Solubility of *p*-Nitrobenzoic Acid in Supercritical Carbon Dioxide with and without Cosolvents

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The solubilities of *p*-nitrobenzoic acid in supercritical carbon dioxide and carbon dioxide + cosolvents were determined at (308, 318, and 328) K and over the pressure range from (8.0 to 21.0) MPa. The effect of cosolvents, cyclohexane, ethanol, cyclohexane + acetone (equal-molar mixture), and acetone on the solubility of *p*-nitrobenzoic acid was studied at a mole fraction of 3.0 % (cosolvents in supercritical mixtures). The solubility data in supercritical carbon dioxide in the absence and presence of cosolvents were correlated by the equations proposed by Mendez-Santiago and Teja with satisfactory agreement, respectively.

Introduction

Recently, supercritical carbon dioxide extraction has been used a great deal in many fields. However, carbon dioxide has limitations resulting from its lack of polarity and associated capacity for specific solvent−solute interactions, which limits its use on the supercritical fluid extraction.[1−3] The addition of small amounts of organic solvents can improve its solvent power.[4−8]

The solubility of a solid is probably the most important property in the optimal design of supercritical fluid extraction processes. *p*-Nitrobenzoic acid is an important medical intermediate. Its solubility data in supercritical carbon dioxide have not been reported. In this work, the effect of temperature and pressure on the solubility has been studied for supercritical carbon dioxide and supercritical carbon dioxide with different cosolvents at a mole fraction of 3.0 %.

Experimental Section

Materials. *p*-Nitrobenzoic acid with a minimum purity of 99.5 % was supplied by the Beijing Chemical Regent Factory. Cyclohexane, ethanol, and acetone were purchased from the Beijing Experimental Chemical Factory. Each had a purity of better than 99.5 %. High-purity carbon dioxide of purity higher than 99.9 % was obtained from Beijing Tianhao Chemical Factory. All chemicals were used without further purification.

Apparatus and Procedure. Figure 1 shows the schematic diagram of the apparatus used; it has been described in detail previously.[4,8] The main part was a high-pressure equilibrium cell with glass wool and stainless steel sintered disks at both ends to prevent physical entrainment of undissolved solute into the saturated supercritical fluid stream. The cell and the preheater coils were immersed in a constant-temperature water bath (ChongQing Yinhe Experimental Instrument Corporation, CS-503), which was controlled to ± 0.5 K. The system temperature was measured by a platinum resistance thermometer with an uncertainty of ± 0.1 K, and the system pressure was measured by a pressure meter (Heise, model CTUSA) with an uncertainty of ± 0.05 MPa. Carbon dioxide was pressured by a syringe pump (Nova, model 5542121) with its operating pressure up to 100 MPa. The pump used for cosolvents was a high-pressure pump (Beijing Weixing Factory, model LB-10C) with an uncertainty of ± 0.01 $\text{mL}\cdot\text{min}^{-1}$ for cosolvents flow rate.

Prior to each measurement, about 40 g (with an uncertainty of 0.0001 g) of solid *p*-nitrobenzoic acid mixed with glass beads was packed into the cell, and the loaded cell was placed into the constant-temperature water bath. Subsequently, carbon dioxide and cosolvents from the vessels were compressed into the mixer heated by electricity coils, and then the supercritical mixtures were introduced into the equilibrium cell from the bottom to a preset temperature and pressure. After about 30 min, the solute and solvent reached phase equilibrium through mass transfer in the equilibrium cell. The saturated supercritical fluid was vented from the top of the cell and then depressurized through an expansion valve wrapped with a coiled heater into two weighed U-type tubes in series. The solid solute was dried in the vacuum oven, and its mass was determined by an electronic scale with an uncertainty of ± 0.1 mg (Ohaus, model AR-2140). The overall volume of carbon dioxide exited from the tube was measured by a calibrated wet-gas flow meter with an uncertainty of ± 1 %. The solubility in terms of mole fraction y_2 or y_2' was given by

$$y_2(y_2') = \frac{\dfrac{m_2}{M_2}}{\dfrac{(P_a - P_w)V_1}{RT_w} + \dfrac{m_2}{M_2}} \qquad (1)$$

where y_2 is the mole fraction of *p*-nitrobenzoic acid in pure supercritical carbon dioxide; y_2' is the mole fraction of solute in supercritical carbon dioxide with cosolvents; m_2 is the mass of the trapped *p*-nitrobenzoic acid; M_2 is the molar mass of *p*-nitrobenzoic acid; P_a is the atmospheric pressure; P_w and T_w are the vapor pressure and the temperature of water contained in the wet-gas flow meter, respectively; V_1 is the gas volume measured by the wet-gas flow meter at the temperature T_w; and R is the gas constant.

It was indispensable to clean all parts of the apparatus thoroughly prior to each measurement with a new cosolvent. It was noteworthy that, by investigating the solubility data against the time and the flow rate, 30 min was sufficient to attaint phase equilibrium at the flow rate of 1000 $\text{mL}\cdot\text{min}^{-1}$.

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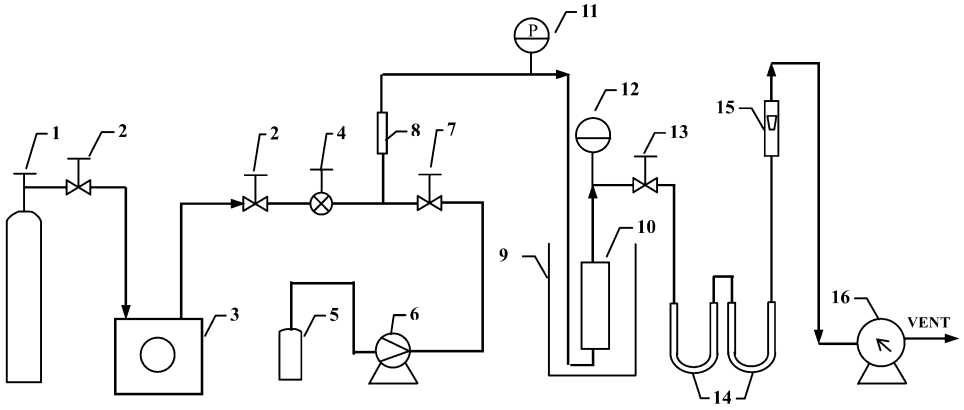

Figure 1. Schematic diagram of the experimental apparatus: 1, CO_2 cylinder; 2, inlet and outlet valves; 3, syringe pump; 4, pressure regulating valve; 5, cosolvent vessel; 6, high-pressure pump; 7, cosolvent metering valve; 8, mixer; 9, constant-temperature water bath; 10, equilibrium cell; 11, pressure meter; 12, resistance thermometer; 13, expansion valve; 14, U-type tube; 15, rotated flow meter; 16, wet-gas flow meter.

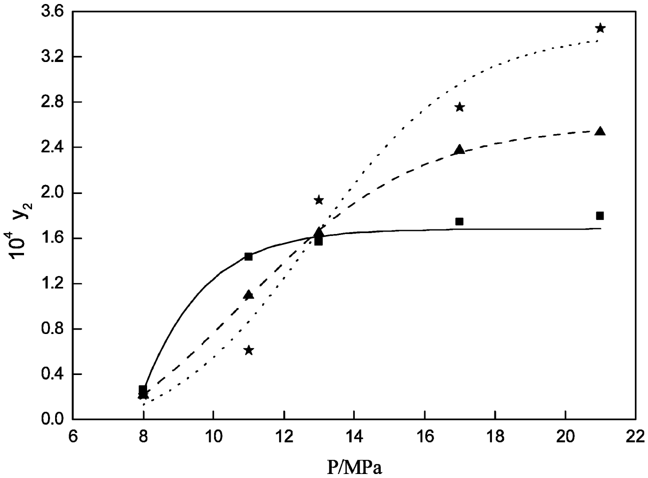

Figure 2. Comparison of experimental solubility data of *p*-nitrobenzoic acid and results correlated by eq 2. ■, exp, — —, cal 308 K; ▲, exp, —, cal 318 K; ★, exp, - - -, cal 328 K.

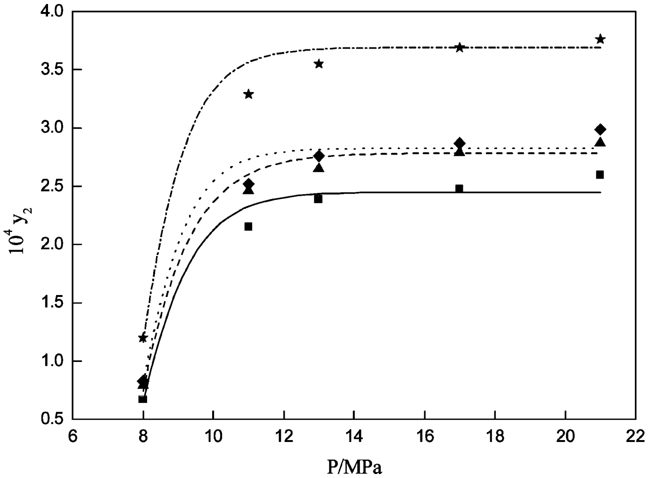

Figure 3. Comparison of experimental solubility data of *p*-nitrobenzoic acid and results correlated by eq 7. Cyclohexane: ■, exp; —, cal. Ethanol: ▲, exp; — —, cal. Cyclohexane + acetone: ◆, exp; - - -, cal. Acetone: ★, exp; — • —, cal.

Table 1. Density ρ_1 and Mole Fraction y_2 of *p*-Nitrobenzoic Acid (2) in Pure Supercritical Carbon Dioxide (1) from $T = 308$ K to 328 K

	T (K)					
	308		318		328	
P/MPa	ρ_1/mol·ml^{-1}	$10^4\,y_2$	ρ_1/mol·ml^{-1}	$10^4\,y_2$	ρ_1/mol·ml^{-1}	$10^4\,y_2$
8.0	0.0097	0.26	0.0051	0.21	0.0047	0.20
11.0	0.0168	1.46	0.0129	1.17	0.0092	0.67
13.0	0.0177	1.63	0.0152	1.68	0.0140	1.95
17.0	0.0191	1.71	0.0178	2.32	0.0161	2.85
21.0	0.0199	1.75	0.0189	2.46	0.0176	3.22

Results and Discussions

The efficiency and reliability of the solubility measurement technique had been testified in our previous work.[4,8] Each reported datum was an average of at least three replicated sample measurement. The solubility data obtained were found to be reproducible within ± 5 %.

Solubility of Solid in Pure Supercritical Carbon Dioxide. The reported data are listed in Table 1 and shown in Figure 2. It is clear that the solubility of *p*-nitrobenzoic acid increased with increasing pressure at each isotherm as expected, and this effect is the greatest for the highest temperature (i.e., the favorable effect of pressure on solubility is 1.7 times larger at 328 K than that at 308 K), which might have originated from the complicated pressure and temperature impaction on the solute vapor pressure and the density of the solvent. By investigating the influence of temperature on the solubility (Figure 2), it could be observed that retrograde behavior existed at about 12.1 MPa.

The results were correlated by the equation proposed by Mendez-Santiago and Teja:[9]

$$T \ln E = A + B\rho \tag{2}$$

where E is the enhancement factor given by

$$E = \frac{y_2 P}{P^{\text{sub}}} \tag{3}$$

where P and T are the system pressure and temperature; P^{sub} is the sublimation of the solute calculated from CSGC−PRV;[10] A and B, which are independent of temperature and needed to be fitted by experimental data, are constants of eq 2; ρ_1 is the density of pure CO_2 and calculated from the EOS proposed by Span and Wagner.[11]

The values of A and B are 1729 and 55356 (with ρ_1 in mol·mL^{-1}, P in bar, and T in K), respectively. The absolute value of average relative deviation (AARD*y*) of eq 2 was 4.68 %.

Solubility of Solid in Modified Supercritical Carbon Dioxide. At the constant temperature of 308 K, the effects of different cosolvents with the same mole fraction of 3.0 % on the solid solubility were studied. The experimental results are presented in Table 2 and illustrated in Figure 3.

Table 2. Cosolvent Effect E and Mole Fraction y_2' of p-Nitrobenzoic Acid (2) in Supercritical Carbon Dioxide (1) with Cosolvents (3) at a Mole Fraction of 3.0 % at 308 K

	308 K			
	cyclohexane	ethanol	cyclohexane + acetone	acetone
P/MPa	$10^4\,y_2'$	$10^4\,y_2'$	$10^4\,y_2'$	$10^4\,y_2'$
8.0	0.67	0.76	0.83	1.20
11.0	2.15	2.46	2.52	3.29
13.0	2.39	2.65	2.76	3.55
17.0	2.48	2.79	2.87	3.63
21.0	2.60	2.87	2.99	3.76
e	1.51	1.70	1.75	2.28

Table 3. Results Correlated by Equation 7[a]

cosolvents	C'	D	n	100 AARDy_2' [b]
cyclohexane	1586.3	61908	5	3.35
ethanol	1632.3	66203	5	2.98
cyclohexane + acetone	1674.0	67883	5	3.56
acetone	1828.7	68497	5	4.17

[a] With ρ_1 in mol·mL^{-1}, P in bar, and T in K. [b] AARDy_2' = $1/N\sum_{i=1}^{N}|(y_2'^{\mathrm{exp}} - y_2'^{\mathrm{cal}})/y_2'^{\mathrm{exp}}|_i$.

To better understand the solubility enhancement, a cosolvent effect e was defined as the ratio of the solubility obtained with cosolvents, $y_2'(P, T, y_3 = 0.03)$, to that obtained without cosolvents at the same temperature and pressure, $y_2(P, T, y_3 = 0)$, and was depicted as

$$e = \frac{y_2'(P, T, y_3 = 0.03)}{y_2(P, T, y_3 = 0)} \tag{4}$$

The results of e were listed in Table 3, from which could be seen that the order of the cosolvent effect was acetone > acetone + cyclohexane (equalmolar) > ethanol > cyclohexane.

The solubility obtained with cosolvents was correlated by the equation also proposed by Mendez-Santiago and Teja:[12]

$$T \ln E' = C + D\rho_1 + Fy_3 \tag{5}$$

where E' was also the enhancement factor, given by

$$E' = \frac{y_2'P}{P^{\mathrm{sub}}} \tag{6}$$

where C, D, and F are constants that need to be fitted, respectively; y_3 is the mole fraction of coslvents in supercritical mixtures (supercritical carbon dioxide + cosolvents), which is also a constant of 0.03 in this work. So Fy_3 could be considered as one constant, and eq 5 could be written as

$$T \ln E' = C' + D\rho_1 \tag{7}$$

where C' is also a constant. The correlated results are presented in Table 3 and illustrated in Figure 3. The overall absolute value of the average deviation was 3.52 %.

Conclusions

The solubilities of p-nitrobenzoic acid in supercritical CO_2 with and without cosolvents were studied over the temperature range from 308 to 328 K and the pressure ranging from 8.0 to 21.0 MPa. The crossover pressure of the system was closed to 12.1 MPa. At the temperature of 308 K and the cosolvent mole fraction of 3.0 %, the order of the cosolvent effect was acetone > acetone + cyclohexane (equalmolar) > ethanol > cyclohexane. The experimental data were correlated by the equations both proposed by Mendez-Santiago and Teja, and the overall deviations between experimental data and correlated results were 4.68 % and 3.52 %, respectively.

Nomenclature

A, B	constants of eq 2
C, D, F	constants of eq 5
C', D	constants of eq 7
y_2	mole fraction of solute in pure supercritical carbon dioxide
y_2'	mole fraction of solute in supercritical carbon dioxide with cosolvents
m_2	mass of the trapped p-nitrobenzoic acid
M_2	molar mass of p-nitrobenzoic acid
P_a	atmospheric pressure
P_w	vapor pressure of water contained in the wet-gas flow meter
V_1	gas volume
R	gas constant
T_w	temperature of water contained in the wet-gas flow meter
T	system temperature
ρ_1	density of pure CO_2
E	enhancement factor of eq 3
P	system pressure
P^{sub}	sublimation of p-nitrobenzoic acid
E'	enhancement factor of eq 6
y_3	mole fraction of coslvents in supercritical mixtures
e	cosolvents effect of eq 4
n	number of datum points
AARDy	absolute value of the average relative deviation

Subscripts

1	carbon dioxide (supercritical fluid)
2	p-nitrobenzoic acid
3	cosolvents

Superscripts

cal	calculated results
exp	experimental results

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