

Mixed Solubilities of 5-Sulfosalicylic Acid and *p*-Aminobenzoic Acid in Supercritical Carbon Dioxide

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The solubilities of pure 5-sulfosalicylic acid and its equal-molar mixture with *p*-aminobenzoic acid in supercritical carbon dioxide were measured at (308 to 328) K and over the pressure range from (8.0 to 21.0) MPa. The effect of temperatures and pressures on the solubility was investigated, and the interaction of the mixed solutes was also studied in this work. The binary and ternary solubility data of 5-sulfosalicylic acid and *p*-aminobenzoic acid were correlated by the Chrastil equation with satisfactory agreement.

Introduction

Supercritical carbon dioxide extraction has been used widely;^{1–4} however, the majority of experimental studies have dealt with binary systems, whereas solubility data of two mixed solutes in supercritical carbon dioxide are much scarcer. It has been demonstrated by some investigators that the solubility of a component in ternary systems was sometimes considerably different from that observed in their respective binary systems.⁵ 5-Sulfosalicylic acid is an important medical intermediate, and *p*-aminobenzoic acid as a vitamin is closely related to human life, but the solubility data of pure 5-sulfosalicylic and its mixture with *p*-aminobenzoic acid in supercritical carbon dioxide have not been reported in the literature. Furthermore, some characteristic functional groups, such as sulfonic and amino, are connected to the molecules of solutes investigated in this work, so the study of their solubilities is also beneficial to our long-term objective, which is to predict the solution properties of solutes with various functional groups in supercritical fluids. This attracted our research group to conduct a further study on the solubilities of pure 5-sulfosalicylic acid and its equal-molar mixture with *p*-aminobenzoic acid in supercritical carbon dioxide.

Experimental Section

Materials. The sources and purities of the experimental reagents are given in Table 1. All of the chemicals were used without further purification.

Apparatus and Procedure. Figure 1 shows the schematic diagram of the apparatus used; it had been described in detail previously.^{6–8} A major part of the apparatus is a high-pressure equilibrium cell with an available volume of 100 mL. The temperature and pressure in the cell were measured by an internal platinum resistance thermometer (Beijing Chaoyang Automatic Instrument Factory, model XMT) and a calibrated pressure meter (Heise, model CTUSA), respectively. The uncertainty for temperature measurement is ± 0.1 K and that for pressure is ± 0.05 MPa. The cell was immersed in a constant-temperature stirred water bath (Chongqing Yinhe Experimental Instrument Corporation, model CS-530), and the temperature (within ± 0.01 K) was maintained constant by a temperature controller. Carbon dioxide was pressurized by a syringe pump

Table 1. Sources and Purities of the Material Used in This Work

substance	source	purity/%
5-sulfosalicylic acid	Beijing Chemical Regent Factory	>99.5
<i>p</i> -aminobenzoic acid	Beijing Chemical Regent Factory	>99.5
carbon dioxide	Beijing Praxair Ltd.	>99.9

(Nova, model 5542121). The total volume of carbon dioxide was measured by the calibrated wet-gas flow meter (Changchun Instrument Factory, model LML-2) with an uncertainty of ± 0.01 L at room temperature and atmospheric pressure during the experiment.

Carbon dioxide from the cylinder was compressed into the buffer, which was heated by an electric coil, and then the supercritical fluid was introduced into the equilibrium cell from the bottom. In the equilibrium cell, the solvent and solute reached equilibrium through mass transfer after about 30 min. Afterward, the saturated carbon dioxide flowed from the top of the cell through an expansion valve (wrapped with a coiled heater) into two U-type tubes in turn.

A model 2100 Unico UV–vis spectrophotometer with 1 cm path length quartz cells was used to determine the mass of the solute settled in the tubes. As the first step, a set of standard solutions was prepared by appropriate dilution of the stock solutions ($5.0 \cdot 10^{-4}$ mol·L⁻¹), and then the calibration curves with regression coefficients of more than 0.999 were obtained at λ_{\max} of the compound (210 nm). Consequently, the weight of the pure 5-sulfosalicylic acid was calculated by an absorbency measurement at λ_{\max} .

Analysis of Mixture. The solubilities of 5-sulfosalicylic acid and *p*-aminobenzoic acid in the ternary systems were also measured with the same apparatus and procedure used for the binary systems. The cumulative absorbance resulted from the comprehensive contribution of both 5-sulfosalicylic acid and *p*-aminobenzoic acid, so each composition of solutes in the ternary system was determined by an absorbency measurement at both wavelengths of 210 and 266 nm (the λ_{\max} of *p*-aminobenzoic acid). Consequently, the ternary solubility of each solute was calculated by a least-squares regression from the relative absorbency at both wavelengths.

Results and Discussion

Each reported datum in the following study was an average of at least three replicated sample measurements. The reproduc-

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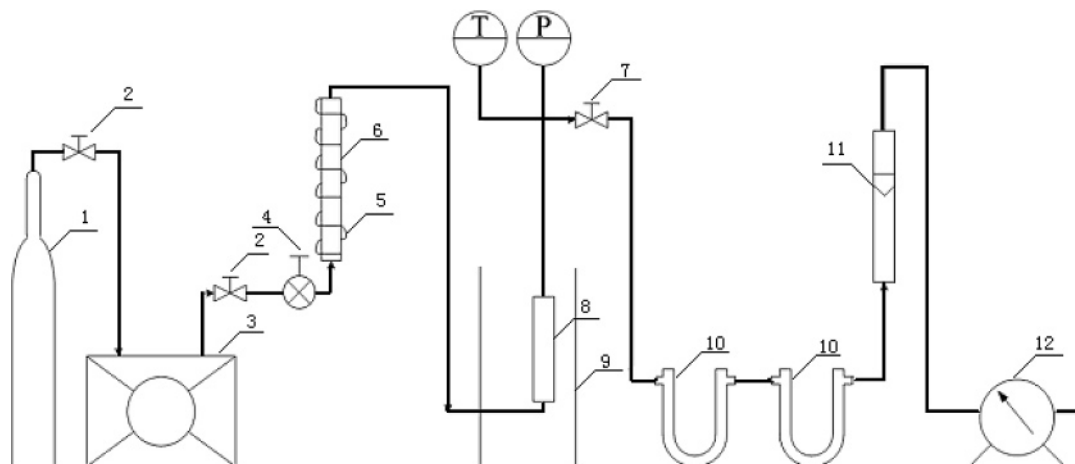


Figure 1. Schematic diagram of the experimental apparatus: 1, CO₂ cylinder; 2, inlet and outlet valves; 3, syringe pump; 4, pressure regulating valve; 5, heating coil; 6, buffer; 7, expansion valve; 8, equilibrium cell; 9, constant-temperature stirred water bath; 10, U-type tube; 11, rotameter; 12, wet-gas flow meter.

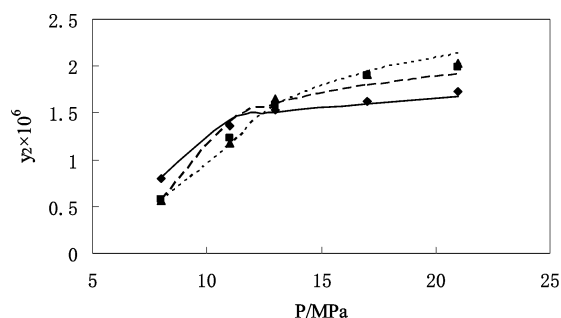


Figure 2. Comparison of the binary solubilities calculated by the Chrastil equation with the experimental data for 5-sulfosalicylic acid: ◆, experimental, —, calculated at $T = 308$ K; ■, experimental, ---, calculated at $T = 318$ K; ▲, experimental, ···, calculated at $T = 328$ K.

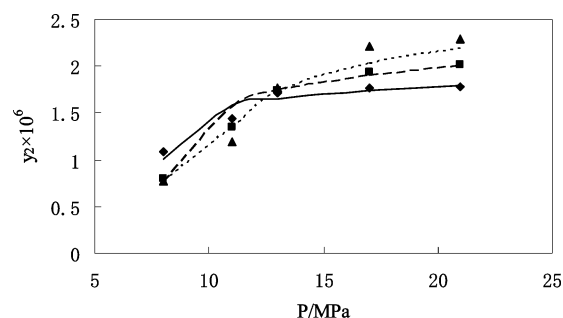


Figure 3. Comparison of the ternary solubilities calculated by the Chrastil equation with the experimental data for 5-sulfosalicylic acid: ◆, experimental, —, calculated at $T = 308$ K; ■, experimental, ---, calculated at $T = 318$ K; ▲, experimental, ···, calculated at $T = 328$ K.

Table 2. Solubility of 5-Sulfosalicylic Acid and *p*-Aminobenzoic Acid in the Binary and Ternary Systems (y_b and y_t)

T K	P MPa	ρ g·L ⁻¹	5-sulfosalicylic acid			<i>p</i> -aminobenzoic acid		
			binary $y_b \cdot 10^6$	ternary $y_t \cdot 10^6$	SE	binary ⁸ $y_b \cdot 10^6$	ternary $y_t \cdot 10^6$	SE
308	8.0	426.8	0.800	1.086	35.78	1.467	2.781	89.55
	11.0	739.2	1.366	1.445	5.79	3.869	3.909	1.04
	13.0	778.8	1.532	1.714	11.89	3.978	4.023	1.14
	17.0	840.4	1.619	1.767	9.13	4.258	4.440	4.28
	21.0	875.6	1.728	1.785	3.30	4.292	4.501	4.87
318	8.0	224.4	0.575	0.797	38.63	1.373	2.015	46.75
	11.0	567.6	1.228	1.352	10.11	3.341	3.488	4.39
	13.0	668.8	1.588	1.744	9.83	3.842	4.066	5.83
	17.0	783.2	1.903	1.941	1.99	4.610	4.858	5.37
21.0	831.6	1.995	2.016	1.08	5.205	5.288	1.59	
328	8.0	206.8	0.565	0.767	35.73	1.302	1.848	41.90
	11.0	404.8	1.177	1.191	1.17	2.406	3.051	26.79
	13.0	616	1.652	1.766	6.90	4.056	4.247	4.72
	17.0	708.4	1.915	2.215	15.64	4.961	5.316	7.16
21.0	774.4	2.030	2.289	12.74	5.661	5.703	0.75	

ibility of the solubility data obtained fell within a range of $\pm 5\%$.

The solubility of pure *p*-aminobenzoic acid in supercritical carbon dioxide was reported in our previous work.⁸ In this work, the solubilities of pure 5-sulfosalicylic acid and its equal-molar mixture with *p*-aminobenzoic acid were measured in supercritical carbon dioxide at temperatures of (308, 318, and 328) K with pressures ranging from (8.0 to 21.0) MPa, and the experimental results are listed in Table 2 and shown in Figures 2 to 5. In both the binary and ternary systems, it is clear that

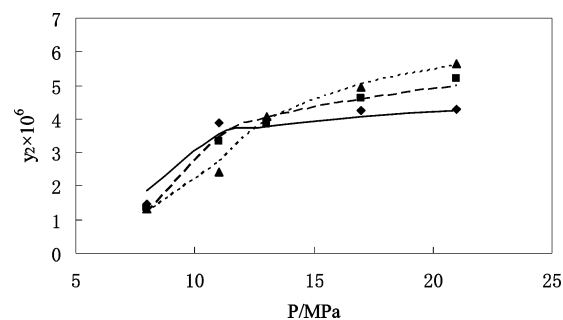


Figure 4. Comparison of the binary solubilities calculated by the Chrastil equation with the experimental data for *p*-aminobenzoic acid: ◆, experimental, —, calculated at $T = 308$ K; ■, experimental, ---, calculated at $T = 318$ K; ▲, experimental, ···, calculated at $T = 328$ K.

the solubilities of pure 5-sulfosalicylic acid in supercritical carbon dioxide increase with increasing pressure at each isotherm. From the effect of temperatures on the solubilities, it is evident that the retrograde behavior exists in the supercritical state. Below the crossover pressure point, solubilities increase with increasing pressure and decrease with increasing temperature; beyond the crossover pressure point, solubilities increase with the increase of both pressure and temperature.

To make easier the comparison of solubility data between the binary and ternary systems, the solubility enhancement (SE) was defined as

$$SE = \frac{y_t - y_b}{y_b} \cdot 100 \quad (1)$$

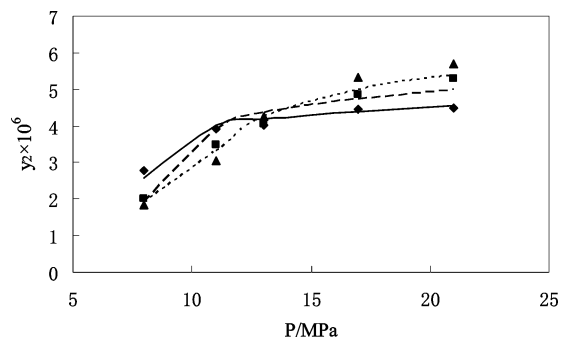


Figure 5. Comparison of the ternary solubilities calculated by the Chrastil equation with the experimental data for *p*-aminobenzoic acid: \blacklozenge , experimental, —, calculated at $T = 308$ K; \blacksquare , experimental, - - -, calculated at $T = 318$ K; \blacktriangle , experimental, \cdots , calculated at $T = 328$ K.

Table 3. Correlated Parameters of Equation 2 for both the Binary and Ternary Systems

	5-sulfosalicylic acid		<i>p</i> -aminobenzoic acid	
	binary	ternary	binary	ternary
k	1.99	1.78	2.14	1.78
a/K	-1834.75	-1488.79	-2079.24	-1329.88
b	-12.30	-11.96	-12.22	-12.13
AARDs/% ^a	3.48	4.87	6.39	4.71

$$^a \text{AARDs}/\% = 1/N \sum_{i=1}^N |s_{\text{calcd}} - s_{\text{exptl}}/s_{\text{exptl}}| \cdot 100.$$

where y_t and y_b are the solubilities of solutes in the ternary and binary systems, respectively. When the solubility of a given solute was studied in the ternary system, in some cases the other solute could be considered as a specific solid cosolvent. Thus, the so-called cosolvent is induced to increase the solubility of the other one in the ternary systems.

To correlate the solubility in pure carbon dioxide, the classical Chrastil equation was applied in this work:⁹

$$s = \rho^k e^{(a/T+b)} \quad (2)$$

$$s = \frac{\rho M_2 y_{b(t)}}{M_1 (1 - y_{b(t)})} \quad (3)$$

s is the solubility of the solute ($\text{g}\cdot\text{L}^{-1}$) and ρ is the density of CO_2 ($\text{g}\cdot\text{L}^{-1}$); their values calculated from the EOS proposed by Span and Wagner¹⁰ are also shown in Table 2. T is the temperature in K, k is the association number of carbon dioxide, and a and b are parameters of eq 2. M_1 and M_2 are the molecular weights of CO_2 and solutes, respectively. Comparisons between the results correlated by eq 2 and the experimental data are

illustrated in Figures 2 to 5. The correlated results of eq 2, which indicate good agreement with the experimental data, are given in Table 3.

Conclusions

The solubilities of pure 5-sulfosalicylic acid and its equal-molar mixture with *p*-aminobenzoic acid in supercritical carbon dioxide are investigated at (308, 318, and 328) K with the pressure ranging from (8.0 to 21.0) MPa. The experimental data of the pure and mixed solutes in supercritical carbon dioxide are correlated by the Chrastil equation, and the average absolute relative deviations between the experimental data and the correlated results in both the binary and ternary systems are 3.48 % and 4.87 % and 6.39 % and 4.71 % for 5-sulfosalicylic acid and *p*-aminobenzoic acid, respectively.

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