

# Bubble-Point Measurement for CO<sub>2</sub> + Vinyl Acetate and CO<sub>2</sub> + Vinyl Acrylate Systems at High Pressures

Hun-Soo Byun\* and Jung-Soo Shin

Department of Chemical Engineering, Yosu National University, Yosu, Chonnam 550-749, South Korea

High-pressure phase behaviors are obtained for CO<sub>2</sub> + vinyl acetate systems at (40, 60, 80, 100, and 120) °C and pressures up to 127 bar and for CO<sub>2</sub> + vinyl acrylate systems at (45, 65, 85, 105, and 125) °C and pressures up to 138 bar. The solubility of CO<sub>2</sub> for the CO<sub>2</sub> + vinyl acetate and CO<sub>2</sub> + vinyl acrylate systems decreases as the temperature increases at constant pressure. The CO<sub>2</sub> + vinyl acetate and CO<sub>2</sub> + vinyl acrylate systems exhibit type-I phase behavior with a continuous mixture-critical curve. The experimental results for CO<sub>2</sub> + vinyl acetate and CO<sub>2</sub> + vinyl acrylate systems were modeled using the Peng–Robinson equation of state. A good fit of the data was obtained with the Peng–Robinson equation with no adjustable parameters for the CO<sub>2</sub> + vinyl acetate system and with two adjustable parameter for the CO<sub>2</sub> + vinyl acrylate system.

## Introduction

The phase behavior data of binary mixtures at high pressure are required for practical use such as in the chemical design and operation of separation processes in the petroleum, related industrial application, and polymer processes, particularly. Recent phase behavior experiments have been reported on the bubble-point and critical-point behavior of mixtures containing supercritical carbon dioxide.<sup>1–3</sup> Also, the supercritical fluid extraction is important as a separation technology.

To design supercritical carbon dioxide + monomer separation processes, one must first characterize the phase behavior of the solute in the supercritical carbon dioxide. Recently, Byun<sup>4</sup> reported phase behavior experimental data for carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate systems at 40–125 °C and pressures up to 136 bar using a static phase equilibria apparatus. Also, the phase behaviors for carbon dioxide + propyl acrylate and carbon dioxide + propyl methacrylate systems were reported by Byun<sup>5</sup> at 40–120 °C. Hasch et al.<sup>6</sup> have performed experimental phase behavior for the ethylene + methyl acrylate system at 15, 30, 75, and 120 °C. The phase behavior experimental data for the ethylene + vinyl acetate system were reported by Lindner and Luft.<sup>7</sup> McHugh et al.<sup>8</sup> studied the phase behavior of butyl acrylate in supercritical carbon dioxide at 35 and 75 °C and pressures up to ~100 bar. The phase behavior of butyl methacrylate and ethyl methacrylate in supercritical carbon dioxide was also studied by Byun and McHugh.<sup>9</sup>

The objective of this work is to obtain experimental data of the high pressure phase behavior information for the system of CO<sub>2</sub> + vinyl acetate and CO<sub>2</sub> + vinyl acrylate mixtures. The vinyl acetate has a dipole moment of 1.7 D,<sup>10</sup> but vinyl acrylate has no experimental or calculated value. The experimental pressure–composition isotherms are presented for the CO<sub>2</sub> + vinyl acetate and CO<sub>2</sub> + vinyl acrylate systems. Also, the pressure–temperature trace of the mixture critical points is presented in the vicinity of

pure CO<sub>2</sub> between the critical point of pure CO<sub>2</sub> and that of vinyl acetate and between critical point of CO<sub>2</sub> and that of vinyl acrylate.

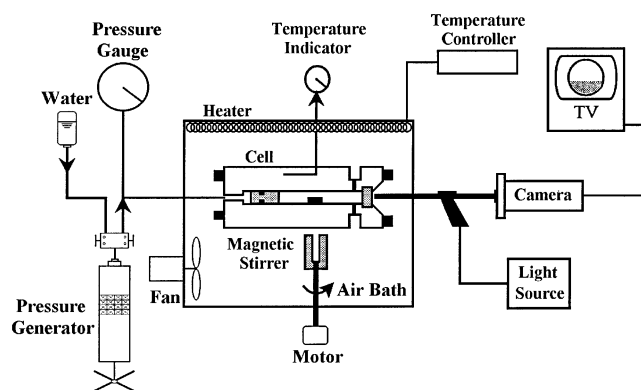
A secondary objective of this work is to compare the Peng–Robinson equation of state<sup>11</sup> with the phase behavior of these systems.

## Experimental Section

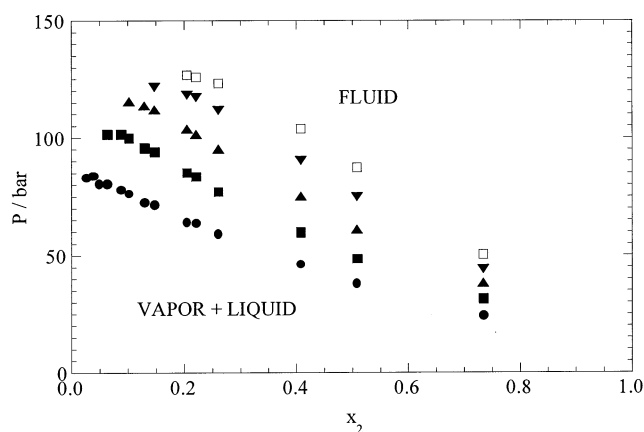
**Apparatus and Procedure.** Figure 1 shows the experimental apparatus used in this work. Phase behavior data were obtained in a high-pressure, variable-volume cell described in detail elsewhere.<sup>12,13</sup> For the CO<sub>2</sub> + vinyl acetate and CO<sub>2</sub> + vinyl acrylate mixtures studied, the empty cell is purged several times with CO<sub>2</sub> and nitrogen to remove traces of air, the liquid vinyl acetate and vinyl acrylate is loaded into the cell to within ±0.002 g using a syringe, and then CO<sub>2</sub> is condensed into the cell to within ±0.004 g using a high-pressure bomb. The solution in the cell is compressed to the desired operating pressure by displacing a movable piston using water pressurized by a high-pressure generator (HIP, model 37-5.75-60). Because the pressure is measured on the water side of the piston, a small correction (±0.7 bar) is added to account for the pressure required to move the piston. The pressure is measured using a Heise pressure gauge (Dresser Ind., model CM-130163, 0–340 bar, accurate to within ±0.3 bar). The system temperature, maintained to within ±0.2 °C, is measured with a platinum-resistance device accurate to within ±0.2 °C (Thermometrics Corp., Class A) placed in a thermowell on the surface of the cell. The contents of the cell are projected onto a video monitor using a camera coupled to a boroscope (Olympus Corp., model F100–038–000–50) placed directly against the sapphire window.

Once thermal equilibrium is maintained in the cell, the contents of the cell are compressed into the one phase region by moving the piston forward. The piston in the cell is slowly adjusted to lower the system pressure into the two-phase region. The phase behavior is obtained in the pressure interval between this two-phase state and the fluid-phase state. The temperature of the system is increased, and then the entire procedure is repeated to obtain

\* To whom correspondence should be addressed. Phone: +82-61-659-3296. Fax: +82-61-653-3659. E-mail: hsbyun@yosu.ac.kr.



**Figure 1.** High-pressure experimental apparatus used in this study.



**Figure 2.** Pressure–composition experimental data for the carbon dioxide + vinyl acetate system obtained in this work: ●, 40 °C; ■, 60 °C; ▲, 80 °C; □, 100 °C; △, 120 °C.

more information without reloading the cell. In this manner, without sampling, an isopleth (constant composition at various temperature and pressure) is obtained. A bubble point is obtained when small bubbles appear in the cell. The phase transition is a mixture critical point if critical opalescence is observed during the transition process and if two phases of equal volume are present when the mixture phase separates.

**Materials.** Carbon dioxide was obtained from Daesung Oxygen Co. (99.99% minimum purity) and used as received. The vinyl acetate (99+% purity) and vinyl acrylate (98% purity) used in this work were obtained from Aldrich Chemical Co. Both components were used without further purification in the experiments.

## Results and Discussion

Bubble- and critical-point data for both the  $\text{CO}_2$  + vinyl acetate and  $\text{CO}_2$  + vinyl acrylate systems are measured and reproduced at least twice to within  $\pm 0.3$  bar and  $\pm 0.2$  °C for a given loading of the cell. The mole fractions are accurate to within  $\pm 0.002$ .

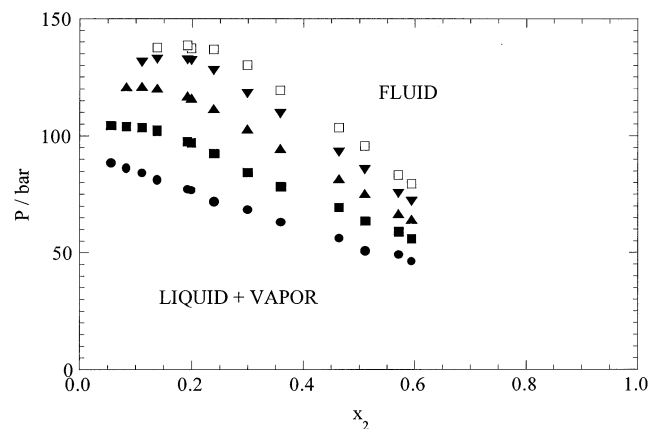
The  $\text{CO}_2$  + vinyl acetate and  $\text{CO}_2$  + vinyl acrylate mole fractions for the solubility isotherms at (40–125) °C have an estimated accumulated error of less than  $\pm 1.0\%$ .

Figure 2 and Table 1 show the experimental pressure–composition ( $P$ – $x$ ) isotherms at (40, 60, 80, 100, and 120) °C and the range of pressures of 24–127 bar for the  $\text{CO}_2$  + vinyl acetate system. Three phases were not observed at any of the five temperatures. As shown in Figure 2, the mixture critical pressures are 83.1 bar (at 40 °C), 101.7

**Table 1.** Experimental Data for the Carbon Dioxide(1) + Vinyl Acetate(2) System<sup>a</sup>

$t/^\circ\text{C}$	$x_2$	$P/\text{bar}$	transition	$t/^\circ\text{C}$	$x_2$	$P/\text{bar}$	transition	
40	0.734	24.6	BP	40	0.102	76.2	BP	
	0.508	38.3	BP		0.087	77.9	BP	
	0.407	46.2	BP		0.063	80.7	BP	
	0.260	59.4	BP		0.049	80.7	BP	
	0.221	63.9	BP		0.039	83.8	BP	
	0.204	64.4	BP		0.037	83.8	BP	
	0.146	71.8	BP		0.027	83.1	CP	
0.128	72.7	BP						
60	0.734	31.8	BP	60	0.146	94.2	BP	
	0.508	48.6	BP		0.128	95.8	BP	
	0.407	60.0	BP		0.102	99.9	BP	
	0.260	77.0	BP		0.087	101.7	BP	
	0.221	83.5	BP		0.063	101.7	CP	
	0.204	85.1	BP					
80	0.734	38.3	BP	80	0.204	103.8	BP	
	0.508	61.0	BP		0.146	112.1	BP	
	0.407	75.2	BP		0.128	113.7	BP	
	0.260	95.3	BP		0.102	115.5	CP	
	0.221	101.5	BP					
100	0.734	44.1	BP	100	0.221	117.3	BP	
	0.508	74.8	BP		0.204	118.3	BP	
	0.407	90.4	BP		0.146	121.7	CP	
	0.260	111.8	BP					
120	0.734	50.3	BP	120	0.260	123.2	BP	
	0.508	87.2	BP		0.221	125.9	BP	
	0.407	103.8	BP		0.204	126.8	CP	

<sup>a</sup> BP is a bubble point and CP is a critical point.



**Figure 3.** Experimental data isotherms for the carbon dioxide + vinyl acrylate system obtained in this work: ●, 45 °C; ■, 65 °C; ▲, 85 °C; □, 105 °C; △, 125 °C.

bar (at 60 °C),  $\sim 115.5$  bar (at 80 °C),  $\sim 121.7$  bar (at 100 °C), and  $\sim 126.8$  bar (at 120 °C). The  $P$ – $x$  isotherms shown in Figure 2 are consistent with those expected for a type I system<sup>14,15</sup> where a maximum occurs in the critical mixture curve. The solubility of  $\text{CO}_2$  decreases as temperatures shift higher under constant pressure.

Figure 3 and Table 2 show the phase experimental data at (45, 65, 85, 105, and 125) °C and for pressures up to 138 bar for the  $\text{CO}_2$  + vinyl acrylate mixture. As shown in Figure 3, the mixture critical pressures are  $\sim 104.0$  bar (at 65 °C), 121.0 bar (at 85 °C), 131.4 bar (at 105 °C), and 137.6 bar (at 125 °C). Also, the pressure of each mixture–critical point continually increases as the temperature increases. The  $\text{CO}_2$  + vinyl acrylate system does not exhibit three phases at any of the five temperatures investigated. The mixture–critical curve for the  $\text{CO}_2$  + vinyl acrylate system exhibits a pressure maximum in  $P$ – $T$  space.

**Table 2. Experimental Data for the Carbon Dioxide(1) + Vinyl Acrylate(2) System<sup>a</sup>**

<i>t</i> /°C	<i>x</i> <sub>2</sub>	<i>P</i> /bar	transition	<i>t</i> /°C	<i>x</i> <sub>2</sub>	<i>P</i> /bar	transition
45	0.594	46.2	BP	45	0.199	76.7	BP
	0.570	49.1	BP		0.192	77.2	BP
	0.510	51.0	BP		0.138	81.4	BP
	0.463	56.2	BP		0.111	84.1	BP
	0.358	65.3	BP		0.083	86.5	BP
	0.299	68.5	BP		0.055	113.8	BP
0.239	72.1	BP					
65	0.594	55.9	BP	65	0.199	97.0	BP
	0.570	59.1	BP		0.192	97.6	BP
	0.510	63.6	BP		0.138	102.4	BP
	0.463	69.3	BP		0.111	103.6	BP
	0.358	78.5	BP		0.083	104.0	BP
	0.299	84.3	BP		0.055	104.5	CP
0.239	92.5	BP					
85	0.594	64.3	BP	85	0.239	111.6	BP
	0.570	66.7	BP		0.199	116.0	BP
	0.510	75.4	BP		0.192	116.9	BP
	0.463	81.7	BP		0.138	120.3	BP
	0.358	94.7	BP		0.111	121.0	BP
	0.299	102.9	BP		0.083	121.0	CP
105	0.594	71.9	BP	105	0.239	127.8	BP
	0.570	75.3	BP		0.199	132.2	BP
	0.510	85.6	BP		0.192	132.4	BP
	0.463	93.1	BP		0.138	132.8	BP
	0.358	109.5	BP		0.111	131.4	CP
	0.299	118.1	BP				
125	0.594	79.5	BP	125	0.299	130.2	BP
	0.570	83.2	BP		0.239	136.8	BP
	0.510	95.7	BP		0.199	137.4	BP
	0.463	103.5	BP		0.192	138.6	CP
	0.358	119.5	BP		0.138	137.6	DP

<sup>a</sup> BP is a bubble point and CP is a critical point.

**Table 3. Pure Component Critical Properties with the Peng–Robinson Equation of State<sup>10,16,17</sup>**

component	<i>M</i> <sub>w</sub>	<i>t</i> <sub>c</sub> /°C	<i>P</i> <sub>c</sub> /bar	acentric factor
carbon dioxide	44.01	31.1	73.9	0.225
vinyl acetate	86.09	251.85	43.5	0.3384
vinyl acrylate	98.1	279.43	39.7	0.3345

The experimental phase behavior curves obtained in this work are modeled using the Peng–Robinson equations of state. The Peng–Robinson equations are briefly described here. The Peng–Robinson equations of state<sup>11</sup> are used with the following mixing rules:

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - k_{ij})$$

$$b_{\text{mix}} = \sum_i \sum_j x_i x_j b_{ij}$$

$$b_{ij} = 0.5[(b_{ii} b_{jj})] (1 - \eta_{ij})$$

where  $k_{ij}$  and  $\eta_{ij}$  are binary interaction parameters that are determined by fitting  $P$ - $x$  isotherms curves and  $a_{ij}$  and  $b_{ii}$  are pure component parameters as defined by Peng and Robinson.<sup>11</sup> The expression for the fugacity coefficient using these mixing rules is given by Peng and Robinson<sup>11</sup> and is not reproduced here. Table 3 lists the pure component critical temperatures, critical pressures, and the acentric factors for carbon dioxide,<sup>10,16</sup> vinyl acetate,<sup>10,17</sup> and vinyl acrylate<sup>10</sup> that are used with the Peng–Robinson equation of state. The properties of vinyl acrylate were calculated due to Ambrose group contributions by the Lydersen method.<sup>10</sup>

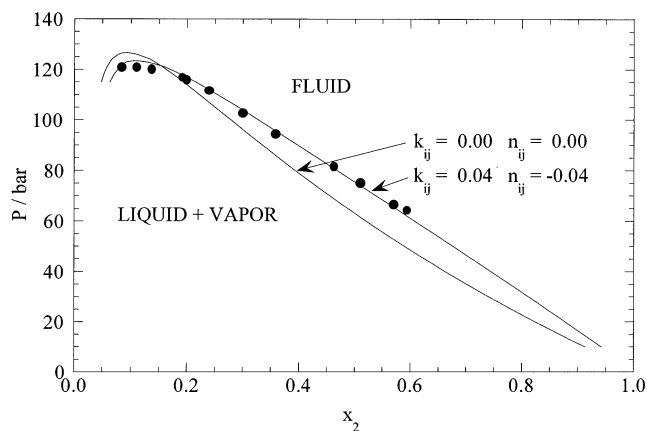
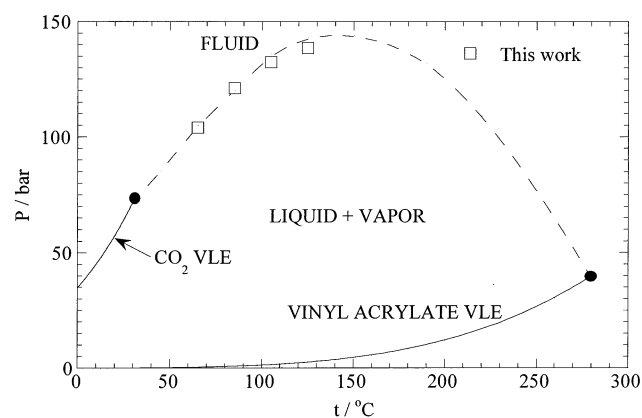
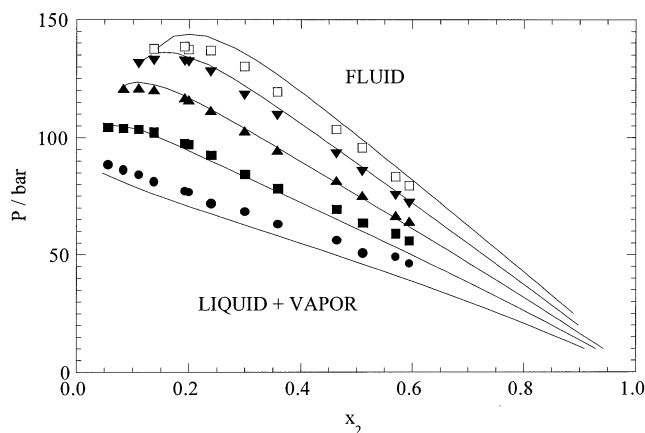
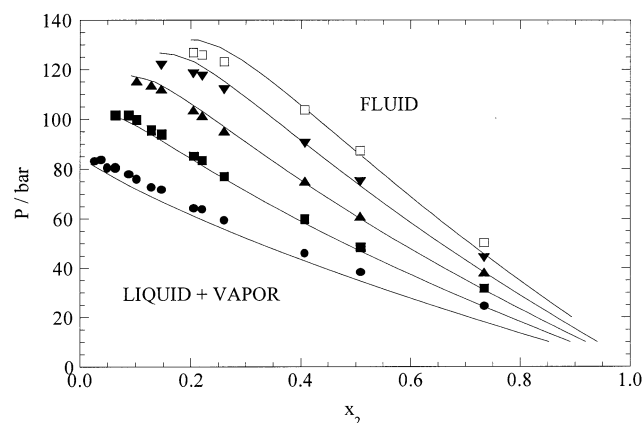
**Figure 4.** Comparison of the best fit of Peng–Robinson equation of state to carbon dioxide + vinyl acrylate system obtained in this work (●) at 85 °C.**Figure 5.** Pressure–temperature diagram for the carbon dioxide + vinyl acrylate system. The solid line and the solid circles represent the vapor–liquid line and the critical point for pure carbon dioxide and vinyl acrylate. The open squares are critical points determined from isotherms measured in this study. The dashed line represents calculated values obtained using the Peng–Robinson equation of state with  $k_{ij}$  equal to 0.04 and  $\eta_{ij}$  equal to -0.04.

Figure 4 shows a comparison of CO<sub>2</sub> + vinyl acrylate experimental results with the calculated data obtained using Peng–Robinson equation of state at 85 °C. A reasonable fit of data is obtained over most of the composition range even if no binary interaction parameters are used. However, if two mixture parameters,  $k_{ij} = 0.04$  and  $\eta_{ij} = -0.04$ , are used, the fit of the experimental results is significantly better. We compared the experimental results with calculated  $P$ - $x$  isotherms at temperatures of (45, 65, 105, and 125) °C for the CO<sub>2</sub> + vinyl acrylate system using the adjusted values of  $k_{ij}$  and  $\eta_{ij}$  determined at 85 °C. Figure 5 shows a comparison of experimental with calculated data at the temperatures of the CO<sub>2</sub> + vinyl acrylate mixture. A reasonable fit of data are obtained with the Peng–Robinson equation using two adjustable mixture parameters for the CO<sub>2</sub> + vinyl acrylate system at (45–85) °C. However, mixture critical point for the CO<sub>2</sub> + vinyl acrylate system shows a little difference in the comparison of experimental result with calculated value at temperature of 105 and 125 °C.

As shown in Figure 5, the solid lines represent the vapor pressure for pure CO<sub>2</sub><sup>10,16</sup> and vinyl acrylate.<sup>10</sup> The vapor pressure of vinyl acrylate is obtained by the Lee–Kesler method.<sup>10</sup> The boiling point of vinyl acrylate is obtained from Aldrich Chemical Co.



**Figure 6.** Comparison of the experimental data (symbols) for the carbon dioxide (1) + vinyl acrylate (2) system with calculations (solid lines) obtained using the Peng–Robinson equation of state with  $k_{ij}$  equal to 0.04 and  $\eta_{ij}$  equal to  $-0.04$ : ●, 45 °C; ■, 65 °C; ▲, 85 °C; ▼, 105 °C; □, 125 °C.

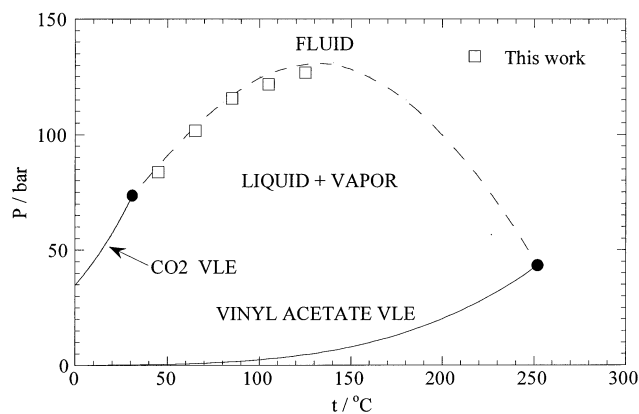


**Figure 7.** Comparison of the experimental data (symbols) for the carbon dioxide (1) + vinyl acetate (2) system with calculations (solid lines) obtained using the Peng–Robinson equation of state with  $k_{ij}$  and  $\eta_{ij}$  equal to 0.0: ●, 40 °C; ■, 60 °C; ▲, 80 °C; ▼, 100 °C; □, 120 °C.

Figure 6 shows a comparison of experimental with calculated  $P$ – $x$  isotherms at temperatures of (45, 65, 85, 105, and 125) °C for the carbon dioxide + vinyl acrylate system. These isotherms are calculated using the adjusted values of  $k_{ij}$  equal to 0.04 and  $\eta_{ij}$  equal to  $-0.04$  determined at 85 °C in the same way as above.

Figure 7 shows predicted  $P$ – $x$  isotherms for the  $\text{CO}_2$  + vinyl acetate mixture at (40, 60, 80, 100, and 120) °C using the Peng–Robinson equation of state with  $k_{ij}$  and  $\eta_{ij}$  equal to 0.0. These adjusted values of the mixture parameters are obtained by fitting the 80 °C isotherm and a reasonable fit between the experimental and calculated results. The remaining isotherms are calculated using the same values of the mixture interaction parameters. The calculated mixture-critical curve is type I, in agreement with experimental results.

Figure 8 shows the mixture-critical curve for the  $\text{CO}_2$  + vinyl acetate system, experimental and calculated results by the Peng–Robinson equation of state. As shown in Figure 8, the solid lines represent the vapor pressure for pure  $\text{CO}_2$ <sup>10,16</sup> and vinyl acetate.<sup>16,17</sup> The solid circles represent the critical point for pure  $\text{CO}_2$  and vinyl acetate.<sup>16,17</sup> The upper part of the dash line indicates single phase (fluid), and the lower part of that does two phase (vapor–liquid). The open squares are for the mixture-critical points determined from isotherms measured in this



**Figure 8.** Pressure–temperature diagram for the carbon dioxide + vinyl acetate system. The solid line and the solid circles represent the vapor–liquid line and the critical point for pure carbon dioxide and vinyl acetate. The open squares are mixture-critical points determined from isotherms measured in this study. The dashed line represents calculated values obtained using the Peng–Robinson equation of state with  $k_{ij}$  and  $\eta_{ij}$  equal to 0.0.

experiment. The dash lines represent the calculated value obtained using the Peng–Robinson equation of state.

## Conclusions

The phase behavior of  $\text{CO}_2$  + vinyl acetate and  $\text{CO}_2$  + vinyl acrylate systems has been studied using a high-pressure, variable-volume view cell. These two systems exhibit type I phase behavior, which is characterized by an uninterrupted critical mixture curve. The  $\text{CO}_2$  + vinyl acetate and  $\text{CO}_2$  + vinyl acrylate mixtures do not exhibit three phases at any five temperatures. The Peng–Robinson equation of state is capable of accurately predicting the phase behavior for both of these two systems using no and two temperature-independent mixture interaction parameters.

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