J. Chem. Eng. Data **2006,** *51,* 1436−1440

High-Pressure Phase Behavior for Pentyl Acrylate and Pentyl Methacrylate in Supercritical Carbon Dioxide

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High-pressure phase behavior is obtained for CO_2 + pentyl acrylate systems at (313.15, 333.15, 353.15, 373.15, and 393.15) K and pressures up to 16.8 MPa and for CO_2 + pentyl methacrylate systems at (313.15, 333.15, 353.15, 373.15, and 393.15) K and pressures up to 17.4 MPa. The solubility of monomers for the CO_2 + pentyl acrylate and CO_2 + pentyl methacrylate systems increase as the temperature increases at constant pressure. The CO_2 + pentyl acrylate and CO_2 + pentyl methacrylate systems exhibit type-I phase behavior. The experimental results for CO_2 + pentyl acrylate and CO_2 + pentyl methacrylate systems were correlated with the Peng−Robinson equation of state using a van der Waals one-fluid mixing rule including two adjustable parameters. A good fit of the data was obtained with the Peng−Robinson equation for CO_2 + pentyl acrylate and CO_2 + pentyl methacrylate systems. Critical constants (P_c, T_c, and ω) were predicted with the Joback method and the Lee−Kesler method.

Introduction

Knowledge of phase equilibrium data in binary mixtures containing supercritical fluids is required for practical use such as in the chemical separation process, related industrial application, and the polymerization process. The chemical separation processes based on supercritical fluid phase behavior are supported by abundant theoretical background and experimental data.[1] For phase behavior experiments, we have recently reported on the the bubble point, dew point, and critical point behavior of binary (meth)acrylate mixtures in supercritical carbon dioxide.[2−4] To design a supercritical carbon dioxide + monomer mixture for separation processes, one must first characterize the phase behavior of the monomer in the supercritical carbon dioxide.

Acrylate and methacrylate are widely used in modern plastics technology. The (meth)acrylate and polymers are used mainly for a variety of applications such as prostheses, contact lenses, photopolymer printing plates, adhesives, and coating.[5]

The phase behavior experimental data for the ethylene + pentyl acrylate system were reported by Lindner and Luft.[6] McHugh et al.[7] studied the phase behavior of butyl acrylate in supercritical carbon dioxide at (318.15 and 348.15) K and pressure up to ∼10.0 MPa. The phase behavior of butyl methacrylate and ethyl methacrylate in supercritical carbon dioxide was also studied by Byun and McHugh.[8] Recently, Byun and Lee[9] reported phase behavior experimental data for the carbon dioxide + decyl acrylate and carbon dioxide + decyl methacrylate systems at (313.15 to 393.15) K and pressure up to 18.9 MPa using a static phase equilibria apparatus. Also, the phase behavior for the carbon dioxide + hexyl acrylate and carbon dioxide + hexyl methacrylate systems were reported by Byun et al.[10] at (313.15 to 393.15) K.

However, phase behavior of the CO_2 + monomer system was very important in determining the initial polymerization condition because particle formation and particle size distribution of polymer are directly affected. Also, for monomer extraction from polymer, phase behavior experimental data for CO_2 + monomer mixtures are necessary.[11]

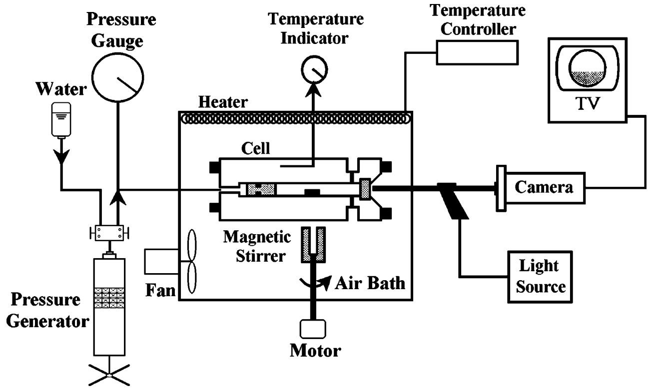

Figure 1. High-pressure experimental apparatus used in this study.

The objective of this work was to obtain experimental data of the high-pressure phase behavior information for the system of CO_2 + pentyl acrylate and CO_2 + pentyl methacrylate mixtures. The experimental pressure−composition isotherms are presented for the CO_2 + pentyl acrylate and CO_2 + pentyl methacrylate systems**.** The pressure−temperature trace of the mixture critical points is presented in the vicinity of pure CO_2 not only between the critical point of pure CO_2 and that of pentyl acrylate but also between the critical point of CO_2 and that of pentyl methacrylate. The other objective of this work was to compare the Peng−Robinson equation of state (PR-EOS)[12] with the phase behavior of the CO_2 + pentyl acrylate and CO_2 + pentyl methacrylate systems.

Experimental Section

***Apparatus and Procedure*.** Figure 1 shows the experimental apparatus used in this work. Phase behavior data were obtained using variable-volume cell at high pressure. The cell has a 1.59 cm i.d., a 7.0 cm o.d., and a working volume of ∼28 cm^3. This apparatus has been described in detail elsewhere.[13,14] For the CO_2 + pentyl acrylate and CO_2 + pentyl methacrylate mixtures studied, the empty cell is purged several times with CO_2 and

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10.1021/je060122s CCC: $33.50

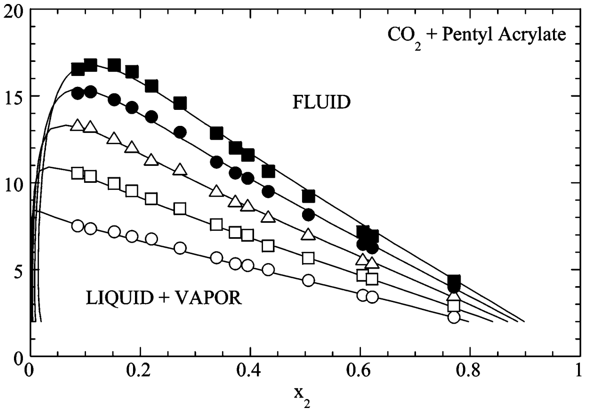

Figure 2. Comparison of the experimental data (symbols) for the CO_2 (1) + pentyl acrylate (2) system with calculations (solid lines) obtained using the Peng−Robinson equation of state with k_{ij} equal to 0.0293 and η_{ij} equal to −0.0448: ○, 313.15 K; □, 333.15 K; △, 353.15 K; ●, 373.15 K; ■, 393.15 K.

N_2 to remove traces of organic substance or air; the pentyl acrylate and pentyl methacrylate are loaded using a syringe (accurate to within ± 0.002 g); and CO_2 is condensed using a high-pressure bomb (accurate to within ± 0.004 g). The solution in the cell is compressed to the desired operating pressure by displacing the movable piston using water pressurized by a high-pressure generator (HIP, model 37-5.75-60). The pressure is measured using a Heise pressure gauge (Dresser Ind., model CM-130163, 0−34.0 MPa, accurate to within ± 0.03 MPa). The temperature of the system is maintained to within ± 0.2 K. Also, it is measured with a platinum-resistance device accurate to within ± 0.2 K (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 fluid-phase state. A bubble point pressure was obtained at the moment small vapor bubbles first appear in the cell, and dew point was obtained at the moment a fine mist appears 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. The temperature of system is increased, and then the entire procedure is repeated to obtain more information without reloading the cell.

Materials. Carbon dioxide was obtained from Daesung Oxygen Co. (99.8 % minimum purity) and used as received. The pentyl acrylate (97 % purity; CAS Registry No. 2998-23-4) and the pentyl methacrylate (98 % purity; CAS Registry No. 2849-98-1) used in this work were obtained from Scientific Polymer Products. Both components were used without further purification in the experiments.

Results and Discussion

High-pressure phase behavior data for both the CO_2 + pentyl acrylate and CO_2 + pentyl 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 CO_2 + pentyl acrylate and CO_2 + pentyl methacrylate mole fraction for the solubility isotherms at (313.15 to 393.15) K have an estimated accumulated error of less than ± 1.0 %.

Table 1. Experimental Data for the Carbon Dioxide (1) + Pentyl Acetate (2) System[a]

x_2	P/MPa	transition	x_2	P/MPa	transition
T = 313.15 K					
0.770	2.27	BP	0.338	5.70	BP
0.621	3.43	BP	0.272	6.26	BP
0.605	3.53	BP	0.220	6.79	BP
0.506	4.39	BP	0.184	6.93	BP
0.432	5.00	BP	0.152	7.18	BP
0.395	5.24	BP	0.109	7.38	BP
0.373	5.35	BP	0.086	7.53	BP
T = 333.15 K					
0.770	2.91	BP	0.338	7.58	BP
0.621	4.45	BP	0.272	8.52	BP
0.605	4.67	BP	0.220	9.09	BP
0.506	5.65	BP	0.184	9.54	BP
0.432	6.57	BP	0.152	9.96	BP
0.395	6.99	BP	0.109	10.37	BP
0.373	7.14	BP	0.086	10.55	BP
T = 353.15 K					
0.770	3.56	BP	0.338	9.55	BP
0.621	5.41	BP	0.272	10.79	BP
0.605	5.61	BP	0.220	11.35	BP
0.506	7.06	BP	0.184	12.09	BP
0.432	8.07	BP	0.152	12.59	BP
0.395	8.72	BP	0.109	13.25	BP
0.373	8.96	BP	0.086	13.34	CP
T = 373.15 K					
0.770	4.00	BP	0.338	11.20	BP
0.621	6.27	BP	0.272	12.93	BP
0.605	6.47	BP	0.220	13.83	BP
0.506	8.16	BP	0.184	14.35	BP
0.432	9.51	BP	0.152	14.80	BP
0.395	10.27	BP	0.109	15.24	CP
0.373	10.58	BP	0.086	15.17	DP
T = 393.15 K					
0.770	4.34	BP	0.338	12.89	BP
0.621	6.95	BP	0.272	14.62	BP
0.605	7.19	BP	0.220	15.59	BP
0.506	9.26	BP	0.184	16.41	BP
0.432	10.68	BP	0.152	16.80	CP
0.395	11.61	BP	0.109	16.79	DP
0.373	12.03	BP	0.086	16.55	DP

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

Figure 2 and Table 1 show the experimental pressure−composition ($P-x$) isotherms at (313.15, 333.15, 353.15, 373.15, and 393.15) K, and the range of pressures of (2.2 to 16.8) MPa for the CO_2 + pentyl acrylate system. Three phases were not observed at any of the five temperatures. As shown in Figure 2, the mixture critical pressures are 13.34 MPa (at 353.15 K), ∼15.24 MPa (at 373.15 K), and ∼16.80 MPa (at 393.15 K). The $P-x$ isotherms shown in Figure 2 are consistent with those expected for a type-I system[15,16] where a maximum occurs in the critical mixture curve. The solubility of CO_2 in the liquid phase decreases as temperatures shift higher under constant pressure.

Figure 3 and Table 2 show the phase experimental data at (313.15, 333.15, 353.15, 373.15, and 393.15) K and for pressures up to 17.4 MPa for the CO_2 + pentyl methacrylate mixture. As shown in Figure 3, the mixture critical pressures are 13.28 MPa (at 353.15 K) and 17.48 MPa (at 393.15 K). Also, the pressure of each mixture critical point continually increases as the temperature increases. The CO_2 + pentyl methacrylate system does not exhibit three phases at any of the five temperatures investigated.

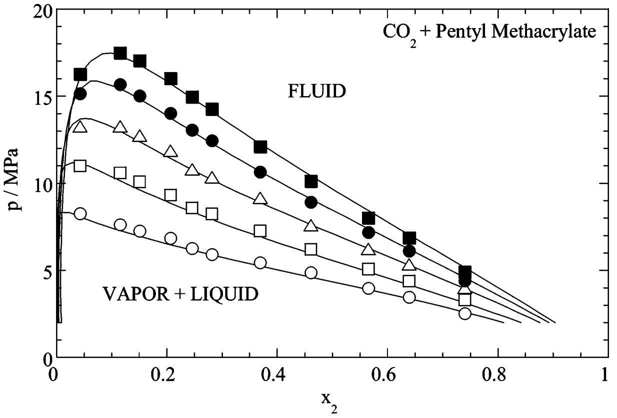

Figure 3. Comparison of the experimental data (symbols) for the CO$_2$ (1) + pentyl methacrylate (2) system with calculations (solid lines) obtained using the Peng−Robinson equation of state with k_{ij} equal to 0.0140 and η_{ij} equal to −0.0531: ○, 313.15 K; □, 333.15 K; △, 353.15 K; ●, 373.15 K; ■, 393.15 K.

The experimental phase behavior curves obtained in this work are modeled using the PR-EOS. The Peng−Robinson equations are briefly described here. The PR-EOS[12] is used with the following mixing rules:

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j a_{ij} \tag{1}$$

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

$$b_{\text{mix}} = \sum_i \sum_j x_i x_j b_{ij} \tag{3}$$

$$b_{ij} = 0.5[(b_{ii} + b_{jj})](1 - \eta_{ij}) \tag{4}$$

where k_{ij} and η_{ij} are binary interaction parameters that are determined by fitting $P-x$ isotherm curves and a_{ii} and b_{ii} are pure component parameters as defined by Peng and Robinson.[12] The expression for the fugacity coefficient using these mixing rules is given by Peng and Robinson[12] and is not reproduced here. Objection function[17] (OBF) and root-mean-square relative deviation (RMSD) percent of this calculation were defined by

$$\text{OBF} = \sum_i^N \left(\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}}\right)^2 \tag{5}$$

$$\text{RMSD (\%)} = \sqrt{\frac{\text{OBF}}{\text{ND}}} \times 100 \tag{6}$$

ND in eq 6 means the number of data point. Table 3 lists the pure component critical temperatures, critical pressures, and the acentric factors (ω) for carbon dioxide,[18,19] pentyl acrylate,[19] and pentyl methacrylate[19] that are used with the PR-EOS. The properties of pentyl acrylate and pentyl methacrylate were calculated by the Joback group-contribution method.[19] Also, the vapor pressures were calculated by the Lee−Kesler method.[19]

Figure 4 shows a comparison between the experimental result of carbon dioxide + pentyl acrylate and the calculated value obtained using the Peng−Robinson equation at a temperature of 353.15 K. The binary interaction parameters of PR-EOS are fitted by the experimental data at 353.15 K. The values of the optimized parameters of the PR-EOS for the carbon dioxide + pentyl acrylate system are $k_{ij} = 0.0293$ and $\eta_{ij} = -0.0448$. The RMSD at 353.15 K was 1.37 % of the 14 bubble points.

Table 2. Experimental Data for the Carbon Dioxide (1) + Pentyl Methcrylate (2) System[a]

x_2	P/MPa	transition	x_2	P/MPa	transition
		T = 313.15 K			
0.740	2.54	BP	0.245	6.28	BP
0.639	3.47	BP	0.206	6.85	BP
0.565	3.99	BP	0.150	7.26	BP
0.461	4.88	BP	0.115	7.63	BP
0.369	5.46	BP	0.043	8.28	BP
0.281	5.93	BP			
		T = 333.15 K			
0.740	3.32	BP	0.245	8.59	BP
0.639	4.39	BP	0.206	9.32	BP
0.565	5.08	BP	0.150	10.08	BP
0.461	6.20	BP	0.115	10.59	BP
0.369	7.28	BP	0.043	11.00	BP
0.281	8.24	BP			
		T = 353.15 K			
0.740	4.00	BP	0.245	10.79	BP
0.639	5.35	BP	0.206	11.89	BP
0.565	6.23	BP	0.150	12.73	BP
0.461	7.59	BP	0.115	13.26	BP
0.369	9.17	BP	0.043	13.28	CP
0.281	10.35	BP			
		T = 373.15 K			
0.740	4.41	BP	0.245	13.07	BP
0.639	6.13	BP	0.206	14.02	BP
0.565	7.19	BP	0.150	15.02	BP
0.461	8.93	BP	0.115	15.67	BP
0.369	10.66	BP	0.043	15.14	DP
0.281	12.45	BP			
		T = 393.15 K			
0.740	4.92	BP	0.245	14.97	BP
0.639	6.88	BP	0.206	16.01	BP
0.565	8.03	BP	0.150	17.05	BP
0.461	10.13	BP	0.115	17.48	CP
0.369	12.10	BP	0.043	16.28	DP
0.281	14.28	BP			

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

Table 3. Pure Component Critical Properties with the Peng−Robinson Equation of State[18,19]

component	M_w	T_c/K	P_c/MPa	ω
carbon dioxide	44.01	304.25	7.39	0.225
pentyl acrylate	142.20	612.31	2.66	0.5253
pentyl methacrylate	156.23	638.09	2.42	0.5691

Figure 2 compared experimental results with calculated $P-x$ isotherms at temperatures of (313.15, 333.15, 353.15, 373.15, and 393.15) K for the carbon dioxide + pentyl acrylate system using the optimized values of k_{ij} and η_{ij} determined at 353.15 K. As shown in Figure 2, a good fit of the data are obtained with the Peng−Robinson equation using an adjustable mixture parameters for the carbon dioxide + pentyl acrylate system. The RMSD at five temperatures (313.15, 333.15, 353.15, 373.15, and 393.15) K for the carbon dioxide + pentyl acrylate system was 1.96 % of the 67 bubble points.

Figure 3 shows a comparison of experimental with calculated $P-x$ isotherms at temperature of (313.15, 333.15, 353.15, 373.15, and 393.15) K for the carbon dioxide + pentyl methacrylate system. In the same way as above, these isotherms are calculated using the optimized values of $k_{ij} = 0.0140$ and $\eta_{ij} = -0.0531$ determined at 353.15 K (bubble point data = 10, RMSD = 1.19 %). The RMSD at five temperatures for the carbon dioxide + pentyl methacrylate system was 2.02 % of the 52 bubble points.

Figure 5 shows the mixture critical curve for the carbon dioxide + pentyl acrylate system predicted by the PR-EOS. The calculated mixture critical curve is type-I, in good agreement

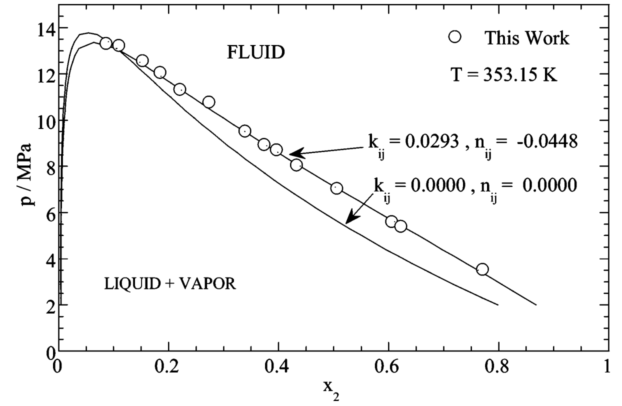

Figure 4. Comparison of the best fit of Peng−Robinson equation of state to CO_2 (1) + pentyl acrylate (2) system obtained in this work (○) at 353.15 K.

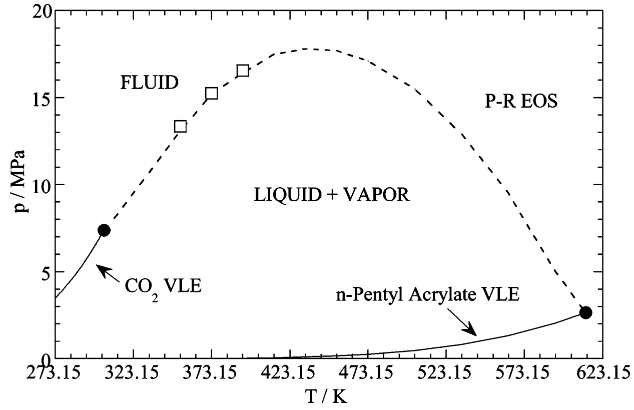

Figure 5. Pressure-temperature diagram for the CO_2 (1) + pentyl acrylate (2) system; the solid line and the solid circles represent the vapor−liquid line and the critical point for pure CO_2 and pentyl acrylate; the open squares are critical points determined from isotherms measured in this study; the dashed line represents calculated values obtained using the Peng−Robinson equation of state with $k_{ij} = 0.0293$ and $\eta_{ij} = -0.0448$.

with experimental observations at five temperatures. In Figure 5, the solid lines represent the vapor pressure for pure carbon dioxide[18] and pentyl acrylate.[19] The solid circles represent the critical point for pure carbon dioxide and pentyl acrylate. The dashed lines represent the calculated value obtained using the PR-EOS. The above part of the dashed line is single phase (fluid), the below part vapor−liquid (two phases). The open squares are for the mixture critical points determined from isotherms measured in this experiment.

Figure 6 shows the mixture critical curve for the carbon dioxide + pentyl methacrylate system predicted by the PR-EOS. The mixture critical curves calculated by the two mixture parameters are type-I. In Figure 6, the solid lines for the vapor pressure for pure pentyl methacrylate was obtained by the Lee−Kesler method.[19] The dashed lines represent calculations obtained using the PR-EOS, with $k_{ij} = 0.0140$ and $\eta_{ij} = -0.0531$.

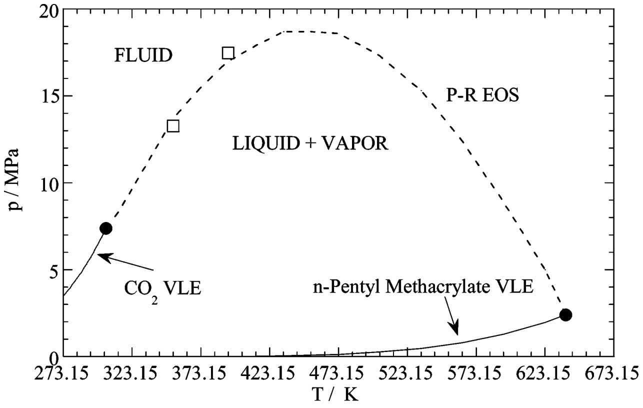

Figure 6. Pressure−temperature diagram for the CO_2 (1) + pentyl methacrylate (2) system; the solid line and the solid circles represent the vapor−liquid line and the critical point for pure CO_2 and pentyl methacrylate; the open squares are mixture-critical points determined from isotherms measured in this study; the dashed line represents calculated values obtained using the Peng−Robinson equation of state with $k_{ij} = 0.0140$ and $\eta_{ij} = -0.0531$.

Conclusions

The pressure−composition isotherm data of the CO_2 + pentyl acrylate and CO_2 + pentyl methacrylate systems have 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 CO_2 + pentyl acrylate and CO_2 + pentyl methacrylate mixtures do not exhibit three phases at any of the five temperatures. The PR-EOS is capable of accurately predicting the phase behavior for both of these two systems using two temperature-independent mixture interaction parameters. The agreement between calculated and experimental mixture critical curves is reasonably good using two optimized parameters with the PR-EOS. We obtained good correlation results. RMSD (%) for the CO_2 + pentyl acrylate system was 1.96 % and for the CO_2 + pentyl methacrylate system was 2.02 %.

Literature Cited

(1) Wichterle, I. Phase equilibria with supercritical component. *Pure Appl. Chem.* **1993**, *65*, 1003−1008.

(2) Byun, H. S. High-pressure phase behavior of CO_2 + propyl acrylate and CO_2 + propyl methacrylate systems. *Fluid Phase Equilib.* **2002**, *198*, 299−312.

(3) Byun, H. S.; Shin, J. S. Bubble-point measurement for CO_2−vinyl acetate and CO_2−vinyl acrylate. *J. Chem. Eng. Data* **2003**, *48*, 97−101.

(4) Byun, H. S. Bubble-point measurement for CO_2 + methyl acrylate and CO_2 + ethyl acrylate systems at high pressures. *J. Chem. Eng. Data* **2002**, *47*, 357−360.

(5) Waegemaekers, T. H. J. M.; Bensink, M. P. M. Non-mutagenicity of 27 aliphatic acrylate esters in the salmonella-microsome test. *Mutat. Res.* **1984**, *137*, 95−102.

(6) Lindner, A.; Luft, G. Studies of phase behavior of mixtures of ethylene and pentyl acrylate. *Ber. Bunsen-Ges. Phys. Chem.* **1975**, *79*, 414−418.

(7) McHugh, M. A.; Rindfleisch, F.; Kuntz, P. T.; Schmaltz, C.; Buback, M. Cosolvent effect of alkyl acrylate on the phase behavior of poly(alkyl acrylate)-supercritical CO_2 mixtures. *Polymer* **1998**, *39*, 6049−6052.

(8) Byun, H. S.; McHugh, M. A. Impact of "free" monomer concentration on the phase behavior of supercritical carbon dioxide−polymer mixtures. *Ind. Eng. Chem. Res.* **2000**, *39*, 4658−4662.

(9) Byun, H. S.;. Lee, D. H. Phase behavior of binary and ternary mixtures of poly(decyl acrylate)−supercritical solvents−decyl acrylate and poly(decyl methacrylate)−CO_2−decyl methacrylate systems. *Ind. Chem. Eng. Res.* **2006**, *45*, 3373−3380.

(10) Byun, H. S.; Kim, J. G.; Yang, J. S. Phase behavior on the poly[hexyl (meth)acrylate]−supercritical solvents−monomer mixtures at high pressures. *Ind. Chem. Eng. Res.* **2002**, *47*, 359−362.

(11) Kwon, S.; Bae, W.; Kim, H. High-pressure phase behavior of CO_2 + *N*-vinyl caprolactam and CO_2 + *N*-methyl caprolactam systems. *J. Chem. Eng. Data* **2005**, *50*, 1560−1563.

(12) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−63.

(13) Byun, H. S.; Choi, M. Y.; Lim, J. S. High-pressure phase behavior and modeling of binary mixtures for alkyl acetate in supercritical carbon dioxide. *J. Supercrit. Fluids* (in press).

(14) Lee, C. W.; Jung, C. Y.; Byun, H. S. High-pressure phase behavior of carbon dioxide + 1-methyl-2-pyrrolidinone and carbon dioxide + 1-ethyl-2-pyrrolidinone systems. *J. Chem. Eng. Data* **2004**, *49*, 53−57.

(15) Scott, R. L.; van Konynenburg, P. B. Static properties of solutions—van der Waals and related models for hydrocarbon mixtures. *Discuss. Faraday Soc*. **1970**, *49*, 87−97.

(16) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed.; Butterworth: Stoneham, MA, 1993.

(17) Kuester, J. L.; Mize, J. H. *Optimization Techniques with Fortran*; McGraw-Hill: New York, 1973.

(18) Vargaftik, N. B. *Handbook of Physical Properties of Liquid and Gases*; Springer-Verlag: Berlin, 1983.

(19) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Liquids and Gases*, 4th ed.; McGraw-Hill: New York, 1987.

Received for review March 14, 2006. Accepted May 14, 2006. The authors gratefully acknowledge the financial support from the Korea Ministry of Commerce, Industry & Energy and the Korea Energy Management Corporation to the superfund project.

JE060122S