Phase Behavior and Modeling of Supercritical Carbon Dioxide−Organic Acid Mixtures

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Pressure−composition isotherms are obtained for binary mixtures of carbon dioxide with formic acid, acetic acid, butyric acid, valeric acid, caproic acid, and caprylic acid at temperatures of 35.0−120.0 °C and pressures up to 250 bar. The accuracy of the experimental apparatus was tested by comparing the measured phase equilibrium data of the carbon dioxide−acetic acid system at 40.0 and 60.0 °C with those of Laugier et al. These six carbon dioxide−polar solute systems exhibit type I phase behavior, which is characterized by an uninterrupted critical mixture curve that has a maximum in pressure. In each system, the mixture critical point increases as the temperatures increases, and also the mixture critical pressure increases as the molecular weight increases. On the contrary, the carbon dioxide−formic acid system shows a higher mixture critical pressure compared with those of the other systems. The experimental data are modeled using both the statistical associating fluid theory (SAFT) and the Peng−Robinson (P−R) equation of state. The SAFT equation of state reasonably models the pressure−composition isotherms for these six systems only if two temperature-independent mixture parameters are used for each system. The P−R equation of state calculated the phase behavior with one or two temperature-independent mixture parameters.

Introduction

The phase behavior of mixtures containing carbon dioxide is important for industrial applications, especially for the analysis of supercritical extraction using carbon dioxide. In particular, the process design requires the knowledge of phase equilibrium diagrams over a wide range of pressures and temperatures. The advance of supercritical fluid extraction development is often dependent on new thermodynamic data on vapor−liquid, liquid−liquid−vapor, and liquid−liquid equilibria. However, it is important to determine three-phase equilibria in the binary system

Carboxylic acids from formic acid to the 22-carbon long-chain acids are economically important. Formic acid, acetic acid, and butyric acid are manufactured in large quantities from petrochemical feedstocks. The higher acids are derived from animal fats, vegetable oils, or fish oils, for which there are significant industrial applications. The shorter to higher chain carboxyl acids are polymorphic with a unit cell containing dimers formed by hydrogen bonding between carboxyl groups.[1]

The first part of this work is to expand the high-pressure, experimental database for carbon dioxide−solute mixtures by investigating mixtures of carbon dioxide with six polar compounds: formic acid, which has a moderate dipole moment of 1.5 D;[2] acetic acid, which has a dipole moment of 1.7 D;[3] butyric acid, which is expected to have a dipole moment of 1.5 D;[2] valeric acid, which has a dipole moment of 1.6 D at 20 °C;[3] caproic acid, which is expected to have a dipole moment of 1.13 D at 25 °C(1.31 D at 60 °C);[4] and caprylic acid, which has a dipole moment of 1.15 D at 25 °C (1.31 D at 60 °C).[4] Also presented is a portion of the pressure−temperature ($P-T$) trace of the mixture critical curve for the carbon dioxide−valeric acid and carbon dioxide−caproic acid 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 of the solvent.[5−9]

A detailed description of the characteristics of this type of phase behavior can be found in Scott and Konynenburg[10] and McHugh and Krukonis.[11]

The $P-T$ region of interest for the mixture critical measurements is limited to the vicinity of the critical point of pure carbon dioxide where the strength of acid−acid polar interactions and the propensity of acid dimerization are expected to be much greater than at higher temperatures. Recently, Byun et al.[12−14] have performed phase behavior experiments for mixtures containing carbon dioxide and polar solutes.

In the second part of this work, the resulting experimental data are modeled using both the statistical associating fluid theory (SAFT)[15−20] and the Peng−Robinson (P−R) equation of state.[11,21]

The phase behavior experimental data for the carbon dioxide−acid systems provides an especially stringent test of the SAFT model as solute acid was found to form dimers in solution by Pimentel and McClellan.[22] The P−R equation of state is used because it is a well-known benchmark equation of state that is easily implemented and programmed, even though it only specifically accounts for dispersion interactions. It is possible to use the P−R equation of state to model the phase behavior of mixtures with species that form hydrogen bonds if the mixture parameters are temperature-dependent, although this approach can give spurious results when the calculations are performed on systems for which little experimental information is available.[9]

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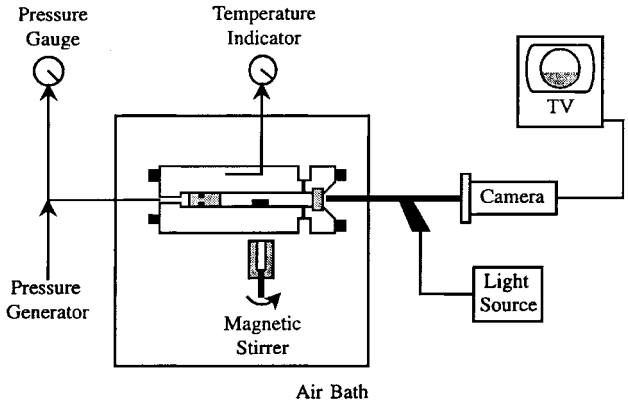

Figure 1. Experimental system for measurement of bubble, dew, and critical points.

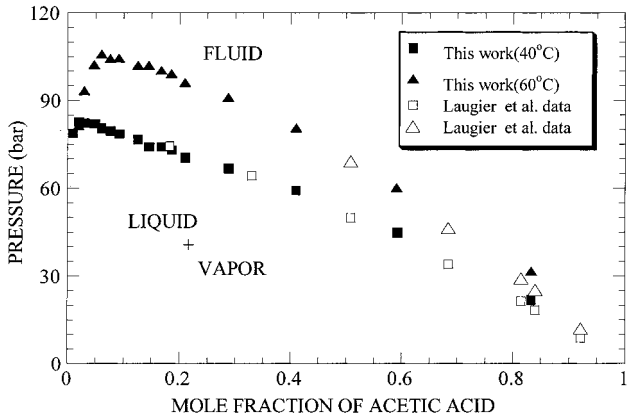

Figure 2. Comparison of mole fraction for the CO_2−acetic acid system obtained in this study and Laugier et al. at 40.0 and 60.0 °C.

Experimental Section

Apparatus and Procedure. The experimental apparatus and techniques used in this work are described in detail by Byun et al.[12,13] Figure 1 shows the experimental apparatus used here. Bubble- and dew-point curves are obtained using a high-pressure, variable-volume cell (1.59 cm i.d. × 7.0 cm o.d., ∼28 cm^3 working volume). A 1.9 cm thick sapphire window is fitted in the front part of the cell to allow for visual observation of the bubble-point and dew-point transitions. The cell is capable of operating to pressures of 3000 bar.

The empty cell is purged several times with nitrogen followed by carbon dioxide to ensure that all of the air is removed. The desired amount of liquid solute is loaded into the cell to within ±0.002 g using a syringe, and carbon dioxide is transferred into the cell gravimetrically 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 Inc., model 37-5.75-60). The pressure within the cell is measured with a Heise gauge (Dresser Ind., model CM-35790, 0-690 bar, accurate to within ±0.7 bar). The temperature of the cell is measured using a platinum resistance thermometer (Thermometrics Corp., Class A) and a digital multimeter (Yokogawa, model 7563, accurate to within ±0.005%). The system temperature is maintained to within ±0.1 °C and is measured to within ±0.2 °C with a thermometer placed in a thermowell on the surface of the cell. CO_2−organic acid solute mole fractions have an estimated accumulated error of less than ±1.0%. The solution in the cell is stirred by a magnetic stir bar, which is activated by an external magnet beneath the cell. The mixture inside the cell is 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.

To reach thermal equilibrium, the cell is maintained at the temperature of interest for a period of at least 30−40 min. At a fixed temperature, the mixture in the cell is compressed to a single phase, and the pressure is then slowly decreased until a second phase appeared. A bubble point is obtained if a small bubble appears in the cell, and a dew point is obtained if a fine mist appears in the cell. The 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. The formic acid (methanoic acid, CH_2O_2; CAS, 64-18-16; 96.0% purity), acetic acid (ethanoic acid, $C_2H_4O_2$; CAS, 64-19-7; 99.8% purity), butyric acid (butanoic acid, $C_4H_8O_2$; CAS, 107-92-6; >99 % purity), valeric acid (pentanoic acid, $C_5H_{10}O_2$; CAS, 109-52-4, >99 % purity), caproic acid (hexanoic acid, $C_6H_{12}O_2$; CAS, 142-62-1, >99.5 % purity), and caprylic acid (octanoic acid, $C_8H_{16}O_2$; CAS, 124-7-2, >99.5 % purity) used in this work were obtained from Aldrich Chemical Co. Carbon dioxide was obtained from Deasung Oxygen Co. (99.9% minimum purity, CP grade). Both components were used without further purification in the experiments.

Experimental Results

To verify the accuracy and reproducibility of the experimental apparatus, we measured phase behavior data for a binary carbon dioxide−acetic acid mixture with the same mole fractions as a mixture measured previously by Laugier el al.[23] at 40.0 and 60.0 °C.

As shown in Figure 2, the experimental data were in good agreement with those of Laugier et al.[23]

Bubble- and dew-point data for the six systems CO_2−formic acid, CO_2−acetic acid, CO_2−butyric acid, CO_2−valeric acid, CO_2−caproic acid, and CO_2−caprylic acid are reproduced to within ±0.3 bar at least twice for a given loading of the cell. Tables 1−6 present the data obtained in this work for the CO_2−formic acid, CO_2−acetic acid, CO_2−butyric acid, CO_2−valeric acid, CO_2−caproic acid, and CO_2−caprylic acid systems. The mole fractions are accurate to within ±0.002. The mole fractions for the solubility isotherms at 35−120 °C are arranged according to the value of at least two independent data points that have an accumulated error of less than 1.0%.

Table 1 shows the experimental pressure−composition (P−x) isotherms at 40.0, 60.0, 80.0, 100.0, and 120.0 °C and for the range of pressures from 33 to 264 bar for the CO_2−formic acid system. Three phases were not observed at any of the five temperatures. The P−x isotherms shown in Table 1 are consistent with those expected for a type-I system[10,11] where a maximum occurs in the critical mixture curve. Table 2 shows the experimental P−x isotherms at 40.0, 60.0, 80.0, 100.0, and 120.0 °C and for the range of pressures from 18 to 170 bar for the carbon dioxide−acetic acid system. Again, type-I phase behavior is observed.

Table 3 presents the phase behavior experimental data at 40.0, 60.0, 80.0, 100.0, and 120.0 °C and for pressures up to 190 bar for the CO_2−butyric acid mixture. As shown in Table 3, the mixture critical

Table 1. Pressure−Composition Data Obtained in This Study for the CO_2−Formic Acid System

mole fraction formic acid	P (bar)	transition[a]	mole fraction formic acid	P (bar)	transition[a]
T = 40.0 °C			T = 60.0 °C		
0.869	33.8	BP	0.869	44.1	BP
0.639	45.3	BP	0.639	82.0	BP
0.494	61.3	BP	0.494	108.2	BP
0.438	63.7	BP	0.438	116.3	BP
0.358	68.6	BP	0.358	132.4	BP
0.338	72.6	BP	0.338	133.8	BP
0.304	73.4	BP	0.304	134.9	BP
0.259	74.1	BP	0.259	136.8	BP
0.189	74.1	BP	0.189	136.8	CP
0.163	75.5	BP	0.163	127.7	DP
0.130	76.8	BP	0.130	117.4	DP
0.127	76.5	BP	0.127	118.5	DP
0.119	77.5	BP	0.119	117.0	DP
0.109	78.2	BP	0.109	115.3	DP
0.094	78.2	BP	0.094	111.0	DP
0.073	79.6	BP	0.073	106.8	DP
0.037	81.0	CP			
0.018	74.1	DP			
T = 80.0 °C			T = 100.0 °C		
0.869	56.2	BP	0.869	70.3	BP
0.639	126.1	BP	0.639	162.8	BP
0.494	165.5	BP	0.494	209.3	BP
0.438	165.3	BP	0.438	216.7	BP
0.358	183.7	BP	0.358	224.1	BP
0.338	184.8	BP	0.338	225.3	BP
0.304	188.2	BP	0.304	229.9	CP
0.259	188.8	CP	0.259	228.5	DP
0.189	176.8	DP	0.189	209.9	DP
0.163	159.2	DP	0.163	187.1	DP
0.130	154.4	DP	0.130	153.3	DP
0.127	144.0	DP			
0.119	144.0	DP			
0.109	143.8	DP			
0.094	131.5	DP			
T = 120.0 °C					
0.869	91.8	BP			
0.639	200.8	BP			
0.494	245.8	BP			
0.438	252.6	BP			
0.358	259.84	BP			
0.338	264.5	CP			
0.304	260.9	DP			
0.259	256.1	DP			
0.189	232.6	DP			

[a] BP is a bubble point, DP is a dew point, and CP is a critical point.

pressures are 88.4 bar (at 40.0 °C), 113.4 bar (at 60.0 °C), 143.9 bar (at 80 °C), 168.2 bar (at 100.0 °C), and 187.1 bar (at 120.0 °C). The carbon dioxide−butyric acid system is not observed to include three phases at any of the five temperatures.

Table 4 shows the bubble- and dew-point data at 40.0−120.0 °C and for pressures up to 205 bar for the CO_2−valeric acid system. As shown in Table 4, the pressure of each mixture critical point continually increases with increasing temperature. Therefore, the mixture critical curve for the CO_2−valeric acid system exhibits a pressure maximum in $P-T$ space.

Table 5 presents the phase behavior experimental data at 35.0−100.0 °C and for the range pressures from 25 to 205 bar for the CO_2−caproic acid mixture. In the same manner as above, the $P-x$ isotherms shown in Table 5 are consistent with those expected for a type I system. As shown in Table 5, the mixture critical pressures are 78.1 bar at 35.0 °C, 114.9 bar at 55.0 °C, ∼158.6 bar at 75 °C, and 198.6 bar at 100.0 °C. The solubility of carbon dioxide decreases as temperatures shift higher under constant pressure.

Table 2. Pressure−Composition Data Obtained in This Study for the CO_2−Acetic Acid System

mole fraction acetic acid	P (bar)	transition[a]	mole fraction acetic acid	P (bar)	transition[a]
T = 40.0 °C			T = 60.0 °C		
0.832	27.6	BP	0.832	33.7	BP
0.591	45.1	BP	0.591	60.3	BP
0.410	59.3	BP	0.410	80.6	BP
0.288	66.8	BP	0.288	91.0	BP
0.209	70.6	BP	0.209	96.1	BP
0.185	73.0	BP	0.185	99.2	BP
0.167	74.1	BP	0.167	100.3	BP
0.145	74.1	BP	0.145	101.9	BP
0.126	76.8	BP	0.126	102.0	BP
0.091	78.6	BP	0.091	104.5	BP
0.076	79.6	BP	0.076	104.4	BP
0.061	80.6	BP	0.061	105.8	CP
0.047	82.0	BP	0.047	102.3	DP
0.030	82.3	BP	0.030	93.4	DP
0.020	82.7	CP	0.020	81.3	DP
0.010	78.8	DP	0.010	−	
T = 80.0 °C			T = 100.0 °C		
0.832	39.6	BP	0.832	46.5	BP
0.591	78.2	BP	0.591	96.8	BP
0.410	104.4	BP	0.410	126.5	BP
0.288	118.2	BP	0.288	141.6	BP
0.209	123.0	BP	0.209	145.7	BP
0.185	124.4	BP	0.185	147.1	BP
0.167	125.4	BP	0.167	148.4	BP
0.145	127.1	BP	0.145	148.5	CP
0.126	127.7	CP	0.126	145.4	DP
0.091	127.0	DP	0.091	135.8	DP
0.076	125.7	DP	0.076	124.7	DP
0.061	118.6	DP	0.061	−	
0.047	103.7	DP	0.047	−	
T = 120.0 °C					
0.832	53.7	BP			
0.591	113.4	BP			
0.410	148.5	BP			
0.288	163.0	BP			
0.209	165.5	BP			
0.185	165.4	CP			
0.167	164.3	DP			
0.145	159.8	DP			
0.126	153.0	DP			

[a] BP is a bubble point, DP is a dew point, and CP is a critical point.

Table 6 presents the phase behavior experimental data at 35.0, 55.0, 75.0, and 100.0 °C and for pressures up to 240 bar for the CO_2−caprylic acid mixture. The solubility of caprylic acid increases as temperatures shift higher under constant pressure.

Modeling

The experimental data obtained in this work are modeled using both the Peng−Robinson and the statistical associating fluid theory (SAFT) equations of state. The two equations of state are briefly described here. The Peng−Robinson equation of state[21] 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 binary parameters that

Table 3. Pressure−Composition Data Obtained in This Study for the CO_2−Butyric Acid System

mole fraction butyric acid	P (bar)	transition[a]	mole fraction butyric acid	P (bar)	transition[a]
T = 40.0 °C			T = 60.0 °C		
0.750	30.3	BP	0.750	37.2	BP
0.480	56.2	BP	0.480	76.8	BP
0.322	68.5	BP	0.322	94.7	BP
0.201	75.8	BP	0.201	104.2	BP
0.169	76.8	BP	0.169	106.5	BP
0.154	78.6	BP	0.154	107.9	BP
0.137	81.0	BP	0.137	109.3	BP
0.098	82.2	BP	0.098	110.3	BP
0.077	83.0	BP	0.077	111.3	BP
0.058	84.4	BP	0.058	112.7	BP
0.040	86.5	BP	0.040	113.4	BP
0.021	87.2	BP	0.021	113.4	CP
0.017	88.2	BP	0.017	112.2	DP
0.009	88.4	BP	0.009	110.0	DP
0.003	88.4	CP	0.003	−	
0.001	87.4	DP	0.001	−	
T = 80.0 °C			T = 100.0 °C		
0.750	45.1	BP	0.750	53.7	BP
0.480	98.2	BP	0.480	116.8	BP
0.322	122.7	BP	0.322	148.2	BP
0.201	134.7	BP	0.201	160.8	BP
0.169	136.8	BP	0.169	162.3	BP
0.154	137.2	BP	0.154	163.7	BP
0.137	138.9	BP	0.137	164.7	BP
0.098	142.2	BP	0.098	166.9	BP
0.077	143.1	BP	0.077	168.2	CP
0.058	143.9	CP	0.058	167.7	DP
0.040	139.6	DP	0.040	164.7	DP
0.021	130.9	DP	0.021	145.4	DP
0.017	121.6	DP	0.017	113.4	DP
T = 120.0 °C					
0.750	63.1	BP			
0.480	137.5	BP			
0.322	172.0	BP			
0.201	185.5	BP			
0.169	187.6	BP			
0.154	188.3	BP			
0.137	189.6	BP			
0.098	189.5	DP			
0.077	188.2	DP			
0.058	187.1	DP			
0.040	182.3	DP			
0.021	96.1	DP			

[a] BP is a bubble point, DP is a dew point, and CP is a critical point.

Table 4. Pressure−Composition Data Obtained in This Study for the CO_2−Valeric Acid System

mole fraction valeric acid	P (bar)	transition[a]	mole fraction valeric acid	P (bar)	transition[a]
T = 40.0 °C			T = 60.0 °C		
0.788	25.8	BP	0.788	32.7	BP
0.600	50.6	BP	0.600	61.0	BP
0.373	67.9	BP	0.373	95.1	BP
0.218	77.9	BP	0.218	109.9	BP
0.193	78.6	BP	0.193	111.3	BP
0.188	80.3	BP	0.188	112.1	BP
0.152	81.0	BP	0.152	113.3	BP
0.133	81.7	BP	0.133	114.4	BP
0.117	82.7	BP	0.117	116.8	BP
0.097	83.4	BP	0.097	117.9	BP
0.086	83.7	BP	0.086	118.3	BP
0.068	83.7	BP	0.068	118.2	BP
0.052	84.4	BP	0.052	119.4	BP
0.021	85.1	BP	0.021	120.6	BP
0.018	85.6	BP	0.018	120.1	CP
0.011	85.6	BP			
0.005	85.4	BP			
0.003	84.8	DP			
T = 80.0 °C			T = 100.0 °C		
0.788	39.6	BP	0.788	47.9	BP
0.600	75.5	BP	0.600	90.6	BP
0.373	127.6	BP	0.373	156.2	BP
0.218	146.1	BP	0.218	175.4	BP
0.193	148.5	BP	0.193	177.0	BP
0.188	149.2	BP	0.188	178.8	BP
0.152	149.2	BP	0.152	179.1	BP
0.133	151.3	BP	0.133	180.2	BP
0.117	152.9	BP	0.117	181.8	BP
0.097	154.0	BP	0.097	180.5	BP
0.086	154.0	BP	0.086	180.7	CP
0.068	154.7	BP	0.068	178.2	DP
0.052	153.4	CP	0.052	171.0	DP
0.021	147.2	DP			
0.018	145.3	DP			
T = 120.0 °C					
0.788	53.4	BP			
0.600	104.4	BP			
0.373	179.6	BP			
0.218	200.9	BP			
0.193	203.4	BP			
0.188	204.4	BP			
0.152	205.0	BP			
0.133	206.0	BP			
0.117	207.9	BP			
0.097	206.1	DP (CP)			
0.086	202.8	DP			
0.068	192.3	DP			

[a] BP is a bubble point, DP is a dew point, and CP is a critical point.

are determined by fits of the pressure−composition data and a_{ii} and b_{ii} are the pure component parameters as defined by Peng and Robinson.[21] The expression for the fugacity coefficient using these mixing rules is given by McHugh and Krukonis[11] and is not reproduced here. Table 7 lists the pure component critical temperatures, critical pressures, and the acentric factors for carbon dioxide, formic acid, acetic acid, butyric acid, valeric acid, caproic acid, and caprylic acid that are used with the Peng−Robinson equation of state.

As an illustration, Figure 3 shows a comparison of the carbon dioxide−butyric acid experimental results with calculations obtained using P−R 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. However, if two mixture parameters, $k_{ij} = -0.015$ and $\eta_{ij} = -0.050$, are used, the fit of the experimental results is significantly better. We compared the experimental results with calculated $P-x$ isotherms at temperatures of 40.0, 60.0, 100.0, and 120.0 °C for the carbon dioxide−butyric acid system using the optimized values of k_{ij} and η_{ij} determined at 80 °C. For all of the other systems, these were applied to the calculation by the same method.

Figure 4 shows a comparison of the experimental and calculated data at temperatures of 35.0, 55.0, and 100 °C for the carbon dioxide−caproic acid mixture. These isotherms are calculated using the optimized values of $k_{ij} = 0.000$ and $\eta_{ij} = -0.035$ determined at 75 °C. A good fit of the data is obtained with the P−R equation using one adjustable mixture parameter for the carbon dioxide−caproic acid system.

Figure 5 shows the predicted $P-x$ isotherms for the carbon dioxide−caprylic acid mixture at 35.0, 55.0, 75.0, and 100 °C using the P−R equation of state with k_{ij} equal to 0.025 and η_{ij} equal to −0.015. These optimized values of the mixture parameters are obtained by fitting the 75.0 °C isotherm and minimizing the error between the experimental and calculated results. As for the

Table 5. Pressure−Composition Data Obtained in This Study for the CO_2−Caproic Acid System

mole fraction caproic acid	P (bar)	transition[a]	mole fraction caproic acid	P (bar)	transition[a]
T = 35.0 °C			T = 55.0 °C		
0.751	25.3	BP	0.751	32.7	BP
0.618	37.2	BP	0.618	48.2	BP
0.493	47.5	BP	0.493	68.9	BP
0.386	58.9	BP	0.386	80.3	BP
0.279	66.2	BP	0.279	96.3	BP
0.223	69.1	BP	0.223	100.3	BP
0.173	71.2	BP	0.173	105.8	BP
0.137	73.7	BP	0.137	109.9	BP
0.101	73.8	BP	0.101	112.8	BP
0.093	74.2	BP	0.093	112.5	BP
0.077	74.9	BP	0.077	113.4	BP
0.076	75.1	BP	0.076	113.7	BP
0.058	75.1	BP	0.058	113.9	BP
0.055	75.8	BP	0.055	113.1	BP
0.054	76.3	BP	0.054	114.1	BP
0.039	75.3	BP	0.039	114.9	BP
0.023	78.0	BP	0.023	113.0	DP
0.012	79.1	BP	0.012	111.1	DP
0.006	78.1	CP	0.006	106.8	DP
0.003	78.0	DP	0.003	101.0	DP
T = 75.0 °C			T = 100.0 °C		
0.751	40.5	BP	0.751	51.5	BP
0.618	61.2	BP	0.618	77.9	BP
0.493	80.5	BP	0.493	101.1	BP
0.386	104.7	BP	0.386	134.7	BP
0.279	129.1	BP	0.279	167.1	BP
0.223	135.8	BP	0.223	178.2	BP
0.173	145.1	BP	0.173	186.1	BP
0.137	150.2	BP	0.137	193.7	BP
0.101	152.0	BP	0.101	199.3	BP
0.093	152.3	BP	0.093	200.9	BP
0.077	154.0	BP	0.077	203.2	BP
0.076	154.4	BP	0.076	−	BP
0.058	158.7	BP	0.058	204.8	BP
0.055	−		0.055	−	BP
0.054	157.0	BP	0.054	203.3	BP
0.039	158.6	DP	0.039	198.6	CP
0.023	148.9	DP	0.023	188.5	DP
0.012	138.2	DP	0.012	150.1	DP
0.006	122.5	DP	0.006	106.8	DP
0.003	−		0.003	101.0	DP

[a] BP is a bubble point, DP is a dew point, and CP is a critical point.

carbon dioxide−butyric acid system previously, both parameters are necessary to obtain a reasonable fit of the 75.0 °C isotherm. The remaining isotherms are calculated using the same values of the two mixture parameters.

Figure 6 shows the mixture critical curve for the carbon dioxide−valeric acid system predicted by the SAFT and P−R equations of state. The calculated mixture critical curve is type-I, in agreement with the experimental observations. As shown in Figure 6, the solid lines represent the vapor pressure for pure carbon dioxide[2] and valeric acid.[24] The solid circles represent the critical point for pure carbon dioxide and valeric acid.[2] The upper part of the dashed line is a single phase (fluid); the lower part is two phases (vapor−liquid). The open circles are the mixture critical points determined from isotherms measured in this experiment. The dashed lines represent the calculated value obtained using the SAFT and P−R equations of state. Both mixture parameters are then obtained for the case of the SAFT equation, with k_{ij} equal to −0.060 and η_{ij} equal to 0.050, and for the case of the P−R equation, with k_{ij} equal to 0.005 and η_{ij} equal to −0.045. The process of obtaining optimum mixture parameters is identical with the method in the carbon dioxide−butyric acid system. The SAFT equation of state will be discussed later.

Table 6. Pressure−Composition Data Obtained in This Study for the CO_2−Caprylic Acid System

mole fraction caprylic acid	P (bar)	transition[a]	mole fraction caprylic acid	P (bar)	transition[a]
T = 35.0 °C			T = 55.0 °C		
0.759	23.3	BP	0.759	29.5	BP
0.641	34.1	BP	0.641	43.6	BP
0.495	47.2	BP	0.495	63.7	BP
0.361	62.2	BP	0.361	86.0	BP
0.237	73.0	BP	0.237	107.9	BP
0.191	75.5	BP	0.191	115.9	BP
0.141	75.8	BP	0.141	125.1	BP
0.135	76.8	BP	0.135	125.6	BP
0.113	77.9	BP	0.113	128.7	BP
0.085	77.5	BP	0.085	134.7	BP
0.071	78.0	BP	0.071	135.9	BP
0.058	78.0	BP	0.058	136.8	BP
0.041	78.0	BP	0.041	136.7	CP
0.035	78.9	BP	0.035	133.6	DP
0.029	77.7	BP	0.029	132.0	DP
0.025	78.4	BP	0.025	−	
0.020	78.4	BP	0.020	129.7	DP
0.014	78.4	BP	0.014	126.5	DP
0.006	79.7	CP	0.006	118.4	DP
0.002	77.2	DP	0.002	108.5	DP
0.001	76.7	DP	0.001	−	
T = 75.0 °C			T = 100.0 °C		
0.759	37.4	BP	0.759	45.2	BP
0.641	54.4	BP	0.641	66.1	BP
0.495	80.1	BP	0.495	100.6	BP
0.361	112.0	BP	0.361	142.7	BP
0.237	147.3	BP	0.237	189.7	BP
0.191	158.2	BP	0.191	203.3	BP
0.141	171.9	BP	0.141	219.5	BP
0.135	173.2	BP	0.135	219.6	BP
0.113	175.7	BP	0.113	225.9	BP
0.085	179.2	BP	0.085	237.7	BP
0.071	182.9	BP	0.071	237.9	BP
0.058	185.4	CP	0.058	240.1	DP
0.041	181.8	DP	0.041	−	
0.035	180.7	DP	0.035	235.4	DP
0.029	175.9	DP	0.029	230.5	DP
0.025	−		0.025	−	
0.020	−		0.020	−	
0.014	167.8	DP	0.014	197.5	DP
0.006	150.9	DP	0.006	166.6	DP
0.002	122.3	DP	0.002	−	
0.001	−	DP	0.001		

[a] BP is a bubble point, DP is a dew point, and CP is a critical point.

Table 7. Pure Component Parameters[2,24] Used with the Peng−Robinson Equation of State

component	T_c (°C)	P_c (bar)	acentric factor
carbon dioxide	31.1	73.9	0.225
formic acid	306.9	73.9	0.4730
acetic acid	319.6	57.8	0.4624
butyric acid	354.9	44.2	0.6041
valeric acid	377.9	38.1	0.6269
caproic acid	393.9	33.5	0.6701
caprylic acid	418.9	26.9	0.7792

The SAFT equation of state, which is based on thermodynamic perturbation theory, explicitly accounts for molecular size, association energy, and mean-field attractive energy. A molecule is represented as a covalently bonded chain of segments. The molar, residual Helmholtz free energy of a mixture is determined from a mean-field attractive perturbation term, added to terms accounting for the connectiveness of the hard

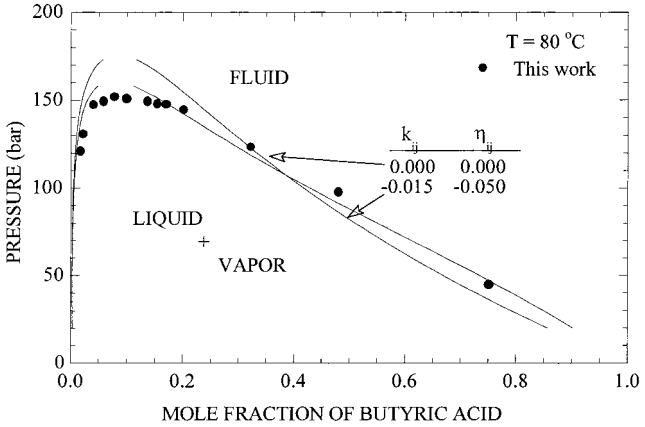

Figure 3. Comparison of the best fit of the Peng−Robinson equation of state for the CO_2−butyric acid system at 80 °C.

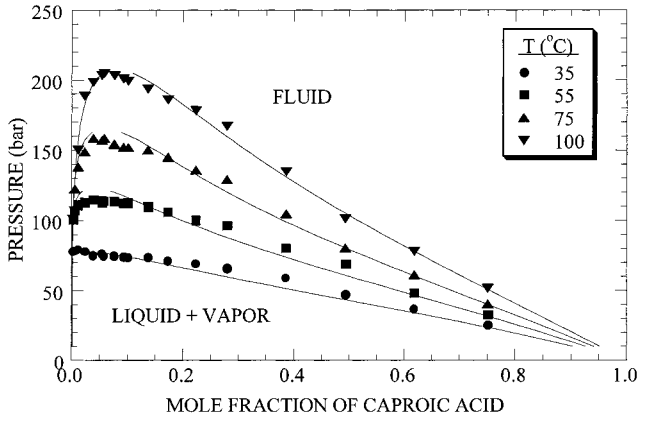

Figure 4. Comparison of the experimental data (symbols) for the CO_2−caproic acid system with calculations (solid lines) obtained with the Peng−Robinson equation of state with k_{ij} equal to 0.000 and η_{ij} equal to −0.035.

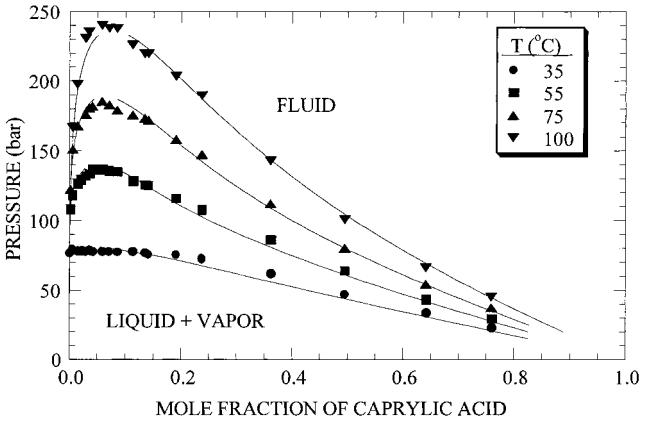

Figure 5. Comparison of the experimental data (symbols) for the CO_2−caprylic acid system with calculations (solid lines) obtained with the Peng−Robinson equation of state with k_{ij} equal to 0.025 and η_{ij} equal to −0.015.

segments in the chain, the hard-sphere repulsion of segments, and the energy of site−site specific interactions of association of the molecules in solution.[15−20] A detailed description of the mathematical form for these terms can be found elsewhere.[17,18] With SAFT, it is possible to account explicitly for hydrogen bonding and complexation between molecules in a mixture.

For each pure component, there are potentially five parameters in the SAFT equation of state: v^{oo}, the temperature-independent volume of a segment; u^o/k, the temperature-independent energy of attraction between

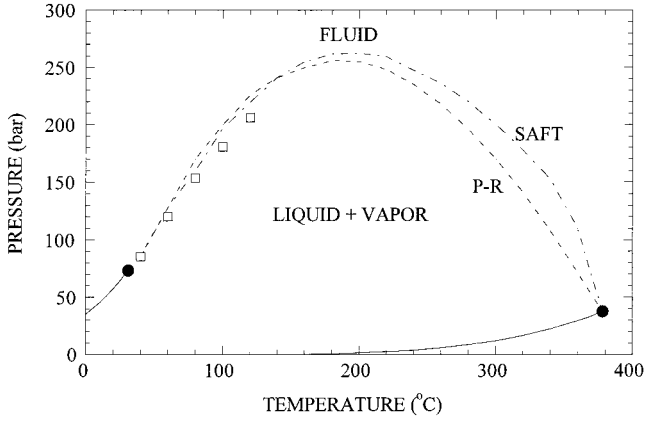

Figure 6. Pressure−temperature diagram for the CO_2−valeric acid system. The solid lines and solid circles represent the vapor−liquid lines and the critical points for pure CO_2 and valeric acid.[2] The open circles are critical points determined from isotherms measured in this study. The dashed lines represent calculation obtained using the SAFT equation of state with k_{ij} equal to −0.060 and η_{ij} equal to 0.050 and the Peng−Robinson equation of state with k_{ij} equal to 0.005 and η_{ij} equal to −0.045.

Table 8. Pure Components Parameters Used with the SAFT Equation of State[a]

component	v^{oo} (mL/mol)	m	u^o/k (K)	ϵ/k (K)	v (mL/mol)
carbon dioxide	13.578	1.417	216.08	0	0
formic acid	15.0	1.341	333.28	7522	0.03447
acetic acid	14.5	2.132	290.73	3941	0.80507
butyric acid	13.0	3.800	268.93	4155	0.06802
valeric acid	12.0	4.719	248.63	4322	0.08660
caproic acid	12.0	5.482	243.39	4683	0.03991
caprylic acid	12.0	6.628	240.41	4745	0.04124

[a] The carbon dioxide parameters were obtained from Huang and Radosz,[17] and the methanoic acid, ethanoic acid, butanoic acid, pentanoic acid, hexanoic acid, and octanoic acid parameters, obtained by Huang and Radosz,[17] are substituted for formic acid, acetic acid, butyric acid, valeric acid, caproic acid, and caprylic acid.

two segments; m, the number of segments in a molecule; ϵ/k, the energy of association between sites on a molecule, and v, the volume of site−site association. For the systems considered here, ϵ/k and v are nonzero only for hydrogen-bonding molecules. Table 8 lists the pure component values for carbon dioxide, formic acid, acetic acid, butyric acid, valeric acid, caproic acid, and caprylic acid used in the calculation presented here.

The extension of the SAFT equation of state to multicomponent mixtures is straightforward, with mixing rules required only for the dispersion term in the equation of state. Detailed derivations of the a^{chain} and a^{assoc} terms for mixtures have been given by Huang and Radosz[17,18] and are not reproduced here. The mixing rule for the temperature-dependent segment energy is

$$v^o = \sum_i \sum_j x_i x_j m_i m_j v_{ij}^o$$

where

$$v_{ij}^o = \frac{1}{8}[(v_i^o)^{1/3} - (v_j^o)^{1/3}]^3$$

and

$$\frac{u}{kT} = \frac{\sum_i \sum_j x_i x_j m_i m_j \left[\frac{u_{ij}}{kT}\right] v_{ij}^{o}}{\sum_i \sum_j x_i x_j m_i m_j v_{ij}^{o}}$$

where

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

and m is the average segment size for mixtures. This quantity is defined as

$$m = \sum_i \sum_j x_i x_j m_{ij}$$

where

$$m_{ij} = \frac{1}{2}(m_i + m_j)(1 - \eta_{ij})$$

Figure 7 shows a comparison of the experimental and calculated $P-x$ isotherms at temperatures of 40.0, 60.0, 80.0, 100.0, and 120.0 °C for the carbon dioxide−acetic acid system. These isotherms are calculated using the optimized values of k_{ij} equal to −0.050 and η_{ij} equal to 0.065 determined at 80 °C in the same manner as above. With two adjustable parameters, the critical pressure predicted at 80 °C is ∼15 bar higher than that of the experimental data. The predicted critical pressures are ∼20 bar higher at a temperature of 100 °C. The critical pressures predicted by the SAFT equation of state are reasonably accurate for the 40.0 and 60.0 °C data.

Figure 8 shows a comparison of the experimental and calculated values obtained with the SAFT equation of state with k_{ij} equal to −0.075 and η_{ij} equal to 0.005 for the carbon dioxide−caprylic acid system. These $P-x$ isotherms are calculated using the optimized values obtained at 75 °C. Good agreements are obtained between experimental and calculated results with the SAFT equation using two adjustable parameters for the carbon dioxide−caprylic acid system.

Figure 9 shows the mixture critical curve for the carbon dioxide−caproic acid system predicted by the SAFT and P−R equations of state. The mixture critical curves calculated by the two mixture parameters are type-I, and three phases (LLV) are not observed. As shown Figure 9, the dashed lines represent the results obtained using the SAFT equation of state with $k_{ij} = -0.075$ and $\eta_{ij} = 0.030$ and the Peng−Robinson equation with $k_{ij} = 0.000$ and $\eta_{ij} = -0.035$. The agreement between the calculated and experimental mixture critical curves is reasonably good using two adjustable parameters with the SAFT equation of state and one adjustable parameter with the P−R equation of state.

Conclusions

High-pressure phase behavior data of carbon dioxide−acid systems are obtained at 35.0−120.0 °C and for a pressure range of 23−250 bar for binary mixtures. The carbon dioxide−formic acid, carbon dioxide−acetic acid, carbon dioxide−butyric acid, carbon dioxide−valeric acid, carbon dioxide−caproic acid, and carbon dioxide−caprylic acid systems exhibit type-I phase behavior, which is characterized by an uninterrupted critical mixture curve. Also, three phases were not observed for any of the systems studied. The SAFT equation of state is capable of accurately predicting the phase behavior for the six polar systems studied using two temperature-independent mixture parameters. The P−R equation of state models the pressure−composition isotherms for the six carbon dioxide−acid systems reasonably well

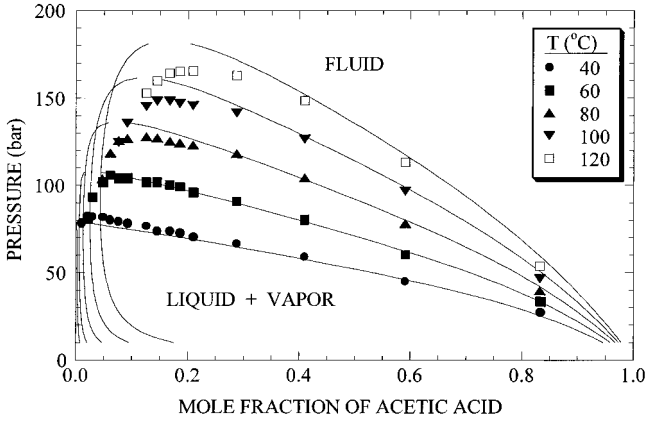

Figure 7. Comparison of the experimental data (symbols) for the CO_2−acetic acid system with calculations (solid lines) obtained with the SAFT equation of state with k_{ij} equal to −0.050 and η_{ij} equal to 0.065.

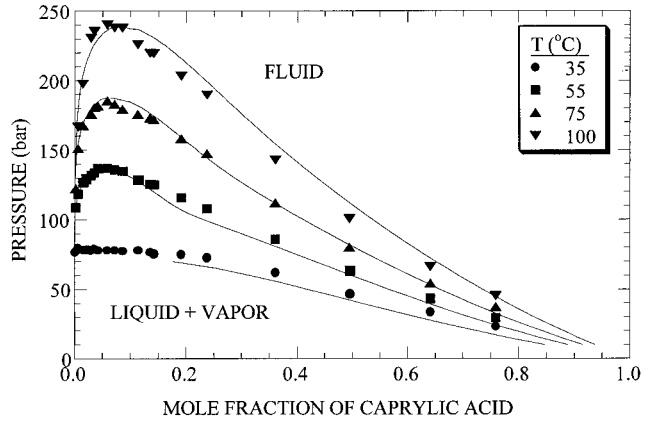

Figure 8. Comparison of the experimental data (symbols) for the CO_2−caprylic acid system with calculations (solid lines) obtained with the SAFT equation of state with k_{ij} equal to −0.075 and η_{ij} equal to 0.005.

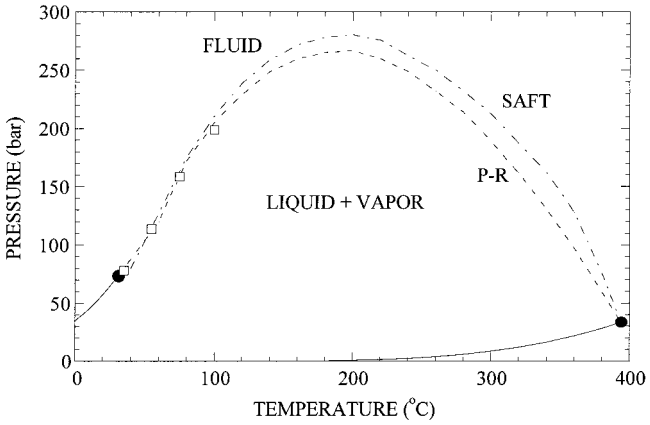

Figure 9. Pressure−temperature diagram for the CO_2−caproic acid system. The solid lines and solid circles represent the vapor−liquid lines and the critical points for pure CO_2 and caproic acid.[24] The open circles are critical points determined from isotherms measured in this study. The dashed lines represent calculations obtained using the SAFT equation of state with k_{ij} equal to −0.075 and η_{ij} equal to 0.030 and the Peng−Robinson equation of state with k_{ij} equal to 0.000 and η_{ij} equal to −0.035.

using one or two temperature-independent mixture parameters. Also, the P−R equation provided a good model for the carbon dioxide−acid systems because the equation does not explicitly account for dimerization of the acid molecules.

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