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Phase Behavior of Carbon Dioxide + Methyl Acrylate and Carbon Dioxide + Ethyl Acrylate Systems at High Pressures

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Pressure−composition isotherms are obtained for binary mixtures of carbon dioxide + methyl acrylate systems at (40, 60, 80, 100, and 120) °C and pressures to 132 bar and for carbon dioxide + ethyl acrylate systems at (45, 65, 85, 105 and 125) °C and pressures up to 136 bar. The solubility of methyl acrylate and ethyl acrylate for the carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate systems increases as the temperatures increases at constant pressure. The carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate systems have continuous critical mixture curves that exhibit maximums in pressure at temperatures between the critical temperatures of carbon dioxide and methyl acrylate or ethyl acrylate. The carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate systems exhibit type I phase behavior, characterized by a continuous critical line from pure carbon dioxide to the second component with a maximum in pressure. The experimental results for the carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate systems have been modeled using the Peng−Robinson equation of state. A good fit of the data is obtained with the Peng−Robinson equation using an adjustable parameter.

Introduction

Recently, we have performed phase behavior experiments for mixtures containing supercritical carbon dioxide.[1−4] The bubble- and dew-point behaviors of mixtures containing supercritical carbon dioxide are important for industrial application, supercritical fluid extraction, and process design. The advance of supercritical fluid extraction development is often dependent on new thermodynamics data on vapor−liquid, liquid−liquid−vapor, and liquid−liquid equilibria. However, it is important to determine three-phase equilibria in the binary system.

The first part of this work is the high-pressure experimental data for carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate mixtures by investigating mixtures of carbon dioxide with two compounds: methyl acrylate and ethyl acrylate. Also presented is a portion of the pressure−temperature (*P*, *T*) trace of the mixture critical curve for the carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate systems measured in the vicinity of the critical point of pure carbon dioxide. It has long been known that three-phase, liquid−liquid−vapor regions occur with carbon dioxide + alcohol systems and with low-molecular-weight hydrocarbon solvent + alcohol mixtures near the critical lines of the solvent.[5−9] A detailed description of the characteristics of this type of phase behavior can be found in Scott and van Konynenburg[10] and McHugh and Krukonis.[11] Also, to provide phase behavior information for high-pressure process design purposes, the measured bubble- and dew-point data of binary systems are modeled using the Peng−Robinson equation of state. These results can give valuable information for rational design and operation of the supercritical region.

Experimental Section

Apparatus and Procedure. Figure 1 shows a schematic diagram of the experimental apparatus. The main component of the experimental apparatus is a high pressure, variable-volume cell which is constructed of a high-nickel-content austenitic steel (Nitronic 50, 5.7 cm o.d., 1.59 cm i.d., a working volume of ~28 cm^3) and is capable of operating to pressure of 2000 bar. A 1.9 cm thick sapphire window is fitted in the front part of the cell to allow observation of the phases. Typically, the liquid methyl acrylate or ethyl acrylate is loaded into the cell to within ±0.002 g using a syringe after the empty cell is purged several times with carbon dioxide to remove trances of air. Carbon dioxide is then added to the cell to within ±0.004 g using a high-pressure bomb.

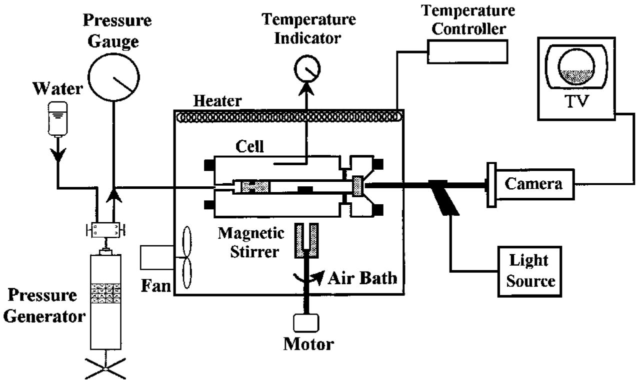

Figure 1. Schematic diagram of the high-pressure experimental apparatus used in this study.

The solution in the cell was compressed to the desired pressure by moving a piston located within the cell. The piston was moved using water pressurized by a high-pressure generator (HIP, model 37-5.75-60). Because the pressure is measured on the water side of piston, a small correction (0.7 bar) is added to account for the pressure required to move the piston. The pressure of the mixture was measured with a Heise gauge (Dresser Ind., model CM-53920, 0−340 bar) accurate to ±0.4 bar. The temperature of the cell, which was typically maintained to within ±0.2 °C, was measured using a platinum-resistance thermometer (Thermometrics Corp., class A) and a digital multi-

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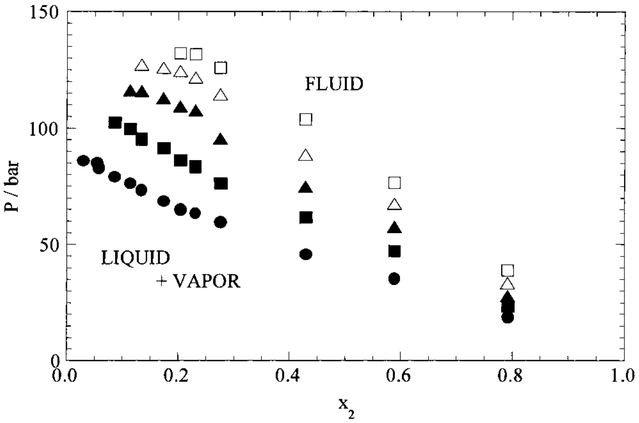

Figure 2. Experimental data isotherms for the carbon dioxide−methyl acrylate system obtained in this work: ●, 45 °C; ■, 65 °C; ▲, 85 °C; △, 105 °C; □, 125 °C.

meter (Yokogawa, model 7563, accurate to ±0.005%). The mixture inside the cell can be viewed on a video monitor using a camera coupled to a borescope (Olympus Corp., model F100-038-000-50) placed against the outside of the sapphire window. A fiberoptic cable connected to a high-density illuminator (Dolan-Jenner Industries, Inc., model 180) and to the borescope was used to transmit light into the cell. The solution in the cell was well mixed using a magnetic stir bar activated by an external motor beneath the cell.

At a fixed temperature, the solution in the cell was compressed to a single phase. The solution was maintained in the single-phase region at the desired temperature for at least 30 min for the cell to reach phase equilibrium. The pressure was then slowly decreased until a second phase appears. A bubble point pressure was obtained when small vapor bubbles appear first in the cell. Critical points are obtained by adjusting the temperature and pressure of the mixture until critical opalescence was observed along with equal liquid and vapor volume upon the formation of the second phase.

Materials Carbon dioxide was obtained from Daesung Oxygen Co. (99.9% minimum purity) and used as received. The methyl acrylate (99.5% purity) and ethyl acrylate (99.5% purity) used in this work were obtained from Junsei Chemical Co. Both components were used without further purification in the experiments.

Experimental Results and Discussion

Bubble- and critical-point data for both the carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate systems are measured and reproduced at least twice to within ±0.4 bar and 0.2 °C for a given loading of the cell. The mole fractions are accurate to ±0.002.

The carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate mole fraction for the solubility isotherms at (40−125) °C are arranged according to the value of at least two independent data points that have an estimated accumulated error of less than ±1.0%.

Figure 2 and Table 1 show the experimental pressure−composition (P, x) isotherms at (45, 65, 85, 105 and 125) °C and the range of pressures of 19−132 bar for the carbon dioxide + methyl acrylate system. Three phases were not observed at any of the five temperatures studied. Although the characteristics of the P, x isotherms appear to be consistent with those expected for a type I system, the lowest temperature isotherm is too far away from the critical point of pure carbon dioxide to make any definitive statement concerning whether this mixture indeed exhibits type I behavior.[10,11]

Table 1. Experimental Data of Liquid Phase for the Carbon Dioxide (1) + Methyl Acrylate (2) System

t/°C	x_2	P/bar	transition[a]	x_2	P/bar	transition[a]
45	0.792	19.0	BP	0.134	73.5	BP
	0.589	35.6	BP	0.113	76.2	BP
	0.429	45.9	BP	0.085	79.0	BP
	0.275	59.7	BP	0.057	83.1	BP
	0.231	63.5	BP	0.054	85.2	BP
	0.203	65.2	BP	0.029	85.9	BP
	0.173	68.6	BP			
65	0.792	23.5	BP	0.203	86.2	BP
	0.589	47.2	BP	0.173	91.4	BP
	0.429	64.5	BP	0.134	95.5	BP
	0.275	76.2	BP	0.113	99.7	BP
	0.231	83.8	BP	0.085	102.4	CP
85	0.792	27.9	BP	0.203	109.3	BP
	0.589	57.6	BP	0.173	112.8	BP
	0.429	74.8	BP	0.134	115.9	BP
	0.275	95.5	BP	0.113	116.2	CP
	0.231	107.6	BP			
105	0.792	33.5	BP	0.231	121.7	BP
	0.589	67.6	BP	0.203	124.5	BP
	0.429	88.6	BP	0.173	125.9	BP
	0.275	114.5	BP	0.134	127.2	CP
125	0.792	39.0	BP	0.275	125.9	BP
	0.589	76.6	BP	0.231	131.7	BP
	0.429	103.8	BP	0.203	132.1	CP

[a] BP is a bubble point and CP is a critical point.

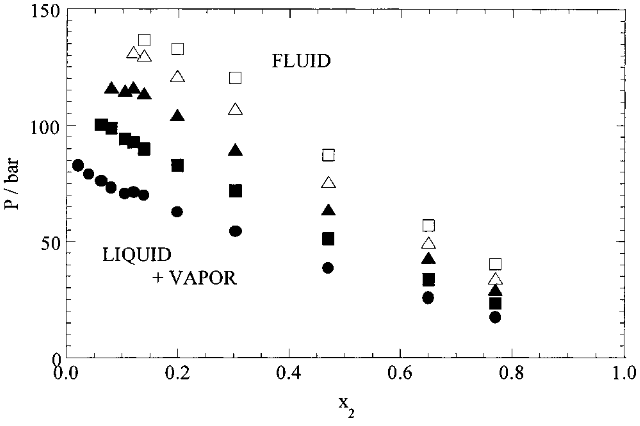

Figure 3. Pressure−composition isotherms for the carbon dioxide−ethyl acrylate system obtained in this work: ●, 40 °C; ■, 60 °C; ▲, 80 °C; △, 100 °C; □, 120 °C.

Figure 3 and Table 2 show the experimental P, x isotherms at (40, 60, 80, 100, and 120) °C for the carbon dioxide + ethyl acrylate system. The P, x isotherms shown in Figure 3 are consistent with the characteristics expected for a type I system where a maximum occurs in the critical mixture curve. The solubility of carbon dioxide for ethyl acrylate decreases as the temperature increased at constant pressure. Also, the mixture critical points for the carbon dioxide + ethyl acrylate system increased as the temperature increases.

Figure 4 presents the experimentally determined pressure−temperature (P, T) trace of the mixture critical curve in the vicinity of the critical point of carbon dioxide. The mixture critical curves of the two dashed lines in Figure 4 represent calculations obtained by using the Peng−Robinson equation of state, which is discussed later. There were no three-phase regions observed during the gathering of either P, x or P, T data for the carbon dioxide + ethyl acrylate system. Also, the carbon dioxide + ethyl acrylate system exhibits type I behavior. This observation is inter-

Table 2. Experimental Data of Liquid Phase for the Carbon Dioxide (1) + Ethyl Acrylate (2) System

t/°C	x_2	P/bar	transition[a]	x_2	P/bar	transition[a]
40	0.770	17.6	BP	0.119	71.4	BP
	0.650	26.0	BP	0.104	70.7	BP
	0.470	38.6	BP	0.080	73.5	BP
	0.302	54.5	BP	0.061	76.2	BP
	0.198	62.8	BP	0.040	79.0	BP
	0.138	70.0	BP	0.021	83.1	CP
60	0.770	23.5	BP	0.138	90.1	BP
	0.650	33.9	BP	0.119	92.8	BP
	0.470	51.4	BP	0.104	94.1	BP
	0.302	72.1	BP	0.080	99.0	BP
	0.198	83.1	BP	0.061	100.4	CP
80	0.770	29.3	BP	0.138	113.8	BP
	0.650	43.1	BP	0.119	116.2	BP
	0.470	63.8	BP	0.104	114.8	BP
	0.302	89.7	BP	0.080	116.2	CP
	0.198	104.5	BP			
100	0.770	34.1	BP	0.198	121.0	BP
	0.650	49.6	BP	0.138	130.0	BP
	0.470	75.9	BP	0.119	131.4	CP
	0.302	107.2	BP			
120	0.770	40.4	BP	0.302	120.4	BP
	0.650	56.9	BP	0.198	132.8	BP
	0.470	87.2	BP	0.138	136.6	CP

[a] BP is a bubble point and CP is a critical point.

Table 3. Pure Component Critical Properties with the Peng–Robinson Equation of State[14–16]

component	M_w	t_c/°C	P_c/bar	acentric factor
carbon dioxide	44.01	31.1	73.9	0.225
methyl acrylate	86.09	262.8	42.5	0.3475
ethyl acrylate	100.12	279.8	36.8	0.3776

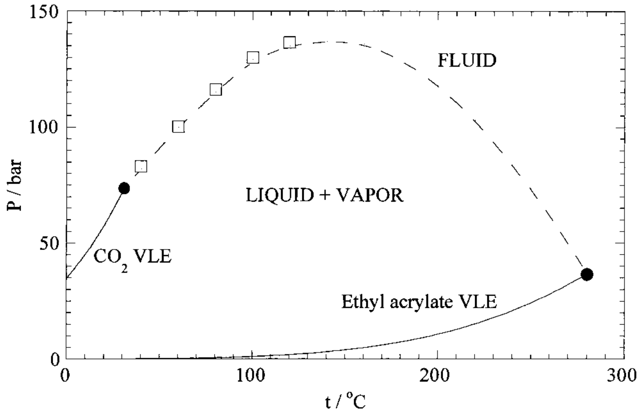

Figure 4. Pressure–temperature diagram for the carbon dioxide–ethyl acrylate system. The solid line and the solid circles represent the vapor–liquid line and the critical point for pure carbon dioxide and ethyl acrylate. The open squares are critical points determined from isotherms measured in this study. The dashed line represents calculated values obtained using the Peng–Robinson equation of state with η_{ij} equal to −0.05.

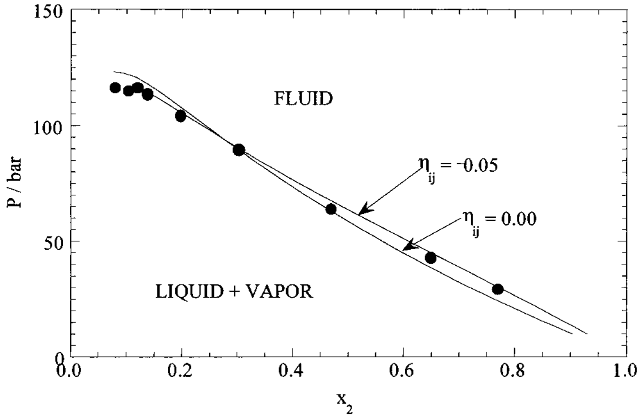

Figure 5. Comparison of the best fit of Peng–Robinson equation of state to carbon dioxide–ethyl acrylate system obtained in this work (●) at 80 °C.

esting considering that carbon dioxide–alkanol systems typically exhibit LLV behavior at temperatures near the critical point of carbon dioxide.[5] The biggest difference between the acrylates and alcohol is that acrylates are only polar whereas alcohols can form linear, hydrogen-bonded multimers.[12]

The experimental data obtained in this work is modeled using the Peng–Robinson equation of state. This equation is briefly described here. The Peng–Robinson equation[13] of state is 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 η_{ij} are interaction mixture parameters that are determined by fitting pressure–composition data and a_{ii} and b_{ii} are pure component parameters as defined by Peng and Robinson. The expression for the fugacity coefficient using these mixing rules is given by Peng and Robinson[13] and is not reproduced here. Table 3 lists the pure component critical temperatures, critical pressures, and the acentric factors for carbon dioxide, methyl acrylate, and ethyl acrylate that are used with the Peng–Robinson equation of state.[14,15]

Figure 5 shows a comparison of carbon dioxide + ethyl acrylate experimental results with calculations obtained using Peng–Robinson equation at a temperature of 80 °C. A reasonable fit of the data is obtained over most of the composition range even if no mixture parameters are used. But if one mixture parameter, $k_{ij} = 0.000$ and $\eta_{ij} = -0.050$, is used, the fit of the experimental results is significantly better. We compared the experimental results with calculated P, x isotherms at temperatures of (40, 60, 100, and 120) °C for the carbon dioxide + ethyl acrylate system using the adjusted values of k_{ij} and η_{ij} determined at 80 °C. As shown in Figure 6, a good fit of the data is obtained with the Peng–Robinson equation using adjustable mixture parameters for the carbon dioxide + ethyl acrylate system.

Figure 7 shows a comparison of experimental and calculated P, x isotherms at temperature of (45, 65, 85, 105, and 125) °C for the carbon dioxide + methyl acrylate system. These isotherms are calculated using the adjusted values of k_{ij} equal to 0.000 and η_{ij} equal to −0.050 determined at 85 °C with the same manner as above.

Figure 8 shows the mixture-critical curve for the carbon dioxide + methyl acrylate system predicted by the Peng–Robinson equation of state. The calculated mixture-critical curve is type I, in agreement with experimental observations. As shown in Figure 8, the solid lines represent the vapor pressure for pure carbon dioxide[14,15] and methyl acrylate.[16] The solid circles represent the critical point for pure carbon dioxide and methyl acrylate. The upper part of the dash line is single phase (fluid); the lower part is two phase (vapor–liquid). The open squares are the

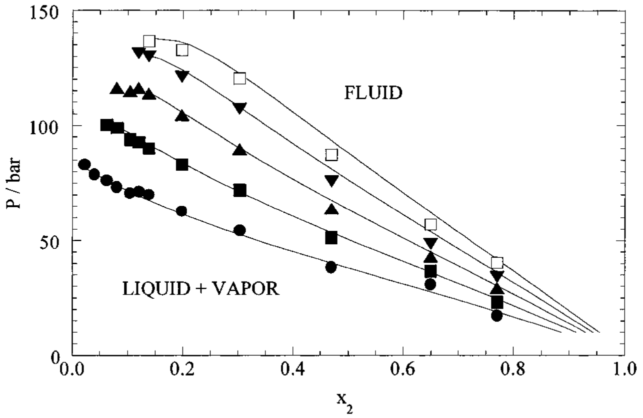

Figure 6. A comparison of the expermental data (symbols) for the carbon dioxide–ethyl acrylate system with calculations (solid lines) obtained using the Peng–Robinson equation of state with η_{ij} equal to −0.05: ●, 40 °C; ■, 60 °C; ▲, 80 °C; ▼, 100 °C; □, 120 °C.

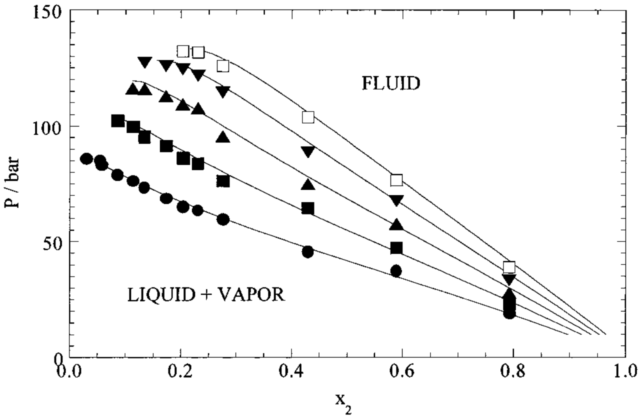

Figure 7. A comparison of the expermental data (symbols) for the carbon dioxide–methyl acrylate system with calculations (solid lines) obtained using the Peng–Robinson equation of state with η_{ij} equal to −0.05: ●, 45 °C; ■, 65 °C; ▲, 85 °C; ▼, 105 °C; □, 125 °C.

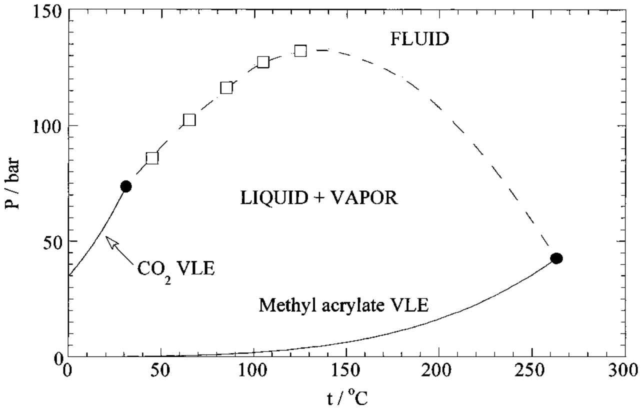

Figure 8. Pressure–temperature diagram for the carbon dioxide–methyl acrylate system. The solid line and the solid circles represent the vapor–liquid line and the critical point for pure carbon dioxide and methyl acrylate. The open squares are critical points determined from isotherms measured in this study. The dashed line represents calculated values obtained using the Peng–Robinson equation of state with η_{ij} equal to −0.05.

mixture-critical points determined from isotherms measured in this experiment. The dash lines represent the calculated value obtained using the Peng–Robinson equation of state. The mixture parameters are then obtained from the case Peng–Robinson equation, with k_{ij} equal to 0.000 and η_{ij} equal to −0.050.

Conclusions

High-pressure phase behavior data for carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate systems are obtained at 40–125 °C and a pressure range of 17–136 bar for binary mixtures. The carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate systems exhibit type I phase behavior, which is characterized by an uninterrupted critical-mixture curve. Also three phases were not observed in any of the systems studied.

The Peng–Robinson equation of state models the pressure–composition isotherms for two carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate systems reasonably well using independent-temperature mixture parameters. Also The Peng–Robinson equation did a good job modeling for the carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate systems.

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