Solubility of 3,5-Dinitrobenzoic Acid in Supercritical Carbon Dioxide with Cosolvent at Temperatures from (308 to 328) K and Pressures from (10.0 to 21.0) MPa

Zhao Tang, Jun-su Jin,* Ze-ting Zhang, Xiang-yun Yu, and Jing-nian Xu

College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China

The solid solubility of 3,5-dinitrobenzoic acid in supercritical carbon dioxide with cosolvent, ethanol, ethyl acetate, *n*-propanol, and ethylene glycol was measured using a flow-type apparatus at temperatures from (308 to 328) K and in the pressure range of (10.0 to 21.0) MPa. The mole fraction of cosolvent was 0.015, 0.035, and 0.055, respectively. The experimental results showed that the equilibrium solubility of 3,5-dinitrobenzoic acid can be effectively enhanced in the presence of all cosolvents. A semiempirical model, the Sovova model, was modified by adding a function of temperature (*T*). The accuracy of the modified Sovova model was tested and verified by the solubility data of 17 kinds of solid compounds from the literature. In addition, the modified Sovova model was successfully used to correlate the experimental solubility data of 3,5-dinitrobenzoic acid in supercritical carbon dioxide with different cosolvents, and the average absolute relative deviation (AARD) ranged from (2.2 to 8.8) %.

Introduction

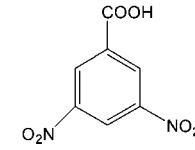
Supercritical fluid (SCF) is an excellent fluid for its good diffusivity and solvent capacity above its critical point. SCF technology has been developing rapidly in the last 20 years and has been widely applied in dyeing, food processing, pharmaceutical industries, wastewater treatment, separation processes, chemical reactions, and materials processing.[1−6]

Supercritical carbon dioxide ($SCCO_2$) is a promising solvent for supercritical fluid extraction (SFE) technology because of its moderate critical properties ($P_c = 7.38$ MPa and $T_c = 304$ K) and their environmental benefits, such as nontoxicity, nonflammability, inertness, and inexpensitivity. However, the solvent power of $SCCO_2$ is limited for most polar, high molecular weight, and nonvolatile organic substances, due to its lack of polarity and associated capacity for specific solvent−solute interactions.[7−9] As shown from the experimental results in the literature, the solvent power of $SCCO_2$ can be enhanced by adding a small amount of polar cosolvent.[10−14]

Solid solubility data in $SCCO_2$ are essential for the separation of solid compounds, especially for biomolecules and pharmaceuticals. However, it is noticed that more experimental data for the solubilities of organic and pharmaceutical compounds in $SCCO_2$ are still needed. The study of phase equilibrium is still the key point in SCF technology.[15−17]

3,5-Dinitrobenzoic acid is an important intermediate for organic synthesis. It is widely applied to synthesize several kinds of drug molecules in pharmaceutical industry, such as sulfa chrysoidine, ampicillin, and adipiodone. However, no solubility data of this pharmaceutical solid in $SCCO_2$ with or without cosolvent have been listed in previous literature. Therefore, it is important to measure the solubility of 3,5-dinitrobenzoic acid in $SCCO_2$ with or without cosolvent. In addition, our research group has been studying the solid solubilities of benzoic acid with different functional groups from the 1990s.[18−20] In this paper, double nitro-functional groups were investigated.

Table 1. Formula and Structure of Solid Compound

Compound	formula	molecular structure
3, 5-dinitrobenzoic acid	$C_7H_4N_2O_6$	

In our previous work, the solubility data of 3,5-dinitrobenzoic acid in pure $SCCO_2$ were measured and correlated.[21] In this work, the solubility of 3,5-dinitrobenzoic acid in $SCCO_2$ with cosolvent was investigated at (308, 318, and 328) K from (10.0 to 21.0) MPa. Ethanol, ethyl acetate, *n*-propanol, and ethylene glycol were used as a cosolvent, respectively. A new modified Sovova model was developed, verified, and compared with the original Sovova model[22] by the solubility data of 18 kinds of solid compounds from this work and literature.

Experimental Section

Materials. Carbon dioxide with a minimum purity of 0.999 was purchased from Beijing Praxair Industrial Gas Co., Ltd. 3,5-Dinitrobenzoic acid ($C_7H_4N_2O_6$, CAS 99-34-3, Table 1) with an assessed minimum purity of 0.99 (mass fraction) was purchased from Beijing Hengye Zhongyuan Chemical Co., Ltd. Ethanol, ethyl acetate, *n*-propanol, and ethylene glycol (analytical reagent) were purchased from Beijing Chemical Reagent Factory. All chemicals were used without further purification.

Apparatus and Procedure. The solubility of 3,5-dinitrobenzoic acid in $SCCO_2$ with cosolvent was measured using a dynamic flow technique with ultraviolet spectrophotometer analysis. A schematic diagram of the experimental apparatus is shown in Figure 1.

Pure CO_2 was first supplied to a high-pressure surge flask from a cylinder by the compressor (Nova, model 5542121).

* Corresponding author. Tel.: +86-10-64434788. Fax: +86-10-64436781. E-mail: jinjs@mail.buct.edu.cn.

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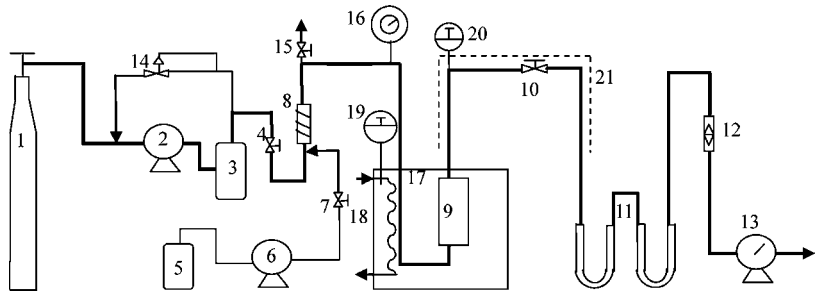

Figure 1. Schematic diagram of the experimental apparatus: 1, CO_2 cylinder; 2, compressor; 3, surge flask; 4, pressure-regulating valve; 5, cosolvent vessel; 6, high-pressure pump; 7, cosolvent regulating valve; 8, preheating and mixing cell; 9, high-pressure equilibrium cell; 10, decompression sampling valve; 11, U-shape tube; 12, rotated flow meter; 13, wet-gas flow meter; 14, back pressure valve; 15, safety valve; 16, pressure gauge; 17, constant-temperature stirred water bath; 18, preheating coils; 19, temperature controller; 20, thermometer; 21, heating coils.

Table 2. Solubility S and y of 3,5-Dinitrobenzoic Acid in Pure $SCCO_2$ as Functions of Temperature (T) and Pressure (p)

T/K	p/MPa	$10^6\ y_1$	$10^5\ S$/g·L^{-1}
308	10.0	0.58	0.52
	12.0	0.73	0.64
	15.0	0.94	0.83
	18.0	1.08	0.95
	21.0	1.09	0.96
318	10.0	0.48	0.42
	12.0	1.17	1.03
	15.0	1.69	1.49
	18.0	2.14	1.89
	21.0	2.30	2.03
328	10.0	0.44	0.39
	12.0	1.31	1.16
	15.0	2.65	2.34
	18.0	3.57	3.15
	21.0	4.21	3.72

Table 3. Solubility S and y of 3,5-Dinitrobenzoic Acid in $SCCO_2$ with Different Cosolvents (Ethanol, Ethyl Acetate, *n*-Propanol, Ethylene Glycol) and Solubility Enhancement Effect e of Different Cosolvents in Mole Fraction $y_3 = 0.035$ and Temperature $T = 318$ K as a Function of Pressure (p)

cosolvent	p/MPa	$10^5\ y_2$	$10^4\ S$/g·L^{-1}	e
ethanol	10.0	0.77	0.69	16.25
	12.0	2.29	2.04	19.61
	15.0	3.94	3.52	23.28
	18.0	5.22	4.66	24.36
	21.0	5.91	5.27	25.69
ethyl acetate	10.0	0.14	0.12	2.92
	12.0	0.77	0.67	6.56
	15.0	1.68	1.47	9.93
	18.0	3.17	2.78	14.77
	21.0	4.36	3.82	18.93
n-propanol	10.0	0.63	0.55	13.27
	12.0	1.76	1.53	15.05
	15.0	2.88	2.50	17.03
	18.0	3.99	3.46	18.62
	21.0	4.93	4.28	21.42
ethylene glycol	10.0	0.08	0.07	1.67
	12.0	0.40	0.35	3.44
	15.0	1.18	1.02	6.98
	18.0	2.26	1.95	10.53
	21.0	2.93	2.53	12.74

Then, CO_2 entered into a preheating and mixing cell with an electric coil so that its temperature and pressure could reach to the operating condition. Alternatively, in the experiments with cosolvent, the cosolvent flowed to the same cell by a high-pressure pump (Beijing Weixing Factory, model LB-10C) with the accuracy of ± 0.01 mL·min^{-1} by a cosolvent regulating valve. Lastly, the $SCCO_2$ with cosolvent entered into an high-pressure equilibrium cell loaded by (40 or 50) g of solute with glass beads and stainless steel sintered disks at both ends to prevent physical entrainment of undissolved solute. The cell was immersed into a constant-temperature stirred water bath (Chongqing Yinhe Experimental Instrument Corporation, model CS-530), which was controlled to ± 0.5 K by a temperature controller. The temperature and pressure in the cell were measured by a calibrated internal platinum resistance thermometer (Beijing Chaoyang Automatic Instrument Factory, model, XMT) and a calibrated pressure gauge (Heise, model CTUSA), respectively. The uncertainty for temperature measurement is ± 0.1 K, and that for pressure is ± 0.05 MPa. In the high-pressure equilibrium cell, the solvent and solute reached equilibrium after about 30 min.

Table 4. Solubility S and y of 3,5-Dinitrobenzoic Acid in $SCCO_2$ with Ethyl Acetate and Solubility Enhancement Effect e of Ethyl Acetate as Functions of Temperature (T), Pressure (p), and Mole Fraction of Cosolvent (y_3)

p/MPa	$10^5\ y_2$	$10^4\ S$/g·L^{-1}	e
	$T = 308$ K	$y_3 = 0.035$	
10.0	0.35	0.30	5.95
12.0	0.57	0.50	7.85
15.0	0.91	0.80	9.75
18.0	1.36	1.20	12.60
21.0	1.55	1.36	14.28
	$T = 318$ K	$y_3 = 0.035$	
10.0	0.14	0.12	2.92
12.0	0.77	0.67	6.56
15.0	1.68	1.47	9.93
18.0	3.17	2.78	14.77
21.0	4.36	3.82	18.93
	$T = 328$ K	$y_3 = 0.035$	
10.0	0.06	0.05	1.35
12.0	0.69	0.60	4.54
15.0	2.65	2.33	10.02
18.0	5.44	4.77	15.25
21.0	8.29	7.27	19.67
	$T = 318$ K	$y_3 = 0.015$	
10.0	0.09	0.08	1.54
12.0	0.29	0.26	2.50
15.0	0.75	0.65	4.40
18.0	1.24	1.09	5.80
21.0	1.51	1.32	6.55
	$T = 318$ K	$y_3 = 0.055$	
10.0	0.20	0.18	3.67
12.0	1.01	0.88	8.64
15.0	3.04	2.66	17.96
18.0	5.46	4.78	25.45
21.0	6.84	5.99	29.70

$SCCO_2$ was expanded into atmospheric pressure through a decompression sampling valve (wrapped with heating coils). The solid compound was separated from the CO_2 and collected by two U-shaped tubes in turn. The volume and flow rate of CO_2 were measured by a calibrated wet-gas flow meter

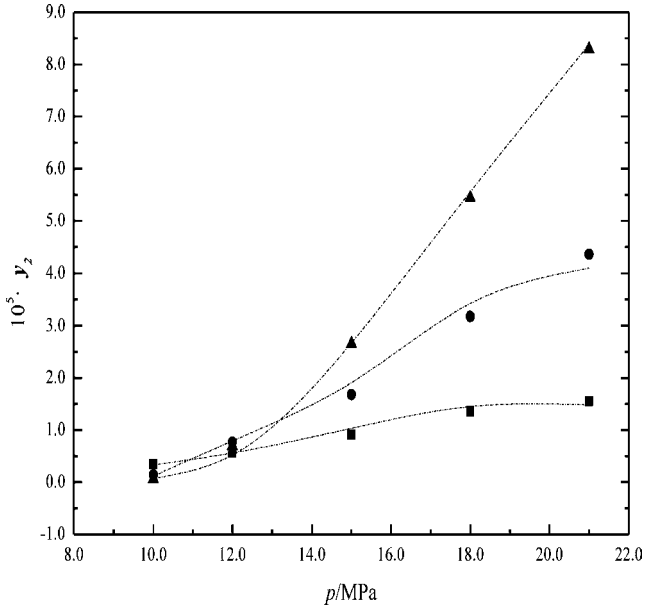

Figure 2. Comparison of experimental solubility of 3,5-dinitrobenzoic acid in $SCCO_2$ with cosolvent ethyl acetate in mole fraction of 0.035 as a function of pressure and the calculated results using modified Sovova model: ■, $T = 308$ K; ●, $T = 318$. K; ▲, $T = 328$ K; and ⋯, calculated using the modified Sovova model.

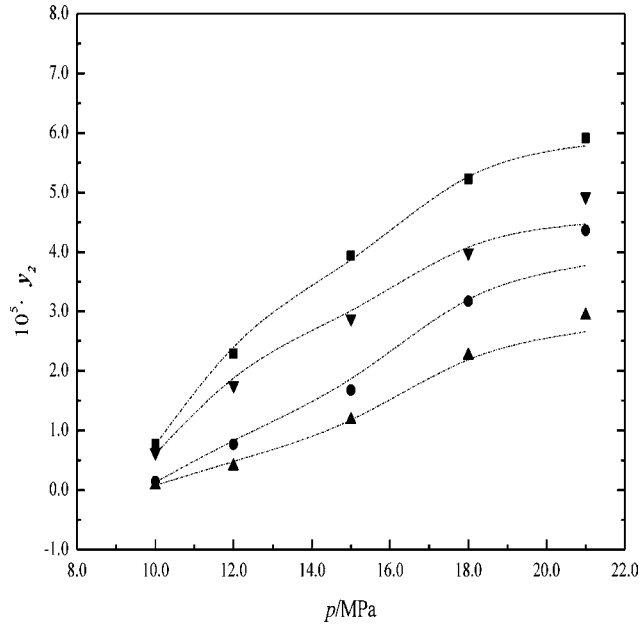

Figure 3. Comparison of experimental solubility of 3,5-dinitrobenzoic acid in $SCCO_2$ with different cosolvents in mole fraction of 0.035 at $T = 318$ K as a function of pressure and the calculated results using the modified Sovova model: ■, ethanol; ▼, *n*-propanol; ●, ethyl acetate; ▲, ethylene glycol; and ⋯, calculated using the modified Sovova model.

(Changchun Instrument Factory, model LML-2) and a rotated flow meter, respectively. The total volume of CO_2 was measured with an uncertainty of ± 0.01 L at room temperature and atmospheric pressure during the experiment. The flow rate in the range of (0.3 to 0.5) $L \cdot min^{-1}$ was adopted in this work to establish the conditions under which equilibrium would be maintained.

The amount of 3,5-dinitrobenzoic acid in solution was analyzed by ultraviolet spectrophotometer (UNICO, model UV-2100) at a fixed wavelength 268 nm. Experiments were performed to establish a calibration curve, and the regression coefficient of the calibration curve was better than 0.9995.

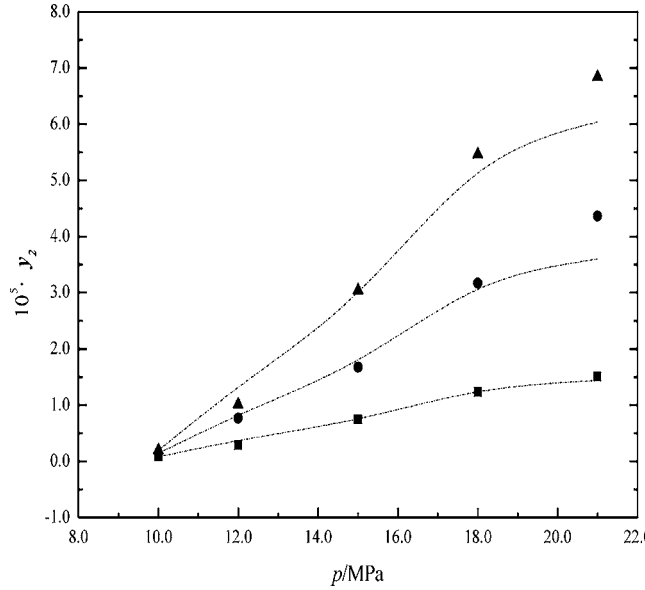

Figure 4. Comparison of experimental solubility of 3,5-dinitrobenzoic acid in $SCCO_2$ with cosolvent ethyl acetate at $T = 318$ K as a function of pressure and the calculated results using the modified Sovova model: ■, mole fraction of 0.015; ●, mole fraction of 0.035; ▲, mole fraction of 0.055; and ⋯, calculated using modified Sovova model.

Table 5. Correlation Parameters (*k*, *m*, and *n*) and Number of Data Points *N* Using the Sovova Model

cosolvent	*k*	*m*	*n*	*N*	AARD/%
ethyl acetate[a]	$2.5160 \cdot 10^{10}$	1.2069	2.3263	15	8.8
ethyl acetate[b]	$ky_3^m = 1.8368 \cdot 10^7$ ($y_3 = 0.035$)		2.0913	15	39.8
ethanol	$ky_3^m = 1.4192 \cdot 10^3$ ($y_3 = 0.035$)		1.3138	5	2.2
n-propanol	$ky_3^m = 8.4489 \cdot 10^2$ ($y_3 = 0.035$)		1.2946	5	5.3
ethylene glycol	$ky_3^m = 2.1239 \cdot 10^{11}$ ($y_3 = 0.035$)		2.8275	5	7.0

[a] With different mole fractions at 318 K. [b] With a mole fraction of 0.035 at different temperatures.

Table 6. Correlated Parameters (*k*, *m*, *b*, and *n*) and Number of Data Points *N* Using the Modified Sovova Model

cosolvent	*k*	*m*	*b*	*n*	*N*	AARD/%
ethyl acetate[a]	$ky_3^m = 1.5717 \cdot 10^{-2}$ ($y_3 = 0.035$)		$8.7480 \cdot 10^3$	2.5817	15	8.0

[a] With a mole fraction of 0.035 at different temperatures.

Results and Discussion

Equilibrium Solubility. The reliability of the experimental apparatus was verified by measuring the solubilities of solid solutes in our previous work.[23,24] Each reported data point in this work was the average of at least three replicated sample measurement to ensure the accuracy. The uncertainty of each measurement was within ± 5 %.

The experimental solid solubility data of 3,5-dinitrobenzoic acid in pure $SCCO_2$[21] are listed in Table 2. In this work, the solubility data of 3,5-dinitrobenzoic acid in $SCCO_2$ with cosolvent at (308, 318, and 328) K at pressures between (10.0 and 21.0) MPa are listed in Tables 3 and 4, respectively. It can be seen that the mole fraction solubility of 3,5-dinitrobenzoic acid with ethyl acetate (mole fraction of 0.055) at 328 K and 21.0 MPa reaches values of up to $8.29 \cdot 10^{-5}$, which corresponds to a mass fraction solubility of $7.27 \cdot 10^{-4}$.

The crossover pressure region has been observed, as shown in Figure 2. It is from (11.0 to 13.0) MPa for 3,5-dinitrobenzoic acid in $SCCO_2$ with ethyl acetate (mole fraction of 0.035). Below the crossover pressure, the solubility decreases with increasing temperature, whereas an opposite trend was exhibited at pressures higher than the crossover pressure. The crossover

Table 7. Correlated Results with the Number of Data Points *N* of the Solubility Data from the Literature Using the Sovova Model and Modified Sovova Model at Different Temperatures (*T*), Pressures (*p*), and Mole Fractions of Cosolvent

	T	*p*	cosolvent			AARD/%		
compound	K	MPa	mole fraction	*N*	refs	lit.[a]	S-model[b]	S′-model[c]
disperse yellow 54	353.2, 393.2	15−30	ethanol (0.01)	7	25	Chrastil 6.6, M-T 16.7	6.25	2.15
	353.2, 393.2	15−30	ethanol (0.03)	7	25	Chrastil 7.5, M-T 14.4	8.57	3.47
	353.2, 393.2	15−30	ethanol (0.05)	7	25	Chrastil 4.3, M-T 11.0	12.86	7.18
anthracene	313, 333	12−35	ethane (0.05, 0.1)	93	26		5.35	4.71
	313, 333	12−35	propane (0.05, 0.1)	86	26		6.08	5.84
	313, 333	11.5−35	butane (0.05, 0.1)	87	26		6.60	6.86
	313, 333	13.7−31	methanol (0.05, 0.1)	37	26		8.74	7.40
phenanthrene	313, 333	10.7−35	ethane (0.05, 0.1)	71	26		4.91	4.88
	313, 333	10.7−33.8	propane (0.05, 0.1)	63	26		7.87	5.02
	313, 333	10.3−35	butane (0.05, 0.1)	50	26		9.79	6.90
	313, 333	10.8−25	methanol (0.05, 0.1)	32	26		5.34	5.34
pyrene	313, 333	11−34	ethane (0.05, 0.1)	102	26		3.98	3.88
	313, 333	10.7−31.7	propane (0.05, 0.1)	97	26		8.74	6.53
	313, 333	10.3−32.2	butane (0.05, 0.1)	101	26		9.38	6.69
	313, 333	11−32	methanol (0.05, 0.1)	45	26		7.12	4.84
aspirin	318.2, 328.2	12−20	methanol (0.03)	8	27	PR-EOS 16.9−19.8	7.77	7.63
	318.2, 328.2	12−20	ethanol (0.03)	8	27	PR-EOS 14.3−22.3	5.75	5.73
	318.2, 328.2	12−20	acetone (0.03)	8	28	Chrastil 5.42, K-J 7.72	4.70	3.03
behenic acid	308.2, 318.2	8−16	ethanol (0.0121−0.0667)	40	29		12.86	12.87
	318.2, 328.2	9−16	pentane (0.0189−0.0716)	36	30		23.84	20.18
	308.2, 318.2	8−16	*n*-octane (0.0103−0.0666)	39	30		22.84	13.17
β-carotene	313.2, 323.2, 333.2	15−28	ethanol (0.003−0.0237)	17	31	their work 5	3.84	3.25
	313.2, 323.2, 333.2	20−28	vegetable oil (0.003−0.0237)	17	31	their work 12	9.28	7.87
C.I. disperse violet 1	353.2, 393.2	15−30	ethanol (0.01)	7	32	Chrastil 6.8, M-T 15	5.53	2.43
	353.2, 393.2	15−30	ethanol (0.03)	7	32	Chrastil 7.8, M-T 16.3	5.49	2.36
	353.2, 393.2	15−30	ethanol (0.05)	7	32	Chrastil 6.2, M-T 13.3	7.40	1.48
2-naphthol	308.1, 318.1, 328.1	10−30	acetone (0.036)	18	33		17.93	8.96
	308.1, 318.1, 328.1	10−30	ethanol (0.036)	18	33		14.67	5.51
	308.1, 318.1, 328.1	10−30	cyclohexane (0.036)	18	33		5.76	5.67
anthracene	308.1, 318.1, 328.1	10−30	acetone (0.04)	15	33		6.15	6.35
	308.1, 318.1, 328.1	10−30	ethanol (0.04)	15	33		3.71	3.62
	308.1, 318.1, 328.1	10−30	cyclohexane (0.04)	15	33		3.02	2.56
p-toluene sulfonic acid	308.1, 318.1, 328.1	11−21	ethanol (0.035)	15	34	Chrastil 11.1, M-T 4.6	12.55	3.62
sulfanilamide	308.1, 318.1, 328.1	11−21	ethanol (0.035)	15	34	Chrastil 5.6, M-T 6.5	8.91	4.90
octadecanoic acid	308, 318	12.8−22.6	3-methyl-1-butanol (0.0073)	10	35	M-T 1.9	8.54	2.43
	308, 318	12.8−22.6	ethanol (0.0073)	10	35	M-T 2.14	8.13	2.67
hexadecanoic acid	308, 318	12.8−22.6	3-methyl-l-butanol (0.0073)	10	35	M-T 1.48	4.70	0.83
	308, 318	12.8−22.6	ethanol (0.0073)	10	35	M-T 1.96	5.62	0.88
disperse orange 3	353.2, 373.2, 393.2	16−30	ethanol (0.055)	16	36	Chrastil 37.6, their work 22	27.77	28.72
disperse blue 79	353.2, 373.2, 393.3	16−30	ethanol (0.055)	9	36	Chrastil 14.6, their work 6.09	22.66	8.37
solvent brown 1	353.2, 373.2, 393.2	16−30	ethanol (0.055)	17	36	Chrastil 16.6, their work 10.4	10.53	10.07
C.I. disperse blue 56	353.2, 393.2	15−30	ethanol (0.01)	7	37	Chrastil 7.9	2.94	2.00
	353.2, 393.2	15−30	ethanol (0.03)	7	37	Chrastil 5.7	2.36	1.71
	353.2, 393.2	15−30	ethanol (0.05)	7	37	Chrastil 6.3	7.38	3.21
total	308.0	8−35	12[d] (0.003−0.1)	1311			8.96	5.99

[a] Calculated from the literature models. PR-EOS is the Peng−Robinson equation of state. M-T is the Méndez-Santiago and Teja model. [b] Sovova model. [c] Modified Sovova model. [d] The number of cosolvents.

phenomena could be attributed to the competitions between solute's vapor pressure and solvent's density, whose temperature dependences are in opposite directions. At the crossover point, these two competitive factors affect balance.

Cosolvent Effects. Ethanol, ethyl acetate, *n*-propanol, and ethylene glycol are commonly used as cosolvents with stronger polarity. Ethanol and ethyl acetate are green cosolvents, with better volatility.

The solubility enhancement effect can be quantified by *e*, which is defined as the ratio of the solubility obtained with cosolvent, y_2 (p, T, y_3), to that obtained without cosolvent at the same temperature and pressure, y_1 (p, T, $y_3 = 0$):

$$e = \frac{y_2(p, T, y_3)}{y_1(p, T, y_3 = 0)} \quad (1)$$

where y_1 is the mole fraction of solute in pure $SCCO_2$,[21] which is listed in Table 2, y_2 is the mole fraction of solute in $SCCO_2$ with cosolvent, y_3 is the mole fraction of cosolvent in $SCCO_2$, p is pressure (MPa), and T is temperature (K).

From Figure 3, it is clear that the solubility of 3,5-dinitrobenzoic acid increases in the presence of all cosolvents at 318 K. The increase of solvent density and intermolecular interactions are the major factors that contribute to the cosolvent effect. The values of *e* of all cosolvents are figured out in Table 3. The order of the solubility enhancement is ethanol > *n*-propanol > ethyl acetate > ethylene glycol. For example, the values of *e* of ethanol, *n*-propanol, ethyl acetate, and ethylene glycol at 318 K and 15.0 MPa are 23.28, 17.03, 9.93, and 6.98, respectively. Ethylene glycol, ethanol, and *n*-propanol molecules have higher intermolecular interactions such as hydrogen

bonding ability than ethyl acetate. However, from the molecular structures of ethylene glycol and 3,5-dinitrobenzoic acid, it is shown that the steric hindrance between them may inhibit to form hydrogen bonds. As a result, ethanol and *n*-propanol molecules are able to form hydrogen bonds with 3,5-dinitrobenzoic acid more easily. These reasons may impact the solubility enhancement effect of cosolvents.

From Table 4, the values of *e* of ethyl acetate are figured out at different temperatures with different mole fractions. As shown in Table 4 and Figure 4, the solubility enhancement increases with an increase of ethyl acetate's concentration, and the maximum value of *e* is close to 30. In addition, it is clear that the value of *e* increases with increasing temperature above the crossover pressure, which indicated that the cosolvent effect of ethyl acetate can be enhanced by improving the temperature of experimental conditions. Such results illuminate that the magnitude of the cosolvent effect was dependent on the cosolvent, solute, and experimental conditions.

Data Correlation. In this work, the Sovova model[22] and the modified Sovova model were used to correlate the equilibrium solubility data of 3,5-dinitrobenzoic acid in $SCCO_2$ with cosolvent.

Sovova Model. A commonly used semiempirical model, the Sovova model, which was widely used to correlate the solubility of solids in $SCCO_2$ with cosolvent, was applied in this work to correlate the equilibrium solubility data. The Sovova model was expressed as:

$$y_2 - y_1 = k y_3^{\,m} y_1^{\,n} \tag{2}$$

where y_2 is the mole fraction solubility of solute in $SCCO_2$ with cosolvent, y_1 is the mole fraction solubility of solute in pure $SCCO_2$, and y_3 is the mole fraction of cosolvent in $SCCO_2$. In eq 2, *k*, *m*, and *n* are parameters independent of temperature and pressure, which needed to be fitted by experimental data.

The average absolute relative deviation (AARD (%)) of the model from experimental data was calculated according to the following formula:

$$\mathrm{AARD}(\%) = \frac{100}{N}\sum_{i=1}^{n}\frac{|y_{\mathrm{cal}} - y_{\mathrm{exp}}|}{y_{\mathrm{exp}}} \tag{3}$$

where y_{cal} is the calculated value of the mole fraction solubility of solute, y_{exp} is the experimental value of the mole fraction solubility of solute, and *N* is the number of experimental points.

The correlated results and optimal parameters of the experimental solubility data using the Sovova model are presented in Table 5. From Table 5, it is shown that the equilibrium solubility data of 3,5-dinitrobenzoic acid in $SCCO_2$ with ethanol, *n*-propanol, and ethylene glycol (mole fraction of 0.035) at 318 K are satisfactorily correlated from the Sovova model with the values of AARD/% of 2.2, 5.3, and 7.0, respectively. In addition, the equilibrium solubility data with ethyl acetate (variant mole

Table 8. Correlated Parameters (*k*, *m*, and *n*) of the Solubility Data of Different Compounds with Different Cosolvents from the Literature Using the Sovova Model

compound	cosolvent	*k*	*m*	*n*
disperse yellow 54	ethanol ($y_3 = 0.01$)	$1.7662 \cdot 10^{-3}$		0.6340
	ethanol ($y_3 = 0.03$)	$3.1059 \cdot 10^{-2}$		0.7631
	ethanol ($y_3 = 0.05$)	$1.3176 \cdot 10^{-1}$		0.8198
anthracene	ethane ($y_3 = 0.05, 0.1$)	$2.9940 \cdot 10^{-1}$	1.0358	0.7908
	propane ($y_3 = 0.05, 0.1$)	1.4986	1.4455	0.7698
	butane ($y_3 = 0.05, 0.1$)	3.6703	1.3438	0.8549
	methanol ($y_3 = 0.05, 0.1$)	$1.8202 \cdot 10^{-1}$	1.2242	0.4916
phenanthrene	ethane ($y_3 = 0.05, 0.1$)	$5.2419 \cdot 10^{-1}$	0.8643	0.8132
	propane ($y_3 = 0.05, 0.1$)	1.9436	1.2001	0.7597
	butane ($y_3 = 0.05, 0.1$)	2.0424	1.0402	0.7604
	methanol ($y_3 = 0.05, 0.1$)	2.0719	0.7816	0.8166
pyrene	ethane ($y_3 = 0.05, 0.1$)	$9.6793 \cdot 10^{-2}$	1.1016	0.5790
	propane ($y_3 = 0.05, 0.1$)	$1.3016 \cdot 10^{-1}$	1.2644	0.4691
	butane ($y_3 = 0.05, 0.1$)	$1.3718 \cdot 10^{-1}$	1.1919	0.4511
	methanol ($y_3 = 0.05, 0.1$)	1.5356	0.8556	0.8319
aspirin	methanol ($y_3 = 0.03$)	$1.1962 \cdot 10^{-1}$		0.5368
	ethanol ($y_3 = 0.03$)	$6.3563 \cdot 10^{-2}$		0.4602
	acetone ($y_3 = 0.03$)	$1.3281 \cdot 10^{-2}$		0.4114
behenic acid	ethanol ($y_3 = 0.0121$–0.0667)	$4.3379 \cdot 10^{2}$	1.7356	0.8233
	pentane ($y_3 = 0.0189$–0.0716)	$4.5059 \cdot 10^{2}$	1.8901	0.9179
	n-octane ($y_3 = 0.0103$–0.0666)	$2.8221 \cdot 10^{4}$	1.7019	1.3053
β-carotene	ethanol ($y_3 = 0.003$–0.0237)	$5.3760 \cdot 10^{-3}$	0.4625	0.4614
	vegetable oil ($y_3 = 0.003$–0.0237)	$1.0078 \cdot 10^{-4}$	0.2962	0.3555
C.I. disperse violet 1	ethanol ($y_3 = 0.01$)	$1.5983 \cdot 10^{-4}$		0.5092
	ethanol ($y_3 = 0.03$)	$2.6763 \cdot 10^{-2}$		0.7973
	ethanol ($y_3 = 0.05$)	$4.0410 \cdot 10^{-2}$		0.7880
2-naphthol	acetone ($y_3 = 0.036$)	$1.1264 \cdot 10^{-2}$		0.4594
	ethanol ($y_3 = 0.036$)	$5.0223 \cdot 10^{-2}$		0.4612
	cyclohexane ($y_3 = 0.036$)	$5.9223 \cdot 10^{-3}$		0.3331
anthracene	acetone ($y_3 = 0.04$)	$7.5049 \cdot 10^{-6}$		–0.1223
	ethanol ($y_3 = 0.04$)	$2.7823 \cdot 10^{-5}$		–0.0459
	cyclohexane ($y_3 = 0.04$)	$3.6321 \cdot 10^{-4}$		0.1867
p-toluene sulfonic acid	ethanol ($y_3 = 0.035$)	$1.2731 \cdot 10^{2}$		1.3445
sulfanilamide	ethanol ($y_3 = 0.035$)	$9.5544 \cdot 10^{-3}$		0.6506
octadecanoic acid	3-methyl-1-butanol ($y_3 = 0.0073$)	$6.5042 \cdot 10^{-2}$		0.7120
	ethanol ($y_3 = 0.0073$)	$1.7431 \cdot 10^{-1}$		0.7641
hexadecanoic acid	3-methyl-1-butanol ($y_3 = 0.0073$)	$3.4026 \cdot 10^{-1}$		0.9366
	ethanol ($y_3 = 0.0073$)	$5.7846 \cdot 10^{-1}$		0.9328
disperse orange 3	ethanol ($y_3 = 0.055$)	$4.6941 \cdot 10^{-1}$		0.7690
disperse blue 79	ethanol ($y_3 = 0.055$)	$6.3139 \cdot 10^{-1}$		0.8685
solvent brown 1	ethanol ($y_3 = 0.055$)	1.0245		0.8932
C.I. disperse blue 56	ethanol ($y_3 = 0.01$)	$5.5931 \cdot 10^{-3}$		0.8288
	ethanol ($y_3 = 0.03$)	$2.2067 \cdot 10^{-2}$		0.8183
	ethanol ($y_3 = 0.05$)	$3.0885 \cdot 10^{-2}$		0.7890

Table 9. Correlated Parameters (*k*, *m*, *b*, and *n*) of the Solubility Data of Different Compounds with Different Cosolvents from the Literature Using the Modified Sovova Model

compound	cosolvent	k (k', k'')	m	b	n
disperse yellow 54	ethanol ($y_3 = 0.01$)	$7.8276 \cdot 10^{-1}$		$-3.0360 \cdot 10^{3}$	0.4694
	ethanol ($y_3 = 0.03$)	$8.8422 \cdot 10^{-1}$		$-1.6700 \cdot 10^{3}$	0.6725
	ethanol ($y_3 = 0.05$)	4.9259		$-1.8040 \cdot 10^{3}$	0.7223
anthracene	ethane ($y_3 = 0.05, 0.1$)	$1.5192 \cdot 10^{-3}$	1.0341	$2.5258 \cdot 10^{3}$	1.0623
	propane ($y_3 = 0.05, 0.1$)	$5.1800 \cdot 10^{-1}$	1.4453	$5.0183 \cdot 10^{2}$	0.8223
	butane ($y_3 = 0.05, 0.1$)	$1.2077 \cdot 10^{1}$	1.3410	$-5.6479 \cdot 10^{2}$	0.7963
	methanol ($y_3 = 0.05, 0.1$)	$1.8590 \cdot 10^{-3}$	1.4812	$2.2574 \cdot 10^{3}$	0.6685
phenanthrene	ethane ($y_3 = 0.05, 0.1$)	$1.1480 \cdot 10^{2}$	0.8621	$-1.7746 \cdot 10^{3}$	0.7970
	propane ($y_3 = 0.05, 0.1$)	$1.3394 \cdot 10^{4}$	1.1933	$-2.9954 \cdot 10^{3}$	0.6943
	butane ($y_3 = 0.05, 0.1$)	$3.0433 \cdot 10^{3}$	1.0511	$-2.4425 \cdot 10^{3}$	0.7155
	methanol ($y_3 = 0.05, 0.1$)	2.2722	0.7770	$-3.3207 \cdot 10^{1}$	0.8170
pyrene	ethane ($y_3 = 0.05, 0.1$)	0.7550	1.0993	$-6.8256 \cdot 10^{2}$	0.5725
	propane ($y_3 = 0.05, 0.1$)	$2.4014 \cdot 10^{2}$	1.2768	$-2.4533 \cdot 10^{3}$	0.4533
	butane ($y_3 = 0.05, 0.1$)	$1.1617 \cdot 10^{2}$	1.1909	$-2.2503 \cdot 10^{3}$	0.4231
	methanol ($y_3 = 0.05, 0.1$)	$2.1935 \cdot 10^{-3}$	1.2013	$2.5491 \cdot 10^{3}$	0.8688
aspirin	methanol ($y_3 = 0.03$)	$6.9644 \cdot 10^{-4}$		$1.6814 \cdot 10^{3}$	0.5434
	ethanol ($y_3 = 0.03$)	$3.8647 \cdot 10^{-2}$		$1.6257 \cdot 10^{2}$	0.4609
	acetone ($y_3 = 0.03$)	$8.2597 \cdot 10^{-1}$		$-1.3495 \cdot 10^{3}$	0.4061
behenic acid	ethanol ($y_3 = 0.0121$–0.0667)	2.1620	1.8189	$2.0233 \cdot 10^{3}$	0.9005
	pentane ($y_3 = 0.0189$–0.0716)	$6.8221 \cdot 10^{9}$	1.4398	$-5.8872 \cdot 10^{3}$	0.8948
	n-octane ($y_3 = 0.0103$–0.0666)	$1.5170 \cdot 10^{15}$	1.5764	$-9.2380 \cdot 10^{3}$	0.9183
β-carotene	ethanol ($y_3 = 0.003$–0.0237)	$1.0266 \cdot 10^{-2}$	0.4234	$-4.7444 \cdot 10^{2}$	0.4200
	vegetable oil ($y_3 = 0.003$–0.0237)	$1.0679 \cdot 10^{9}$	4.1707	$-3.1167 \cdot 10^{4}$	–5.4506
C.I. disperse violet 1	ethanol ($y_3 = 0.01$)	$4.5934 \cdot 10^{-1}$		$-3.3293 \cdot 10^{3}$	0.4334
	ethanol ($y_3 = 0.03$)	$7.3927 \cdot 10^{-1}$		$-1.3874 \cdot 10^{3}$	0.7657
	ethanol ($y_3 = 0.05$)	$8.0711 \cdot 10^{-1}$		$-1.2519 \cdot 10^{3}$	0.7595
2-naphthol	acetone ($y_3 = 0.036$)	$1.2564 \cdot 10^{6}$		$-6.1678 \cdot 10^{3}$	0.3434
	ethanol ($y_3 = 0.036$)	$1.7201 \cdot 10^{-5}$		$2.6560 \cdot 10^{3}$	0.5112
	cyclohexane ($y_3 = 0.036$)	$6.2345 \cdot 10^{-4}$		$7.4933 \cdot 10^{2}$	0.3472
anthracene	acetone ($y_3 = 0.04$)	$4.0497 \cdot 10^{-4}$		$-1.2536 \cdot 10^{3}$	–0.1177
	ethanol ($y_3 = 0.04$)	$1.4489 \cdot 10^{-5}$		$2.0509 \cdot 10^{2}$	–0.0466
	cyclohexane ($y_3 = 0.04$)	$9.8053 \cdot 10^{-5}$		$4.1161 \cdot 10^{2}$	0.1852
p-toluene sulfonic acid	ethanol ($y_3 = 0.035$)	$5.6995 \cdot 10^{-1}$		$2.4149 \cdot 10^{3}$	1.5484
sulfanilamide	ethanol ($y_3 = 0.035$)	$1.4731 \cdot 10^{-1}$		$2.2738 \cdot 10^{3}$	1.3146
octadecanoic acid	3-methyl-1-butanol ($y_3 = 0.0073$)	$9.6344 \cdot 10^{4}$		$-5.4743 \cdot 10^{3}$	0.3431
	ethanol ($y_3 = 0.0073$)	$8.2270 \cdot 10^{3}$		$-4.1465 \cdot 10^{3}$	0.4846
hexadecanoic acid	3-methyl-1-butanol ($y_3 = 0.0073$)	$4.4343 \cdot 10^{4}$		$-4.6704 \cdot 10^{3}$	0.5253
	ethanol ($y_3 = 0.0073$)	$1.6840 \cdot 10^{4}$		$-4.0760 \cdot 10^{3}$	0.5738
disperse orange 3	ethanol ($y_3 = 0.055$)	$1.2814 \cdot 10^{1}$		$-1.1907 \cdot 10^{3}$	0.7772
disperse blue 79	ethanol ($y_3 = 0.055$)	$4.5548 \cdot 10^{-4}$		$2.6253 \cdot 10^{3}$	0.8546
solvent brown 1	ethanol ($y_3 = 0.055$)	9.4064		$-9.1312 \cdot 10^{2}$	0.8735
C.I. disperse blue 56	ethanol ($y_3 = 0.01$)	$4.0185 \cdot 10^{-1}$		$-2.2591 \cdot 10^{3}$	0.7023
	ethanol ($y_3 = 0.03$)	$6.7308 \cdot 10^{-3}$		$6.2755 \cdot 10^{2}$	0.8535
	ethanol ($y_3 = 0.05$)	$1.4652 \cdot 10^{-3}$		$1.6110 \cdot 10^{3}$	0.8792

fraction) at 318 K are satisfactorily correlated from the Sovova model with the value of AARD/% of 8.8. However, the equilibrium solubility data with ethyl acetate (mole fraction of 0.035) at different temperatures are not well-correlated from the Sovova model with the value of AARD/% of 39.8. By means of the linear regression analysis of the experimental data, we found that, when the mole fraction of cosolvent (y_3) remained invariant, eq 2 with three adjustable parameters (k, m, and n) transformed into eq 4 with two adjustable parameters (k' and n, where $k' = k{y_3}^m$). This transformation may lead to the decline of the relation's degree and accuracy. To solve this problem, we try to modify the Sovova model.

$$y_2 - y_1 = k'{y_1}^n \tag{4}$$

Modified Sovova Model. The Sovova model is expressed with three adjustable parameters (k, m, and n) in eq 2. It is clear that y_2 is related with y_1 and y_3 but not related with temperature (T). When y_3 remains invariant with T changing, the number of equation's parameters will decrease. Therefore, we added a function of temperature (T) to modify the model as shown in eq 5:

$$y_2 - y_1 = k{y_3}^m{y_1}^n e^{b/T} \tag{5}$$

here y_1, y_2, and y_3 are the same as those in eq 2 and T is temperature (K). In eq 5, k, m, n, and b are the equation's parameters independent of temperature and pressure.

With regards to the equilibrium solubility data of these groups, two new parameters, k' and k'', are defined, respectively: $k' = k{y_3}^m$ (at constant y_3); $k'' = ke^{b/T}$ (at constant T). As a result, eq 5 transforms into eq 6 or 7, respectively.

$$y_2 - y_1 = k'{y_1}^n e^{b/T} \tag{6}$$

$$y_2 - y_1 = k''{y_3}^m{y_1}^n \tag{7}$$

As shown in eq 6 or 7, the modified Sovova model is still expressed with three adjustable parameters with y_3 or T invariant. The equilibrium solubility data of these groups were correlated using the modified Sovova model again. For the equilibrium solubility data of 3,5-dinitrobenzoic acid in $SCCO_2$ with ethanol, *n*-propanol, and ethylene glycol (mole fraction of 0.035) at 318 K and with ethyl acetate (variant mole fraction) at 318 K, the modified Sovova model is expressed as eq 7, which is similar to eq 2. Therefore, the correlated results and optimal parameters of these data using the modified Sovova model are the same as those in Table 5. For the equilibrium solubility data with ethyl acetate (mole fraction of 0.035) at different temperatures, the modified Sovova model is expressed as eq 6. The correlated result and optimal parameters of the equilibrium solubility data

of this group using the modified Sovova model are presented in Table 6. From Table 6, the value of AARD/% decreases from 39.8 to 8.0. Figures 2 to 4 show the comparisons of the equilibrium solubility data of these groups and the calculated results using the modified Sovova model. Correlation results with optimally fitted parameters using the modified Sovova model are satisfactory.

Verification of the Modified Sovova Model. To verify the accuracy of the modified Sovova model, the experimental solubility data of 17 kinds of solid compounds in $SCCO_2$ with cosolvent from the literature are found out.[25−37] Temperature, pressure range, and the mole fraction of cosolvent of experiments are taken from the literature and listed in Table 7. In addition, the values of AARD/% have been calculated for all compounds by the Sovova model and modified Sovova model. The solubilities of these solid compounds have been measured in a pressure range from (8.0 to 35.0) MPa, a temperature range from (308.0 to 393.2) K, and the mole fraction of cosolvent range from 0.003 to 0.1. In total, 1311 pieces of experimental solubility data in $SCCO_2$ with 12 different kinds of cosolvents have been applied.

Table 7 shows a comparison of the models from the literature, the Sovova model, and the modified Sovova model. It is observed that the agreement with the experimental data is satisfactory. The total values of AARD/% from the Sovova model and modified Sovova model are 8.96 and 5.99, respectively. As can be seen, the solubilities of most of these solid compounds in $SCCO_2$ with cosolvent are correlated quite accurately using the Sovova model and modified Sovova model. However, some compounds are not well-correlated with the values of AARD/% in the range of (10.07 to 28.71), such as behenic acid, disperse orange 3, and solvent brown 1. The high deviation may result from the strong interaction between cosolvents, and these solid compounds could not be reflected by the Sovova model and modified Sovova model. As shown in Table 7, these results (AARD/%) were still better than the ones which were correlated using the models from the literature. Furthermore, for most of the ternary systems ($SCCO_2$ + solute + cosolvent), correlation results of the solubilities are satisfactory by the Sovova model and modified Sovova model, especially for the modified Sovova model. The correlated parameters of the solubility data from the literature using the Sovova model and modified Sovova model are listed in Tables 8 and 9, respectively.

Conclusions

The solubility of 3,5-dinitrobenzoic acid in $SCCO_2$ with cosolvent at temperatures from (308 to 328) K and pressures from (10.0 to 21.0) MPa was investigated in this study. Ethanol, ethyl acetate, *n*-propanol, and ethylene glycol were used as a cosolvent in $SCCO_2$, respectively. The crossover pressure region for the ternary system ($SCCO_2$ + 3,5-dinitrobenzoic acid + ethyl acetate) was from (11.0 to 13.0) MPa. The values of enhancement effect *e* of different cosolvents in $SCCO_2$ were figured out at different temperatures with different mole fractions. The maximum value of *e* was close to 30. The Sovova model was modified by adding a function of temperature (*T*). The measured equilibrium solubility data in $SCCO_2$ with different cosolvents were satisfactorily correlated from the modified Sovova model with the values of AARD/% in the range of (2.2 to 8.8). Seventeen kinds of solid compounds in $SCCO_2$ with cosolvent from the literature were correlated from the Sovova model and modified Sovova model. The total values of AARD/% from Sovova model and modified Sovova model were 8.96 and 5.99, respectively.

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