Phase Equilibrium and Density of CO$_2$ + Acetic Acid Systems from 308.15 to 338.15 K and 15 to 45 MPa

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ABSTRACT: Using a high-pressure phase equilibrium apparatus and vibrating-tube densimeter, phase transition pressures of CO$_2$ (1) + acetic acid (2) binary systems with $x_2$ = 0.000, 0.107, 0.163, 0.222, and 1.000 were measured under temperatures from 308.15 to 338.15 K. Besides, the densities at the same composition and temperature under pressure from 15 to 45 MPa were also detected, and the volumes of mixing ($\Delta V_m$) were calculated. Three prediction models (SRK EOS, PC-SAFT EOS, and TS model) were introduced to predict and correlate the density of binary systems, which was found to have positive relationships with temperature and acetic acid concentration and a negative relationship with pressure. Thereinto, the variation trend of CO$_2$ density with pressure tends to be excessive reaction rate, leading to well pipe corrosion. The situation. 7 At present, supercritical CO$_2$ fracturing and enhanced oil recovery have already become the hotspots in field development.8,9 And it is urgently needed to investigate the phase behavior and density of the CO$_2$ + acetic acid binary system, which could provide technology support for supercritical CO$_2$ application in oil field development.

1. INTRODUCTION

Recently, supercritical CO$_2$ utilization technology in the extraction process has gained much attention.10,11 It was reported that the transformation of glycerol, as the main byproduct of biodiesel, via the esterification of glycerol and acetic acid could be efficient in high-value downstream product synthesis, such as that of monoglycerate, diglycerate, and triglycerate. During the process, an extra amount of acetic acid residual needs to be extracted to further maximize the resource utilization.3 The supercritical CO$_2$ extraction process is an efficient, ecological, stable, and cheap technology that could be used in acetic acid extraction. Thus, the phase behavior and density of CO$_2$ + acetic acid should be carefully investigated to provide basic data and experimental guide for further application.4,5 Moreover, in oil field development, acidification is an efficient route for carbonate reservoir production improvement.6 However, the general acidification process possesses an excessive reaction rate, leading to well pipe corrosion. The introduction of acetic acid could effectively avoid this situation.7 At present, supercritical CO$_2$ fracturing and enhanced oil recovery have already become the hotspots in oil field development. In the deep formation, CO$_2$ and acetic acid, which have an interaction, could benefit the acidification, fracturing, and enhanced oil recovery processes.8,9 And it is urgently needed to investigate the phase behavior and density of the CO$_2$ + acetic acid binary system, which could provide technology support for supercritical CO$_2$ application in oil field development.

In reported supercritical CO$_2$ high-pressure phase equilibrium and density measurement methods, visible phase transition pressure measurement and vibrating-tube densimeter measurement, which have the advantage of user-friendly control and nonsampling, have gained much attention.10,11 The Peng–Robinson (PR) EOS,12 Soave–Redlich–Kwong (SRK) EOS,13 and Tait equation14 are generally used as the equation of state or empirical model of phase transition pressure and density. As reported by Gross et al., the perturbed-chain statistical associating fluid theory equation of state (PC-SAFT EOS) has good prediction for a high-pressure CO$_2$ system.15,16 Besides, Toscani and Szwarz reported that a six-parameter empirical model (TS model) could also correlate well with density experimental values under high pressure.17 Physically, the accurate determination of phase behavior and thermodynamic properties of a given gas–liquid mixture depends on the $\alpha$ function, binary interaction parameters, mixing rules, and volume translation strategy.18–21 The original SRK EOS and PR EOS have a relatively large deviation in the prediction of saturated vapor pressure and liquid density. The modification of saturated vapor pressure is carried out by using the $\alpha$ function.22,23 In principle, the existing $\alpha$ functions can be
classified as Soave-type \(^{13,24}\) and logarithm-type.\(^{25}\) The Soave-type \(\alpha\) function has been found to be the most widely used one for the two-parameter cubic EOSs. However, the traditional Soave-type \(\alpha\) function cannot satisfy a basic requirement, that is, it does not exhibit a limiting behavior as the reduced temperature approaches infinity. For this reason, Heyen proposed the logarithmic-type \(\alpha\) function.\(^{26}\) Through the improvement of Trebble and Bishnoi\(^{25}\) and Twu et al.,\(^{25,27}\) this kind of \(\alpha\) function has been able to solve this problem, and the prediction accuracy has been further improved. Since then, Li and Yang combined the advantages of the two types and obtained a new \(\alpha\) function that could better predict the vapor pressure of both pure substance and alkane solvent—CO\(_2\)—heavy oil systems.\(^{28}\) Recently, Chen and Yang optimized the reduced temperature for acentric factor in \(\alpha\) function associated with PR EOS and SRK EOS to improve vapor pressure prediction for heavy hydrocarbon compounds.\(^{29}\) These new \(\alpha\) functions can significantly improve the prediction accuracy of phase behavior not only for small molecules but also for complex heavy hydrocarbon components.

At present, the existing cubic EOS can provide reliable prediction for many thermodynamic properties of various substances but cannot give an accurate calculation of liquid volume.\(^{30}\) To reduce this error, Martin\(^{31}\) first introduced the concept of volume translation, and Peneloux et al. suggested a constant volume correction in SRK EOS.\(^{32}\) This method can still be used to evaluate the liquid density in supercritical CO\(_2\)\(^{33}\) and other systems.\(^{34,35}\) Further research shows that the temperature-dependent volume translation model\(^{36,37}\) and temperature–volume–dependent volume translation model\(^{38,39}\) can improve the prediction accuracy. Recently, Chen and Li have fully exploited the potential of the distance function to improve the accuracy of the volume translation SRK EOS in predicting the density of saturated and single-phase liquids.\(^{18}\)

To predict the density of mixed systems, binary interaction parameters and mixing rules are often used by regression of experimental results.\(^{40}\) Starting from the original van der Waals mixing rule,\(^{1,12}\) a series of studies of SRK EOS and PR EOS mixed rules, such as the Huron–Vidal mixing rule,\(^{41}\) MHV2 mixing rule,\(^{42}\) PHV mixing rule,\(^{43}\) Wong–Sandler mixing rule,\(^{44}\) and its modified type.\(^{45}\) These modified mixing rules and the \(\alpha\) function and volume translation we mentioned before make the SRK EOS and PR EOS still have considerable vitality.

To the best of our knowledge, for the CO\(_2\) + acetic acid binary system, the investigation of density under high pressure is still rare.\(^{5}\) In this work, the combination of a self-designed high-pressure phase equilibrium apparatus with a vibrating-tube densimeter was introduced to detect the phase transition pressures of CO\(_2\) (1) + acetic acid (2) binary with \(x_2 = 0.107, 0.163,\) and 0.222, and densities of unitary and binary systems at temperature of 308.15, 318.15, 328.15, and 338.15 K and pressure of 15.00, 20.00, 25.00, 30.00, 35.00, 40.00, and 45.00 MPa. At the same time, the \(\alpha\) function, binary interaction parameters, mixing rules, and volume translation strategy are used for accurately determining phase transition pressures and density by using SRK EOS, PR EOS, and PC-SAFT EOS followed by density correlation with the TS model and volume of mixing calculation.

### 2. MODELING

The phase transition pressure of the CO\(_2\) + acetic acid binary systems was predicted by modifying the \(\alpha\) function of SRK EOS and PR EOS. In addition, the SRK EOS, PC-SAFT EOS, and TS model were introduced to predict and correlate the densities of CO\(_2\) + acetic acid unitary and binary systems for experimental reliability validation. And volumes of mixing (\(\Delta V_m\)) in binary system were also investigated.

#### 2.1. SRK EOS

SRK EOS\(^{13}\) has the expression of:

\[
p = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b)}
\]

where \(p\), \(T\), and \(V_m\) are the pressure, temperature, and molar volume, respectively. \(R\) is the ideal gas constant. \(a\) and \(b\) are parameters.

For pure components, the expressions for \(a\) and \(b\) are:

\[
a_i = \alpha(T_i, \omega) \times 0.42747 \frac{R^2T_i^{1/2}}{P_i}
\]

\[
b_i = 0.08664 \frac{RT_i}{P_i}
\]

where \(\alpha(T_i, \omega)\) is the \(\alpha\) function, which is dependent upon both the reduced temperature \(T_i\) and the acentric factor \(\omega\). \(T_i\) is the critical temperature, and \(P_i\) is the critical pressure. In this paper, the Soave-type \(\alpha\) function\(^{13}\) used in the SRK EOS is given by:

\[
\alpha = \left[ 1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)(1 - T_i^{0.5}) \right]^2
\]

For mixed systems, \(a\) could be decided by adding the standard quadratic mixing term \(a_0\) and asymmetric (polar) term \(a_1\) together.

\[
a = a_0 + a_1
\]

Expressions of \(a_0, a_1,\) and \(b\) are shown below:

\[
a_0 = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (a_i a_j)^{0.5} (1 - \eta_{ij})
\]

\[
a_1 = \sum_{i=1}^{n} x_i \left( \sum_{j=1}^{n} x_j ((a_i a_j)^{0.5} l_{ij})^{1/3} \right)^3
\]

\[
b = \sum_{i=1}^{n} x_i b_i
\]

In the expressions, \(x_i\) is the mole fraction, and \(\eta_{ij}\) and \(l_{ij}\) are the binary interaction parameters that could be obtained from density—composition regression. Another three parameters, \(a_0\), \(a_1\), and \(b_0\) are denoted in SRK EOS especially for the pure system.

In this paper, since it is necessary to calculate the density of the liquid phase, the volume translation proposed by Peneloux\(^{32}\) was used to correct the molar volume:

\[
V_m = V_{m0} - c
\]

\[
c = \sum_{i=1}^{n} x_i c_i
\]
\[
c_i = 0.40768 \frac{RT_i}{p_i} (0.29411 - Z_{RAi})
\]

where \( V_{mol} \) is the molar volume calculated by the equation of state without the correction, \( c \) is the Peneloux volume correction term, and \( c_i \) is the Peneloux volume correction term for pure components, calculated from the critical temperature \( (T_c) \) and pressure \( (p_c) \) and the Rackett parameter \( (Z_{RA}) \).

2.2. PR EOS. The expression of the PR EOS is:

\[
p = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)}
\]

For pure components, the expressions for \( a \) and \( b \) are:

\[
a_i = \alpha(T_i, \omega) \times 0.45724 \frac{RT^2_{ci}}{p_i}
\]

\[
b_i = 0.077797 \frac{RT_{ci}}{p_i}
\]

Here, we use the \( \alpha \) function modified by Li and Yang to improve phase transition pressure prediction. The expression of this \( \alpha \) function used in the PR EOS is given by:

\[
\alpha = \exp\{ (0.13280 - 0.05052\omega + 0.25948\omega^2)(1 - T_c) + 0.81769 \ln[1 + (0.31355 + 1.86745\omega - 0.52604\omega^2)(1 - T_c^{(0.5)})] \}
\]

The mixing rule and volume translation are the same as in SRK EOS, and the meanings of each variable in eqs 12 to 15 are the same as those in Section 2.1.

2.3. PC-SAFT EOS. In PC-SAFT EOS, compressibility factor \( Z \) is related to ideal gas \( (Z_{id} = 1) \), hard-chain \( (Z^{hc}) \), segment dispersion \( (Z^{disp}) \), and association \( (Z^{assoc}) \), which could be expressed as below:

\[
Z = 1 + Z^{hc} + Z^{disp} + Z^{assoc}
\]

Generally speaking, the non-association molecule could be presented by three parameters from the pure system, which are the number of spheres in the chain \( (m) \), the diameter of the spheres \( (\sigma) \), and the segment energy parameter \( (\varepsilon/k) \). For the association molecule, another two parameters, the effective association volume \( (k^{bh}) \) and the association energy \( (\varepsilon^{ab}) \), should also be used. For \( CO_2 \) and acetic acid used in this work, \( CO_2 \) as a non-association molecule, has weak polarity, while acetic acid is an association molecule with strong polarity. The detailed information about these two molecules is listed in Table 1.

Table 1. PC-SAFT EOS Pure-Component Parameters Used in This Work

| Component | \( M \) (g·mol\(^{-1}\)) | \( m^{m/}(M\) (mol·g\(^{-1}\)) | \( \sigma \) (Å) | \( \varepsilon_i \) (Å\(^{-1}\)) | \( k^{ab} \) | \( \varepsilon^{ab} \) (K\(^{-1}\)) | Ref. |
|-----------|------------------|------------------|---------|------------------|------------------|------------------|-----|
| CO\(_2\)   | 44.01            | 0.0471           | 2.7852  | 169.21           | 221.59           | 0.07555          | 15  |
| acetic acid| 60.05            | 0.0223           | 3.8582  | 15               | 3044.4           |                  | 16  |

\[
\varepsilon_i = (\varepsilon_i^0)^{0.5}(1 - k_i)
\]

\[
\varepsilon^{AB} = 0.5 \times (\varepsilon^{A,B} + \varepsilon^{A,B})
\]

\[
k^{AB} = (k^{AB} + k^{AB})^{0.5} \times \frac{2(\sigma_i \times \sigma_j)^{0.5}}{\sigma_i + \sigma_j}
\]

Among them, \( k_{ij} \) is a binary interaction parameter, as the function of temperature, which could be used to correlate crossing dispersion energy between different molecules. In this work, \( k_{ij} \) is obtained by regressing the experimental data of density.

2.4. Toscani–Szwarc (TS) Model. The TS model is an empirical density correlation model with six adjusted parameters, which shows good correlation results in this work. The model could be expressed as below:

\[
\rho = \frac{A_1 - A_2 T + p + A_3 p^{0.5}}{A_4 + A_5 p + A_6 p^{0.5}}
\]

In the model, \( \rho, p, \) and \( T \) are the mass density in kg·m\(^{-3}\), pressure in MPa, and temperature in K, respectively. \( A_1 - A_6 \) are the six adjusted parameters, which could be calculated by regressing experimental data.

2.5. Deviation Analysis. Absolute average deviation (AAD), mean deviation (bias), standard deviation (SDV), and root mean square (RMS) are used for deviation analysis between experimental and calculated data. These four deviations could be expressed as follows:

\[
\Delta Y = \left( \frac{Y_{exp} - Y_{cal}}{Y_{exp}} \right) \times 100\%
\]

\[
AAD = \frac{1}{n} \sum_{i=1}^{n} |\Delta Y_i| \times 100\%
\]

\[
Bias = \frac{1}{n} \sum_{i=1}^{n} (\Delta Y_i) \times 100\%
\]

\[
SDV = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (\Delta Y_i - bias)^2} \times 100\%
\]

\[
RMS = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (\Delta Y_i)^2} \times 100\%
\]

Among them, \( Y_{exp} \) and \( Y_{cal} \) represent the experimental and calculated value, respectively.

2.6. Volumes of Mixing (\( \Delta V_m \)). Volumes of mixing (\( \Delta V_m \)) of the binary system are calculated with the density difference between the mixture and pure chemicals (excess volume), which could be expressed in the following:

\[
\Delta V_m = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2}
\]
In the expression, $\Delta V_m$ and $\rho$ are denoted as volumes of mixing and mixture density, respectively. Besides, $x_i$, $M_i$, and $\rho_i$ represent the molar fraction, molar weight, and density of the pure system, respectively, with $i = 1$ as CO$_2$ and $i = 2$ as acetic acid.

2.7. Calculation Method. The SRK EOS, PR EOS, PC-SAFT EOS, and TS model were calculated and decided by the commercial software Aspen Plus V11 and MATLAB. All the parameters were correlated with the Marquardt-Levenberg algorithm of least squares optimization.

3. RESULTS AND DISCUSSION

3.1. Phase Transition Pressure. Density measurement has meaning only when the system is homogenous. Thus, herein, the measurement for phase transition pressure was used further for density measurement. The results are listed in Table 2.

The pressure–composition phase diagram of the CO$_2$ (1) + acetic acid (2) binary system could be found in Figure 1. In this figure, solid dots stand for the experimental data, red lines represent the SRK EOS calculation results with $\eta_{ij} = 0.024$ and $l_{ij} = 0$ using the Soave-type $\alpha$ function, and black lines express the PR EOS calculation results with $\eta_{ij} = 0$ and $l_{ij} = 0$ using the $\alpha$ function modified by Li and Yang. It clearly shows that PR EOS has a better ability in phase transition pressure prediction compared with that of SRK EOS. The AAD values of PR EOS and SRK EOS are 3.72 and 5.31%, respectively, indicating that the modified $\alpha$ function can better predict the results of phase transition pressure of the CO$_2$ + acetic acid binary system.

The phase transition pressure, which is only used for further density measurement under high pressure, would not be discussed further in this work.

3.2. Density. In this work, the SRK EOS, PR EOS, PC-SAFT EOS, and TS model were used to calculate the density of CO$_2$ + ethyl acetate systems comparing with the experimental results. Among them, the AAD values of SRK EOS and PR EOS are about the same. To save space, only the calculation results using SRK EOS, PC-SAFT EOS, and TS models are presented in the following paper.

3.2.1. Experimental Results. Density measurement results for CO$_2$, acetic acid, and CO$_2$ (1) + acetic acid (2) systems are listed in Table 3. It could be found that the densities for all the systems have a positive relationship with pressure and negative relationship with temperature. The density of CO$_2$ is more boosted, the difficulty of compression for CO$_2$ also increases. These correspond with the gas characteristics under high pressure.\textsuperscript{11,49} Besides, the density of acetic acid is found to

| Table 2. Phase Transition Pressure for the CO$_2$ (1) + Acetic Acid (2) Binary System |
|-----------------------------------|-------------------|-------------------|-------------------|-------------------|
| $p$ (MPa) | $x_2 = 0.000$ | $x_2 = 0.107$ | $x_2 = 0.163$ | $x_2 = 0.222$ |
| $T = 308.15$ K | 7.14 | 8.41 | 9.68 | 10.92 |
| $T = 318.15$ K | 6.42 | 7.70 | 8.98 | 10.29 |
| $T = 328.15$ K | 6.07 | 7.29 | 8.50 | 9.78 |
| $T = 338.15$ K | 5.83 | 7.06 | 8.30 | 9.53 |

Table 3. Experimental Data for the Densities of CO$_2$ (1) + Acetic Acid (2) Systems\textsuperscript{a}

| $p$ (MPa) | $x_2 = 0.000$ | $x_2 = 0.107$ | $x_2 = 0.163$ | $x_2 = 0.222$ |
|-----------|-------------------|-------------------|-------------------|-------------------|
| $T = 308.15$ K | 806 | 914 | 950 | 978 |
| $T = 318.15$ K | 853 | 944 | 974 | 997 |
| $T = 328.15$ K | 890 | 969 | 994 | 1013 |
| $T = 338.15$ K | 920 | 990 | 1012 | 1028 |
| $T = 348.15$ K | 944 | 1009 | 1028 | 1042 |
| $T = 358.15$ K | 965 | 1025 | 1042 | 1055 |
| $T = 368.15$ K | 989 | 1041 | 1055 | 1066 |

\textsuperscript{a}Uncertainty: $u(T) = 0.05$ K, $u(p) = 0.02$ MPa, and $u(\rho) = 4.6$ kg m$^{-3}$.
have a positive linear relationship with pressure, which is similar with the characteristic of liquids, such as water and ethanol.50–52

3.2.2. Calculation Results and Deviation Analysis. SRK-EOS and PC-SAFT EOS were used to predict the density of CO$_2$ + acetic acid unitary and binary systems, and the TS model was also introduced for correlation. All the adjusted parameters of the TS model are listed in Table 4. The calculation results and deviation analysis of four statistical values—AAD, bias, SDV, and RMS—from different models are presented in Table 5. Comparison of density—pressure curves obtained from calculation with experimental data is shown in Figure 2. For clarity, only prediction curves calculated from SRK-EOS with $n_{ij} = 0.024$ and $l_{ij} = 0$ and from PC-SAFT EOS with $k_{ij} = 0.061$ are used herein for comparison.

From Table 5 and Figure 2, it could be illustrated that SRK EOS and PC-SAFT EOS have good integral prediction ability for unitary and binary systems, with overall AAD of 1.75 and 0.92%, respectively. Between them, SRK EOS has a relatively larger prediction deviation for unitary system, although the Peneloux volume correction has been used, with AAD for pure CO$_2$ and pure acetic acid of 2.92 and 5.26%, respectively, which might be caused by the simplicity of its expressions. For pure CO$_2$ and pure acetic acid systems, SRK EOS and PC-SAFT EOS have greater prediction deviation at higher temperature and lower pressure, while for binary systems, the prediction accuracy of the two equations of state is the highest at medium pressure (30 MPa). On the whole, the prediction accuracy of two kinds of EOS for the binary system is obviously better than that of the unitary system. It should be noticed here that the TS model, as a simple model with six adjusted parameters, could correlate well with experimental results of density under high pressure, which has an AAD value of only 0.10%.

3.2.3. Calculation of $\Delta V_m$. Volumes of mixing ($\Delta V_m$) could be used to evaluate the deviation between mixture and ideal state. In this work, eq 17 was used to calculate the $\Delta V_m$ of the CO$_2$ (1) + acetic acid (2) system with $x_2 = 0.107$, 0.163, and 0.222, and the results are listed in Table 6. It can be clearly seen that all the $\Delta V_m$ under the conditions used herein are negative. This might be caused by the formation of Lewis acid—base interaction between CO$_2$ and acetic acid.53,54 With strong affinity between CO$_2$ and carboxyl of acetic acid, CO$_2$ molecules could easily insert into the gap between acetic acid molecules and thus cause negative values of $\Delta V_m$.55

By comparison of the $\Delta V_m$ under different temperatures and pressures, the absolute values of $\Delta V_m$ were found to increase with temperature increase or pressure release. This might be caused by the lower density of the mixture system and bigger intermolecular space at relative high temperature (338.15 K) and low pressure (15 MPa), leading to the increase of absolute value of $\Delta V_m$.56

4. CONCLUSIONS

A high-pressure phase equilibrium apparatus was introduced to measure the transition phase pressure of CO$_2$ (1) + acetic acid (2) at 308.15–338.15 K, and PR EOS was found to have a better prediction ability in transition phase pressure than SRK EOS by the modified $\alpha$ function. Besides, a vibrating-tube densimeter was used for CO$_2$ (1) + acetic acid (2) density measurement with $x_2 = 0.000$, 0.107, 0.163, 0.222, and 1.000 at 308.15–338.15 K and 15–45 MPa. By calculation of $\Delta V_m$, the SRK EOS, PC-SAFT EOS, and TS model were applied to predict and correlate the density results.

The densities of all systems were found to have positive relationships with temperature and acetic acid concentration but a negative relationship with pressure. Therein, the CO$_2$ density would flatten under high pressure, which is in accordance with the characteristics of gases under high pressure generally reported. The SRK EOS, PC-SAFT EOS, and TS model have good prediction and correlation performance for densities of pure CO$_2$, pure acetic acid, and CO$_2$ + acetic acid binary systems, with AAD values of 1.75, 0.92, and 0.10%, respectively. The $\Delta V_m$ are all negative values, and their absolute values increased with temperature increase or pressure decrease. This might be caused by the Lewis acid—base relationship formation between CO$_2$ and carbonyl of acetic acid.

All the experimental and calculation data obtained herein could provide a theoretical guide and data foundation for supercritical CO$_2$ utilization in extraction and oil field exploration.

5. EXPERIMENTAL SECTION

5.1. Chemicals. All chemicals used in this work are listed in Table 7 and are not further purified.

5.2. Structure of the High-Pressure Phase Equilibrium Apparatus. The visible and volume-variable high-pressure phase equilibrium apparatus was used to measure the phase behavior and density of CO$_2$ and acetic acid systems. The apparatus was built by Jiangsu Haian Oilfield Scientific Instrument Co., Ltd, and modified somewhat by our group to satisfy the demand for density measurement under high pressure. The detailed composition and operation method of this supercritical CO$_2$ phase equilibrium device, which is shown in Figure 3, have been described in our previous works.57,58

A brief introduction would be given here. The apparatus is composed of a supercharging device (including piston pump, piston cylinder, etc.), high-pressure visible unit (including high-pressure autoclave, sapphire window, servo motor controller, etc.), temperature and pressure control system.

| parameters       | $x_1 = 0.000$ | $x_1 = 0.107$ | $x_1 = 0.163$ | $x_1 = 0.222$ | $x_1 = 1.000$ |
|------------------|---------------|---------------|---------------|---------------|---------------|
| $A_1$ (MPa)      | 1.163 $\times$ 10$^6$ | 67.97         | 86.16         | 128.5         | 107.6         |
| $A_1$ (MPa K$^{-1}$) | 1.273 $\times$ 10$^4$ | 0.1902        | 0.2176        | 0.3302        | 0.07561       |
| $A_1$ (MPa m$^{3}$kg$^{-1}$) | 1.034 $\times$ 10$^8$ | 2.592         | 4.161         | 12.84         | $-3.899$      |
| $A_2$ (m$^3$kg$^{-1}$) | $-3432$      | 0.0177        | 0.0232        | 0.02982       | 0.0812        |
| $A_4$ (MPa$^{1/2}$m$^{1/2}$kg$^{-1}$) | $-49.8$      | 0.0006575     | 0.0006347     | 0.0004251     | 0.0008208     |
| $A_6$ (MPa$^{1/2}$m$^{1/2}$kg$^{-1}$) | 1476         | 0.004117      | 0.005413      | 0.01477       | $-0.003613$   |

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Table 4. Adjusted Parameters for the TS Models for Densities of CO$_2$ (1) + Acetic Acid (2) Systems
Table 5. Calculated Results and Deviation Analysis of Density of the CO2 (1) + Acetic Acid (2) Systema

| p (MPa) | $\rho_{cal}$ (kg m$^{-3}$) | $\Delta Y_i \times 100$ | $\rho_{cal}$ (kg m$^{-3}$) | $\Delta Y_i \times 100$ | $\rho_{cal}$ (kg m$^{-3}$) | $\Delta Y_i \times 100$ |
|---------|-----------------------------|------------------------|-----------------------------|------------------------|-----------------------------|------------------------|
| T = 308.15 K |
| 15.00 | 909 | 0.55 | 917 | -0.33 | 915 | -0.13 |
| 20.00 | 940 | 0.42 | 944 | -0.03 | 945 | -0.11 |
| 25.00 | 967 | 0.21 | 966 | 0.31 | 970 | -0.08 |
| 30.00 | 990 | 0.02 | 985 | 0.51 | 991 | -0.10 |
| 35.00 | 1010 | -0.12 | 1001 | 0.79 | 1009 | 0.02 |
| 40.00 | 1028 | -0.29 | 1017 | 0.78 | 1026 | -0.11 |
| 45.00 | 1044 | -0.29 | 1030 | 1.06 | 1040 | 0.10 |
| T = 318.15 K |
| 15.00 | 861 | 0.58 | 872 | -0.69 | 865 | 0.12 |
| 20.00 | 899 | 0.44 | 905 | -0.22 | 901 | 0.22 |
| 25.00 | 929 | 0.32 | 931 | 0.11 | 931 | 0.12 |
| 30.00 | 955 | 0.10 | 953 | 0.31 | 956 | 0.00 |
| 35.00 | 978 | -0.01 | 972 | 0.61 | 977 | 0.10 |
| 40.00 | 998 | -0.20 | 989 | 0.70 | 996 | -0.04 |

a: Calculated results with the SRK EOS, PC-SAFT EOS, and TS model.
Table 5. continued

| $x_2 = 0.163$ | $x_2 = 1.000$ |
|---------------|---------------|
| **SRK EOS**   | **SRK EOS**   | **PC-SAFT EOS** | **PC-SAFT EOS** | **TS model** | **TS model** |
| $p$ (MPa)     | $\rho_{ad}$ (kg m$^{-3}$) | $\Delta Y_1 \times 100$ | $\Delta Y_2 \times 100$ | $\rho_{ad}$ (kg m$^{-3}$) | $\Delta Y_1 \times 100$ | $\rho_{ad}$ (kg m$^{-3}$) | $\Delta Y_1 \times 100$ |
| 45.00         | 981            | 0.11            | 976            | 0.41            | 980            | 0.04            |
| AAD (%)       | 0.13           | 0.50            | 0.06           |
| bias (%)      | 0.12           | -0.02           | 0.00           |
| SDV (%)       | 0.11           | 0.76            | 0.08           |
| RMS (%)       | 0.15           | 0.71            | 0.07           |
| **SRK EOS**   | **SRK EOS**   | **PC-SAFT EOS** | **PC-SAFT EOS** | **TS model** | **TS model** |
| $p$ (MPa)     | $\rho_{ad}$ (kg m$^{-3}$) | $\Delta Y_1 \times 100$ | $\Delta Y_2 \times 100$ | $\rho_{ad}$ (kg m$^{-3}$) | $\Delta Y_1 \times 100$ | $\rho_{ad}$ (kg m$^{-3}$) | $\Delta Y_1 \times 100$ |
| 45.00         | 1011           | 4.44            | 1004           | 1.70            | 1059           | -0.10           |
| 20.00         | 1015           | 4.78            | 1048           | 1.69            | 1066           | -0.03           |
| 25.00         | 1019           | 5.03            | 1055           | 1.68            | 1074           | -0.09           |
| 30.00         | 1023           | 5.28            | 1061           | 1.76            | 1080           | -0.07           |
| 35.00         | 1026           | 5.52            | 1068           | 1.66            | 1087           | -0.07           |
| 40.00         | 1030           | 5.68            | 1074           | 1.65            | 1093           | -0.09           |
| 45.00         | 1033           | 5.92            | 1080           | 1.64            | 1098           | 0.01            |

Gas could be supercharged through the piston pump and piston cylinder that are not shown in Figure 1. With the servo motor to control the piston, the volume and pressure of visible unit could be varied. The temperature of visible unit was adjusted by the oil bath. The deviation caused by observation could be minimized with the introduction of photosensitive resistance that could vary accompanied by system turbidity.

Uncertainty: $u(T) = 0.05$ K, $u(p) = 0.02$ MPa, and $u(\rho) = 4.6$ kg m$^{-3}$.

![Image](https://dx.doi.org/10.1021/acsomega.0c05462)
The density measurement unit includes a vibrating-tube densimeter and evaluation unit (DMATM HPM and mPDS-5, provided by Anton Paar Co., Ltd.), a pressure sensor, a temperature detector, a computer, and a circulating pump. The vibrating-tube densimeter is a U-shaped pipe made of Hastelloy C-276 alloy. The density of as-detected fluid could be thus decided by the relationship between oscillation period and mass of vibrating tube.

The phase equilibrium device and density measurement unit can bear a maximum temperature of 423 K and maximum pressure of 50 MPa. The uncertainties of temperature, pressure, and density measurement are ±0.05 K, ±0.02 MPa, and 4.6 kg·m⁻³, respectively.

5.3. Method for Phase Equilibrium and Density Measurement. The measurement method for phase transition pressure and density of the CO₂ + acetic acid system is listed herein. First of all, a certain amount of acetic acid was...

Figure 2. Density–pressure curves of CO₂ (1) + acetic acid (2) unitary and binary systems. Symbols represent experimental data from this work. Solid and dash lines represent the density calculated using the SRK EOS and PC-SAFT EOS, respectively. The black, red, blue, and magenta dots and lines represent temperatures of 308.15, 318.15, 328.15, and 338.15 K, respectively.
added into the visible unit followed by high-pressure CO$_2$ that was introduced by a supercharging device. The mass of CO$_2$ in the visible device could be detected by the balance. After temperature setting, the pressure of as-detected fluid was modulated. When the system became bright and homogenous, the pressure at the moment was just higher than that of its phase transition point. Subsequently, the pressure was released until phase separation occurred. The pressure of the phase transition point could be exactly confirmed by the variation of photosensitive resistance.

After the end of phase transition pressure measurement, the circulating pump was opened to transport the fluid through the vibrating-tube densimeter. Instantaneous density under different temperature and pressure could be measured by the photosensitive resistance.

Table 6. $\Delta V_m$ (cm$^3$mol$^{-1}$) for CO$_2$ (1) + Acetic Acid (2) Binary Systems at Different Temperatures and Pressures

| $p$ (MPa) | $x_1 = 0.107$ | $x_1 = 0.163$ | $x_1 = 0.222$ |
|-----------|----------------|----------------|----------------|
| $T = 308.15$ K |
| 15.00 | −4.805 | −5.876 | −6.440 |
| 20.00 | −3.662 | −4.498 | −4.932 |
| 25.00 | −2.957 | −3.605 | −3.935 |
| 30.00 | −2.480 | −3.031 | −3.286 |
| 35.00 | −2.230 | −2.680 | −2.893 |
| 40.00 | −1.999 | −2.391 | −2.599 |
| 45.00 | −1.665 | −1.967 | −2.136 |
| $T = 318.15$ K |
| 15.00 | −7.160 | −8.612 | −9.273 |
| 20.00 | −4.322 | −5.423 | −6.005 |
| 25.00 | −3.486 | −4.326 | −4.803 |
| 30.00 | −2.880 | −3.567 | −3.972 |
| 35.00 | −2.441 | −2.979 | −3.304 |
| 40.00 | −2.096 | −2.579 | −2.862 |
| 45.00 | −1.822 | −2.249 | −2.443 |
| $T = 328.15$ K |
| 15.00 | −10.865 | −12.614 | −13.337 |
| 20.00 | −5.738 | −7.236 | −7.938 |
| 25.00 | −4.011 | −5.135 | −5.728 |
| 30.00 | −3.523 | −4.357 | −4.818 |
| 35.00 | −2.692 | −3.384 | −3.785 |
| 40.00 | −2.401 | −2.976 | −3.283 |
| 45.00 | −1.866 | −2.394 | −2.670 |
| $T = 338.15$ K |
| 15.00 | −16.788 | −19.259 | −19.861 |
| 20.00 | −7.688 | −9.655 | −10.531 |
| 25.00 | −5.008 | −6.386 | −7.142 |
| 30.00 | −3.621 | −4.720 | −5.333 |
| 35.00 | −2.815 | −3.688 | −4.181 |
| 40.00 | −2.499 | −3.194 | −3.642 |
| 45.00 | −2.016 | −2.604 | −2.966 |

Table 7. Specifications of Pure Components

| reagent | CAS number | supplier | mass fraction | purification | analysis method |
|---------|------------|----------|---------------|--------------|-----------------|
| CO$_2$  | 124-38-9   | Qingdao Tianyuan Gas Co., Ltd. | >0.9999 | none | GC$^a$ |
| acetic acid | 64-19-7  | Guangdong Xilong Chemical Co., Ltd. | >0.998 | none | GC$^a$ |

$^a$Gas chromatography.

5.4. Comparison with Results in the Reference. Experimental data regarding the investigation of a CO$_2$ + acetic acid system under high pressure are very rare; thus, only the density of the pure CO$_2$ system would be compared herein. From Figure 4, it could be found that the deviation of experimental data and the ones in the reference is small with an absolute average deviation (AAD) of 1.80%, which indicates the reliability of this work.

5.5. Establishment of Experimental Conditions. This work was based on the density and phase behavior investigation by mixing a large amount of CO$_2$ with a little acetic acid. Here, 0.107, 0.163, and 0.222 of acetic acid molar fraction were chosen. The temperature was controlled at...
308.15, 318.15, 328.15, and 338.15 K. Meanwhile, it would have significance for density measurement provided that the pressure is higher than the miscibility pressure. Thus, pressure was set as 15.00, 20.00, 25.00, 30.00, 35.00, 40.00, and 45.00 MPa.

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Notes
The authors declare no competing financial interest.

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