J. Chem. Eng. Data **2005,** *50,* 385−389

Phase Behavior of the Binary Mixture of Cyclohexyl Acrylate and Cyclohexyl Methacrylate in Supercritical Carbon Dioxide

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Pressure−composition isotherms are obtained for binary mixtures of carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems at (313.2, 333.2, 353.2, 373.2, and 393.2) K and pressures up to 20.6 MPa. The solubility of cyclohexyl acrylate and cyclohexyl methacrylate for the carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems increases as the temperature increases at constant pressure. The carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate 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 + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate 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 two adjustable interaction parameters for each system.

Introduction

Phase behavior information for mixtures containing supercritical fluids is required for practical uses such as plant design and operation of separation process in the petroleum, natural gas, and related fields. The bubble-, critical-, and dew-point behavior of mixtures containing supercritical carbon dioxide is important for industrial application, supercritical fluid extraction, and process design. Recently, solubility experiments have been carried out for mixtures containing supercritical carbon dioxide to examine bubble-, dew-, and critical-point behavior.[1−4] Advances in supercritical fluid extraction development are often dependent on new thermodynamic data on vapor−liquid, liquid−liquid−vapor, and liquid−liquid equilibria.

Phase behavior data with the carbon dioxide + alkyl (meth)acrylate system were reported by McHugh et al.[5,6,8] and Byun.[7] These miscibility data for the supercritical carbon dioxide + monomer system have important conditions needed for polymer synthesis and polymerization processes. McHugh et al.[5] used a static apparatus and reported two-phase separation for the carbon dioxide + butyl acrylate system. Byun and McHugh[6] used a static apparatus and presented the liquid−vapor equilibria curves for carbon dioxide + butyl methacrylate and carbon dioxide + ethyl methacrylate mixtures. Byun[7] reported the solubility curve for the carbon dioxide + methyl acrylate and carbon dioxide + ethyl acrylate systems. Lora and McHugh[8] presented the phase behavior for a carbon dioxide + methyl methacrylate solution.

The first part of this work is the high-pressure experimental data for carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate mixtures by investigating mixtures of carbon dioxide with two components. Also, pressure−temperature (*P*−*T*) diagrams of the mixture critical curve are presented for the carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems in the vicinity of the critical point of pure carbon dioxide. Also, to provide phase behavior information for high-pressure process design purposes the measured bubble-, critical-, and dew-point data of binary systems are modeled using the Peng−Robinson equation of state. These results can provide valuable information for the rational design and operation of the supercritical region.

Experimental Section

Apparatus and Procedure. Phase behavior data are obtained with a high-pressure, variable-volume cell described in detail elsewhere.[9,10] The main component of the experimental apparatus is a high pressure, variable-volume cell that is constructed of high-nickel-content austenitic steel (Nitronic 50; 5.7-cm o.d., 1.59-cm i.d., and working volume of ∼28 cm^3) and is capable of operating up to a pressure of 100 MPa. A 1.9-cm-thick sapphire window is fitted into the front part of the cell to allow for phase observation. Typically, a quantity of liquid cyclohexyl acrylate or cyclohexyl methacrylate was loaded into the cell to within an accuracy of ±0.002 g by using a syringe after the empty cell was purged several times with carbon dioxide to remove air. Carbon dioxide was then added to the cell to within an accuracy of ±0.004 g by using a high-pressure bomb.

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) The pressure of the mixture was measured with a Heise gauge (Dresser Ind., model CM-53920, 0 to 34.0 MPa) accurate to ±0.03 MPa. The temperature of the cell, which was typically maintained to within ±0.2 K, was measured using a platinum resistance thermometer (Thermometrics Corp., Class A) and a digital multimeter (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 (Olympus

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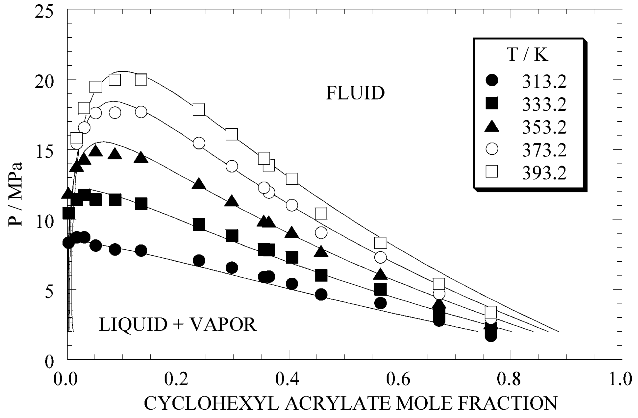

Figure 1. Comparison of the experimental data (symbols) for the carbon dioxide + cyclohexyl acrylate system with calculated data (solid lines) obtained with the Peng−Robinson equation of state with $k_{ij} = 0.031$ and $\eta_{ij} = 0.006$.

Optical Co., model ILK-5) 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 40 min for the cell to reach phase equilibrium. The pressure was then slowly decreased until the bubble, dew, and critical points appears. A bubble-point pressure was obtained when small bubbles appear in the cell, and a dew point was obtained if a fine mist appears in the cell. In either case, the composition of the predominant phase present in the cell was equal to the overall solution composition because the mass present in the second phase was considered to be negligible. The mixture critical point is defined as the pressure and temperature at which critical opalescence is observed for a slight change in either pressure or temperature, and also at the mixture critical point, a slight change in temperature (<0.2 K) and pressure (<0.03 MPa) causes the single supercritical fluid phase to separate into a 50 vol % liquid phase and 50 vol % vapor phase.

Materials. Carbon dioxide was obtained from Daesung Oxygen Co.(99.9% minimum purity) and was used as received. The cyclohexyl acrylate (minimum 85 mass % purity) and cyclohexyl methacrylate (~98.0 mass % purity) used in this work were obtained from Polysciences Inc. Both components were used without further purification in the experiments.

Experimental Results and Discussion

Bubble-, critical-, and dew-point curves for both the carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems are measured and reproduced at least twice to within ±0.03 MPa and 0.2 K for a given loading of the cell. The mole fractions are accurate to within ±0.002. The carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate mixtures for the solubility isotherms at (313.2 to 393.2) K 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 1 and Table 1 show the experimental pressure−composition ($P-x$) isotherms at (313.2, 333.2, 353.2, 373.2, and 393.2) K and the range of pressures of (1.7 to 20.0) MPa for the carbon dioxide + cyclohexyl acrylate system. As shown in Figure 1, 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.[11,12]

Figure 2 and Table 2 show the experimental phase behavior of $P-x$ isotherms at (313.2, 333.2, 353.2, 373.2, and 393.2) K for the carbon dioxide + cyclohexyl methacrylate system. The $P-x$ isotherms shown in Figure 2 are consistent with the characteristics expected for a type-I system where a maximum occurs in the critical mixture curve at (313.2, 333.2, 353.2, 373.2, and 393.2) K. As shown in Figure 2, the solubility of carbon dioxide for the carbon dioxide + cyclohexyl methacrylate system decreases as the temperature increases at constant pressure. Also, the mixture critical points (8.64 MPa at 313.2 K; 12.21 MPa at 333.2 K; 15.45 MPa at 353.2 K; 18.21 MPa at 373.2K; and 20.59 MPa at 393.2K) for the carbon dioxide + cyclohexyl methacrylate system increase as the temperature increases.

Figure 3 presents the experimentally determined pressure−temperature ($P-T$) trace of the mixture critical curve in the vicinity of the critical point of carbon dioxide.[13,14] The mixture critical curves shown by the dashed lines in Figure 3 represent the calculation using the Peng−Robinson equation of state, which is discussed later. The calculated mixture critical curve of the carbon dioxide + cyclohexyl acrylate system exhibits type-I behavior, in agreement with the experimental observation.

The experimental data obtained in this work were correlated with the Peng−Robinson equation of state using van der Waals one-fluid mixing rules including two binary interaction parameters. This equation of state is briefly described here. The Peng−Robinson equation of state[15] is used with the mixing rules given by

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \tag{1}$$

$$a(T) = a(T_c)\,\alpha(T_r,\omega) \tag{2}$$

$$a(T_c) = 0.45724\frac{R^2T_c^2}{P_c} \tag{3}$$

$$\alpha = [1 + m(1 - \sqrt{T_r})^2] \tag{4}$$

$$m = 0.37464 + 1.5422\omega - 0.26992\omega^2 \tag{5}$$

$$b = 0.07780\left(\frac{RT_c}{P_c}\right) \tag{6}$$

$$a_{mix} = \sum_i\sum_j x_i x_j a_{ij} \tag{7}$$

$$a_{ij} = (a_{ii}a_{jj})^{1/2}(1 - k_{ij}) \tag{8}$$

$$b_{mix} = \sum_i\sum_j x_i x_j b_{ij} \tag{9}$$

$$b_{ij} = 0.5[(b_{ii} + b_{jj})](1 - \eta_{ij}) \tag{10}$$

These two binary interaction parameters, k_{ij} and η_{ij}, were determined by regression experimental data with the Peng−Robinson equation of state. The expression for the fugacity coefficient using these mixing rules is given by Peng and Robinson[15] and is not reproduced here. The

Table 1. Experimental Data for the Carbon Dioxide + Cyclohexyl Acrylate System Measured in This Study

mole fraction of the cyclohexyl acrylate	P/MPa	transition	mole fraction of the cyclohexyl acrylate	P/MPa	transition	mole fraction of the cyclohexyl acrylate	P/MPa	transition
T = 313.2 K								
0.002	8.35	DP	0.133	7.78	BP	0.405	5.41	BP
0.017	8.74	CP	0.237	7.07	BP	0.458	4.66	BP
0.030	8.72	BP	0.297	6.55	BP	0.564	4.03	BP
0.051	8.14	BP	0.355	5.89	BP	0.670	2.78	BP
0.086	7.86	BP	0.363	5.93	BP	0.764	1.69	BP
T = 333.2 K								
0.002	10.47	DP	0.133	11.13	BP	0.405	7.31	BP
0.017	11.43	DP	0.237	9.64	BP	0.458	6.02	BP
0.030	11.76	CP	0.297	8.85	BP	0.564	5.03	BP
0.051	11.43	BP	0.355	7.86	BP	0.670	3.33	BP
0.086	11.41	BP	0.363	7.85	BP	0.764	2.26	BP
T = 353.2 K								
0.002	11.90	DP	0.133	14.47	BP	0.405	9.10	BP
0.017	13.83	DP	0.237	12.59	BP	0.458	7.74	BP
0.030	14.35	DP	0.297	11.35	BP	0.564	6.14	BP
0.051	14.93	CP	0.355	9.91	BP	0.670	4.05	BP
0.086	14.72	BP	0.363	9.86	BP	0.764	2.59	BP
T = 373.2 K								
0.017	15.43	DP	0.237	15.47	BP	0.458	9.07	BP
0.030	16.55	DP	0.297	13.81	BP	0.564	7.29	BP
0.051	17.50	DP	0.355	12.28	BP	0.670	4.69	BP
0.086	17.64	DP	0.363	11.95	BP	0.764	2.95	BP
0.133	17.67	BP	0.405	11.02	BP			
T = 393.2 K								
0.017	15.79	DP	0.237	17.85	BP	0.458	10.41	BP
0.030	17.93	DP	0.297	16.09	BP	0.564	8.31	BP
0.051	19.46	DP	0.355	14.35	BP	0.670	5.40	BP
0.086	19.95	DP	0.363	13.85	BP	0.764	3.35	BP
0.133	19.98	BP	0.405	12.90	BP			

objection function (obf) and root-mean-squared relative deviation (rmsd) percent of this calculation are defined by

$$\text{obf} = \sum_i^N \left(\frac{P_{\text{exptl}} - P_{\text{calcd}}}{P_{\text{exptl}}}\right)^2 \text{ at given } T \text{ and } x_i \quad (11)$$

$$\text{rmsd}(\%) = \sqrt{\frac{\text{obf}}{N_{\text{D}}}} \times 100 \quad (12)$$

N_{D} in eq 12 means the number of data points. We used Marquardt[16] to optimize the objection function. All isotherms were included for the calculation.

Table 3 lists the pure-component critical temperatures, critical pressures, and acentric factors for carbon dioxide, cyclohexyl acrylate, and cyclohexyl methacrylate that are used with the Peng−Robinson equation of state in this work.[13,14] The boiling points of cyclohexyl acrylate and cyclohexyl methacrylate were obtained from Polysciences Inc. The properties of cyclohexyl acrylate and cyclohexyl methacrylate were calculated by the Joback group-contribution method.[13] Also, the vapor pressures were calculated by the Lee−Kesler method.[13]

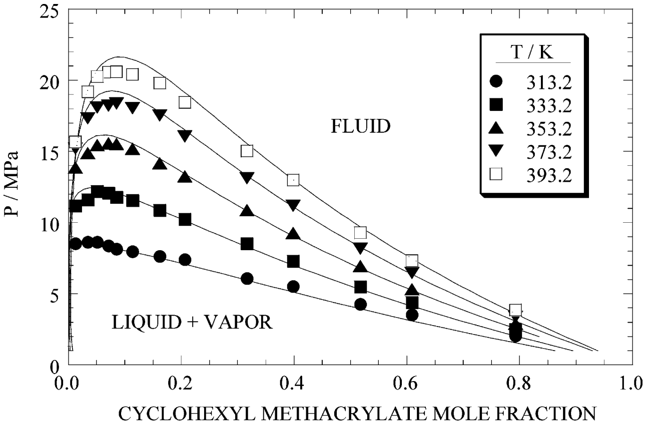

Figure 2. Comparison of the experimental data (symbols) for the carbon dioxide + cyclohexyl methacrylate system with calculated data (solid lines) obtained with the Peng−Robinson equation of state with k_{ij} = 0.033 and η_{ij} = −0.013.

Figure 4 shows a comparison of the experimental results of carbon dioxide−cyclohexyl acrylate with calculated value obtained using the Peng−Robinson equation at a temperature of 353.2 K. The binary interaction parameters of the Peng−Robinson equation of state are fit by the experimental data at 353.2 K. The values of the optimized parameters (bubble-point data = 11, rmsd = 4.15%) of the Peng−Robinson equation of state for the carbon dioxide + cyclohexyl acrylate system are k_{ij} = 0.031 and η_{ij} = 0.006.

We compared the experimental results with calculated $P-x$ isotherms at temperatures of (313.2, 333.2, 373.2, and 393.2) K for the carbon dioxide + cyclohexyl acrylate system using the optimized values of k_{ij} and η_{ij} determined at 353.2 K. As shown in Figure 1, a good fit of the data is obtained with the Peng−Robinson equation using adjustable mixture parameters for the carbon dioxide + cyclohexyl acrylate system. The rmsd at five temperatures (313.2, 333.2, 353.2, 373.2 and 393.2) K for the carbon dioxide + cyclohexyl acrylate system was 5.93% of the 56 bubble points.

Figure 2 shows a comparison of experimental with calculated $P-x$ isotherms at temperature of (313.2, 333.2, 353.2, 373.2, and 393.2) K for the carbon dioxide + cyclohexyl methacrylate system. These isotherms are calculated using the optimized values (bubble-point data = 10, rmsd = 1.82%) of k_{ij} = 0.033 and η_{ij} = −0.013 determined at 353.2 K in the same way as above. The rmsd at five temperatures for the carbon dioxide + cyclohexyl methacrylate system was 9.29% of the 49 bubble points.

Table 2. Experimental Data for the Carbon Dioxide + Cyclohexyl Methacrylate System Measured in This Study

mole fraction of the cyclohexyl methacrylate	P/MPa	transition	mole fraction of the cyclohexyl methacrylate	P/MPa	transition	mole fraction of the cyclohexyl methacrylate	P/MPa	transition
$T = 313.2$ K								
0.012	8.52	DP	0.114	7.97	BP	0.399	5.52	BP
0.034	8.64	CP	0.162	7.62	BP	0.518	4.28	BP
0.050	8.62	BP	0.206	7.40	BP	0.609	3.52	BP
0.071	7.97	BP	0.317	6.07	BP	0.793	2.03	BP
0.085	8.14	BP						
$T = 333.2$ K								
0.012	11.17	DP	0.114	11.57	BP	0.399	7.31	BP
0.034	11.62	DP	0.162	10.86	BP	0.518	5.50	BP
0.050	12.21	CP	0.206	10.24	BP	0.609	4.40	BP
0.071	11.78	BP	0.317	8.52	BP	0.793	2.52	BP
0.085	11.79	BP						
$T = 353.2$ K								
0.012	13.86	DP	0.114	15.19	BP	0.399	9.26	BP
0.034	14.88	DP	0.162	14.17	BP	0.518	6.93	BP
0.050	15.45	CP	0.206	13.24	BP	0.609	5.31	BP
0.071	15.28	BP	0.317	10.88	BP	0.793	2.90	BP
0.085	15.31	BP						
$T = 373.2$ K								
0.012	15.21	DP	0.114	18.05	BP	0.399	11.17	BP
0.034	17.33	DP	0.162	17.53	BP	0.518	8.17	BP
0.050	18.10	DP	0.206	16.05	BP	0.609	6.47	BP
0.071	18.21	CP	0.317	13.12	BP	0.793	3.36	BP
0.085	18.07	BP						
$T = 393.2$ K								
0.012	15.66	DP	0.114	20.41	BP	0.399	12.98	BP
0.034	19.19	DP	0.162	19.79	BP	0.518	9.29	BP
0.050	20.26	DP	0.206	18.45	BP	0.609	7.33	BP
0.071	20.59	CP	0.317	15.03	BP	0.793	3.85	BP
0.085	20.59	BP						

Figure 3 shows the mixture critical curve for the carbon dioxide + cyclohexyl acrylate system predicted by the Peng–Robinson equation of state. The calculated mixture critical curve is type-I, in good agreement with experimental observations at five temperatures. In Figure 3, the solid lines represent the vapor pressure for pure carbon dioxide [13,14] and cyclohexyl acrylate.[13] The solid circles represent the critical point for pure carbon dioxide and cyclohexyl acrylate. The upper part of the dashed line is single-phase, and the lower part is vapor–liquid. Open squares are used for the mixture critical points determined from isotherms measured in this experiment. The dashed lines represent the calculated value obtained using the Peng–Robinson equation of state.

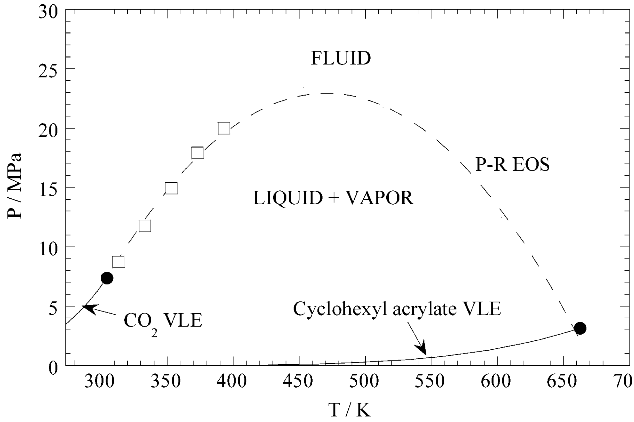

Figure 3. Pressure–temperature diagram for the carbon dioxide + cyclohexyl acrylate system. The solid line and solid circles represent the vapor–liquid lines and the critical points, respectively, for pure carbon dioxide and cyclohexyl acrylate. The open squares represent mixture critical points determined from isotherms measured in this study. The dashed lines represent the calculation using the Peng–Robinson equation of state with $k_{ij} = 0.031$ and $\eta_{ij} = 0.006$.

Table 3. Pure-Component Parameters for the Peng–Robinson Equation of State[13,14]

compound	M_w	T_c/K	P_c/MPa	ω
carbon dioxide	44.01	304.3	7.39	0.225
cyclohexyl acrylate	154.21	662.46	3.17	0.4226
cyclohexyl methacrylate	168.24	685.79	2.71	0.4641

Figure 5 shows the mixture critical curve for the carbon dioxide + cyclohexyl methacrylate system predicted by the Peng–Robinson equation of state. The mixture critical curves calculated by the two mixture parameters are type-I. In Figure 5, the solid lines for the vapor pressure for pure cyclohexyl methacrylate were obtained by the Lee–Kesler method.[13] The dashed lines represent the calculation using the Peng–Robinson equation of state, with $k_{ij} = 0.033$ and $\eta_{ij} = -0.013$. The agreement between cal-

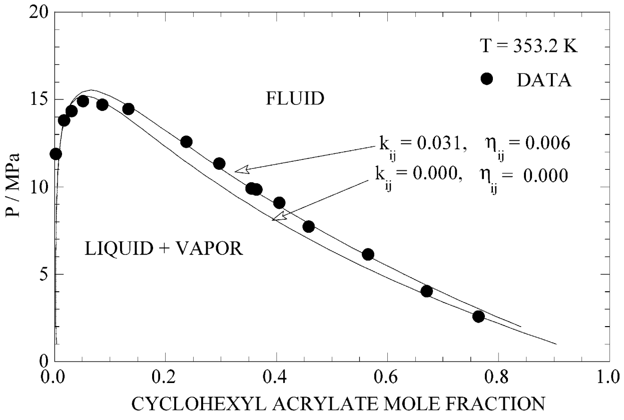

Figure 4. Comparison of the best fit of the Peng–Robinson equation of state to the carbon dioxide + cyclohexyl acrylate system at 353.2 K.

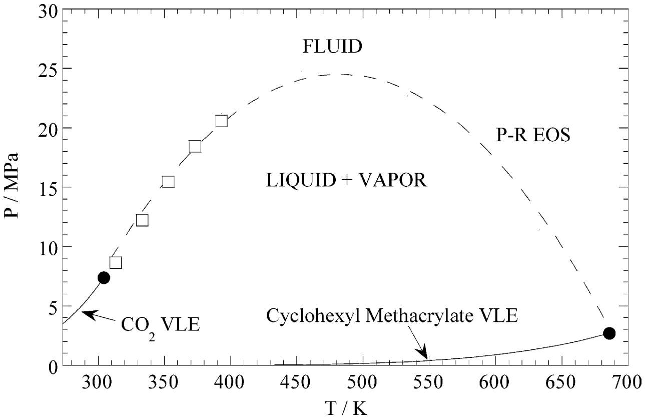

Figure 5. Pressure−temperature diagram for the carbon dioxide + cyclohexyl methacrylate system. The solid line and solid circles represent the vapor−liquid lines and the critical points, respectively, for pure CO_2 and cyclohexyl methacrylate. The open squares represent mixture critical points determined from isotherms measured in this study. The dashed lines represent the calculation using the Peng−Robinson equation of state with $k_{ij} = 0.033$ and $\eta_{ij} = -0.013$.

culated and experimental mixture critical curves is reasonably good using two optimized parameters with the Peng−Robinson equation of state.

Conclusions

High-pressure phase behavior data of carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems are obtained from (313.2 to 393.2) K in the pressure range of (1.7 to 20.6) MPa for binary mixtures. The carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems exhibit type-I phase behavior, which is characterized by an uninterrupted mixture critical curve. For carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems, we did not observe three-phase behavior. The solubility of cyclohexyl acrylate and cyclohexyl methacrylate in the carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems increases as the temperature increases at constant pressure. The Peng−Robinson equation of state models the pressure−composition isotherms for two carbon dioxide + cyclohexyl acrylate and carbon dioxide + cyclohexyl methacrylate systems reasonably well using the independent-temperature mixture parameters.

List of Symbols

a = attraction parameter
b = van der Waals covolume
k = binary interaction parameter
m = characteristic constant in eq 4
P = pressure
R = gas constant
T = temperature
V = volume
x = mole fraction

Greek Letters

α = scaling factor defined by eq 2
η = secondary binary interaction parameter
ω = acentric factor

Subscripts

c = critical property
calcd = calculated
exptl = experimental
m = mixture
r = reduced property

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Received for review June 21, 2004. Accepted November 22, 2004. The authors gratefully acknowledge the financial support from the Korea Ministry of Commerce, Industry & Energy and the Korea Energy Management Corporation to superfund project.

JE0497707