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Cloud-Point and Vapor−Liquid Behavior of Binary and Ternary Systems for the Poly(dodecyl acrylate) + Cosolvent and Dodecyl Acrylate in Supercritical Solvents

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High-pressure phase behavior data were reported for poly(dodecyl acrylate) [P(DDA)] in propane, propylene, butane, 1-butene, and dimethyl ether (DME), as well as for the P(DDA) + dodecyl acrylate (DDA) (or DME) in CO_2. Cloud-point curves for P(DDA) in C_4 hydrocarbons were about 90 K higher than P(DDA) + C_3 hydrocarbon curves, at a fixed pressure of about 10.0 MPa. The cloud-point curve for the P(DDA) + DME mixture was located between C_3 and C_4 hydrocarbons at pressures below about 20.0 MPa. The location of the P(DDA) + CO_2 cloud-point curve shifts to lower temperatures and pressures upon the addition of DDA or DME. High-pressure phase equilibrium data were presented for the CO_2 + DDA system at temperatures ranging from (313.2 to 393.2) K and pressures up to about 26.14 MPa. The CO_2 + DDA system exhibits type I phase behavior with a continuous critical mixture curve and was adequately modeled using the Peng−Robinson equation of state.

Introduction

Supercritical fluids (SCFs) have been used as solvents in polymer purification, polymeric materials production, fractionation, and polymerization processes; they further play roles as environmentally friendly solvents for cleaning, powder formation, and solution coating.[1−3] Research into the experimental phase behavior of monomers in SCF solvents has been valuable for the plant design of chemical processes by providing information on polymer size and conditions.[4,5] Acrylate-based polymers are widely used in modern plastic technology. Along with monomers, acrylate polymers are used mainly in prostheses, contact lenses, adhesives, and coatings.[6]

Previous work has revealed that the phase boundary for binary mixtures consisting of polymer in SCF solvent shifted to lower pressures upon the addition of cosolvent in the solution.[7−9] Albrecht et al.[7] has reported cloud-point pressures for binary sub- and SCF solutions containing either saturated or unsaturated polyisoprene in ethane, ethylene, propane, propylene, and dimethyl ether (DME) up to 423.2 K and 140 MPa. McHugh et al.[8] determined experimental cloud-point data for poly(butyl acrylate) + and poly(2-ethylhexyl acrylate) + CO_2 + cosolvent mixtures. Experimental phase behavior data for the poly(decyl acrylate) + CO_2 + decyl acrylate (or DME) mixtures were reported by Byun and Lee.[9] In addition, the phase equilibria of CO_2 + alkyl acrylate systems have been revealed by several researchers. McHugh et al.[8] studied the phase equilibria of butyl acrylate in supercritical carbon dioxide at (308.2 and 348.2) K and at pressures up to about 10.0 MPa. The phase equilibria of decyl acrylate[9] and hexyl acrylate[10] in supercritical carbon dioxide were also reported by Byun et al. A detailed description of type I of phase behavior along with its characteristics can be found in the reports by Scott and von Konynenburg[11] and McHugh and Krukonis.[12] To provide phase behavior information for the design of high-pressure processes, measured bubble- and dew-point data of binary systems are modeled using the Peng−Robinson equation of state.[13] These results can give valuable information for the rational design and operation of the supercritical region.

Table 1. Critical Temperatures, Critical Pressures, Critical Densities, Polarizabilities, Dipole Moments, and Quadrupole Moments of Solvents Used in This Study[7,14−18]

solvents	T_c K	p_c MPa	ρ_c $kg \cdot m^{-3}$	$\alpha \cdot 10^{30}$ m^3	$\mu \cdot 10^{30}$ $C \cdot m$	$Q \cdot 10^{40}$ $C \cdot m^2$
carbon dioxide	304.3	7.38	469	2.65	0.00	−14.34
propane	342.9	4.25	217	6.29	0.27	4.00
propylene	365.1	4.62	236	6.26	1.23	8.34
butane	425.3	3.80	228	8.14	0.00	0.00
1-butene	419.6	3.97	234	8.24	1.13	8.34
DME	400.0	5.30	258	5.22	4.34	4.00

The focus of this work is to determine the impact of dodecyl acrylate (DDA) cosolvent on the phase behavior of poly(dodecyl acrylate) [P(DDA)] + supercritical CO_2. Cloud-point data are obtained regarding the effect of DME cosolvent on the P(DDA) + supercritical CO_2 binary system. Binary cloud-point curves are also obtained for P(DDA) in supercritical propane, propylene, butane, 1-butene, and DME. These data show the effect of solvent polarity on the location of cloud-point curves.

Table 1 lists the critical temperature (T_c), critical pressure (p_c), acentric factor (ω), polarizability (α), dipole moment (μ), and quadrupole moment (Q) of each solvent and cosolvent used in this study.[7,14−18] C_3 (propane and propylene) hydrocarbons (or C_4 hydrocarbons) have similar critical properties and polarizabilities. In addition, a double bond within C_3- and C_4-hydrocarbons generates significant quadrupole moments that favor interaction with polar DDA groups in the polymer. Hence, quadrupole interactions, which are essentially independent of dispersion interactions, can be evaluated by comparing cloud-point curves from each pair of alkane and alkene solvents. DME has a significant dipole moment that allows the effect of dipole interactions to be compared with that of quadrupole interactions found with alkenes and CO_2.

Monomers DDA and DME are used as cosolvents with CO_2. Tsang and Streett[19] previously reported a thorough experimental

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data set for the CO_2 + DME binary system, which has a continuous critical-mixture curve and a maximum pressure of 8.0 MPa at about 320.2 K. Since there are no data from the literature available on these mixtures, vapor−liquid equilibria data for the CO_2 + DDA binary mixture were obtained to complement the P(DDA) + CO_2 + DDA data presented here. These data complement the P(DDA) + CO_2 + DME data obtained in the current study. Therefore, the binary phase behavior data for CO_2 with DDA or DME show if any one of the three binary mixtures form multiple phases in the pressure−temperature−composition (p, T, x) regions in which the cosolvents are used. The CO_2 + DDA experimental data were fit to the Peng−Robinson equation of state[13] to calculate phase boundary curves at elevated operating temperatures and pressures.

Experimental Section

Materials. CO_2 (mass fraction purity > 0.998) was obtained from Daesung Industrial Gases Co., propane (mass fraction purity >0.980) from LG Gas (E1), and propylene (mass fraction purity > 0.996), butane (mass fraction purity > 0.970), 1-butene (mass fraction purity > 0.995), and DME (mass fraction purity > 0.995) from Yeochun NCC Co. DDA (min mass fraction purity > 0.990; CAS RN 2156-97-0) was obtained from Polysciences, Inc. These materials were used with no further purification. Poly(dodecyl acrylate) [P(DDA)] (M_w = about 44 000; M_w/M_n: 1.6; T_g = 243.2 K; CAS RN 26246-92-4) was obtained from Scientific Polymer Product, Inc. Upon arrival, the P(DDA) was in a toluene solution, and the polymer solution was placed under vacuum for at least 10 h in the rotary evaporator (Tamato Scientific Co., model RE-47) for toluene removal.

Apparatus and Procedure. Vapor−liquid equilibrium and cloud-point curves were obtained using a high-pressure, variable-volume cell described in detail elsewhere.[20,21] The experimental apparatus was used to construct the $p-x$ isotherms for the DDA + CO_2 binary mixtures[20] and the cloud-point curves for the polymer + SCF solvent + cosolvent mixtures.[21] The mixture in the view cell was compressed to the desired pressure by an internal piston displaced with water in a high-pressure generator (model: HIP 37-5.75-60). The mixture pressure in the view cell was measured with a Heise gauge (model: Dresser CM-108952, (0 to 345.0) MPa, accurate to ± 0.35 MPa; model: Dresser CM-53920, (0 to 34.0) MPa, accurate to ± 0.03 MPa).

The bubble point, dew point, and critical point were measured for the CO_2 + DDA system. The solution in the cell is compressed to one phase at a fixed temperature. The inside solution is maintained in the one-phase region for at least (30 to 40) min to reach phase equilibrium. The pressure is then slowly decreased until a two-phase region appears. A bubble point is obtained when small vapor bubbles appear first in the cell, while a dew point is obtained if a fine mist appears in the cell. Critical points are obtained by adjusting the temperature and pressure of the mixture until critical opalescence is observed along with equal liquid and vapor volume upon the formation of the two phase.

Cloud points were measured for each polymer solution at a fixed P(DDA) concentration of $w = 5.0 \pm 1.0$ %, which is typical for polymer + SCF solvent studies. The cell was loaded with polymer to within ± 0.001 g, which was then purged with nitrogen followed by CO_2 to ensure that all of the air was removed. DDA was injected into the cell to within ± 0.002 g using a syringe, followed by a gravimetric transfer of supercritical solvents into the cell to within ± 0.004 g using a high-pressure bomb. The system temperature was typically maintained within a range ± 0.2 K below 473 K. Cloud points were measured and reproduced at least twice to within ± 0.28 MPa and ± 0.3 K. Vapor−liquid equilibrium data for the CO_2 + DDA mixtures were measured and reproduced at least twice to within ± 0.03 MPa and ± 0.2 K. Mole fractions of monomer are accurate to ± 0.002.

Table 2. Experimental Cloud-Point Data for the P(DDA) (1) + Solvent (2) System Measured in This Study[a]

T/K	p/MPa
$w_1 = 0.056$, $w_2 = 0.944$ (Propane)	
333.9	8.79
354.2	12.93
375.2	16.72
395.0	19.66
413.8	22.24
435.1	24.66
455.6	26.38
$w_1 = 0.051$, $w_2 = 0.949$ (Propylene)	
333.4	7.76
354.1	12.24
375.4	16.38
395.4	20.17
413.3	22.59
435.2	25.35
454.7	27.76
$w_1 = 0.054$, $w_2 = 0.946$ (1-Butene)	
394.6	3.97
413.5	6.72
434.0	9.83
453.7	12.72
$w_1 = 0.050$, $w_2 = 0.950$ (n-Butane)	
392.1	4.31
413.5	7.76
433.1	10.66
454.6	13.28
$w_1 = 0.047$, $w_2 = 0.953$ (DME)	
374.3	3.62
392.3	7.76
413.2	12.03
432.5	15.35
454.5	18.10

[a] w_i is the mass fraction.

Experimental Results and Discussion

Phase Behavior for P(DDA) + SCF Solvent Mixture. Table 2 and Figure 1 show the cloud points of P(DDA) dissolved in supercritical propane, propylene, butane, 1-butene, and DME. The cloud-point behavior for the P(DDA) + C_3 hydrocarbons (propane and propylene), + C_4 hydrocarbons (butane and 1-butene), and + DME mixture exhibit lower critical solution temperature (LCST) type curves with positive slopes. The phase behavior for the P(DDA) + C_3 hydrocarbon mixture is presented at temperatures ranging from (333 to 453) K and pressures ranging from (6.5 to 27.5) MPa. The cloud-point behavior for the P(DDA) + C_4 hydrocarbons systems is presented at the temperature range of (393 to 453) K and pressure range of (3.0 to 13.0) MPa. At 423 K, the phase behavior boundary has a pressure difference of about 15.0 MPa due to the difference in polarizability between C_3 hydrocarbons (about $6.3 \cdot 10^{-30}$ m^3) and C_4 hydrocarbons (about $8.2 \cdot 10^{-30}$ m^3), as shown in Table 1.

Phase Behavior for P(DDA) + SCF CO_2 + DDA Mixture. Table 3 and Figure 2 show the cloud-point behavior of the P(DDA) + CO_2 + DDA systems. P(DDA) does dissolve in pure CO_2 at a temperatures higher than 463 K and pressures

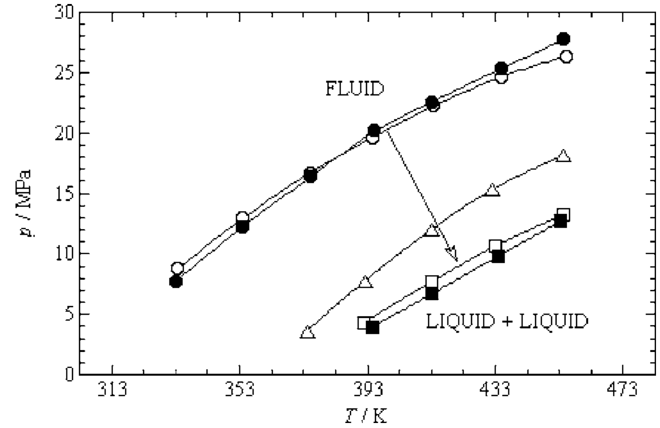

Figure 1. Phase behavior of P(DDA) dissolved in supercritical propane, propylene, butane, 1-butene, and dimethyl ether (DME). The mass fraction of polymers is about $w_1 = 0.05$ for each solution. ○, propane; ●, propylene; □, butane; ■, 1-butene; △, DME.

Table 3. Experimental Cloud-Point Curve for the P(DDA) (1) + CO_2 (2) + DDA (3) System with Different DDA Content Measured in This Study[a]

T/K	p/MPa
$w_1 = 0.052$, $w_3 = 0.00$	
456.9	205.28
459.0	169.55
460.5	157.07
463.4	150.14
$w_1 = 0.055$, $w_3 = 0.080$	
408.9	179.48
411.0	140.86
413.6	126.38
417.0	116.17
437.1	105.62
451.9	101.59
$w_1 = 0.051$, $w_3 = 0.148$	
371.5	181.90
372.6	121.55
375.6	104.72
383.6	90.41
396.5	82.79
412.1	79.14
435.8	76.00
456.0	76.10
$w_1 = 0.053$, $w_3 = 0.207$	
342.3	145.21
342.8	104.31
346.2	85.17
356.8	69.86
374.9	62.14
394.3	59.62
413.7	59.76
434.0	60.21
453.3	60.90
$w_1 = 0.047$, $w_3 = 0.260$	
315.5	75.35
323.7	61.35
336.2	51.90
356.9	45.69
375.4	46.38
395.2	46.72
415.6	47.76
437.2	49.66
455.8	50.86

[a] w_i is the mass fraction.

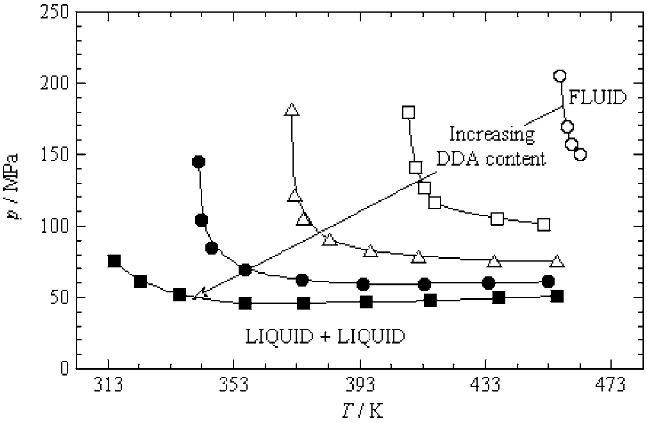

Figure 2. Impact of the DDA monomer (on a polymer-free basis) on the phase behavior of the P(DDA) (1) + CO_2 (2) + $w_3 = x$ DDA (3) system. The mass fraction of polymer is about $w_1 = 0.05$ for each solution. ○, $w_3 = 0.00$; □, $w_3 = 0.08$; △, $w_3 = 0.148$; ●, $w_3 = 0.207$; ■, $w_3 = 0.260$.

Table 4. Experimental Cloud-Point (CP), Bubble-Point (BP), and Liquid−Liquid−Vapor (LLV) Data for the P(DDA) (1) + CO_2 (2) + DDA (3) System Measured in This Study[a]

T/K	p/MPa	transition
	$w_1 = 0.054$, $w_3 = 0.398$	
	Cloud-Point Transition	
395.1	24.93	CP
412.3	26.93	CP
432.9	28.55	CP
	Bubble-Point Transition	
362.9	20.54	BP
376.6	22.38	BP
	Liquid−Liquid−Vapor	
394.2	24.01	LLV

[a] w_i is the mass fraction.

higher than about 150 MPa. The cloud-point behavior for P(DDA) in supercritical CO_2 shows an upper critical solution temperature (UCST) curve.[22] When $w_3 = 0.080$ or $w_3 = 0.148$ DDA were added to the solution, the cloud-point curve exhibited UCST-type phase behavior with negative slopes. P(DDA) + CO_2 + $w_3 = 0.080$ DDA and P(DDA) + CO_2 + $w_3 = 0.148$ DDA systems did not dissolve at below temperatures of (403 and 363) K, respectively. As temperatures are increased above (413 or 383) K, the cloud-point pressure decreases, but only to 75.0 ± 5.0 MPa and 105.0 ± 5.0 MPa at 433 K. With $w_3 = 0.207$ or $w_3 = 0.260$ DDA in solution, the cloud-point curves are essentially flat at about 60 MPa ($w_3 = 0.207$ DDA) and 50 MPa ($w_3 = 0.260$ DDA), respectively, in a temperature range of (353 to 453) K. The cloud-point curves for the P(DDA) + CO_2 + $w_3 = 0.207$ and $w_3 = 0.260$ DDA systems exhibit upper-lower critical solution temperature (U-LCST) region phase behavior from a negative to positive slope.

Table 4 and Figure 3 show the impact of $w_3 = 0.398$ DDA monomer on the phase behavior of the P(DDA) + CO_2 solution. At 413 K, the phase boundary has shifted the pressure lower as the concentration of DDA increases. The P(DDA) + CO_2 + $w_3 = 0.398$ DDA phase behavior curve intersects the liquid → liquid + vapor (LV) curve at about 383 K and 23.0 MPa. These results clearly demonstrate that obtaining a single phase extending over a large temperature range at modest pressures is possible if sufficient amounts of free acrylate monomer are added to the solution.

Vapor−Liquid Equilibria for the SCF CO_2 + DDA Mixture. Table 5 and Figure 4 show the experimental pressure−composition (p, x) isotherms at temperatures of (313.2, 333.2, 353.2, 373.2, and 393.2) K and pressures in the range of (2.5 to 26.14) MPa for the CO_2 + DDA system. The three phases were not observed at any of the five temperatures studied.

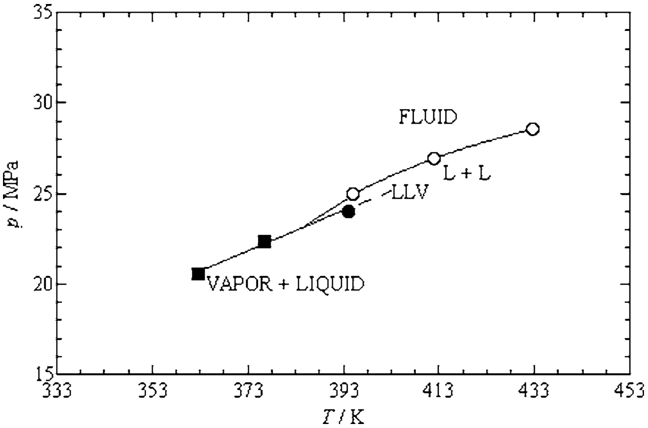

Figure 3. Impact of $w_3 = 0.398$ DDA monomer (on a polymer-free basis) on the phase behavior of the P(DDA) (1) + CO_2 (2) system. ○, fluid → liquid + liquid transition; ■, fluid → liquid + vapor transition; ●, liquid + liquid (L + L)→ liquid$_1$ + liquid$_2$ + vapor (LLV) transition; ----, suggested extension of the LLV line.

The (p, x) isotherms shown in Figure 4 are consistent with the characteristics expected for type I phase behavior, in which a maximum occurs in the critical locus. The experimental data in the (p, x) isotherms obtained in this work are modeled using the Peng−Robinson equation of state.[13] Table 6 lists the pure component critical temperatures, critical pressures, and the acentric factors of the CO_2[14] and DDA[14] used with the Peng−Robinson equation of state.[13] The properties of DDA were calculated by the Joback group-contribution methods.[14] Also, the vapor pressures were calculated by the Lee−Kesler method.[14] Values for the two binary interaction parameters were determined by applying (nonlinear least-squares) regression to the experimental data at 353.2 K using the Peng−Robinson equation of state and by minimizing the objection function (OBF).

$$\mathrm{OBF} = \sum_{i}^{N} \left(\frac{P_{\mathrm{exp}} - P_{\mathrm{cal}}}{P_{\mathrm{exp}}} \right)^2$$

Figure 4 compares the experimental results for the CO_2 + DDA system with calculated values obtained by the Peng−Robinson equation at a temperature of 353.2 K. The values of the adjusted parameters for the CO_2 + DDA system are $k_{ij} = 0.035$ and $\eta_{ij} = 0.030$. As shown in Figure 4, we used these adjusted values to compare experimental results with calculated (p, x) isotherms for the CO_2 + DDA system at temperatures of (313.2, 333.2, 373.2, and 393.2) K. A good fit of the data was obtained using the Peng−Robinson equation and adjustable mixture parameters for the CO_2 + DDA system. Figure 5 compares the experimental data with the critical mixture curves calculated by the Peng−Robinson equation of state for the CO_2 + DDA system. The experimental data and calculated critical mixture curve is type I[11] and in agreement with experimental observations.

Table 5. Experimental Data for the Carbon Dioxide (1) + DDA (2) System Measured in This Study[a]

x_2	p/MPa	transition
	T/K = 313.2	
0.009	9.62	BP
0.014	9.59	BP
0.026	9.52	BP
0.050	9.32	BP
0.075	9.16	BP
0.107	8.81	BP
0.148	8.38	BP
0.262	6.62	BP
0.407	4.76	BP
0.501	3.42	BP
0.566	2.85	BP
0.649	2.31	BP
	T/K = 333.2	
0.009	15.07	CP
0.014	15.07	BP
0.026	15.02	BP
0.050	14.52	BP
0.075	13.86	BP
0.107	13.11	BP
0.148	12.16	BP
0.262	9.07	BP
0.407	6.09	BP
0.501	4.44	BP
0.566	3.60	BP
0.649	2.84	BP
	T/K = 353.2	
0.009	19.19	DP
0.014	19.88	CP
0.026	19.67	BP
0.050	18.98	BP
0.075	18.34	BP
0.107	17.56	BP
0.148	16.22	BP
0.262	11.63	BP
0.407	7.46	BP
0.501	5.59	BP
0.566	4.28	BP
0.649	3.33	BP
	T/K = 373.2	
0.009	22.76	DP
0.014	23.20	DP
0.026	23.31	CP
0.050	22.62	BP
0.075	22.03	BP
0.107	21.24	BP
0.148	19.78	BP
0.262	13.86	BP
0.407	8.84	BP
0.501	6.36	BP
0.566	4.80	BP
0.649	3.60	BP
	T/K = 393.2	
0.009	25.10	DP
0.014	26.01	DP
0.026	26.14	DP
0.050	25.56	BP
0.075	24.97	BP
0.107	24.12	BP
0.148	22.40	BP
0.262	16.03	BP
0.407	10.21	BP
0.501	7.02	BP
0.566	5.37	BP
0.649	3.99	BP

[a] BP is the bubble point, CP the critical point, and DP the dew point. x_i is the mole fraction.

Phase Behavior for the P(DDA) + SCF CO$_2$ + DME Mixture. Figure 6 and Table 7 show the phase behavior in the P(DDA) + CO_2 + DME mixture. A single-phase region in the P(DDA) + CO_2 mixture was obtained at temperatures in the range of (418.2 to 473.2) K and at very high pressures such as 192.2 MPa (at 418.2 K), while that in the P(DDA) + DME mixture was obtained at temperatures in the range of (373.2 to 453.2) K and at relatively low pressures higher than 17.8 MPa (at 453.2 K). The pressure difference between two systems is due to the presence of a dipole moment in DME [$4.34 \cdot 10^{-30}$ C·m] and CO_2 [$0.0 \cdot 10^{-30}$ C·m], as shown in Table 1. The P(DDA) + CO_2 + $w_3 = 0.094$ and $w_3 = 0.184$ DME mixtures

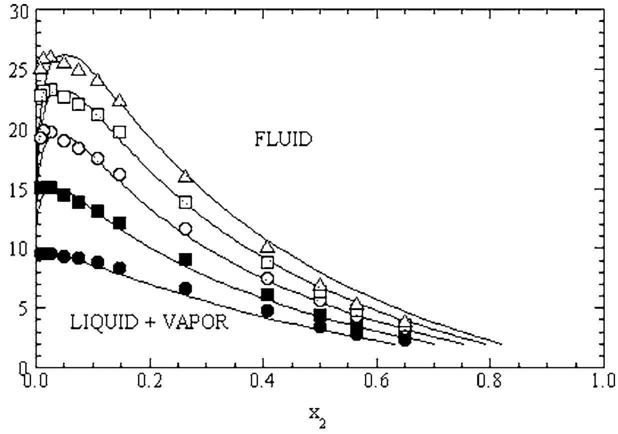

Figure 4. Comparison of experimental data (symbols) for the CO_2 (1) + DDA (2) system with calculated data (solid lines) obtained using the Peng−Robinson equation of state with $k_{ij} = 0.035$ and $\eta_{ij} = 0.030$. ●, 313.2 K; ■, 333.2 K; ○, 353.2 K; □, 373.2 K; △, 393.2 K.

Table 6. Pure-Component Parameters for the Peng−Robinson Equation of State

compound	M_w	T_c/K	p_c/MPa	ω
carbon dioxide	44.01	304.3	7.38	0.225
DDA	240.4	764.7	1.47	0.775

show UCST-type behavior of a negative slope, while their pressures increase rapidly below about 423.2 K. With w_3 = 0.293 DDA added to the solution, the cloud-point curve exhibited UCST region phase behavior that maintains a negative slope. The P(DDA) + CO_2 + w_3 = 0.412 DME system shows U-LCST-type behavior from a negative slope to positive slope. The cloud-point pressure remains virtually constant at 50 MPa over a temperature range from (333.2 to 453.2) K. The location in which the curve demonstrates U-LCST type behavior is mainly controlled by entropic contributions, which are sensitive to the changes in pressure. This type of behavior is probably due to the difference in free volume among P(DDA), CO_2, and DME. Tsang and Streett[19] previously reported a thorough experimental data set for the CO_2 + DME binary system which has a continuous critical-mixture curve with a maximum pressure of 8.0 MPa at about 320 K. They also demonstrated that the Peng−Robinson equation of state[13] provides a very adequate representation of the experimental data if a k_{ij} value of −0.020 is used. These DME + CO_2 data complement the P(DDA) + CO_2 + DME data obtained in the current study.

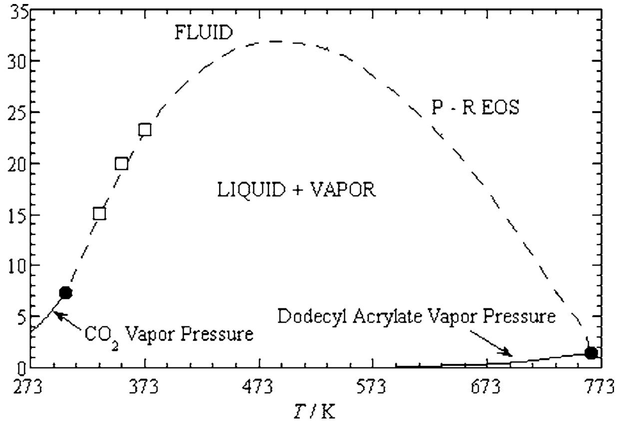

Figure 5. Plot of pressure against temperature for the CO_2 + DDA system. Solid lines and circles represent the vapor−liquid lines and critical points for pure CO_2 and DDA. Open squares are mixture critical points determined from isotherms measured in this work. Dashed lines represent calculations obtained using the Peng−Robinson equation of state with k_{ij} equal to 0.035 and η_{ij} equal to 0.030.

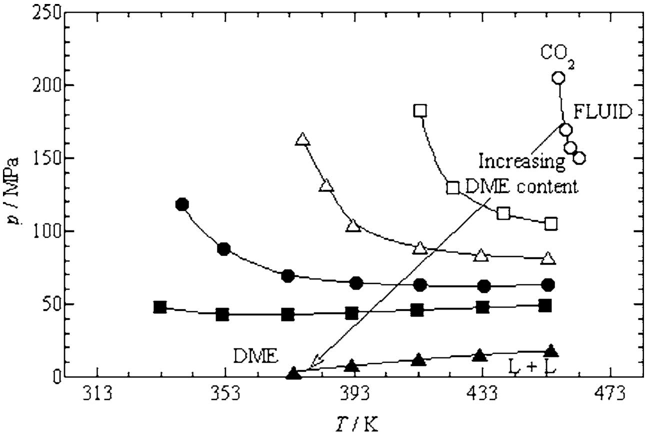

Figure 6. Phase behavior for the P(DDA) + CO_2 + $w_3 = x$ DME system. The mass fraction of polymer is about $w_1 = 0.05$ for each solution. ○, w_3 = 0.000; □, w_3 = 0.094; △, w_3 = 0.184; ●, w_3 = 0.293; ■, w_3 = 0.412; ▲, w_3 = 1.00.

Table 7. Experimental Cloud-Point Data for the P(DDA) (1) + CO_2 (2) + DME (3) System with Different DME Content Measured in This Study[a]

T/K	p/MPa
$w_1 = 0.050$, $w_3 = 0.094$	
413.7	182.59
424.0	129.83
439.7	111.90
454.6	105.17
$w_1 = 0.050$, $w_3 = 0.184$	
377.3	163.62
384.7	131.55
393.1	103.97
414.0	88.79
432.8	83.62
453.7	81.55
$w_1 = 0.047$, $w_3 = 0.293$	
339.6	118.10
352.8	87.76
372.5	69.83
393.7	64.66
413.6	62.93
433.7	62.59
453.8	63.28
$w_1 = 0.046$, $w_3 = 0.412$	
332.9	48.10
352.3	43.28
372.6	42.93
392.4	44.31
412.9	46.03
433.3	47.76
452.6	49.28

[a] w_i is the mass fraction.

Comparison of Cloud-Point Curves for the Polymer + SCF CO_2 Mixture. Figure 7 shows the comparison of experimental cloud-point curves for mixtures of poly(hexyl acrylate) [P(HA), M_w = 90 000, T_g = 216.2 K],[10] poly(octyl acrylate) [P(OA), M_w = 100 000, T_g = 208.2 K],[23] poly(decyl acrylate) [P(DA), M_w = 130 000, T_g = unknown],[9] and P(DDA) [M_w = 50 000, T_g = 243.2 K] in supercritical CO_2. As shown in Figure 7, we presented the weight-average molecular weight (M_w) and glass transition temperature (T_g) of the polymers. A comparison of the cloud-point curves of P(HA), P(OA), P(DA), and P(DDA) shows that the cloud-point temperature increases smoothly as the length of the alkyl tail is increased, a result

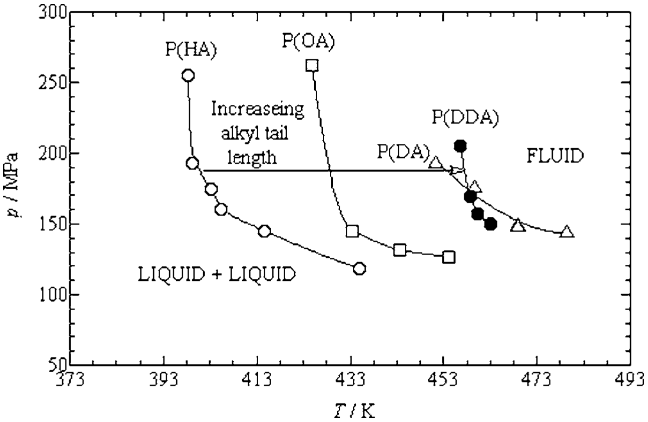

Figure 7. Impact of the straight chain alkyl tail of the acrylate group on the cloud-point curves of poly(hexyl acrylate) [P(HA), $M_w = 90\,000$, $T_g = 216.2$ K], poly(octyl acrylate) [P(OA), $M_w = 100\,000$, $T_g = 208.2$ K], poly(decyl acrylate) [P(DA), $M_w = 130\,000$, T_g = unknown], and P(DDA) [$M_w = 50\,000$, $T_g = 243.2$ K] in supercritical CO_2. T_g is the glass transition temperature, and M_w is the weight-average molecular weight.

similar to the one discussed by Rindfleisch et al.[22] As the alkyl tail on the acrylate increases, the polarity effectively decreases since the reduced dipole moment is in inverse proportion to the square root of the molar volume. From the ordering of the curves in the pressure−temperature space, it is quite clear that M_w nor T_g decides on the cloud-point behavior. If it were, the P(DDA) + CO_2 curve would be at the lowest temperature. The P(DDA), however, turns up clearly in pressure at 455 K. This suggests that CO_2 is so polar that it cannot dissolve P(DDA) even at this very high temperature. On the contrary, as the straight alkyl tail of the acrylate is decreased, polymers remain in solution at lower temperatures and fixed pressures, suggesting that quadrupole−dipole interactions between the acrylate group and CO_2 are favorable for solubility.

Conclusions

The cloud-point curves for the binary mixtures of P(DDA) in supercritical propane, propylene, butane, 1-butene, and DME are presented at temperatures from (333 to 456) K and at pressures from (3.62 to 26.38) MPa. Experimental cloud-point data of the P(DDA) + CO_2 + DDA mixture were obtained at temperatures below 463 K and pressures up to 205.3 MPa. With $w_3 = 0.398$ DDA, the phase behavior curve shows vapor−liquid, liquid−liquid, and liquid−liquid−vapor equilibria. The cloud-point curve shows an LCST-type phase behavior. Furthermore, the effect of DME on the P(DDA) + $w_3 = (0.094$ to $0.412)$ DME system in supercritical CO_2 is presented at temperatures below 455 K and at pressures ranging from (43 to about 183) MPa. The effect of the straight chain alkyl tail of the acrylate group was examined in cloud-point curves of P(HA), P(OA), P(DA), and P(DDA) in supercritical CO_2. Morever, cloud-point curves of P(DDA) and the P(DDMA) + CO_2 mixture were used to compare the effects of the DDA and DDMA cosolvents. The vapor + liquid equilibrium data of the CO_2 + DDA binary system is shown at temperatures ranging from (313.2 to 393.2) K and at pressures up to 26.14 MPa. The CO_2 + DDA system exhibits type I phase behavior and not liquid−liquid−vapor behavior. Experimental data for the CO_2 + DDA system were correlated with two adjustable parameters provided by the Peng−Robinson equation of state.

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