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Equilibrium solubility of pure and mixed 3,5-dinitrobenzoic acid and 3-nitrobenzoic acid in supercritical carbon dioxide

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ARTICLE INFO

Article history: Received 8 October 2010 Received in revised form 26 January 2011 Accepted 30 January 2011 Available online 18 February 2011

Keywords: Solubility 3,5-Dinitrobenzoic acid 3-Nitrobenzoic acid Mixture Supercritical carbon dioxide

1. Introduction

Supercritical fluid (SCF) technology has gained a rapid growth for the past few decades, and has been widely applied in food processing, pharmaceutical industries, separation processes, chemical reaction and a variety of extractions [1]. Carbon dioxide (CO₂) is a solvent of choice in SCF technology because it is inexpensive, nontoxic, readily available in relatively pure form, and has moderate critical constants (7.38 MPa and 304 K). Supercritical carbon dioxide (SCCO₂) has strong solvent power, high diffusivity and low viscosity. These unique properties make SCCO₂ an attractive solvent for many industrial separation and purification processes, especially in the pharmaceutical industry [2].

3,5-Dinitrobenzoic acid (3,5-DNBA) and 3-nitrobenzoic acid (m-NBA) are important pharmaceutical intermediate materials for the pharmaceutical industry. 3,5-DNBA is mainly used for the synthesis of sulfachrysoidine and the detection of ampicillin. m-NBA is used for the production of agricultural chemicals and dyes, in particular for the synthesis of procaine hydrochloride, procaine ammonium salts, and amino-nitro benzoic acid. These two aromatic compounds are similar in production and application processes, and benzoic acid is their common raw material in industry [3]. It reports that benzoic acid reacts with a three mole ratio of the BF₃·N₂O₅ complex in carbon tetrachloride in 36 h at 70 °C to form 3,5-DNBA (70% yield) and m-NBA (9.3% yield). The mixture products of 3,5-

ABSTRACT

The solid solubility of pure 3,5-dinitrobenzoic acid (3,5-DNBA) and 3-nitrobenzoic acid (m-NBA) and their equal-weight mixture in supercritical carbon dioxide (SCCO₂) was measured using a flow-type apparatus at 308, 318, and 328 K and in the pressure range of 10.0–21.0 MPa. The solubility enhancement *SE* of mixed 3,5-DNBA and m-NBA in the ternary system has been observed. The mixture separation factor μ and the separation efficiency *HE* were investigated. A modified Kumar–Johnston (K–J) model was proposed for correlating the solubility of solid compounds in SCCO₂. The experimental solubility data of pure and mixed solutes in SCCO₂ were successful to be correlated by Chrastil model, the modified Adachi–Lu model, K–J model and new proposed model. Solubility data from 23 different solid compounds were taken from literature. The accuracy of the proposed model was evaluated by correlating 13 binary systems, 13 ternary systems, and 1 quaternary system. The modified K–J model satisfactorily correlated the experimental results for the solubility of all these compounds in SCCO₂ within 5.11% AARD.

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DNBA and *m*-NBA should be separated before further reaction and preparation of single pure compound. Thus, it is a necessary step to separate the mixture of 3,5-DNBA and *m*-NBA in industry.

For the separation and purification of pharmaceutical materials using SCCO₂ extraction technology, it is important to determine the solubility of solid compounds in SCCO₂. Many recent literature have reviewed the solubility data of solid compounds in SCCO₂ [4,5]. However, no solubility data of pure or mixed 3,5-DNBA and *m*-NBA in SCCO₂ have been listed in previous literature.

Because the experimental determination of the solubility of solid compounds in SCCO₂ at various temperatures and pressures is time consuming, modeling of the solubility data in SCCO₂ is essential. Models used for correlating the solubility data can be broadly classified as equation of state (EOS) based models and semi-empirical models [6,7]. EOS based models like cubic equation of state or perturbed equations need large and complicated computational methods and the knowledge of the solid properties (macroscopic critical properties and sublimation pressure are needed for cubic equations of state are normally not available for many complex pharmaceutical compounds, which are determined by group contribution methods [8,9]. Due to several drawbacks, an error is produced in their estimations.

On the other hand, semi-empirical equations, like density based models, only need available independent variables like pressure, temperature and density of pure SCF instead of solid properties. They are based on simple error minimization. The only drawback is the semi-empirical character, which means that solubility data are needed [10]. Recently, many semi-empirical models such as

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^{0040-6031/\$ -} see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.tca.2011.01.039

Table 1 Chemical structures of solid compounds.



^a $T_{\rm m}$ is the melting point of compound searching from the website of Chem YQ.

Chrastil model [11], Méndez-Santiago and Teja model [12], Bartle model [13], Gordillo model [14], del Valle and Aguilera model [15], Adachi and Lu model [16], Sparks model [17], Kumar and Johnston (K–J) model [18], and Yu model [19] are used for correlating the solubility data of solid compounds in SCCO₂. However, it is still uncertain which is the best model to predict more accurately for the solubility data of solid solutes in SCCO₂, especially for the mixtures of solid solutes.

Thus, an excellent mathematical modeling of solubility data in SCF could provide better understanding of the dissolution phenomenon and can be used for solubility prediction at interested pressures and temperatures after measuring a minimum number of experimental data, which could speed up the development of SCF technology.

In this work, the solubility of pure and mixed 3,5-DNBA and *m*-NBA in SCCO₂ was measured at 308, 318, and 328 K over a pressure range from 10.0 to 21.0 MPa. The optimal operation for the separation of 3,5-DNBA and *m*-NBA using SCCO₂ extraction technology was investigated. The experimental solubility data were correlated by Chrastil model, the modified Adachi and Lu model, and K–J model. A modified semi-empirical model with four parameters based on K–J model was developed and used to correlate the solubility data of 25 different solid compounds from this work and literature.

2. Experimental methods

2.1. Chemicals and raw materials

Carbon dioxide (CAS 124-38-9) (more than 99.9% mass fraction) was purchased from Beijing Praxair Industrial Gas Co., Ltd. 3,5-DNBA ($C_7H_4N_2O_6$, CAS 99-34-3) and *m*-NBA ($C_7H_5NO_4$, CAS 121-92-6) with an assessed minimum mass purity of 99% (analytical purity) were purchased from Beijing Hengye Zhongyuan Chemical Co., Ltd. The chemical structures and melting points of solid compounds are shown in Table 1. All chemicals were used without further purification.

2.2. Experimental procedure

The solubility of 3,5-DNBA and *m*-NBA in SCCO₂ was measured using a dynamic flow technique with ultraviolet spectrophotometer analysis. A schematic diagram of the experimental apparatus is shown in Fig. 1.

CO₂ supplied to a high-pressure surge flask from a cylinder was pressurized by the compressor (Nova, model 5542121). Highpressured CO₂ entered into a preheating and mixing cell with a heating electric coil so that its temperature and pressure could reach to the operating condition. SCCO₂ entered into a highpressure equilibrium cell with an available volume of 150 mL from the bottom consecutively, which was loaded 40 or 50 g of packed solute mixed with the glass beads and stainless steel sintered disks at both ends to prevent physical entrainment of undissolved solute. The high-pressure equilibrium cell was immersed in a constanttemperature stirred water bath with preheating coils (Chongqing Yinhe Experimental Instrument Corporation, model CS-530), which was controlled to $\pm 0.5 \text{ K}$ by a temperature controller. The temperature and pressure in the cell was 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.



Fig. 1. Schematic diagram of the experimental apparatus: 1, CO₂ cylinder; 2, compressor; 3, high-pressure surge flask; 4, pressure regulating valve; 5, preheating and mixing cell; 6, high-pressure equilibrium cell; 7, decompression sampling valve; 8, U-shaped tube; 9, rotated flow meter; 10, wet-gas flow meter; 11, back pressure valve; 12, safety valve; 13, pressure gauge; 14, constant-temperature stirred water bath; 15, preheating coils; 16, temperature controller; 17, thermometer; 18, heating coils.

SCCO₂ flowed out from the top of the equilibrium cell through a decompression sampling valve (wrapped with heating coils) and the solid compound was separated from CO₂ and collected by two U-shaped tubes in turn. From experimental observation, nearly all the solute was collected in the first U-shaped tube, and scarcely little precipitated in the second U-shaped tube. 3,5-DNBA is hardly soluble in water and very soluble in ethanol, while *m*-NBA is both soluble in water or ethanol. As a result, the solvent used to wash the analytes in the U-shaped tubes was the mixed solvent of ethanol and water (the volume ratio of ethanol and water = 1:3). The total volume of CO₂ released during the experiment was measured by a calibrated wet gas flow meter (Changchun Instrument Factory, model LML-2) with an uncertainty of ± 0.01 L at room temperature and atmospheric pressure.

To make sure the reliability of the experimental procedure, the equilibrium time and the suitable flow rate of CO_2 was determined, respectively. The flow rate experiments with a rotated flow meter were carried out before. The results showed that when the flow rate of CO_2 was in the range of $0.3-1.0 \,\mathrm{L\,min^{-1}}$, the equilibrium of system would be maintained. The average flow rate of $0.6 \,\mathrm{L\,min^{-1}}$ in this work was adopted. At a suitable flow rate of CO_2 , the solubility of solutes was measured after 20, 30, 40, 50, and 60 min, respectively. The results showed that the solubility was nearly invariable after 30 min, which shows that the system had reached equilibrium. Therefore, all of the data were measured after 30 min.

2.3. Analytical methods and solubility measurements

UV spectrophotometer (UNICO, model UV-2100) method was used to analyze the amount of solutes collected in the U-shaped tubes. The reference solution was the mixed solvent of ethanol and water (the volume ratio of ethanol and water = 1:3). The maximum UV absorption λ_{max} of the sample was detected at a wavelength of 263 nm for 3,5-DNBA and 268 nm for *m*-NBA, respectively. A calibration curve was used to establish the concentration of solute with the regression coefficient better than 0.9995. The solubility of solute was determined by the concentration of solute and the flow volume of SCCO₂, and the solubility of solute in mole fraction was calculated according to the following formula:

$$y = \frac{S \times M_1}{S \times M_1 + \rho \times M_2} \tag{1}$$

where *S* is the solubility of solute (gL^{-1}) , M_1 and M_2 are the molecular weights of CO₂ and solute $(gmol^{-1})$, respectively, ρ is the density of CO₂ at room temperature and normal atmospheric pressure (gL^{-1}) , and *y* is the mole fraction solubility of the solute.

For the solubility measurements of mixed 3,5-DNBA and *m*-NBA in SCCO₂, the cumulative absorbance was resulted from the comprehensive contribution of both 3,5-DNBA and *m*-NBA. Thus, each composition of solutes in the ternary system $(3,5-DNBA + m-NBA + SCCO_2)$ was determined by an absorbency measurement at both wavelengths of 268 nm (the maximum wavelength of *m*-NBA) and 237 nm (obtained by detecting the wavelength to acquire a maximum absorption difference with the absorption at 268 nm) using UV spectrophotometer. Consequently, the solubility of each solute was calculated by a least-squares regression from the relative absorbency at both wavelengths.

The reliability of the experimental apparatus was verified by measuring the solubility of solid solutes in our previous work [20,21]. 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 $\pm 5\%$.

3. Theoretical section

3.1. Empirical models

Chrastil model [11] is one of the most frequently used densitybased models, which indicates that the relationship between the solute solubility (S, gL^{-1}) in SCF and the solvent density (ρ_1 , gL^{-1}) and temperature (T, K) as:

$$\ln S = A_0 \ln \rho_1 + \frac{A_1}{T} + A_2 \tag{2}$$

where A_0 - A_2 are the model constants that can be estimated from experimental solubility data in SCF. A_0 is an association constant describes the number of SCF molecules in the solvated complex, A_1 is a function of the enthalpy of salvation and vaporization, and A_2 is a function of the association number and molecular weights of the solute and SCF.

Adachi and Lu [16] modified Chrastil's model to better model the solubility of triglycerides. Chrastil assumed the association number A_0 to be constant and independent of density. Adachi and Lu changed the association number A_0 to a second-order polynomial of density. They proposed that the association constant A_0 could be expressed as $A_0 = e_0 + e_1\rho_1 + e_2\rho_1^2$. They found that a significant reduction in variation between experimental and calculated solubility data could be achieved for some systems by modifying the association number A_0 .

Sparks et al. [17] found that Adachi and Lu modified the term for the association constant A_0 in Chrastil model so that it became a quadratic function of density. However, when values of the modified A_0 were calculated for several solid-SCCO₂ systems [16] and plotted against reduced density, an interesting trend can be observed. Though A_0 was generated from a quadratic function, the change of A_0 with density is somewhat linear for each compound. Therefore, Adachi and Lu model can be simplified (with insignificant loss of efficacy) to the following form as $A_0 = e_0 + e_1\rho_1$. Therefore, the solubility of solute (S, gL^{-1}) in SCF can be correlated to the solvent density (ρ_1 , gL^{-1}) and temperature (T, K) by the modified Adachi and Lu model:

$$\ln S = (B_0 + B_1 \rho_1) \ln \rho_1 + \frac{B_2}{T} + B_3$$
(3)

where $B_0 - B_3$ are the model constants.

Kumar and Johnston [18] pointed out that the linear relationships observed between $\ln y_2$ and $\ln \rho_1$ and in some cases between $\ln y_2$ and ρ_1 are system dependent and neither can be validly generalized. Similar to Eq. (2), the linear expression between $\ln y_2$ and ρ_1 could be given as:

$$\ln y_2 = C_0 \rho_1 + \frac{C_1}{T} + C_2 \tag{4}$$

where y_2 is the mole fraction solubility of solute in SCF, ρ_1 (gL⁻¹) is the solvent density, T(K) is temperature, and C_0-C_2 are the model constants.

K–J model is expressed with three adjustable parameters (C_0 , C_1 and C_2) in Eq. (4). The value of C_1 is related to the total heat ΔH_{total} (heat of solvation ΔH_{sol} , plus heat of vaporization of the solute ΔH_{vap}), which cannot be changed random in the experiment. Parameter C_2 is a constant only acquired from the experimental data. Take into account the viewpoints of Adachi and Lu and Sparks et al. [16,17], the adjustable parameter C_0 should be related with density. Thus, C_0 is defined in this work as $C_0 = D_0 + D_1 \ln \rho_1$, which is linear with $\ln \rho_1$, rather than a constant, as K–J model simulated.

The following empirical model was proposed for the solubility of solid solutes in SCF as:

$$\ln y_2 = (D_0 + D_1 \ln \rho_1)\rho_1 + \frac{D_2}{T} + D_3$$
(5)

Table 2

The mole fraction solubility of pure (y_b) and mixed (y_t) 3,5-DNBA and *m*-NBA in SCCO₂ with the solubility enhancement *SE*, mixture separation factor μ and the separation efficiency *HE* at temperatures of 308, 318, and 328 K and a pressure range of 10.0–21.0 MPa.

<i>T</i> (K)	p(MPa)	$\rho_1^{a}(g/L)$	3,5-DNBA			m-NBA			μ	HE (%)
			$10^6 \cdot y_b$	$10^6 \cdot y_t$	SE (%)	$10^6 \cdot y_b$	$10^6 \cdot y_t$	SE (%)		
308	10.0	714.84	0.58	1.22	110	7.21	7.43	3	6.09	85.90
	12.0	768.42	0.73	2.27	211	14.32	16.85	18	7.42	88.13
	15.0	816.06	0.94	2.69	186	19.44	27.56	42	10.25	91.11
	18.0	848.87	1.08	3.12	189	24.08	33.55	39	10.75	91.49
	21.0	874.40	1.09	3.45	217	25.36	37.71	49	10.93	91.62
			Average		183			30	9.09	89.65
318	10.0	502.57	0.48	0.51	6	3.33	4.43	33	8.69	89.68
	12.0	659.73	1.17	2.45	109	14.94	22.92	53	9.36	90.34
	15.0	743.17	1.69	3.86	128	34.34	40.68	18	10.54	91.33
	18.0	790.18	2.14	5.09	138	47.03	62.60	33	12.30	92.48
	21.0	823.71	2.30	7.11	209	60.68	74.61	23	10.49	91.30
			Average		118			32	10.27	91.03
328	10.0	326.40	0.44	0.45	2	1.44	1.71	19	3.80	79.17
	12.0	506.85	1.31	1.50	15	10.38	12.02	16	8.01	88.91
	15.0	654.94	2.65	4.89	85	46.19	56.08	21	11.47	91.98
	18.0	724.13	3.57	7.23	103	79.59	90.02	13	12.45	92.57
	21.0	768.74	4.21	9.82	133	109.86	121.53	11	12.38	92.52
			Average		67			16	9.62	89.03

^a ρ₁ is the density of pure CO₂ at different experimental pressures and temperatures, which is obtained from the NIST fluid property database.

Table 3

Correlation parameters for the solubility of 3,5-DNBA and *m*-NBA in SCCO₂ for the binary and ternary systems.

	Models	Correlation parameters	AARD (%)
Binary system			
3,5-DNBA	Chrastil model	$A_0 = 2.7982; A_1 = -8755.6; A_2 = -2.0838$	4.75
	Modified Adachi-Lu model	$B_0 = 1.5243$; $B_1 = 0.000314$; $B_2 = -9019.9$; $B_3 = 5.6113$	3.20
	K–J model	$C_0 = 0.004996; C_1 = -9191.4; C_2 = 11.8634$	5.03
	Modified K–J model	$D_0 = 0.02324; D_1 = -0.002476; D_2 = -8999.7; D_3 = 9.8820$	3.22
m-NBA	Chrastil model	$A_0 = 5.3236; A_1 = -10789.4; A_2 = -9.6893$	9.43
	Modified Adachi-Lu model	$B_0 = 2.9892; B_1 = 0.000575; B_2 = -11273.7; B_3 = 4.4120$	5.42
	K–J model	$C_0 = 0.009501; C_1 = -11612.8; C_2 = 19.0637$	9.51
	Modified K–J model	$D_0 = 0.04597$; $D_1 = -0.004948$; $D_2 = -11229.8$; $D_3 = 15.1038$	5.10
Ternary system	-		
3,5-DNBA	Chrastil model	$A_0 = 4.0159; A_1 = -8004.1; A_2 = -11.6981$	12.81
	Modified Adachi-Lu model	$B_0 = 0.4904; B_1 = 0.000869; B_2 = -8735.4; B_3 = 9.5978$	8.71
	K–J model	$C_0 = 0.007270; C_1 = -8732.9; C_2 = 9.5642$	8.57
	Modified K–J model	$D_0 = 0.00962; D_1 = -0.000318; D_2 = -8708.2; D_3 = 9.3095$	8.54
m-NBA	Chrastil model	$A_0 = 5.3242; A_1 = -10259.8; A_2 = -11.1475$	12.25
	Modified Adachi-Lu model	$B_0 = 2.6261; B_1 = 0.000665; B_2 = -10819.6; B_3 = 5.1503$	8.60
	K–J model	$C_0 = 0.009522; C_1 = -11104.0; C_2 = 17.6731$	11.72
	Modified K–J model	$D_0 = 0.03933; D_1 = -0.004044; D_2 = -10790.9; D_3 = 14.4368$	8.58

Table 4

Data references for the compounds considered in this study.

No.	Compound	Formula	<i>T</i> (K)	P(MPa)	Ν	Reference
1	5-Sulfosalicylic acid	C ₇ H ₆ O ₄ S	308-328	8.0-21.0	15	[27]
2	p-Aminobenzoic acid	C ₇ H ₇ NO ₂	308-328	8.0-21.0	15	[27]
3	Ethyl p-hydroxybenzoate	$C_9H_{10}O_3$	308-328	8.0-21.0	15	[28]
4	Ethyl p-aminobenzoate	$C_9H_{11}NO_2$	308-328	8.0-21.0	15	[28]
5	p-Toluenesulfonamide	C ₇ H ₉ NO ₂ S	308-328	11.0-21.0	15	[29]
6	Sulfanilamide	C ₆ H ₈ N ₂ O ₂ S	308-328	11.0-21.0	15	[29]
7	Benzoic acid	$C_7H_6O_2$	308-328	10.1-28.0	18	[30]
8	Salicylic acid	C ₇ H ₆ O ₃	308-328	10.1-28.0	18	[30]
9	Acetylsalicylic acid	$C_9H_8O_4$	308-328	10.1-28.0	18	[30]
10	Medroxyprogesterone acetate	$C_{24}H_{34}O_4$	308-348	12.2-35.5	40	[31]
11	Cyproterone acetate	C24H29ClO4	308-348	12.2-35.5	40	[31]
12	Disperse Red 73	C ₁₈ H ₁₆ N ₆ O ₂	343-383	12.0-28.0	15	[32]
13	Disperse Yellow 119	$C_{15}H_{13}N_5O_4$	343-383	12.0-28.0	15	[32]
14	Cholesteryl benzoate	$C_{34}H_{50}O_2$	308.15-328.15	12.0-24.0	17	[33]
15	Cholesteryl butyrate	$C_{31}H_{52}O_2$	308.15-328.15	12.0-24.0	17	[33]
16	Mono-tert-butyl ethers of glycerol	$C_7 H_{16} O_3$	313.15-348.15	8.0-20.0	14	[34]
17	Di-tert-butyl ethers of glycerol	$C_{11}H_{24}O_6$	313.15-348.15	8.0-20.0	14	[34]
18	Hexachlorobenzene	C ₆ Cl ₆	308-328	9.0-24.06	15	[35]
19	Pentachlorophenol	C ₆ Cl ₅ OH	308-328	9.0-24.06	15	[35]
20	1,10-Decanediol	$C_{10}H_{22}O_2$	308-318	16.38-30.71	10	[36]
21	Benzoic acid	$C_7H_6O_2$	308-318	16.38-30.71	10	[36]
22	Phenanthrene	C ₁₄ H ₁₀	308-318	10.31-23.91	10	[37]
23	Anthracene	C ₁₄ H ₁₀	308-318	10.31-23.91	10	[37]

Table 5

Correlation parameters for the solubility of compounds in SCCO₂ using the modified K–J model.

No.	Compound	D_0	D_1	<i>D</i> ₂	<i>D</i> ₃
Binary system					
1	5-Sulfosalicylic acid	1.4400e-2	-1.7089e-3	-1730.98	-10.1339
2	p-Aminobenzoic acid	9.1885e-3	-9.3986e-4	-2079.81	-8.0072
3	Ethyl p-hydroxybenzoate	4.2332e-2	-5.1802e-3	-4446.84	-1.2031
4	Ethyl p-aminobenzoate	5.3548e-2	-6.4727e-3	-4138.20	-2.0514
5	p-Toluenesulfonamide	-3.1718e-3	7.5725e-4	-3407.34	-0.9067
6	Sulfanilamide	-4.9720e-3	9.6288e-4	-4658.22	-1.4730
7	Benzoic acid	5.9106e-2	-7.0287e-3	-5224.67	0.9408
8	Salicylic acid	1.0870e-2	-7.8654e-4	-5404.26	4.7463
9	Acetylsalicylic acid	-4.0431e-3	1.3068e-3	-5947.86	6.2620
10	Medroxyprogesterone acetate	-4.3570e-2	6.7706e-3	-5125.57	5.3012
11	Cyproterone acetate	-6.2890e-2	9.2829e-3	-2611.14	-0.5895
12	Disperse Red 73	3.2045e-2	-3.8610e-3	-4080.03	-3.9635
13	Disperse Yellow 119	1.8634e-2	-1.8282e-3	-6815.18	3.0222
Ternary system					
1	5-Sulfosalicylic acid	1.0395e-2	-1.2122e-3	-1428.35	-10.4810
	p-Aminobenzoic acid	1.0750e-2	-1.2635e-3	-1259.46	-10.1108
2	Ethyl p-hydroxybenzoate	6.1928e-2	-7.6820e-3	-6028.82	2.4032
	Ethyl p-aminobenzoate	5.7304e-2	-6.9336e-3	-4320.61	-1.7311
3	p-Toluenesulfonamide	-1.1884e-2	2.1132e-3	-5480.40	5.0330
	Sulfanilamide	7.3099e-3	-7.7005e-4	-3210.28	-6.3997
4	Benzoic acid	4.9411e-2	-5.7279e-3	-5143.15	1.4849
	Salicylic acid	3.1613e-2	-3.3639e-3	-5665.65	3.6448
5	Benzoic acid	3.8320e-2	-4.2100e-3	-5917.65	4.8504
	Acetylsalicylic acid	2.7257e-2	-2.5545e-3	-7178.55	7.1142
6	Salicylic acid	2.2175e-2	-2.1601e-3	-5730.32	4.3350
	Acetylsalicylic acid	-8.9059e-4	1.0116e-3	-6546.61	7.7525
7	Medroxyprogesterone acetate	-5.4864e-2	8.0335e-3	-3744.61	3.5130
	Cyproterone acetate	-5.9721e-2	8.6205e-3	-3076.02	1.6648
8	Disperse Red 73	1.6268e-2	-1.6132e-3	-4501.55	-2.2870
	Disperse Yellow 119	4.0710e-3	-8.8115e-5	-4737.14	0.5843
9	Cholesteryl benzoate	7.2903e-2	-8.3326e-3	-7231.02	0.3612
	cholesteryl butyrate	7.9802e-2	-9.0984e-3	-7724.27	-1.8192
10	Mono-tert-butyl ethers of glycerol	4.4042e-2	-5.4756e-3	-2553.57	-3.2763
	Di-tert-butyl ethers of glycerol	3.0442e-2	-3.7524e-3	-1976.88	-4.2448
11	Hexachlorobenzene	1.1040e-1	-1.4062e-2	280.49	-24.4688
	Pentachlorophenol	3.7362e-2	-4.3201e-3	-4792.20	0.2005
12	1,10-Decanediol	-1.8093e-1	2.3854e-2	-6621.34	30.0567
	Benzoic acid	5.4004e-3	-9.3819e-5	-4289.00	3.9268
13	Phenanthrene	7.2043e-2	-8.5736e-3	-5571.79	-0.6192
	Anthracene	9.6274e-2	-1.1723e-2	-5125.50	-7.4187
Quaternary system					
1	Benzoic acid	5.2139e-2	-5.9750e-3	-5879.24	3.1266
	Salicylic acid	5.5034e-2	-6.3209e-3	-6664.57	4.0592
	Acetylsalicylic acid	4.9354e-2	-5.3955e-3	-7475.26	5.7293

where D_0 – D_3 are the model constants, y_2 is the mole fraction solubility of solute in SCF, ρ_1 (gL⁻¹) is the density of pure solvent at different experimental pressures and temperatures, and *T*(K) is temperature.

3.2. Methodology

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

AARD(%) =
$$\frac{100}{n} \sum_{1}^{n} \frac{|y_{cal} - y_{exp}|}{y_{exp}}$$
 (6)

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, *n* is the number of experimental points. The name and version of software that we used to fit the experimental and calculated data was Microsoft Office Excel 2007.

4. Results and discussions

For the binary system $(3,5-DNBA/m-NBA+SCCO_2)$ and the ternary system $(3,5-DNBA+m-NBA+SCCO_2)$ (the mass ratio of

3,5-DNBA and m-NBA = 1:1), the mole fraction solubility data of solutes in SCCO₂ at 308, 318, and 328 K over the pressures range of 10.0–21.0 MPa are all listed in Table 2. The density of CO₂ obtained from the NIST fluid property database is also shown in Table 2. In this work, Chrastil model, the modified Adachi and Lu model, K–J model, and the modified K–J model proposed in our work, Eqs. (2)–(5), were used to correlate the solubility data of solids in SCCO₂.

4.1. Solubility in the binary system

As shown in Table 2 and Fig. 2, the equilibrium solubility of each solid solute increases with increasing pressure at three temperatures (308, 318, and 328 K). It can attribute to the increase of solvent's density with increasing pressure and the specific stronger interactions between solute and solvent molecules at higher pressure. The crossover pressure regions have been observed, as shown in Fig. 2. They are from 10.5 to 11.2 MPa and 11.2–13.0 MPa for 3,5-DNBA and *m*-NBA, respectively. The crossover phenomena could be attributed to the competitions between solute's vapor pressure and solvent's density, whose dependences on temperature are in opposite directions. Below the crossover pressure region, the density effect, sensitive to the solute's vapor pressure, is dominant so that the solute is more soluble at low temperature. However, above the

Table 6

Comparison of AARD of the K–J model, modified K–J model and the models discussed from literature.

Binary system15-suffosalitylic axidChrastil A85.93.4415-suffosalitylic axidChrastil 6.396.495.683BHyl p-introbenzotacChrastil 4.621.795.684BHyl p-sminobenzotacChrastil 3.261.324.025p-7olenesulfonamideChrastil 3.261.761.716Suffanilamide3.000.1948Salitylic add	No.	Compound	Models from literature ^a	K-J1 ^b	K-J ₂ ^c
15-Sulfosalicylic acidChrastil 3.485.953.542p-Aninobenzoia ecidChrastil 5.2914.795.683Ethyl p-IndroxyenzoateChrastil 4.6214.793.685p-Toluenesulfonamide1.797.796Sulfanilamide1.797.797Benzoic acid3.001948Salicylic acid1.651.6110Medroxyprogesterone acetate1.651.6311Oproterone acetate1.8411.1712Disperse Ked 73Chrastil 9; MST 131.819.2813Disperse Ked 73Chrastil 11; MST 139.819.107Average*3.003.033.037P-Aninobenzoia ecidChrastil 4.714.664.597Medroxyprogesterone acetate3.003.033.037P-Aninobenzoia ecidChrastil 4.873.053.567P-Aninobenzoia ecidChrastil 4.873.033.038Ethyl p-Aninobenzoia ecidChrastil 4.873.063.039SulfanilamideChrastil 4.873.053.5614Benzoia ecidChrastil 4.873.103.109Ethyl p-Indiroxybenzate2.033.623.1014Benzoia ecidChrastil 4.873.103.109KalfanilamideChrastil 4.873.103.1015Benzoia ecidChrastil 4.923.103.1016Benzoia ecid	Binary system				
2p-Animobenzoia caidChrastil 6.296.495.263Ethly p-uninobenzoateChrastil 3.2619.324025p-Tolenesulfonamide1.761.776Benzoic caid3.001.948Salirglic caid1.051.61310Medroxyprogesterone acetate1.533.2411Cyproterone acetate1.533.2411Cyproterone acetate1.533.2411Cyproterone acetate1.631.11712Disperse Kel 73Chrastil 9; MST 131.1812.9813Disperse Kel 73Chrastil 11, MST 131.1812.9814Merroysel CarlChrastil 4.875.694.757Merroysel CarlChrastil 4.715.694.557p-Animobenzoia caidChrastil 4.1175.694.557P-Inimobenzoia caidChrastil 4.1175.694.558Parimobenzoia caidChrastil 4.1175.694.558Parimobenzoia caidChrastil 4.212.055.623Parimobenzoia caidChrastil 4.212.055.623SulfanimideChrastil 4.514.641.514Merroysel CarlCarl2.153.135SulfanimideChrastil 1.501.514.446SalirSalir3.162.157Merroysel CarlCarl1.514.447SalirSalir3.163.16 <td>1</td> <td>5-Sulfosalicylic acid</td> <td>Chrastil 3.48</td> <td>5.95</td> <td>3.54</td>	1	5-Sulfosalicylic acid	Chrastil 3.48	5.95	3.54
3Ethylp-hydroxybenzoateChrastil 4.6214.795.684Ethylp-ninobenzoate1.791.795Sulfanilanide1.791.797Benzoic acid3.001.947Benzoic acid1.651.638Salicylic acid1.651.6310Medroxyongesterone acetate1.8411.1712Disperse Ked 73Chrastil 9; MST 131.812.9213Disperse Ked 73Chrastil 11; MST 139.819.9114Disperse Ked 73Chrastil 13; MST 139.819.907Benzoic acidChrastil 4.714.684.597P-Minobenzoia cidChrastil 5.173.565.2738Ethylp-hydroxybenzoateChrastil 6.1571.533.6377Benzoic acidChrastil 6.5572.056.2733p-ToluenesuffonamideChrastil 6.1571.533.6377Benzoic acidChrastil 5.172.302.2158Salicylic acidChrastil 5.172.356.5277Benzoic acidChrastil 1.8, MST 6.31.801.577Benzoic acid2.872.862.878Salicylic acidChrastil 1.8, MST 6.31.801.527Benzoic acid2.872.861.567Benzoic acid2.872.861.568Salicylic acidChrastil 1.9, MST 107.653.629Deleneryl burateChr	2	p-Aminobenzoic acid	Chrastil 6.39	6.49	5.26
4Ethylp-aminobenzateChrastil 3.2619.324.4025p-Toleneaufonamide1.791.791.796Sulfanilamide4.194.0077Benzoic acid3.001.948Salicylic acid1.761.719Acretysalicylic acid1.531.6310Medroxyprogestrome acetate1.539.2311Cyportenone acetate1.539.2411Cyportenone acetate1.8411.1712Disperse Red 73Chrastil 9: MST 1311.819.2813Disperse Red 73Chrastil 11: MST 139.819.007Average'Chrastil 4.714.684.597P-Minobenzoite acidChrastil 4.714.684.592Ethyl p-AnimobenzoiteChrastil 5.012.356.373p-ToleneaufonamideChrastil 5.012.356.373p-ToleneaufonamideChrastil 5.11.311.944Benzoit acid2.302.121.353Salicylic acid2.302.121.374Benzoit acid2.322.657.347Medroxyprogestroma acetate2.221.531.357Medroxyprogestroma acetate2.231.531.547Medroxyprogestroma acetate2.241.793.809Cholesteryl buzzoteChrastil 1.744.648.1810Mone-ret-roturyl ethers of glycerolBartel 5.37 <td>3</td> <td>Ethyl p-hydroxybenzoate</td> <td>Chrastil 4.62</td> <td>14.79</td> <td>5.68</td>	3	Ethyl p-hydroxybenzoate	Chrastil 4.62	14.79	5.68
5p-Toluenesulfonamide1.791.796Sulfamilamide3.001.947Benzoi carid3.001.948Salicylic arid1.651.639Acetylsalicylic arid1.651.6310Medroxyprogesterone acetate1.849.2411Opporterone acetate1.849.2412Disperse Red 73Chrastil 91; MST 139.819.00AverageChrastil 11; MST 139.819.007Average2.005.624.557P-Minobenzoi caidChrastil 4.875.694.758Ethyl p-ApidroxybenzoateChrastil 4.514.684.592Ethyl p-ApidroxybenzoateChrastil 5.613.562.739P-OluenesuffonamideChrastil 6.61MST 8.53.562.739SulfanilamideChrastil 6.714.684.592.3SulfanilamideChrastil 5.613.562.739P-OluenesuffonamideChrastil 5.613.562.7314Benzoi caidChrastil 1.61MST 8.53.182.125Benzoi caid2.202.151.335Benzoi caid2.211.312.996Salicylic acid2.222.551.587Medroxyprogesterone acetate2.222.551.587Medroxyprogesterone acetate2.221.533.5010Mono-tert-bury tetres of glycerolBartle 1.56 </td <td>4</td> <td>Ethyl p-aminobenzoate</td> <td>Chrastil 3.26</td> <td>19.32</td> <td>4.02</td>	4	Ethyl p-aminobenzoate	Chrastil 3.26	19.32	4.02
6Sulfanilamide4.194.077Benzoic acid3.001.948Salkylic acid1.761.719Acetylsalkylic acid1.581.6310Medroxyprogestrome acetate15.389.2411Cyporteome acetate15.389.2412Disperse Red 73Chrastil 9; MST 1318.4811.1712Disperse Red 73Chrastil 9; MST 1318.419.2813Disperse Red 73Chrastil 9; MST 1318.419.287Average ⁴ 8.805.264.577P-Minobenzoic acidChrastil 4714.684.572Ethyl p-hydroxybenzoateChrastil 5.102.356.372Ethyl p-hydroxybenzoateChrastil 5.61 MST 8.53.562.7339-TolleneusilonamideChrastil 5.61 MST 8.53.562.734Benzoic acidChrastil 6.54 MST 8.53.611.574Benzoic acid2.302.121.315Benzoic acid2.372.863.112.996Salkylic acid2.722.651.533.131.907Medroxyprogesterom acetate2.722.651.533.147Medroxyprogesterom acetate2.722.651.533.157Medroxyprogesterom acetate2.303.611.963.837Medroxyprogesterom acetate3.695.601.307Medroxyprogesterom acetate<	5	p-Toluenesulfonamide		1.79	1.79
7Benzoic acid3.001.948Salciylic acid1.761.719Acetylsalicylic acid1.651.6310Medroxyprogestrone acetate15.389.2411Cyproterone acetate1.539.2411Diperse Red 73Chrastil 9; MST 1318.8119.1812Diperse Red 73Chrastil 9; MST 139.819.00Average ^d Neraged8.805.26Ternary systemP-Aminobenzoic acidChrastil 4.716.694.752Ethyl p-hydroxybenzoateChrastil 4.714.684.592Ethyl p-hydroxybenzoateChrastil 4.523.562.733DiffereChrastil 4.523.562.733Sulfaminobenzoic acidChrastil 4.523.562.734Benzoic acidChrastil 4.523.562.735SulfamindeChrastil 4.513.132.994Benzoic acid2.302.123.135Sulfaylic acid2.302.123.135Sulfaylic acid2.722.653.66Salicylic acid2.722.653.67Medroxyprogestrone acetate2.121.633.189Cholesteryl benzoateChrastil 10; MST 108.468.189Cholesteryl benzoateChrastil 6.3; MST 5.3; Bartle 5.5; PR-EOS 9.77.744.917Medroxyprogestrone acetate2.873.663.309	6	Sulfanilamide		4.19	4.07
8Salicylic acid1.761.719Acetylskilylic acid16516310Medroxyprogestrone acetate15392411Cyproterone acetate184811.1712Disperse Red 73Chrastil 9; MST 1311.8192813Disperse Yellow 119Chrastil 9; MST 139.819.10Average ⁴ 8.005.267.305.26Ternary systemFChrastil 4.875.694.751F-Sulfosalicylic acidChrastil 4.714.684.592Ethyl p-hydroxybenzoateChrastil 4.512.356.373p-TolucensulfonamideChrastil 6.573.562.733JuffaniamideChrastil 6.573.562.734Benzoic acidChrastil 6.573.562.735Benzoic acid2.151.333.901.574Benzoic acid2.151.332.866Salicylic acid2.151.312.996Salicylic acid2.722.657Medroxyprogesterone acetate2.722.657Medroxyprogesterone acetate2.722.657Medroxyprogesterone acetate2.732.657Medroxyprogesterone acetate2.873.667Disperse Pellow 119Chrastil 10; MST 108.468.188Disperse Pellow 119Chrastil 4.977.244.917Chrastil 4.973.813.603.8	7	Benzoic acid		3.00	1.94
9Acetylsalicylic acid1.651.6310Medroxyprogesterone acetate15.389.2411Cyproterone acetate15.389.2412Disperse Nellow 119Chrastil 9; MST 1311.819.2813Disperse Yellow 119Chrastil 11; MST 139.819.00AveragedChrastil 4.715.694.757p-Aninoberzoic acidChrastil 4.714.684.592Ethyl p-hydroxyberzoateChrastil 4.714.684.593p-ToluenesulfonamideChrastil 4.523.563.563P-ToluenesulfonamideChrastil 4.523.563.563SulfanilamideChrastil 4.511.312.994Benzoic acid2.151.333.115Benzoic acid2.151.332.125Benzoic acid2.722.652.456Salicylic acid2.722.651.967Medroxyprogesterone acetate2.121.631.968Disperse Ref 73Chrastil 10; MST 108.468.189Cholesteryl buryareChrastil 10; MST 108.468.1810Mono-err-buryl ether	8	Salicylic acid		1.76	1.71
10Medroxyprogeterone acetate15.389.2411Cyproreone acetate18.4811.1712Disperse Red 73Chrastil 9; MST 139.819.30Average ⁴ 8.805.26Ternary system8.805.26Ternary system8.805.2616.SUlfosalicylic acidChrastil 4.876.94.752Ethyl p-hydroxyberozateChrastil 4.714.684.592Ethyl p-hydroxyberozateChrastil 4.522.0595.623p-ToluenesulfonamideChrastil 4.523.562.733sulfanilamideChrastil 4.543.562.734Benzoic acid2.151.332.302.125Benzoic acid2.151.332.992.215Benzoic acid2.151.342.992.996Salicylic acid2.151.342.997Medroxyprogetrone acetate2.722.652.877Medroxyprogetrone acetate2.721.633.147Disperse Red 73Chrastil 10; MST 108.468.189Disperse Yellow 119Chrastil 10; MST 117.767.829Disperse Yellow 119Chrastil 11; MST 117.663.6010Mono-terr-burgl ethers of glycerolBartle 1.4561.6961.03011Heachlorobenzene1.52Medro3.603.8312Disperse Yellow	9	Acetylsalicylic acid		1.65	1.63
11 12Cyproterone acetate18.4811.1712Disperse Ned 73Chrastil 9; MST 1311.819.2813Disperse Vellow 119Chrastil 11; MST 138.809.2014Average ¹ S.805.694.757Partinobenzoic acidChrastil 4.875.694.752Ethyl p-hydroxybenzoateChrastil 4.714.684.592Ethyl p-hydroxybenzoateChrastil 5.012.3.56.373Pariniobenzoic acidChrastil 6.6; MST 8.53.562.733PariniobenzoateChrastil 6.6; MST 8.53.562.734Benzoic acidChrastil 6.6; MST 8.53.562.734Benzoic acid2.151.333.135Benzoic acid2.151.336Salicylic acid2.151.335Benzoic acid2.151.347Medroxyprogestorne acetate2.722.657Medroxyprogestorne acetate2.722.658Disperse Vellow 119Chrastil 11; MST 117.767Medroxyprogestorne acetate2.722.659Cholesteryl burynateChrastil 10; MST 108.468Disperse Vellow 119Chrastil 11; MST 117.767Medroxpyrogestorne acetate2.151.519Cholesteryl burynateChrastil 10; MST 108.4610Dieteryl benzoate6.816.8111Mono-terr-buryl ethers of glycerol <t< td=""><td>10</td><td>Medroxyprogesterone acetate</td><td></td><td>15.38</td><td>9.24</td></t<>	10	Medroxyprogesterone acetate		15.38	9.24
12Disperse Red 73Chrastil 9; MST 1311.819.2813Disperse Yellow 119Chrastil 11; MST 139.819.00AveragedChrastil 11; MST 138.805.26Ternary system-Ninobenzoic acidChrastil 4.714.684.592Ethyl p-hydroxybenzoateChrastil 5.012.356.373p-ToluensuffonamideChrastil 6.51 MS.53.562.733galtanilamideChrastil 6.51 MS.53.562.734Benzoic acidChrastil 6.51 MS.53.052.135Benzoic acidChrastil 6.51 MS.53.062.135Benzoic acidChrastil 6.51 MS.53.062.136Salicylic acid2.151.312.997Acetylsalicylic acid2.151.446Salicylic acid2.121.517Medroxyprogesterone acetate2.121.518Disperse Red 73Chrastil 10; MST 108.468.189Cholesteryl benzoateChrastil 10; MST 108.468.1810Mono-tert-bulyt ethers of glycerolBartle 1.561.6961.03011Hexathlorophenol2.96.895.6013Disperse Yellow 119Chrastil 4.57 MST 6.3; Bartle 5.5; PR-EOS 9.08.475.5510Mono-tert-bulyt ethers of glycerolBartle 1.561.6961.69611Hexathlorophenol6.895.603.8312I.10-DecanedioiPR-EOS 9	11	Cyproterone acetate		18.48	11.17
13Disperse Yellow 119Chrastil 11; MST 139.819.819.10Average ^d 880526Ternary systemChrastil 4.875.694.7515-Sulfosalicylic acidChrastil 4.714.684.592Ethyl p-hydroxybenzoateChrastil 5.0123.356.37Ethyl p-hydroxybenzoateChrastil 6.5; MST 8.53.562.733Benzoic acidChrastil 6.5; MST 8.53.562.733SulfanliamideChrastil 6.5; MST 6.31.801.574Benzoic acid2.151.332.905Benzoic acid2.312.902.236Salicylic acid2.312.902.125Benzoic acid2.151.144Acetylsalicylic acid2.151.446Salicylic acid2.722.657Medroxyprogesterone acetate2.722.657Medroxyprogesterone acetate2.721.638Disperse Pellow 119Chrastil 10: MST 108.468.189Cholesteryl buryrateChrastil 11; MST 117.767.829Cholesteryl buryrateChrastil 6.3: MST 6.3; Bartle 5.5; PR-EOS 9.77.244.9110Mono-terr-buryl ethers of glycerolBarter 1.381.016.2011Hexachlorobenzene6.891.691.691.6912Intra 1.8PR-EOS 9.15.124.7713Menathrene5.821.521.52<	12	Disperse Red 73	Chrastil 9; MST 13	11.81	9.28
Average ^d 8.805.520Ternary system5-Sulfosalicylic acidChrastil 4.875.694.7515-Sulfosalicylic acidChrastil 4.714.684.592Ethyl p-hydroxyberozateChrastil 5.012.336.6373P-fouenesulfonamideChrastil 4.5220.595.623P-fouenesulfonamideChrastil 6.61 MST 8.53.562.734Benzoic acidChrastil 6.61 MST 8.53.601.574Benzoic acidChrastil 6.61 MST 8.53.801.575Benzoic acidChrastil 6.61 MST 8.53.102.126Salicylic acid1.112.992.121.336Salicylic acid1.511.442.872.866Salicylic acid1.511.441.611.647Medroxyprogesterone acetate2.121.631.647Medroxyprogesterone acetate2.121.631.648Disperse Vellow 119Chrastil 10; MST 107.67.829Cholesteryl burgateChrastil 4.531.641.6110Enter-burgl ethers of glycerolBartle 1.4561.691.6311Hexachlorobenzene6.895.603.833.83121.10-DecanediolPR-EOS 9.15.124.7213Hexachlorobenzene6.875.815.725.7214Hexachlorobenzene6.842.873.833.8313I.10-Decanediol<	13	Disperse Yellow 119	Chrastil 11; MST 13	9.81	9.10
Termary Suffosalicylic acid Chrastil 4.87 5.69 4.75 1 9-Aminobenzoic acid Chrastil 4.71 4.68 4.59 2 Ethyl <i>p</i> -hydroxybenzoate Chrastil 5.01 2.35 6.37 2 Ethyl <i>p</i> -hydroxybenzoate Chrastil 4.52 20.59 5.62 3 <i>p</i> -Toluenesuffonamide Chrastil 4.52 3.56 2.73 3 Suffanilamide Chrastil 4.52 3.80 1.57 4 Benzoic acid 2.15 1.33 5 Benzoic acid 2.30 2.12 5 Acetylsalicylic acid 2.87 2.86 6 Salicylic acid 2.72 2.65 7 Acetylsalicylic acid 2.72 2.65 7 Medroxyprogesterone acetate 2.72 2.65 7 Medroxyprogesterone acetate 2.72 2.65 7 Medroxyprogesterone acetate 2.72 2.65 7 Opterone acetate 2.84 7.76 8 Disperse Velo		Average ^d		8.80	5.26
15-Suffosalicylic acidChrastil 4.875.694.75Primobenzoi acidChrastil 4.714.684.592Ethyl p-hydroxybenzoateChrastil 5.0123.356.37Ethyl p-aminobenzoateChrastil 4.5220.595.623p-ToluenesulfonamideChrastil 4.523.562.73SulfanilamideChrastil 1.65; MST 6.31.801.574Benzoic acid2.151.332.915Salicylic acid2.151.332.916Salicylic acid2.872.862.877Medroxyprogesterone acetate2.722.657Medroxyprogesterone acetate2.721.638Disperse Red 73Chrastil 10; MST 108.468.189Chesteryl benzoateChrastil 13; MST 5.3; Bartle 5.5; PR-EOS 9.77.244.9110Mon-terr-burg Heters of glycerolBartle 1.36; MST 5.3; Bartle 5.5; PR-EOS 9.08.475.9510Mon-terr-burg Heters of glycerolBartle 1.4561.696.03011HEXACHOROBENZE3.603.613.6212I.10-DecanediolPR-EOS 9.15.124.7713PR-EOS 9.15.124.774.7214Hexachlorobenzene3.603.613.6115I.10-DecanediolPR-EOS 9.81.521.5214Hexachlorobenzene3.603.613.6115I.10-DecanediolPR-EOS 9.81.524.7216<	Ternary system				
p-Aminobenzoic acidChrastil 4.714.684.592Ethyl p-aminobenzoateChrastil 5.0123.356.37Ethyl p-aminobenzoateChrastil 4.5220.595.623p-ToluenesulfonamideChrastil 6.6; MST 8.53.562.734Benzoic acidChrastil 1.8; MST 6.31.801.574Benzoic acid2.302.125Benzoic acid2.302.126Salicylic acid2.312.99Acetylsalicylic acid2.722.657Medroxyprogesterone acetate2.722.657Medroxyprogesterone acetate2.12516.388Disperse Red 73Chrastil 10; MST 108.468.188Disperse Red 73Chrastil 11; MST 117.767.829Cholesteryl benzoateChrastil 1.3; MST 6.3; Bartle 5.5; PR-EOS 9.77.244.9110Mono-tert-buryl ethers of glycerolBartle 1.8814.016.2011Hzachlorobenzoate6.895.603.603.83121.10-DecanediolPR-EOS 9.15.124.7713Pnenathrene6.895.603.613.6114Acetylasicylic acid2.84.533.613.56131.10-DecanediolPR-EOS 9.81.524.7514Precor 9.98.715.784.543.63151.10-Decanediol8.763.613.5516Precor 9.81.524.753.	1	5-Sulfosalicylic acid	Chrastil 4.87	5.69	4.75
2Ethyl p-aminobenzoateChrastil 5.0123.356.637Ethyl p-aminobenzoateChrastil 4.5220.5956.23p-ToluenesulfonamideChrastil 4.523.562.73SulfanilamideChrastil 1.5; MST 6.31.801.574Benzoic acid2.302.125Benzoic acid2.302.126Acetylsalicylic acid2.372.866Salicylic acid2.372.866Salicylic acid2.372.867Metroxyprogesterone acetate2.722.657Metroxyprogesterone acetate2.231.518Disperse Ref 73Chrastil 10; MST 108.468.188Disperse Ref 73Chrastil 11; MST 117.767.829Cholesteryl blenzoateChrastil 13, MST 5.3; Bartle 5.5; PR-EOS 9.77.244.910Di-tert-butyl ethers of glycerolBartle 14.5616.0610.3010Mono-tert-butyl ethers of glycerolBartle 14.5616.633.83121.0-becanedioPR-EOS 9.15.124.7213Phemanthrene3.603.833.8314Di-tert-butyl ethers of glycerolBartle 13.861.521.5213Phemanthrene3.603.833.8314Di-tert-butyl ethers of glycerolBartle 13.861.521.5215Phemanthrene3.663.633.833.83121.0-becanedioPR-EOS 9.15.12 </td <td></td> <td>p-Aminobenzoic acid</td> <td>Chrastil 4.71</td> <td>4.68</td> <td>4.59</td>		p-Aminobenzoic acid	Chrastil 4.71	4.68	4.59
Ethyl p-aminobenzoateChrastil 4.5220.595.623p-ToluenesulfonamideChrastil 6.6; MST 8.53.562.734Benzoic acidChrastil 1.8; MST 6.31.801.574Benzoic acid2.151.33Salicylic acid3.112.99Acetylsalicylic acid2.722.656Salicylic acid2.722.657Medroxyprogesterone acetate2.722.657Medroxyprogesterone acetate2.722.658Disperse Red 73Chrastil 10; MST 108.468.180Disperse Vellow 119Chrastil 10; MST 108.468.189Cholesteryl buryrateChrastil 6.3; Bartle 5.5; PR-EDS 9.77.244.919Cholesteryl buryrateChrastil 6.3; MST 6.3; Bartle 5.5; PR-EDS 9.08.475.9510Mono-tert-buryl ethers of glycerolBartle 14.5616.6610.3011Hexachlorobenzene6.895.603.83121.10-DecanetiolPR-EOS 9.81.521.524.7713Penzoic acidPR-EOS 9.81.521.521.5213Phennthrene9.845.603.633.8314Anthracene9.284.584.5413Penzoic acid9.845.595.595.5914Hexachlorobenzene6.895.605.5915Practholorobenzene3.612.545.5916Medrobenzene3.635.	2	Ethyl p-hydroxybenzoate	Chrastil 5.01	23.35	6.37
3p-ToluenesulfonamideChrastil 6.6; MST 8.53.562.73SulfanilamideChrastil 1.8; MST 6.31.801.574Benzoic acid2.151.33Salicylic acid2.302.125Benzoic acid2.872.866Salicylic acid2.872.866Salicylic acid2.722.657Medroxyprogesterone acetate2.1216.38Cyprotene acetate2.1216.380 isperse Red 73Chrastil 10; MST 108.468.189Disperse Vellow 119Chrastil 13; MST 6.3; Bartle 5.5; PR-EOS 9.77.244.919Cholesteryl butyrateChrastil 4.9; MST 5.8; Bartle 4.9; PR-EOS 9.08.475.9510Mono-tert-butyl ethers of glycerolBartle 14.5616.9610.3011Hexachlorobenzene6.895.603.833.83121.0-DecanetoidPR-EOS 9.15.124.7713Phenathrene8.811.521.521.5214Hexachlorobenzene6.895.603.8315Preto' 10.0PR-EOS 9.81.521.521.5213Phenathrene9.845.923.533.5720Anthracene2.601.414.444Anthracene2.601.414.7813Preto' 10.0PR-EOS 9.81.521.5214Yerage ⁶ 3.032.573.032.5715Anthracene2.		Ethyl p-aminobenzoate	Chrastil 4.52	20.59	5.62
SuffanilamideChrastil 1.8; MST 6.31.801.574Benzoic acid2.151.33Salicylic acid3.112.99Acetylsalicylic acid2.872.866Salicylic acid2.722.657Medroxyprogesterone acetate2.121.517.7Medroxyprogesterone acetate2.872.868Disperse Red 73Chrastil 10; MST 108.468.189Cholesteryl burzoteChrastil 10; MST 108.468.189Cholesteryl burzoteChrastil 4.9; MST 5.8; Bartle 5.5; PR-EOS 9.77.244.9110mo-tert-butyl ethers of glycerolBartle 13.8814.016.03011Hexachlorobenzene8.309.503.603.83121.10-DecanetiolPR-EOS 9.15.124.7713Phenanthrene9.81.521.521.5213Phenanthrene3.603.833.833.8314AnthracenePR-EOS 9.81.521.521.5213Phenanthrene3.603.603.603.6014Aretrage3.603.613.654.6124Aretrage3.633.613.654.6514Aretrage3.633.613.654.6515Aretrage3.603.633.655.6016Aretrage3.633.655.605.6016Aretrage3.633.655.605.60	3	p-Toluenesulfonamide	Chrastil 6.6; MST 8.5	3.56	2.73
4Benzoic acid2.151.333alicylic acid2.302.125Benzoic acid2.126Salicylic acid2.876Salicylic acid2.877Medroxyprogesterone acetate2.127Medroxyprogesterone acetate2.127Disperse Ref 73Chrastil 10; MST 108.468Disperse Ref 73Chrastil 11; MST 117.769Cholesteryl buryateChrastil 4.5; MST 6.3; Bartle 5.5; PR-EOS 9.77.249Cholesteryl buryateChrastil 4.9; MST 5.8; Bartle 4.9; PR-EOS 9.08.479Cholesteryl buryateBartle 14.5616.9610Mono-tert-buryl ethers of glycerolBartle 14.5616.9611Hexachlorobenzen3.603.83121,10-DecanediolPR-EOS 9.11.521.5213PentachlorophenolFR-EOS 9.81.521.5213Phenanthrene3.032.579Anthracene2.601.4114Acetysalicylic acid2.601.4114Neracei3.032.5713Phenaticei3.032.5714Acetysalicylic acid2.601.4115Acetysalicylic acid3.032.5716Acetysalicylic acid3.032.5717Acetysalicylic acid3.032.5718Acetysalicylic acid3.695.0419Acetysalicylic acid3.695.0410 </td <td></td> <td>Sulfanilamide</td> <td>Chrastil 1.8; MST 6.3</td> <td>1.80</td> <td>1.57</td>		Sulfanilamide	Chrastil 1.8; MST 6.3	1.80	1.57
Salicylic acid2.302.125Benzoic acid3.112.99Acetylsalicylic acid2.872.866Salicylic acid1.511.44Acetylsalicylic acid2.722.657Medroxyprogesterone acetate2.1216.387Medroxyprogesterone acetate2.2817.968Dispers Pellow 119Chrastil 10; MST 108.468.189Dispers Pellow 119Chrastil 11; MST 117.767.829Cholesteryl benzoateChrastil 6.3; MST 6.3; Bartle 5.5; PR-EOS 9.77.244.9110Mon-tert-buryl ethers of glycerolBartle 14.5616.9516.3010Mon-tert-buryl ethers of glycerolBartle 14.5616.9516.3011Hexachlorobenzene3.603.833.833.83121.10-DecanediolPR-EOS 9.15.124.7713PnetachlorophenolPR-EOS 9.81.521.5213Phenathlerene6.142.444.44Quatermary system	4	Benzoic acid		2.15	1.33
5Benzoic acid3.112.99Acetylsalicylic acid2.872.866Salicylic acid2.722.657Medroxyprogesterone acetate2.722.657Medroxyprogesterone acetate2.722.657Medroxyprogesterone acetate2.847.968Disperse Red 73Chrastil 10; MST 108.468.189Cholesteryl bury netChrastil 6.3; MST 6.3; Bartle 5.5; PR-EOS 9.77.244.919Cholesteryl bury netChrastil 6.3; MST 6.3; Bartle 5.5; PR-EOS 9.77.244.9110Mono-tert-butyl ethers of glycerolBartle 14.5616.9610.3011Hexachlorobenzene6.963.833.83121,10-DecanediolPR-EOS 9.15.124.7713Penzoic acidPR-EOS 9.85.124.7513Phenanthrene5.124.751.5213Phenathrene3.482.783.48Quaternary systerISalicylic acid2.601.4114Acetylsalicylic acid2.601.412.6015Salicylic acid3.032.573.632.5716Rerus acide3.633.632.5717Medroxyber3.633.632.5718Rerus acide1.612.601.4119Acetylsalicylic acid3.032.5713Rerus acide3.633.513.6414Acetylsalicylic acid <t< td=""><td></td><td>Salicylic acid</td><td></td><td>2.30</td><td>2.12</td></t<>		Salicylic acid		2.30	2.12
Acetylsalicylic acid2.872.866Salicylic acid1.511.44Acetylsalicylic acid2.722.657Medroxyprogesterone acetate21.2516.38Cyproterone acetate22.8417.968Disperse Red 73Chrastil 10; MST 108.468.189Disperse Yellow 119Chrastil 11; MST 117.767.829Cholesteryl benzoateChrastil 4.9; MST 5.8; Bartle 5.5; PR-EOS 9.77.244.9110Mono-tert-butyl ethers of glycerolBartle 1.3616.9610.30Di-tert-butyl ethers of glycerolBartle 1.3614.016.2011Hexachlorobenzene3.603.833.83121.0-DecanediolPR-EOS 9.13.124.7713Phenanthrene9.861.521.5213Phenanthrene9.861.521.5214Matracene9.863.033.8315Antracene9.861.521.5214Antracene9.861.521.5215Antracene3.603.833.8316Antracene3.603.833.8317Benzoic acidPR-EOS 9.81.521.5218Antracene3.603.633.6319Antracene3.633.633.6310Antracene3.633.633.6313Antracene3.633.633.6314Antracene3.63 <t< td=""><td>5</td><td>Benzoic acid</td><td></td><td>3.11</td><td>2.99</td></t<>	5	Benzoic acid		3.11	2.99
6Salicylic acid1.511.44Acetylsalicylic acid2.722.657Medroxyprogesterone acetate21.2516.38Cyproterone acetate22.8417.968Disperse Red 73Chrastil 10; MST 108.468.180 Disperse Yellow 119Chrastil 11; MST 117.767.829Cholesteryl benzoateChrastil 6.3; MST 6.3; Bartle 5.5; PR-EOS 9.77.244.9110Mono-tert-butyl ethers of glycerolBartle 14.5616.9610.3011Hexachlorobenzene6.895.603.83121.0-DecanediolPR-EOS 9.13.603.8313Pentachlorophenol5.124.7713Phenanthrene9.805.024.5213Phenanthrene6.142.4420Atracene3.032.5720Atracene3.032.5720Atracene3.603.5114Salicylic acid3.032.5720Aterylasicylic acid3.035.11		Acetylsalicylic acid		2.87	2.86
Acetylsalicylic acid 2.72 2.65 7 Medroxyprogesterone acetate 21.25 16.38 Cyproterone acetate 22.84 17.96 8 Dispers Red 73 Chrastil 10; MST 10 8.46 8.18 9 Dispers Yellow 119 Chrastil 11; MST 11 7.76 7.82 9 Cholesteryl benzoate Chrastil 4.9; MST 5.3; Bartle 5.5; PR-EOS 9.7 7.24 4.91 10 Mono-tert-butyl ethers of glycerol Bartle 14.56 16.96 10.30 11 Hexachlorobenzene 6.89 5.60 3.60 3.83 12 1,10-Decanediol PR-EOS 9.1 5.12 4.77 13 Penzacharce 8.9 5.60 3.83 14 1.0-Decanediol PR-EOS 9.1 5.12 4.77 13 Phenanthrene 9.28 1.52 1.52 14 Phenathrene 9.28 3.60 3.83 15 Phenathrene 3.60 3.83 3.61 12 1,10-Decanediol PR-EOS 9.8 1.52 1.52 13 Phenathrene	6	Salicylic acid		1.51	1.44
7 Medroxyprogesterone acetate 21.25 16.38 Cyproterone acetate 22.84 17.96 8 Disperse Red 73 Chrastil 10; MST 10 8.46 8.18 0 Disperse Yellow 119 Chrastil 11; MST 11 7.76 7.82 9 Cholesteryl benzoate Chrastil 6.3; MST 6.3; Bartle 5.5; PR-EOS 9.7 7.24 4.91 10 Mono-tert-butyl ethers of glycerol Bartle 14.56 16.96 10.30 10 Mono-tert-butyl ethers of glycerol Bartle 13.88 14.01 6.20 11 Hexachlorobenzene 6.89 5.60 12 1,10-Decanediol PR-EOS 9.1 5.12 4.77 13 Pentachlorobenzene 6.89 3.60 3.83 13 Phenanthrene 6.14 2.44 13 Phenanthrene 8.03 1.52 1.52 13 Panzoic acid PR-EOS 9.8 1.52 1.52 14 Phenanthrene 3.48 2.78 204ternary system 3.03 2.60 1.41 21 Salicylic acid 3.03 2.		Acetylsalicylic acid		2.72	2.65
Cyproterone acetate 22.84 17.96 8 Dispers Red 73 Chrastil 10; MST 10 8.46 8.18 Dispers Vellow 119 Chrastil 11; MST 11 7.76 7.24 9 Cholesteryl benzoate Chrastil 6.3; MST 6.3; Bartle 5.5; PR-EOS 9.7 7.24 4.91 10 Cholesteryl butyrate Chrastil 4.9; MST 5.8; Bartle 4.9; PR-EOS 9.0 8.47 5.95 10 Mono-tert-butyl ethers of glycerol Bartle 14.56 16.96 10.30 11 Hexachlorobenzene 6.89 5.60 3.83 12 1,10-Decanediol PR-EOS 9.1 5.12 4.77 13 Phenanthrene 6.14 2.45 Anthracene 9.28 3.48 2.78 Quaternary system 1 2.60 1.41 2.57 14 Rezioc acid 2.60 1.41 2.57 14 Rezioc acid 3.48 2.78 2 Salicylic acid 3.03 2.57 3 Salicylic acid 3.03 2.57 4 Acetylsalicylic acid 3.03 2.57	7	Medroxyprogesterone acetate		21.25	16.38
8 Disperse Red 73 Chrastil 10; MST 10 8.46 8.18 Disperse Yellow 119 Chrastil 11; MST 11 7.76 7.82 9 Cholesteryl benzoate Chrastil 6.3; MST 6.3; Bartle 5.5; PR-EOS 9.7 7.24 4.91 Cholesteryl butyrate Chrastil 4.9; MST 5.8; Bartle 4.9; PR-EOS 9.0 8.47 5.95 10 Mono-tert-butyl ethers of glycerol Bartle 14.56 16.96 10.30 Di-tert-butyl ethers of glycerol Bartle 13.88 14.01 6.20 11 Hexachlorobenzene 6.89 5.60 Pentachlorophenol 3.60 3.83 12 1,10-Decanediol PR-EOS 9.1 5.12 4.77 Benzoic acid PR-EOS 9.8 1.52 1.52 13 Phenanthrene 9.28 4.58 Quaternary system 1 3.03 2.57 14 Barcoi acid 3.03 2.57 Acetylsalicylic acid 3.03 2.57 Average ⁶ 7.69 5.04 Average ⁶ 5.04 5.14		Cyproterone acetate		22.84	17.96
Disperse Yellow 119 Chrastil 11; MST 11 7.76 7.82 9 Cholesteryl benzoate Chrastil 6.3; MST 6.3; Bartle 5.5; PR-EOS 9.7 7.24 4.91 Cholesteryl butyrate Chrastil 4.9; MST 5.8; Bartle 5.5; PR-EOS 9.0 8.47 5.95 10 Mono-tert-butyl ethers of glycerol Bartle 14.56 10.696 10.30 Di-tert-butyl ethers of glycerol Bartle 14.56 14.01 6.20 11 Hexachlorobenzene 6.89 5.60 Pentachlorophenol 8.7 3.60 3.83 12 1,0-Decanediol PR-EOS 9.1 5.12 4.77 Benzoic acid PR-EOS 9.1 5.12 4.75 13 Phenanthrene 9.28 4.58 Quaternary system 1.52 1.52 1.52 1 Benzoic acid 3.03 2.57 Average ^e 3.03 2.57 5.04 Acetylsalicylic acid 3.03 2.57 5.04 Average ^e 7.69 5.04 5.12	8	Disperse Red 73	Chrastil 10; MST 10	8.46	8.18
9Cholesteryl benzoate Cholesteryl butyrateChrastil 6.3; MST 6.3; Bartle 5.5; PR-EOS 9.77.244.91Cholesteryl butyrateChrastil 4.9; MST 5.8; Bartle 4.9; PR-EOS 9.08.475.9510Mono-tert-butyl ethers of glycerolBartle 14.5616.9610.30Di-tert-butyl ethers of glycerolBartle 13.8814.016.2011Hexachlorobenzene6.895.603.83121,10-DecanediolPR-EOS 9.15.124.77Benzoic acidPR-EOS 9.81.521.5213Phenanthrene6.142.44Anthracene9.81.521.5213Phenzoic acidPR-EOS 9.81.521.5214Phenanthrene3.603.833.6015Precos 9.81.521.521.5214Anthracene2.601.412.4414Actere3.603.632.7815Phenanthrene3.603.632.5714Antracene3.032.5715Salicylic acid3.032.5716Acetylsalicylic acid3.032.5717Average ⁶ 7.695.0418Total average ^f 5.105.12		Disperse Yellow 119	Chrastil 11; MST 11	7.76	7.82
Cholesteryl butyrate Chrastil 4.9; MST 5.8; Bartle 4.9; PR-EOS 9.0 8.47 5.95 10 Mono- <i>tert</i> -butyl ethers of glycerol Bartle 14.56 16.96 10.30 Di- <i>tert</i> -butyl ethers of glycerol Bartle 13.88 14.01 6.20 11 Hexachlorobenzene 6.89 5.60 Pentachlorophenol 3.60 3.83 12 1,10-Decanediol PR-EOS 9.1 5.12 4.77 Benzoic acid PR-EOS 9.8 1.52 1.52 13 Phenanthrene 6.14 2.44 Anthracene 9.28 4.58 Quaternary system 3.60 3.63 2.78 14 Acetylsalicylic acid 3.03 2.57 Average ^e 7.69 5.04 3.03 2.57	9	Cholesteryl benzoate	Chrastil 6.3; MST 6.3; Bartle 5.5; PR-EOS 9.7	7.24	4.91
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		Cholesteryl butyrate	Chrastil 4.9; MST 5.8; Bartle 4.9; PR-EOS 9.0	8.47	5.95
Di-tert-butyl ethers of glycerolBartle 13.8814.016.2011Hexachlorobenzene6.895.60Pentachlorophenol3.603.83121,10-DecanediolPR-EOS 9.15.1213Benzoic acidPR-EOS 9.81.521.5213Phenanthrene6.142.44Anthracene9.284.58Quaternary system3.612.601.411Acetylsalicylic acid2.601.41Acetylsalicylic acid3.032.57Average ^e 7.695.04Total average ^f 8.035.11	10	Mono-tert-butyl ethers of glycerol	Bartle 14.56	16.96	10.30
11Hexachlorobenzene6.895.60Pentachlorophenol3.603.83121,10-DecanediolPR-EOS 9.15.124.77Benzoic acidPR-EOS 9.81.521.521.5213Phenanthrene6.142.44Anthracene9.284.58Quaternary system32.601.411Benzoic acid2.601.723Salicylic acid2.601.51Acetylsalicylic acid3.032.57Average ^e 7.695.04Total average ^f 5.115.11		Di-tert-butyl ethers of glycerol	Bartle 13.88	14.01	6.20
Pentachlorophenol3.603.83121,10-DecanediolPR-EOS 9.15.124.77Benzoic acidPR-EOS 9.81.521.5213Phenanthrene9.284.24Anthracenc9.289.282.84Quaternary system18enzoic acid3.482.781Benzoic acid2.601.41Acetylsalicylic acid3.032.57Average ^e 7.695.04Total average ^f 5.125.12	11	Hexachlorobenzene		6.89	5.60
12 1,10-Decanediol PR-EOS 9.1 5.12 4,77 Benzoic acid PR-EOS 9.8 1.52 1.52 13 Phenanthrene 6.14 2.44 Anthracene 9.28 4.78 Quaternary system 3.48 2.78 1 Benzoic acid 3.03 2.57 Acetylsalicylic acid 3.03 2.57 Average ^e 7.69 5.04 Total average ^f 5.12 5.12		Pentachlorophenol		3.60	3.83
Benzoic acidPR-EOS 9.81.521.5213Phenanthrene6.142.44Anthracene0.20.32.53Quaternary system83.482.781Benzoic acid3.482.78Salicylic acid2.601.41Acetylsalicylic acid3.032.57Average ^e 7.695.04Total average ^f 5.11	12	1,10-Decanediol	PR-EOS 9.1	5.12	4.77
13Phenanthrene Anthracene6.142.44Quaternary system9.284.581Benzoic acid3.482.78Salicylic acid2.601.41Acetylsalicylic acid3.032.57Average ^e 7.695.04Total average ^f 8.035.11		Benzoic acid	PR-EOS 9.8	1.52	1.52
Anthracene9.284.58Quaternary system7771Benzoic acid3.482.78Salicylic acid2.601.41Acetylsalicylic acid3.032.57Average ^e 7.695.04Total average ^f 8.035.11	13	Phenanthrene		6.14	2.44
Quaternary system 3.48 2.78 1 Benzoic acid 3.60 1.41 Salicylic acid 2.60 1.41 Acetylsalicylic acid 3.03 2.57 Average ^e 7.69 5.04 Total average ^f 8.03 5.11		Anthracene		9.28	4.58
1Benzoic acid3.482.78Salicylic acid2.601.41Acetylsalicylic acid3.032.57Average ^e 7.695.04Total average ^f 8.035.11	Quaternary system				
Salicylic acid2.601.41Acetylsalicylic acid3.032.57Average ^e 7.695.04Total average ^f 8.035.11	1	Benzoic acid		3.48	2.78
Acetylsalicylic acid3.032.57Average ^e 7.695.04Total average ^f 8.035.11		Salicylic acid		2.60	1.41
Average ^e 7.69 5.04 Total average ^f 8.03 5.11		Acetylsalicylic acid		3.03	2.57
Total average ¹ 8.03 5.11		Average ^e		7.69	5.04
		Total average ^t		8.03	5.11

^a Chrastil is Chrastil model; MST is Méndez-Santiago and Teja model; Bartle is Bartle model; PR-EOS is the Peng-Robinson equation of state.

^b K–J₁ is K–J model.

^c $K-J_2$ is the modified K-J model.

^d The average values of AARD for the binary system.

^e The average values of AARD for the ternary and quaternary systems.

^f The total average values of AARD for all systems.

crossover pressure region, solute's vapor pressure becomes dominant at higher temperature and the density of the solvent turns less sensitive to the solute's vapor pressure. At the crossover point, these two competitive factors effect rather.

The solubility data in Table 2 obtained in this study indicate that 3,5-DNBA has lower solubility in SCCO₂ than *m*-NBA. The difference between 3,5-DNBA and *m*-NBA is the increase of a nitro-functional group by comparing their molecular structure. Therefore, the centrosymmetric dimmers are present in the crystal of pure 3,5-DNBA [22], which is the case in the structures of diversity of *m*-NBA. Two polymorphic groups make 3,5-DNBA easier to be a potential hydrogen bond acceptor, which indicates that 3,5-DNBA has higher polarity than *m*-NBA. CO₂ exhibits both non-polar tendencies (low dielectric constant) and 'polar' properties (Lewis acidity, strong quadrupole moment). Due to its structural symmetry, CO₂ does not have a dipole moment, but it does have a substantial quadrupole

moment that operates over a much shorter distance than dipolar interactions. Although CO_2 molecules present a quadrupolar effect, the polarity of CO_2 is still smaller than most of polar solvents [23]. Based on the "like-dissolves-like" principle, the more polar a solute, the lower solubility in CO_2 , the strong polar molecular interaction among the polar 3,5-DNBA molecules impacts on the molecular interaction between 3,5-DNBA and CO_2 , which leads to its lower solubility.

In addition, according to the experimental data of the Table 2, at 328 K, the mole solubility of pure *m*-NBA increases from 1.44×10^{-6} to 109.86 × 10⁻⁶ significantly; however, the mole solubility of the pure 3,5-DNBA increases from 0.44×10^{-6} to 4.21×10^{-6} . McHugh and Paulaitis illustrated the solubility behavior of a solid in SCCO₂ [24]. As they said, A vicinity of upper critical end point (UCEP) of the binary mixture (*m*-NBA + SCCO₂) can be reached, which results to the change in solubility with pressure becomes more drastic.



Fig. 2. Experimental solubility data (Table 2) in the binary system in mole fraction (y_b) with pressure (a) 3,5-DNBA+SCCO₂ and (b) *m*-NBA+SCCO₂ (\blacksquare) 308 K; (\blacklozenge) 318 K; (\blacktriangle) 328 K. (a₁ and b₁) The dash lines and solid lines are model correlations based on Chrastil model and the modified Adachi–Lu model, respectively (Eqs. (2) and (3)) and (a₂ and b₂) The dash lines are model correlations based on K–J model and the modified K–J model, respectively (Eqs. (4) and (5)) and all the correlation parameters are given in Table 3.

4.2. Solubility in the ternary system

The effect of pressure and temperature on the solubility of each solid solute in the ternary systems follows the same trend as that in the binary systems, as shown in Table 2 and Fig. 3. In the ternary system, the crossover pressure region transferred to 12.0-13.0 MPa for 3,5-DNBA and 12.0-13.5 MPa for *m*-NBA, respectively.

In order to make an easier comparison of solubility data between the binary and ternary systems, here the solubility enhancement *SE* was defined as the percentage relative deviation of the ternary solubility from the binary solubility of the component at the same pressure and temperature:

$$SE(\%) = \frac{y_t - y_b}{y_b} \times 100 \tag{7}$$

where y_b and y_t are the mole fraction solubility of solutes in SCCO₂ in the binary and ternary system, respectively.

The values of *SE* of these two solutes in the ternary system are listed in Table 2. The average values of *SE* of 3,5-DNBA at 308, 318, and 328 K are up to 183, 118, and 67, respectively. And the corresponding values of *SE* of *m*-NBA are 30, 32, and 16, respectively. Kurnik and Reid [25] have explained the solubility enhancement in mixed-solid systems in terms of the location of the UCEP. They

argued that the higher solubility would be expected in the ternary system at same temperature because it is closer to the UCEP when in comparison to the binary system.

Comparing the values of *SE* of these two solutes, it indicates that the solubility enhancement of 3,5-DNBA is higher than *m*-NBA in the ternary system, which were also observed similarly on other solid mixtures [25,26]. The molecular interaction between these two solutes and CO₂ may result in the difference. Both 3,5-DNBA and *m*-NBA have stronger molecular polarity than CO₂. Regarding in the ternary system, one solid solute played a "co-solvent" role. Hence two solutes are liable to form the hydrogen bond, which leads to the enhancement of their solubility. However, due to the presence of two polar nitro-functional groups, 3,5-DNBA is a relatively stronger proton donor as well as proton acceptor than *m*-NBA with one nitro-functional group. Therefore, the solubility enhancement of 3,5-DNBA is higher than *m*-NBA in the ternary system.

4.3. Mixture separation

The effect of operating conditions on selectivity is necessary for the optimal design of a separation process. The appropriate condition for separating these two solids in SCCO₂ is confirmed by



Fig. 3. Experimental solubility data (Table 2) in the ternary system (3,5-DNBA + m-NBA + SCCO₂) in mole fraction (y_t) with pressure (a) 3,5-DNBA and (b) m-NBA (\blacksquare) 308 K; (\blacklozenge) 318 K; (\bigstar) 328 K. (a_1 and b_1) The dash lines and solid lines are model correlations based on Chrastil model and the modified Adachi–Lu model, respectively (Eqs. (2) and (3)) and (a_2 and b_2) The dash lines and solid lines are model correlations based on K–J model and the modified K–J model, respectively (Eqs. (4) and (5)) and all the correlation parameters are given in Table 3.

defining the mixture separation factor μ and the separation efficiency *HE* follows:

$$\mu = \frac{y_{31}}{y_{32}} \tag{8}$$

$$HE(\%) = \frac{y_{31}}{y_{31} + y_{32}} \times 100 \tag{9}$$

where y_{31} , y_{32} are the mole fraction solubility of *m*-NBA and 3,5-DNBA in the ternary system (3,5-DNBA+*m*-NBA+SCCO₂), respectively.

The separation factor is based upon the assumption that the solute molecules behave independently of each other. As shown in Table 2, the values of mixture separation factor μ range from 3.80 to 12.45. The separation factor μ isotherms of the mixture as a function of experimental pressure at different temperatures are shown in Fig. 4. As can be seen, the separation factor μ enhanced with increasing pressure at three temperatures. In the lower pressure region (less than 12 MPa), temperature is not the only factor; however, in the higher pressure region (more than 15 MPa), higher temperature enhanced the separating effect. So in a higher pressure region, higher temperature is a positive factor for the separation enhancement in this ternary system.

As shown in Table 2, the average value of *HE* is proximity to 90, which means that the purity of separation can be advanced to 90%. Thus, it could be applied in the separation of the mixture of 3,5-DNBA and *m*-NBA using SCCO₂ technology in the industry separation.

4.4. Model correlation

The correlated results and optimal parameters of the experimental solubility data using Chrastil model, the modified Adachi and Lu model, K–J model, and the modified K–J model, Eqs. (2)-(5), are listed in Table 3 and shown in Figs. 2 and 3. From Table 3, the solubility data of pure 3,5-DNBA and *m*-NBA in SCCO₂ are well correlated by all models, Eqs. (2)-(5), with the values of AARD of (3.20-5.03) and (5.10-9.51), respectively. The existence of the UCEP can be the reason why the correlated results of *m*-NBA with the different models are worse than that of 3,5-DNBA [10]. Compared with the binary system, for the ternary system, the solubility data of mixed 3,5-DNBA and *m*-NBA in SCCO₂ are not well correlated by all models, Eqs. (2)-(5), with the values of AARD of (8.58-12.25), respectively. The molecular interactions in the ternary system are more complicated than that in the binary



Fig. 4. Separation factor μ (Table 2) isotherms of mixture (3,5-DNBA+*m*-NBA) in SCCO₂ with pressure (**■**) 308 K; (**●**) 318 K; (**▲**) 328 K.

system, which may lead to the decline of relations degree and accuracy.

Comparing the values of AARD for all models in Table 3, the modified K–I model proposed in this work (Eq. (5)) correlates the solubility better, which is superior to the existing models, Eqs. (2)–(4). Furthermore, the solubility data of pure and mixed solid solutes in SCCO₂ are correlated better by the modified K–J model (Eq. (5)) and the modified Adachi and Lu model (Eq. (3)) than Chrastil model (Eq. (2)) and K–I model (Eq. (4)). From the expression of models and molecular structures of solid solutes, the reason may result from the complicacy between the solubility of solid solutes and the density of $CO_2(\rho_1)$. Chrastil and K–J models (Eqs. (2) and (4) illuminate that the relationship between the logarithm of solubility (S or y_2) and the solvent's density (ln ρ_1 or ρ_1) is linear. However, the modified K-J and the modified Adachi and Lu models (Eqs. (3) and (5)) indicate the more complicated relationship between the solubility and the solvent's density. Therefore, the modified K-J and the modified Adachi and Lu models (Eqs. (3) and (5)) are more suitable to correlate the solubility data of solid solutes in SCCO₂, especially the modified K–I model (Eq. (5)).

4.5. Verification of the modified K-J model

The solid solubility data of 23 different solid compounds in SCCO₂ were collected from literature [27–37], concluding 13 binary systems, 13 ternary systems, and 1 quaternary system. The solubility data were correlated with K-J model and the modified K-J model (Eqs. (4) and (5)). Table 4 shows the experimental conditions of these compounds from literature. The correlated parameters and results are shown in Tables 5 and 6 along with AARD. It is observed that the new proposed model (Eq. (5)) has successfully correlated the solubility data of all the compounds within 5.11% AARD. Comparing with the correlation result by K-J model (Eq. (4)) with 8.03% AARD, the modified K-J model (Eq. (5)) is superior to K-I model (Eq. (4)) for correlating the solubility of solid compounds in SCCO₂. In addition, as shown in Table 6, for the binary system, the average AARD of the modified K-I model (Eq. (5)) is 5.26; for the ternary and guaternary systems, the average AARD is 5.04, which indicates that the modified K–J model (Eq. (5)) in this study is able to correlate the solubility data of pure and mixed solid compounds with less AARD. Table 6 also shows the comparison of the AARD obtained by the modified K–J model (Eq. (5)) and the models from literature. Therefore, the above results indicate the new proposed model (Eq. (5)) presents more accurate correlation

5. Conclusions

In this work, the solubility of pure 3,5-DNBA and *m*-NBA and their equal-weight mixture in SCCO₂ was determined at 308, 318, and 328 K, over a pressure range from 10.0 to 21.0 MPa. The pressure and temperature effects on solubility in the ternary system were similar to those who obtained in the binary system. The higher polarity of 3,5-DNBA led to its lower solubility in SCCO₂ compared with *m*-NBA both in the binary and ternary systems.

In the ternary system, one solid solute played a "co-solvent" role, which resulted in a significant increase in the solubility of another solute. The effect of solubility enhancement *SE* has been observed. The average values of *SE* of 3,5-DNBA at 308, 318, and 328 K are up to 183, 118, and 67, respectively. And the corresponding values of *SE* of *m*-NBA are 30, 32, and 16, respectively. The results indicate that the solubility enhancement of 3,5-DNBA is higher than *m*-NBA in the ternary system. The mixture separation factor μ and the separation efficiency *HE* were investigated. The maximum values of μ and *HE* were 12.45 and 92.57, respectively, which indicate it is successful to separate the mixture of 3,5-DNBA and *m*-NBA using SCCO₂ technology.

The modified K–J model was proposed for correlating the solubility of solid compounds in SCCO₂. The equilibrium solubility data of pure and mixed solutes in SCCO₂ were correlated by Chrastil model, the modified Adachi and Lu model, K–J model, and the modified K–J model with the values of AARD in ranging of (4.75–12.81), (3.20–8.71), (5.03–11.72), and (3.22–8.58), respectively. The modified K–J model proposed in this work correlates the solubility better, which is superior to another three models. Solubility data from 23 different solid compounds were taken from literature and correlated by K–J model and the modified K–J model in good accuracy. The total average values of AARD from K–J model and the modified K–J model and the modified K–J model were 8.03 and 5.11, respectively.

Acknowledgements

This research was financially supported by the funds awarded by National Natural Science Foundation of China (no. 20776006) and the supports from Petrochina Company Limited through the Applied Research ProProject (no. 2009A-3801-02). The authors are grateful to the support of this research from the Mass Transfer and Separation Laboratory in Beijing University of Chemical Technology.

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