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Solubility of Behenic Acid in Supercritical CO_2 with *n*-Pentane or *n*-Octane Cosolvents

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Solubilities of behenic acid in supercritical (SC) CO_2 with *n*-pentane or *n*-octane cosolvents were measured at 308.15 K, 318.15 K, and 328.15 K in the pressure range from 9.0 MPa to 16.0 MPa and cosolvent concentration range from 0 mol % to 7.5 mol %. The effects of cosolvent concentration, pressure, and temperature on solubility were investigated.

Introduction

Supercritical fluids (SCFs) possess extraordinary properties including high diffusivity, low viscosity, and high compressibility, which make them attractive solvents for many industrial processes. Supercritical (SC) CO_2 is the most popular among SCFs because it is nontoxic, nonflammable, and easy to obtain and has a near-ambient critical temperature. However, the solubility of some strongly polar substances in SC CO_2 is very low, which has become an obstacle for its utilization.

Many researchers have studied the effects of polar cosolvents on the solubilities of polar organic compounds in SC CO_2 (Guan et al., 1998a,b, 1999; Zhong et al., 1997; Koga et al., 1996; Johannsen and Brunner, 1995; Foster et al., 1993; Gurdial et al., 1993; Lemert and Johnston, 1991; Walsh et al., 1987). The mechanism of the effect of a cosolvent on the solubility is very complicated and is not well-understood. However, it is known that a polar cosolvent may interact with a polar solute through hydrogen bonding, dispersion forces, dipole−dipole forces, etc. Studies of the effect of nonpolar cosolvents on the solubility are scarce.

Behenic acid ($CH_3(CH_2)_{20}COOH$) has a large alkyl chain and a polar head. The solubility of behenic acid in pure SC CO_2 is very low (Chrastil, 1982; Yoon et al., 1998); however it can be enhanced by an ethanol cosolvent (Guan et al., 1999). No reports about the effect of nonpolar cosolvents on the solubility of behenic acid in SC CO_2 were found in the literature. It is expected that dispersion forces play a major role in the effect of a nonpolar cosolvent on its solubility. In this work, we studied the solubility of behenic acid in SC CO_2 with *n*-pentane or *n*-octane cosolvents.

Experimental Section

Apparatus and Procedures. The apparatus and experimental procedures for measuring the solubility were described in detail previously (Ke et al., 1996). The apparatus consisted mainly of an optical cell, a gas cylinder, a syringe pump, a digital pressure gauge, a solenoid-operated pump, a vapor sample bomb, a constant-temperature bath, and valves and fittings of various kinds.

The reliability of the apparatus and the procedures were verified by measuring the solubilities of salicylic acid and stearic acid in SC CO_2 and then comparing these results with data reported by others. This was discussed in our previous papers (Ke et al., 1996; Guan et al., 1999). It is estimated that the accuracy of the data is better than ±5%.

Table 1. Solubility of Solute in the SC CO_2−Pentane Mixture and the Apparent Density of CO_2 at 318.15 K

$Y_3 \times 10^2$	$Y_2 \times 10^5$	d_1/(mol·L^{-1})	$Y_3 \times 10^2$	$Y_2 \times 10^5$	d_1/(mol·L^{-1})
9.0 MPa					
0.00	0.59	7.55	3.33	2.63	9.89
2.06	1.20	9.43	5.17	4.10	11.5
9.5 MPa					
0.00	1.05	9.53	4.05	3.98	12.1
2.94	2.24	11.6	5.03	4.22	12.4
10.0 MPa					
0.00	1.26	12.1	4.08	4.37	12.9
1.89	2.14	12.8	5.08	4.47	12.7
11.0 MPa					
0.00	1.82	13.5	3.81	4.57	13.7
2.92	3.24	14.0	5.64	7.76	13.6
13.5 MPa					
0.00	2.95	16.1	3.61	5.61	15.2
2.69	5.37	15.4	4.57	7.94	14.9
16.0 MPa					
0.00	3.55	17.3	3.36	8.51	16.1
2.68	6.46	16.3	4.87	11.2	16.0

Materials. CO_2 with a purity of 99.995% was supplied by Beijing Analytical Instrument Factory; *n*-pentane and *n*-octane were analytical reagent (A.R.) grade (99.7%) produced by Beijing Chemical Plant and were used without further purification. The behenic acid (A.R. grade) was supplied by Beijing Chemical Reagent Co. Before use, it was recrystallized, and the melting range of the purified chemical was determined to be from 353.0 K to 354.9 K.

Results and Discussion

The solubility of behenic acid in SC CO_2 with *n*-pentane or *n*-octane as cosolvent was measured at 308.15 K, 318.15 K, and 328.15 K in the pressure range from 9.0 MPa to 16.0 MPa and the cosolvent concentration range from 0 mol % to 7.5 mol %. There is only one fluid phase under our experimental conditions, which was seen clearly in the optical cell of the experimental apparatus. The results are listed in Tables 1−4, where Y_2 and Y_3 are the mole fractions of the solute and the cosolvents in the fluid phase, respectively; d_1 is the apparent density of CO_2, expressed as moles of CO_2 per liter of the mixture.

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Table 2. Solubility of Solute in the SC CO_2−Pentane Mixture and the Apparent Density of CO_2 at 328.15 K

$Y_3 \times 10^2$	$Y_2 \times 10^5$	d_1/(mol·L^{-1})	$Y_3 \times 10^2$	$Y_2 \times 10^5$	d_1/(mol·L^{-1})
		9.0 MPa			
0.00	0.32	6.82	5.36	2.14	7.90
4.07	1.05	7.05	7.50	6.03	6.89
		9.5 MPa			
0.00	0.63	7.64	6.07	4.33	7.16
3.08	1.95	8.02	7.16	6.31	7.15
		10.0 MPa			
0.00	1.02	7.69	5.17	6.31	8.94
4.34	3.55	8.40	6.15	8.13	9.82
4.66	3.89	8.48			
		11.0 MP			
0.00	1.63	9.96	5.19	10.4	11.1
3.74	6.87	10.4	5.54	13.8	11.5
		13.5 MPa			
0.00	6.17	14.2	4.73	25.1	13.6
3.77	23.1	13.5	5.59	27.5	13.1
		16.0 MPa			
0.00	11.2	15.8	4.13	35.5	14.6
3.53	25.1	14.4	5.59	39.8	14.2

Table 3. Solubility of Behenic Acid in the SC CO_2−*n*-Octane Mixture and the Apparent Density of CO_2 at 308.15 K

$Y_3 \times 10^2$	$Y_2 \times 10^5$	d_1/(mol L^{-1})	$Y_3 \times 10^2$	$Y_2 \times 10^5$	d_1/(mol L^{-1})
		8.0 MPa			
0.00	0.68	11.5	2.14	1.32	14.5
1.03	0.79	13.7	3.04	1.82	14.6
		8.5 MPa			
0.00	0.91	13.9	2.08	1.66	15.3
1.04	1.12	14.9	2.85	2.09	15.2
1.94	1.26	15.4			
		9.5 MPa			
0.00	1.07	15.7	3.06	2.51	15.7
1.03	1.35	15.8	3.24	2.63	15.7
2.06	1.91	16.0			
		11.0 MPa			
0.00	1.23	16.9	2.16	2.19	16.5
1.11	1.58	16.7	3.01	3.16	16.3
		13.5 MPa			
0.00	1.32	18.0	2.89	3.47	17.0
1.15	1.82	17.6	3.06	3.49	16.9
2.05	2.40	17.4			
		16.0 MPa			
0.00	1.38	18.8	1.98	2.51	17.9
0.96	2.09	18.5	2.75	4.07	17.6

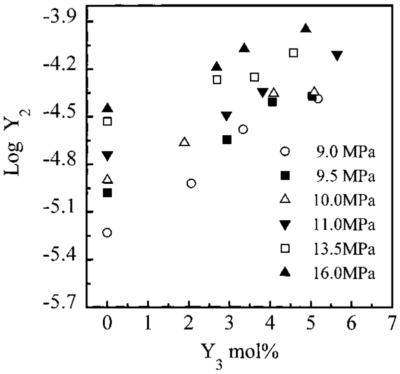

Figure 1. Solubility of behenic acid in the SC CO_2−*n*-pentane mixture at 318.15 K.

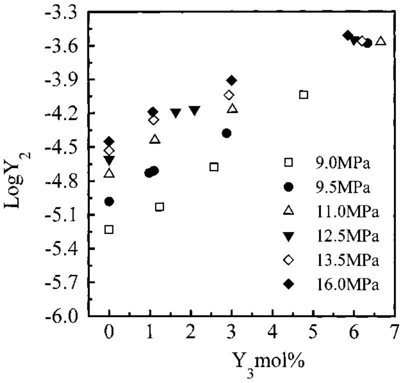

Figure 2. Solubility of behenic acid in the SC CO_2−*n*-octane mixture at 318.15 K.

Table 4. Solubility of Solute in the SC CO_2−*n*-Octane Mixture and the Apparent Density of CO_2 at 318.15 K

$Y_3 \times 10^2$	$Y_2 \times 10^5$	d_1/(mol L^{-1})	$Y_3 \times 10^2$	$Y_2 \times 10^5$	d_1/(mol L^{-1})
		9.0 MPa			
0.00	0.58	8.65	2.57	2.08	10.3
1.24	0.94	9.28	4.77	9.11	11.3
		9.5 MPa			
0.00	1.05	10.5	2.88	4.17	12.7
0.98	1.86	11.3	6.34	26.3	13.3
1.10	1.95	11.5			
		11.0 MPa			
0.00	1.84	14.4	3.02	6.90	14.3
1.12	3.59	14.3	6.66	27.1	14.0
		12.5 MPa			
0.00	2.44	15.6	2.09	6.70	14.8
1.63	6.47	15.2	6.00	28.2	14.6
		13.5 MPa			
0.00	2.92	16.4	2.93	9.20	15.6
1.09	5.45	15.8	6.20	27.8	14.8
		16.0 MPa			
0.00	3.51	17.3	3.00	12.2	15.9
1.07	6.51	16.9	5.85	30.7	15.2

Figure 1 shows the effect of *n*-pentane concentration on the solubility of behenic acid in the CO_2−*n*-pentane system at 318.15 K, which indicates that the solubility increases with cosolvent concentration under the same pressure. *n*-Octane has a similar effect on solubility, as shown in Figure 2. However, *n*-octane enhances the solubility more significantly than *n*-pentane at the same molar concentration, which can be observed from Figures 1 and 2. This can be interpreted qualitatively. The interaction between behenic acid and the cosolvent molecules is mainly due to dispersion forces. The interaction between *n*-octane and behenic acid molecules is stronger because the size of *n*-octane is larger than that of *n*-pentane, which enhances its solubility. On the other hand, SC CO_2 can aggregate with the cosolvent and solute molecules, which causes larger local density around the cosolvent and solute molecules. The aggregation between the solvent and cosolvent molecules reduces the interaction between the cosolvent and solute. The interaction between CO_2 and *n*-octane is stronger than that between CO_2 and *n*-pentane, which is not favorable to enhancing the solubility of behenic acid. The overall effect depends on which of these two factors is dominant. The solubility measurements show that the first factor is dominant; thus *n*-octane affects solubility more significantly.

Figures 3 and 4 show the dependence of the solubility on pressure. The figures demonstrate that at lower pressures or lower cosolvent concentrations, the solubility is a strong function of pressure. At higher pressures and higher cosolvent concentrations the effect is relatively weak because the effect of pressure on the density of the fluid

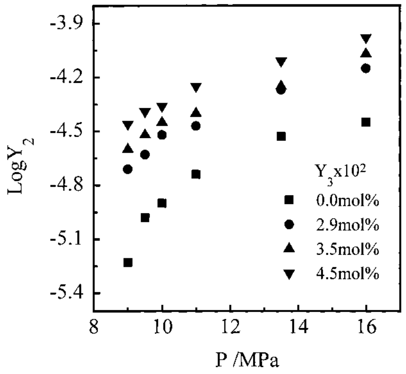

Figure 3. Effect of pressure on the solubility of behenic acid in the SC CO_2−*n*-pentane mixture at 318.15 K.

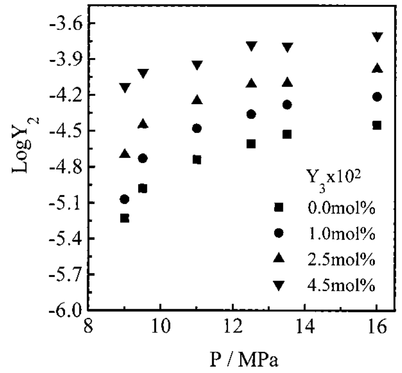

Figure 4. Effect of pressure on the solubility of behenic acid in the SC CO_2−*n*-octane mixture at 318.15 K.

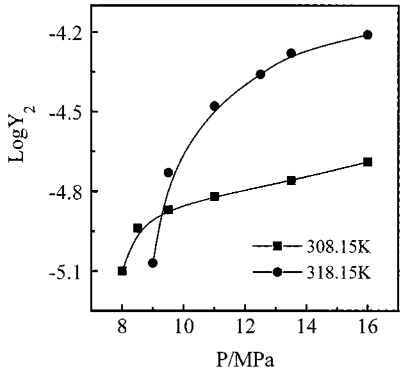

Figure 5. Effect of temperature on the solubility of behenic acid at an *n*-octane concentration of 1.0 mol %.

phase is very limited at these conditions, as shown by the measurements in Tables 1 and 4.

Figure 5 gives the solubility of behenic acid in the CO_2−*n*-octane system at 308.15 K and 318.15 K with an *n*-octane concentration of 1.0 mol %. It can be seen that there is a crossover point at about 9.3 MPa. At a pressure less than this value, the solute is more soluble at the lower temperature; at the higher pressures, the solute is more soluble at a higher temperature. Temperature affects the solubility in the following ways in opposition: the volatility of the solute increases with temperature, which is favorable to increasing the solubility, but, the density of the fluid decreases with temperature, which is not favorable to increasing the solubility. As shown in Tables 3 and 4, the density of CO_2 at 318.15 K is much lower than that at 308.15 K at the lower pressures. Thus, the density effect is dominant, and the solubility decreases with temperature. At higher pressures, the density of CO_2 is not as sensitive to the pressure as that at lower pressures, and the volatility effect becomes dominant and the solubility increases with temperature.

Conclusion

The solubility of behenic acid in SC CO_2−*n*-pentane or in SC CO_2−*n*-octane mixtures increases with cosolvent concentration and pressure. Under similar experimental conditions, *n*-octane affects the solubility more significantly than *n*-pentane. The solubility is more sensitive to pressure at lower pressures.

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