b>(MPa)</b>	<b>(mol/mol)</b>	<b>(MPa)</b>	<b>(mol/mol)</b>
11.42	0.840 (5)	9.51	0.866 (5)	7.12	0.883 (5)
10.55	0.776 (4)	8.55	0.797 (5)	6.42	0.814 (5)
9.48	0.709 (4)	7.70	0.731 (4)	5.83	0.750 (4)
9.30	0.704 (4)	7.56	0.726 (4)	5.74	0.740 (4)
8.51	0.649 (4)	6.95	0.669 (4)	5.32	0.691 (4)
7.53	0.586 (3)	6.12	0.602 (4)	4.87	0.640 (4)
6.12	0.489 (3)	5.16	0.517 (3)	4.08	0.545 (4)
6.35	0.500 (3)	5.29	0.526 (3)	4.17	0.554 (4)
5.18	0.426 (3)	4.42	0.465 (3)	3.31	0.465 (3)
3.95	0.343 (2)	3.11	0.343 (2)	2.35	0.343 (3)
3.96	0.347 (2)	3.12	0.347 (2)	2.35	0.347 (3)

<b>CO<sub>2</sub> + 2-pentanone</b>					
<b><i>T</i> = 353.15 K</b>		<b><i>T</i> = 333.15 K</b>		<b><i>T</i> = 313.15 K</b>	
<b><i>P</i></b>	<b><i>x</i><sub>CO<sub>2</sub></sub></b>	<b><i>P</i></b>	<b><i>x</i><sub>CO<sub>2</sub></sub></b>	<b><i>P</i></b>	<b><i>x</i><sub>CO<sub>2</sub></sub></b>
<b>(MPa)</b>	<b>(mol/mol)</b>	<b>(MPa)</b>	<b>(mol/mol)</b>	<b>(MPa)</b>	<b>(mol/mol)</b>
11.87	0.888 (5)	9.97	0.908 (5)	7.52	0.923 (5)
11.36	0.822 (5)	9.22	0.840 (5)	7.14	0.886 (5)
10.72	0.778 (4)	8.68	0.797 (5)	6.89	0.856 (5)
9.91	0.725 (4)	8.68	0.799 (5)	6.47	0.813 (5)
8.71	0.645 (4)	8.01	0.746 (4)	6.49	0.811 (5)
7.75	0.588 (3)	7.03	0.668 (4)	6.05	0.762 (4)
6.34	0.493 (3)	6.37	0.608 (4)	5.38	0.688 (4)
5.32	0.424 (3)	5.37	0.526 (3)	5.49	0.692 (4)
3.75	0.305 (2)	4.55	0.462 (3)	4.98	0.639 (4)
		2.96	0.305 (2)	4.30	0.558 (4)
				4.23	0.551 (4)
				3.42	0.462 (3)
				2.24	0.305 (3)

<b>CO<sub>2</sub> + 3-pentanone</b>					
<b><i>T</i> = 353.15 K</b>		<b><i>T</i> = 333.15 K</b>		<b><i>T</i> = 313.15 K</b>	
<b><i>P</i></b>	<b><i>x</i><sub>CO<sub>2</sub></sub></b>	<b><i>P</i></b>	<b><i>x</i><sub>CO<sub>2</sub></sub></b>	<b><i>P</i></b>	<b><i>x</i><sub>CO<sub>2</sub></sub></b>
<b>(MPa)</b>	<b>(mol/mol)</b>	<b>(MPa)</b>	<b>(mol/mol)</b>	<b>(MPa)</b>	<b>(mol/mol)</b>
11.79	0.857 (5)	9.65	0.876 (5)	7.22	0.890 (5)
11.52	0.830 (5)	9.36	0.848 (5)	6.98	0.863 (5)
11.53	0.829 (5)	9.33	0.848 (5)	6.97	0.863 (5)
10.65	0.760 (4)	8.56	0.780 (4)	6.42	0.796 (5)
9.97	0.717 (4)	8.07	0.739 (4)	6.09	0.753 (4)

9.98	0.718 (4)	8.08	0.738 (4)	6.09	0.754 (4)
9.11	0.661 (4)	7.42	0.683 (4)	5.64	0.702 (4)
8.10	0.596 (3)	6.66	0.619 (4)	5.14	0.643 (4)
6.49	0.494 (3)	5.45	0.522 (3)	4.32	0.553 (4)
5.51	0.420 (3)	4.93	0.482 (3)	3.64	0.465 (3)
5.43	0.415 (2)	4.76	0.455 (3)	3.54	0.456 (3)
4.13	0.342 (2)	4.68	0.456 (3)	2.51	0.342 (3)
		3.29	0.342 (2)		

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<sup>a</sup> The uncertainties are  $u(T) = 0.04$  K,  $u(P) = 0.01$  MPa, and in case of the mole fraction  $u(x)$  they are given by the number in parentheses, where 0.342 (2) stands for  $0.342 \pm 0.002$  mol/mol.

**Figure 1.** Experimental setup for the present measurements of vapor-liquid equilibria. *VI* indicates a valve, *TW-VI* a three-way valve, PtX a thermometer and PX a pressure transducer.

**Figure 2.** Comparison of vapor-liquid equilibria of CO<sub>2</sub> + acetone at 353.15 K (top), 333.15 K (center), and 353.15 K (bottom) from experiment, correlation by PR+HV+UNIQUAC (—), and prediction by PR+VDW (---). Experimental data were taken from the literature (□ [37-40], ○ [41], ◇ [42], + [43], × [44], ☆ [45], ▽ [46], ◆ [47], ▣ [48], ● [49]) and from this work (▲).

**Figure 3.** Comparison of vapor-liquid equilibria of CO<sub>2</sub> + 3-methyl-2-butanone at 313.15 K, 333.15 K, and 353.15 K from experiment, correlation by PR+HV+UNIQUAC (—), and prediction by PR+VDW (---). The experimental data were taken from the literature (▽ [46]) and from this work (▲).

**Figure 4.** Comparison of vapor-liquid equilibria of CO<sub>2</sub> + 2-pentanone at 313.15 K, 333.15 K, and 353.15 K from experiment, correlation by PR+HV+UNIQUAC (—), and prediction by PR+VDW (---). The experimental data were taken from the literature (▽ [46]) and from this work (▲).

**Figure 5.** Comparison of vapor-liquid equilibria of CO<sub>2</sub> + 3-pentanone at 313.15 K, 333.15 K, and 353.15 K from experimental data measured in this work (▲), correlation by PR+HV+UNIQUAC (—), and prediction by PR+VDW (---).

**Figure 6.** Comparison of vapor-liquid equilibria of CO<sub>2</sub> + acetone (○, dotted line),

CO<sub>2</sub> + 3-methyl-2-butanone ( $\triangle$ , dashed line), CO<sub>2</sub> + 3-pentanone ( $\square$ , long-dashed line), and CO<sub>2</sub> + 2-pentanone ( $\diamond$ , solid line) at 333.15 K between experimental data measured in this work (symbols) and correlation by PR+HV+UNIQUAC (lines). The top figure shows the regular  $P$ - $x_{\text{CO}_2}$  phase diagram and the bottom figure shows a deviation plot where the correlation results of the CO<sub>2</sub> + acetone mixture were used as the baseline, where  $\Delta P(x_{\text{CO}_2}) = P(x_{\text{CO}_2}) - P_{\text{CO}_2+\text{acetone}}^{\text{correlation}}(x_{\text{CO}_2})$  at the same mole fraction  $x_{\text{CO}_2}$ .

Figure 1.

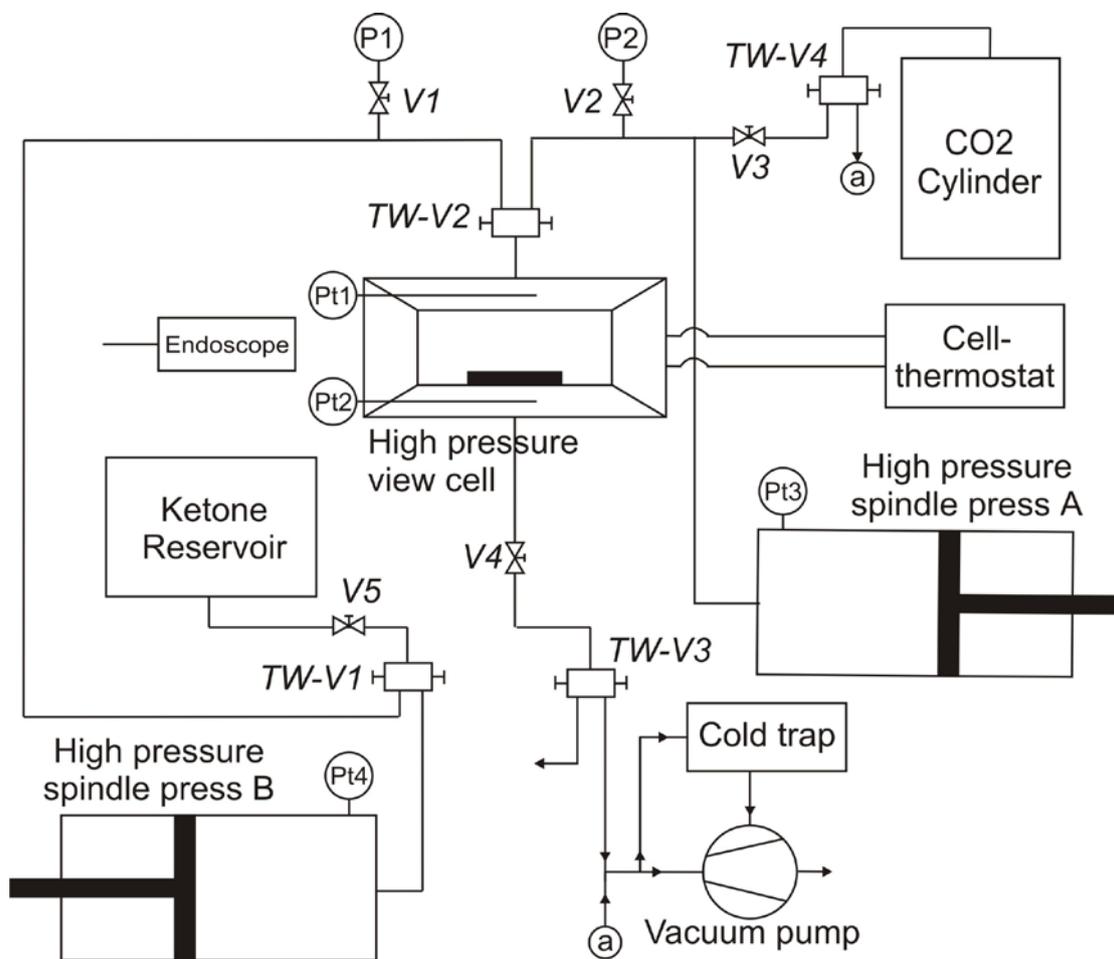


Figure 2.

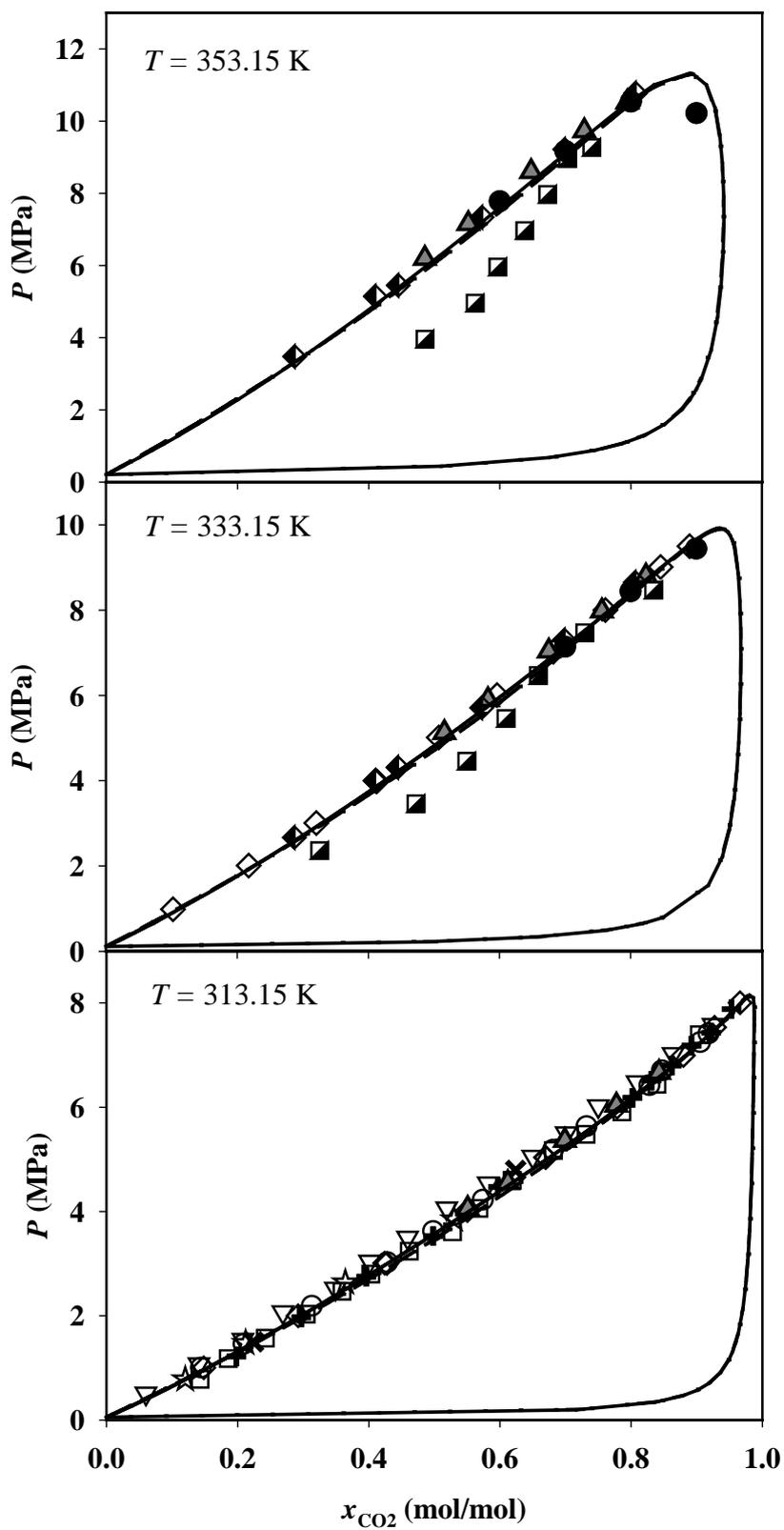


Figure 3.

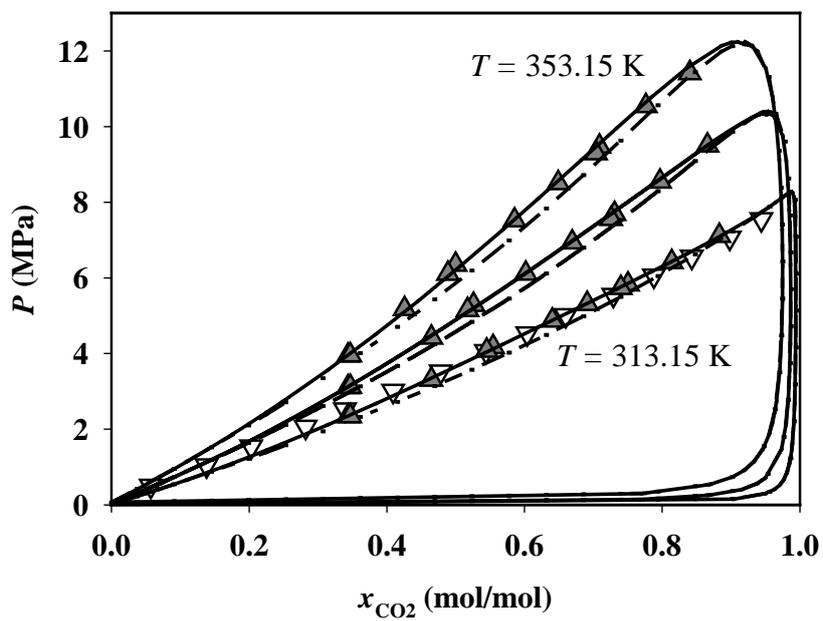


Figure 4.

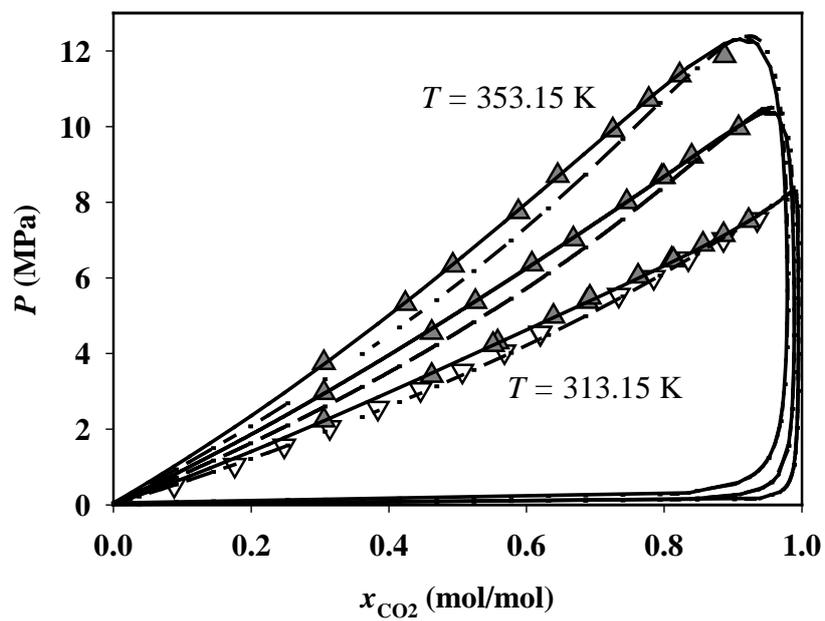


Figure 5.

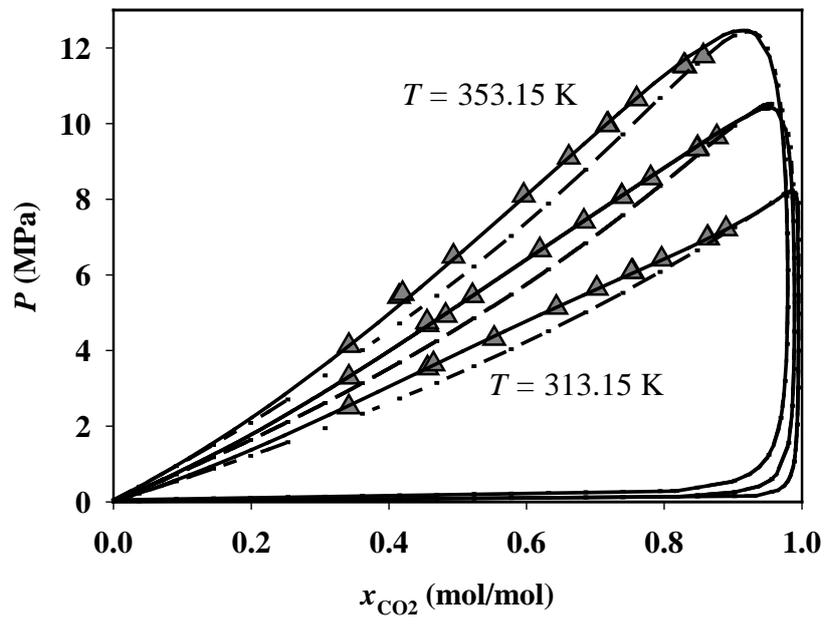


Figure 6.

