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Measurement of High-Pressure Phase Behavior for the Benzyl (Meth)Acrylate in Supercritical Carbon Dioxide from (313.2 to 393.2) K and Pressures from (6 to 24) MPa

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High-pressure phase behavior is obtained for CO_2 (1) + benzyl acrylate (2) and CO_2 (1) + benzyl methacrylate (2) systems at (313.2, 333.2, 353.2, 373.2, and 393.2) K and pressures up to 24.43 MPa. The solubility of monomers for the CO_2 (1) + benzyl acrylate (2) and CO_2 (1) + benzyl methacrylate (2) systems increases as the temperature increases at constant pressure. The CO_2 (1) + benzyl acrylate (2) and CO_2 (1) + benzyl methacrylate (2) systems exhibit type-I phase behavior. The experimental results for CO_2 (1) + benzyl acrylate (2) and CO_2 (1) + benzyl methacrylate (2) systems are correlated with the Peng–Robinson equation of state using a van der Waals one-fluid mixing rule including two adjustable parameters. Critical constants (P_c, T_c, and ω) are predicted with the Joback method and the Lee–Kesler method.

Introduction

Thermodynamic information on the phase behavior for a binary mixture containing supercritical fluids plays an important role in the chemical separation process, supercritical fluid extraction, polymerization condition, and industrial application.[1–3]

Recently, phase behavior experiments have been reported on the bubble-point, dew-point, and critical-point behavior of mixtures containing supercritical carbon dioxide ($scCO_2$).[4,5] $scCO_2$ used in this work is widely used as an environmentally benign solvent which is inexpensive, nonflammable, and nontoxic. Specially, $scCO_2$ has a quadrupole moment, no dipole moment, and a low dielectric constant. $scCO_2$ is a good solvent of low molecular weight in nonpolar molecules. Therefore, phase behavior information for mixtures containing $scCO_2$ is required for practical uses. The acrylate and methacrylate components are widely used in modern plastic technology. The acrylate and methacrylate monomers are used mainly for a variety of applications such as prostheses, contact lenses, photopolymer printing plates, adhesives, and coating.[6]

Phase behavior data for the CO_2 + alkyl (meth)acrylate system were reported by Byun and Choi,[7,8] Lora and McHugh,[9] and McHugh et al.[10] The miscibility for the supercritical CO_2 + monomer system is an important condition needed for polymer synthesis and the polymerization process. Byun and Choi[7] used a static apparatus and presented the liquid–vapor equilibria curves for CO_2 + 2-hydroxypropyl acrylate and CO_2 + 2-hydroxy(ethyl and propyl) methacrylate mixtures at (313.2, 333.2, 353.2, 373.2, and 393.2) K and pressures up to 27.1 MPa. Byun[8] reported the solubility curve for the CO_2 + propyl acrylate and CO_2 + propyl methacrylate system at temperatures from (313.2 to 393.2) K and pressure up to 16.6 MPa. Lora and McHugh[9] presented the phase behavior for the CO_2 + methyl methacrylate system and for the CO_2 + butyl acrylate system[10] at (308.2 and 348.2) K using a static apparatus.

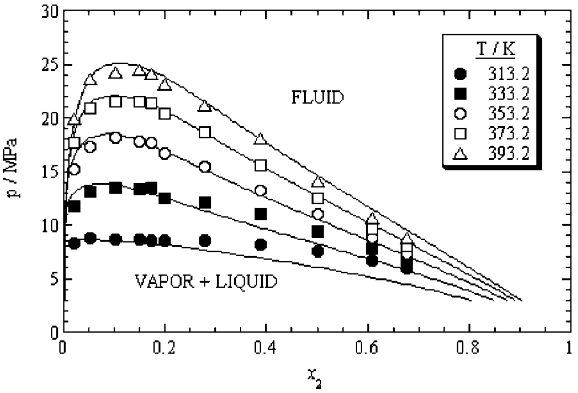

Figure 1. Plot of pressure against mole fraction to illustrate the comparison of the experimental data (symbols) for the carbon dioxide (1) + benzyl acrylate (2) system with calculations (solid lines) obtained with the Peng–Robinson equation of state with k_{ij} equal to 0.042 and η_{ij} equal to –0.052.

The purpose of this work is to obtain the high-pressure experimental data for CO_2 + benzyl acrylate and CO_2 + benzyl methacrylate mixtures by investigating mixtures of CO_2 with two components. Also, the pressure–temperature (*P*–*T*) diagrams of the mixture critical curve are presented for the CO_2 + benzyl acrylate and CO_2 + benzyl methacrylate systems in the vicinity of the critical point of pure CO_2. The experimental data for CO_2 + benzyl acrylate and CO_2 + benzyl methacrylate systems obtained in this work were correlated with the Peng–Robinson equation of state[11] using a van der Waals one-fluid mixing rule including two adjustable parameters. The critical pressure, critical temperature, and acentric factor of benzyl acrylate and benzyl methacrylate are estimated by the Joback and Lydersen method with group contributions, and the vapor pressure is estimated by the Lee–Kesler method.[12]

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Table 1. Experimental Data for the CO_2 (1) + Benzyl Acrylate (2) System[a]

x_2	p/MPa	transition
	T = 313.2 K	
0.020	8.28	DP
0.052	8.72	BP
0.102	8.64	BP
0.151	8.60	BP
0.174	8.58	BP
0.200	8.55	BP
0.278	8.48	BP
0.389	8.16	BP
0.503	7.49	BP
0.609	6.67	BP
0.676	5.90	BP
	T = 333.2 K	
0.020	11.78	DP
0.052	13.14	DP
0.102	13.41	CP
0.151	13.38	BP
0.174	13.48	BP
0.200	12.53	BP
0.278	12.10	BP
0.389	11.00	BP
0.503	9.45	BP
0.609	7.83	BP
0.676	6.47	BP
	T = 353.2 K	
0.020	15.21	DP
0.052	17.35	DP
0.102	18.21	DP
0.151	19.79	BP
0.174	17.67	BP
0.200	16.66	BP
0.278	15.41	BP
0.389	13.28	BP
0.503	11.00	BP
0.609	8.74	BP
0.676	7.24	BP
	T = 373.2 K	
0.020	17.69	DP
0.052	20.86	DP
0.102	21.56	CP
0.151	21.56	BP
0.174	21.41	BP
0.200	20.38	BP
0.278	18.66	BP
0.389	15.60	BP
0.503	12.53	BP
0.609	9.62	BP
0.676	8.09	BP
	T = 393.2 K	
0.020	19.90	DP
0.052	23.62	DP
0.102	24.19	DP
0.151	24.40	CP
0.174	24.03	BP
0.200	23.07	BP
0.278	21.14	BP
0.389	18.03	BP
0.503	14.10	BP
0.609	10.59	BP
0.676	8.74	BP

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

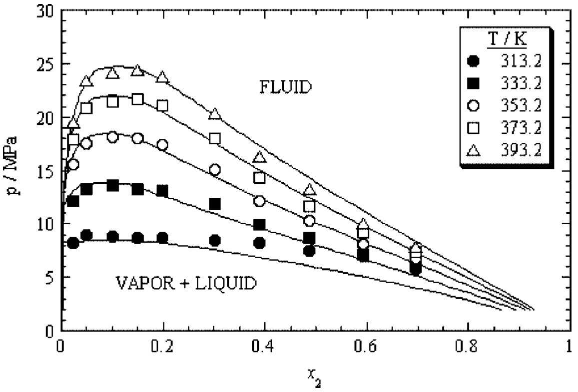

Figure 2. Plot of pressure against mole fraction to illustrate the comparison of the experimental data (symbols) for the carbon dioxide (1) + benzyl methacrylate (2) system with calculations (solid lines) obtained with the Peng–Robinson equation of state with k_{ij} equal to 0.053 and η_{ij} equal to –0.045.

Experimental Section

Apparatus and Procedure. Described in detail elsewhere are the experimental apparatus and techniques used to measure the phase behavior of monomers in supercritical CO_2.[7] A high-pressure, variable-volume view cell, with a 5.7 cm outside diameter, an inside diameter of 1.59 cm, and a working volume of ~28 cm^3, is used to obtain the bubble-, dew-, and critical-point curves and is capable of operating to a pressure of 200.0 MPa. A 1.9 cm thick × 1.9 cm diameter sapphire window is fitted in the front part of the cell to allow observation of the phases. Typically, supercritical carbon dioxide is added to the cell to within ± 0.004 g using a high-pressure bomb. The monomer is loaded into the cell to within ± 0.002 g using a syringe after the empty cell is purged several times with carbon dioxide and nitrogen to remove traces of air and organic matter. The mixture in the cell was compressed to the desired pressure by moving a piston located within the cell. The piston (2.54 cm) 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 the piston, a small correction (0.07 MPa) 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 to 34.0) MPa) accurate to ± 0.02 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.

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 ~ 40) min for the cell to reach phase equilibrium. The pressure was then slowly decreased until a second phase appeared. A bubble point pressure was obtained when small vapor bubbles appeared first in the cell. A dew point was obtained if a fine mist appeared in the cell, and critical points were 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. Benzyl methacrylate (> 98 % purity, CAS RN 2495-37-6) and benzyl acrylate (> 98 % purity; CAS RN 2495-35-4) used in this work were obtained from Scientific Polymer Products, Inc. Two components were used without further purification in the experiments. Carbon dioxide (99.8 % purity) was obtained from Daesung Industrial Gases Co. and used as received.

Results and Discussion

High-pressure phase behavior data for the benzyl acrylate and benzyl methacrylate in supercritical CO_2 are measured and

Table 2. Experimental Data for the CO_2 (1) + Benzyl Methacrylate (2) System[a]

x_2	p/MPa	transition
	T = 313.2 K	
0.024	7.86	DP
0.050	9.00	BP
0.101	8.86	BP
0.151	8.76	BP
0.199	8.65	BP
0.301	8.43	BP
0.390	8.22	BP
0.486	7.48	BP
0.593	6.93	BP
0.696	5.76	BP
	T = 333.2 K	
0.024	12.09	DP
0.050	13.28	DP
0.101	13.62	BP
0.151	13.28	BP
0.199	13.16	BP
0.301	11.85	BP
0.390	9.91	BP
0.486	8.72	BP
0.593	7.14	BP
0.696	6.26	BP
	T = 353.2 K	
0.024	15.62	DP
0.050	17.52	DP
0.101	18.14	CP
0.151	18.03	BP
0.199	17.40	BP
0.301	15.12	BP
0.390	12.10	BP
0.486	10.30	BP
0.593	8.10	BP
0.696	6.72	BP
	T = 373.2 K	
0.024	17.90	DP
0.050	20.81	DP
0.101	21.48	DP
0.151	21.72	BP
0.199	21.07	BP
0.301	17.97	BP
0.390	14.31	BP
0.486	11.69	BP
0.593	9.21	BP
0.696	7.35	BP
	T = 393.2 K	
0.024	19.52	DP
0.050	23.35	DP
0.101	24.17	DP
0.151	24.43	CP
0.199	23.81	BP
0.301	20.40	BP
0.390	16.28	BP
0.486	13.29	BP
0.593	10.00	BP
0.696	7.88	BP

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

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 (1) + benzyl acrylate (2) and CO_2 (1) + benzyl methacrylate (2) mole fractions for the solubility isotherms at (313.2 ~ 393.2) K have an estimated cumulative 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 pressures from (5.90 to 24.40) MPa for the CO_2 (1) + benzyl acrylate (2) system. Three phases were not observed at any of the five temperatures. As shown in Figure 1, the mixture critical pressures are 13.14 MPa (at 333.2 K), 21.56 MPa (at 373.2 K), and 24.40 MPa (at 393.2 K). The P–x isotherms shown in Figure 1 are consistent with those expected for a type-I system[13,14] where a maximum occurs in the critical mixture curve. The solubility of CO_2 decreases as temperatures shift higher under the constant pressure.

Figure 2 and Table 2 show the phase experimental data at (313.2, 333.2, 353.2, 373.2, and 393.2) K and at pressures from (5.76 to 24.43) MPa for the CO_2 (1) + benzyl methacrylate (2) mixture. As shown in Figure 2, the mixture critical pressures are 18.14 MPa (at 353.2 K) and 24.43 MPa (at 393.2 K). Also, the pressure of each mixture-critical point continually increases as the temperature increases. The CO_2 + benzyl methacrylate system does not exhibit three phases at any of the five temperatures investigated. The mixture-critical curve for the CO_2 + benzyl methacrylate system exhibits a pressure maximum in the P–T space.

The experimental data obtained in this work are modeled using the Peng–Robinson equation of state. The Peng–Robinson equations are briefly described here. The Peng–Robinson equation of state[11] 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 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.[11] The expression for the fugacity coefficient using these mixing rules is given by Peng and Robinson[11] and is not reproduced here. The objection function (OBF) and root-mean-square relative deviation (rmsd) percent of this calculation were defined by

$$\text{OBF} = \sum_i^N \left(\frac{P_{\text{exptl}} - P_{\text{calcd}}}{P_{\text{exptl}}} \right)^2$$

We used Marquardt[15] to optimize the objection function. Table 3 lists the pure component critical temperatures, critical pressures, and the acentric factors for carbon dioxide,[12] benzyl acrylate,[12] and benzyl methacrylate[12] that are used with the Peng–Robinson equation of state. The boiling points are obtained by Scientific Polymer Products, Inc. The properties of benzyl acrylate and benzyl methacrylate were calculated by the Joback group contribution method.[12] Also, the vapor pressures were calculated by the Lee–Kesler method.[12]

Figure 3 shows a comparison of the experimental results of carbon dioxide + benzyl acrylate with the calculated values obtained using the Peng–Robinson equation at a temperature

Table 3. Properties of Pure Components

components	molecular weight	molecular formula	T_c/K	P_c/MPa	ω
carbon dioxide	44.01	O=C=O	304.2	7.38	0.225
benzyl acrylate	162.19	$CH_2CHCOOCH_2C_6H_5$	711.9	3.09	0.512
benzyl methacrylate	176.21	$CH_3CH_2CCOOCH_2C_6H_5$	707.6	2.80	0.530

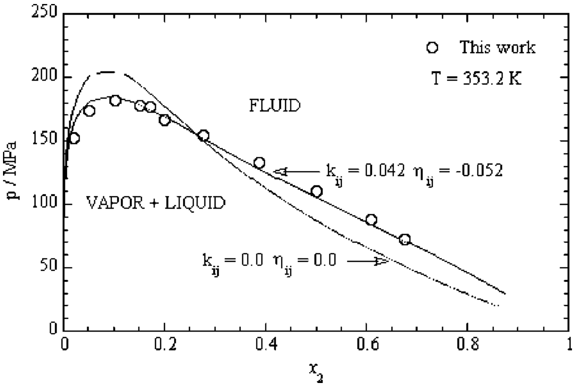

Figure 3. Plot of pressure against mole fraction to illustrate the comparison of the experimental data (symbols) for the carbon dioxide (1) + benzyl acrylate (2) system with calculations obtained from the Peng–Robinson equation of state with k_{ij} and η_{ij} set equal to zero (dashed line) with k_{ij} equal to 0.042 and η_{ij} equal to –0.052 (solid line) at $T = 353.2$ K.

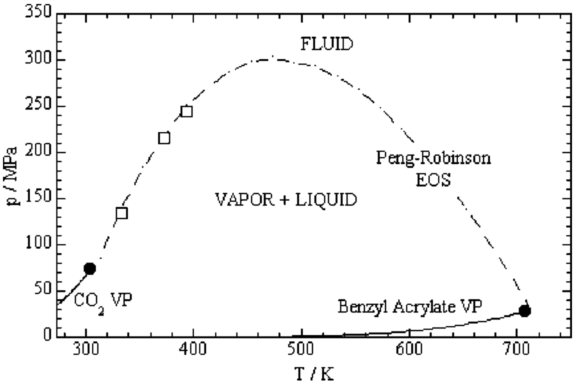

Figure 4. Plot of pressure against temperature for the carbon dioxide + benzyl acrylate system. The solid lines and the solid circles represent the vapor + liquid lines and the critical points for pure carbon dioxide and benzyl acrylate. The open squares are critical points determined from isotherms measured in this work. The dashed lines represent calculations obtained using the Peng–Robinson equation of state with k_{ij} equal to 0.042 and η_{ij} equal to –0.052.

of 353.2 K. The binary interaction parameters of the Peng–Robinson equation of state are fitted by the experimental data at 353.2 K. The values of optimized parameters of the Peng–Robinson equation of state for the carbon dioxide + benzyl acrylate system are $k_{ij} = 0.042$ and $\eta_{ij} = -0.052$.

Figure 1 compares experimental results with calculated *P–x* isotherms at temperatures of (313.2, 333.2, 353.2, 373.2, and 393.2) K for the carbon dioxide + benzyl 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 + benzyl acrylate system.

Figure 2 shows the comparison of experimental results with calculated *P–x* isotherms at temperatures of (313.2, 333.2, 353.2, 373.2, and 393.2) K for the carbon dioxide + benzyl methacrylate system. In the same way as above, these isotherms are calculated using the optimized values of $k_{ij} = 0.053$ and $\eta_{ij} = -0.045$ determined at 353.2 K.

Figure 4 compares the mixture-critical curves of the experimental data with calculated values by the Peng–Robinson equation of state for the carbon dioxide + benzyl acrylate system. The calculated mixture-critical curve is type-I, in good agreement with experimental observations at five temperatures. In Figure 4, the solid lines represent the vapor pressure for pure carbon dioxide[12] and benzyl acrylate.[12] The solid circles represent the critical point for pure carbon dioxide and benzyl acrylate. The upper part of the dashed line is the single phase (fluid), and the lower part is the vapor–liquid phase (two phases). The dashed lines represent the calculated value obtained using the Peng–Robinson equation of state. The open squares are for the mixture-critical points determined from isotherms measured in this experiment.

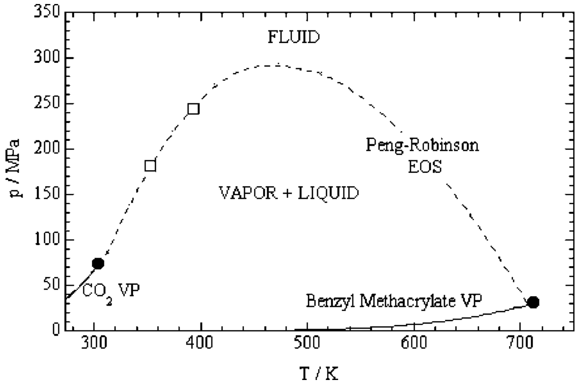

Figure 5. Plot of pressure against temperature for the carbon dioxide + benzyl methacrylate system. The solid lines and the solid circles represent the vapor + liquid lines and the critical points for pure carbon dioxide and benzyl methacrylate. The open squares are critical points determined from isotherms measured in this work. The dashed lines represent calculations obtained using the Peng–Robinson equation of state with k_{ij} equal to 0.053 and η_{ij} equal to –0.045.

Figure 5 shows the mixture-critical curve for the carbon dioxide + benzyl methacrylate system predicted by the Peng–Robinson equation of state. The mixture-critical curves calculated by two mixture parameters are type-I. In Figure 5, the solid lines represented for the vapor pressure of pure benzyl methacrylate were obtained by the Lee–Kesler method.[12] The dashed lines represent calculations obtained using the Peng–Robinson equation of state, with $k_{ij} = 0.053$ and $\eta_{ij} = -0.045$.

Conclusions

The *P–x* isotherm data of CO_2 + benzyl acrylate and CO_2 + benzyl 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 + benzyl acrylate and CO_2 + benzyl methacrylate mixtures do not exhibit three phases at any five temperatures. The Peng–Robinson equation of state is capable of accurately predicting the phase behavior for both of these two systems using two temperature-independent mixture interaction parameters. The agreement between calculated and experimental mixture-critical curves is reasonably good for using two optimized parameters with the Peng–Robinson equation of state.

Literature Cited

(1) Wichterle, I. Phase Equilibria with Supercritical Component. *Pure Appl. Chem.* **1993**, *65*, 1003–1008.

(2) Borch-Jensen, C.; Staby, A.; Mollerup, J. Mutual solubility of 1-butanol and carbon dioxide, ethene, ethane, or propane at a reduced supercritical solvent temperature of 1.03. *J. Supercrit. Fluids* **1994**, *7*, 231–244.

(3) Yeo, S. D.; Kiran, E. Copolymerization of Acrylonitrile with Methyl Methacrylate and 2-Chlorostyrene in Supercritical CO_2. *Macromolecules* **2004**, *37*, 8239–8248.

(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) 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.

(6) 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.

(7) Byun, H. S.; Choi, M. Y.; Lim, J. S. High Pressure Phase Behavior on the Binary Mixture for the 2-Hydroxyethyl Methacrylate, 2-Hydroxypropyl Acrylate and 2-Hydroxypropyl Methacrylate in Supercritical Carbon Dioxide. *J. Chem. Thermodyn.* **2007**, *39*, 855–861.

(8) 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.

(9) Lora, M.; McHugh, M. A. Phase behavior and modeling of the poly(methyl methacrylate)-CO_2-methyl methacrylate system. *Fluid Phase Equilib.* **1999**, *157*, 285–297.

(10) 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.

(11) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *I. E. C. Fundam.* **1976**, *15*, 59–63.

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

(13) 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.

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

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

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