Solubility of *p*-Aminobenzenesulfonamide in Supercritical Carbon Dioxide with Acetone Cosolvent

Jun-su Jin,* Xue-mei Pei, Jia-lin Li, and Ze-ting Zhang

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

Using a flow-type apparatus, the solubilities of *p*-aminobenzenesulfonamide in supercritical carbon dioxide were determined at three different temperatures (308.15, 318.15, and 328.15) K and in the pressure range from (11.0 to 21.0) MPa. The effect of acetone cosolvent on the solubility of *p*-aminobenzenesulfonamide was studied at the mole percents of 3.0 % and 6.0 %. The experimental data in supercritical carbon dioxide without and with cosolvent were satisfactorily correlated with the Chrastil equation and the modified Chrastil equation.

Introduction

Nowadays, supercritical fluid technology has been used widely in many fields, such as food, pharmaceutical, synthesis of carbon nanotubes, polymer processing, and biochemical industries, etc.[1–3] Because carbon dioxide (CO_2) is inert, nontoxic, noninflammable, easy to handle, and especially it has a convenient critical temperature (304.13 K) and critical pressure (7.38 MPa), it is one of the most commonly used supercritical fluids. The solubility of a solid in supercritical fluids is the most important property in the optimal design of supercritical fluid processes, and there are many equilibrium solubility data published in the literature.[4] However, compared to the development of the supercritical fluid technique, the measurements on the solubility of solids in supercritical carbon dioxide (SC CO_2) with and without cosolvents were still insufficient, which severely obstructs the application and development of supercritical fluid technology.

p-Aminobenzenesulfonamide is an important intermediate of sulfa drugs, and it is usually used as a veterinary drug and an antiphlogistic medicine. The solubility data of *p*-aminobenzenesulfonamide in SC CO_2 can not be found in the literature. Furthermore, how the characteristic functional group, sulfonamide, influences the solute solubility in SC CO_2 is one part of our long-term objective, which is to predict the solute solubility with different functional groups in SC CO_2. Therefore, the solubilities of *p*-aminobenzenesulfonamide were measured at (308.15, 318.15, and 328.15) K over the pressure range from (11.0 to 21.0) MPa in SC CO_2 without and with acetone cosolvent. For the SC CO_2 with the mole percent of the 6.0 % acetone system, the influences of temperature on the solubility have also been investigated. The measured solubility data are correlated using the Chrastil and modified Chrastil equation.

Experimental Section

Materials. *p*-Aminobenzenesulfonamide with a minimum purity of 99.5 % was supplied by the Beijing Chemical Reagent Factory. Acetone was purchased from the Beijing Experimental Chemical Factory, and it has a purity of more than 99.5 %. High-purity CO_2 of purity higher than 99.9 % was obtained from Beijing Praxair Industrial Gas Co. Ltd. All chemicals were used without further purification.

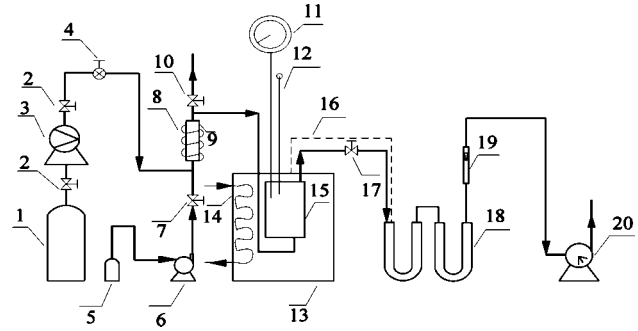

Figure 1. Schematic diagram of the experimental apparatus: 1, CO_2 cylinder; 2, inlet and outlet valves; 3, syringe pump; 4, pressure regulating valve; 5, cosolvent vessel; 6, high-pressure pump; 7, cosolvent metering valve; 8, electric coil; 9, mixer; 10, safety valve; 11, pressure gauge; 12, thermometer;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

Apparatus and Procedure. Figure 1 shows the schematic diagram of the apparatus we used, and the main part is a high-pressure equilibrium cell with an available volume of 100 mL. 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.

CO_2 from the cylinder was compressed by a syringe pump (Nova, model 5542121) into the mixer, which was heated by an electric coil, while the cosolvent was introduced into the same mixer by a high-pressure pump (Beijing Weixing Factory, model LB-10C) with the accuracy of ± 0.01 $mL \cdot min^{-1}$ by regulating the cosolvent metering valve. The SC CO_2 was put into the 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

* To whom correspondence should be addressed. Tel: +86-10-64434788. Fax: +86-10-64436781. E-mail: jinjs@mail.buct.edu.cn.

10.1021/je800700r CCC: $40.75
Published on Web 11/26/2008

Table 1. Solubility of *p*-Aminobenzenesulfonamide in Pure SC CO_2

	T/K					
	308.15		318.15		328.15	
p/MPa	ρ/g·L^{-1}	$S\cdot10^6$/ g·L^{-1}	ρ/g·L^{-1}	$S\cdot10^6$/ g·L^{-1}	ρ/g·L^{-1}	$S\cdot10^6$/ g·L^{-1}
11.0	743.95	1.5024	603.15	1.5925	414.90	1.6747
13.0	785.70	1.5525	693.65	2.1084	571.33	2.3649
15.0	816.06	1.5910	743.17	2.2218	654.94	2.8094
17.0	838.09	1.7257	775.53	2.4745	703.82	2.9272
21.0	873.67	1.8649	822.91	2.6276	767.88	3.3277

into the saturated supercritical fluid stream. In the high-pressure equilibrium cell, the solvent and solute reached equilibrium after about 30 min, and then the saturated SC CO_2 flowed from the top of the equilibrium cell through a decompression sampling valve (wrapped with a heating coil) into two U-shaped tubes in turn. The total volume of CO_2 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 during the experiment. The amount of solubilized solid was determined by UV spectrophotometric analysis (UNICO, model UV-2100) at a fixed wavelength (258 nm). Experiments were performed to establish a calibration curve, and the regression coefficient of the calibration curve is better than 0.9998.

Results and Discussion

The efficiency and reliability of the solubility measurement technique had been testified in our previous work.[5–7] To ensure the accuracy of the data, each reported datum in this work was an average of at least three replicated sample measurement, and the uncertainty of each measurement was within ± 5 %.

Solubility of Solid in Pure SC CO_2. The solubilitiy of *p*-aminobenzenesulfonamide in pure SC CO_2 is listed in Table 1. The typical behavior of the solubility is shown in Figure 2, and it ranges from $1.5024\cdot10^{-6}$ g·L^{-1} at 11.0 MPa and 308.15 K to $3.3277\cdot10^{-6}$ g·L^{-1} at 21.0 MPa and 328.15 K. From Figure 2, we can ascertain that the solubility increases with increasing pressure and temperature over our experimental range, and we also see that the pressure is more important at a higher temperature; this effect may originate from the complicated pressure and temperature effects on the solute vapor pressure and the density of the solvent.

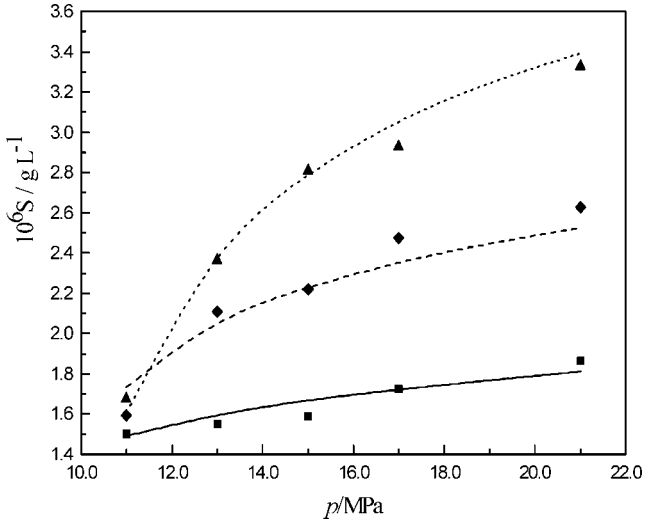

Figure 2. Comparison of experimental solubility data of *p*-aminobenzenesulfonamide and results correlated by the Chrastil equation in pure SC CO_2. ▲ exptl, ···, calcd at 328.15 K; ◆, exptl, - - -, calcd at 318.15 K; ■, exptl, —, calcd at 308.15 K.

Table 2. Solubility of *p*-Aminobenzenesulfonamide in $SCCO_2$ with Different Concentrations of Cosolvent at 318.15 K

	$S'\cdot10^6$/g·L^{-1}		
p/MPa	0 % acetone	3.0 % acetone	6.0 % acetone
11.0	1.5925	2.0734	2.5972
13.0	2.1084	2.6107	3.2755
15.0	2.2218	3.1577	3.4251
17.0	2.4745	3.5522	3.9865
21.0	2.6276	3.8585	4.2012
e	1	1.36	1.59

The solubilities of *p*-aminobenzenesulfonamide in pure SC CO_2 were correlated using the density-based equation proposed by Chrastil,[8] and eq 1 shows the form of the Chrastil equation

$$\ln S = k \ln \rho + a/T + b \tag{1}$$

where *S* is the solubility of the solute (g·L^{-1}); ρ is the density of SC CO_2 (g·L^{-1}) obtained from NIST (http://webbook.nist.gov/chemistry/fluid/); *T* is the temperature in K; *k* is the association number of CO_2; and *a* and *b* are the parameters of eq 1, which can be estimated from the experimental solubility data in pure SC CO_2.

Thus, the solubility of *p*-aminobenzenesulfonamide in SC CO_2 is expressed as follows

$$\ln S = 1.215 \ln \rho - 3966/T - 8.580 \tag{2}$$

The average absolute relative deviation was obtained with AARD = $1/n|(S,\text{calcd} - S,\text{exptl})/S,\text{exptl}|\cdot100$ %, where *n* is the number of experimental points, *S*,calcd is the calculated results, and *S*,exptl is the experimental data. The value of AARD is 2.73 %. As shown in Figure 2, the correlated results have good agreement with the experimental data.

Solubility of Solid in SC CO_2 with Acetone Cosolvent. Because the solubility in pure SC CO_2 of *p*-aminobenzenesulfonamide is very small, we also studied the solute solubility in SC CO_2 with cosolvent. To conveniently express the solubility enhancement induced by cosolvent, a solubility enhancement, *e*, is defined as follows

$$e = \frac{S'(P,T)}{S(P,T)} \tag{3}$$

where $S'(P,T)$ is the solubility containing cosolvent and $S(P,T)$ is the solubility in the absence of cosolvent at the same temperature and pressure. The value of the solubility enhancement, *e*, depends on temperature, pressure, concentration, and the nature of the cosolvent.

In this work, we investigated the solubility enhancement of different concentrations of acetone cosolvent, and the experimental results are presented in Table 2 and shown in Figure 3. From Table 2, it can be seen that at the temperature of 318.15 K the order of the solubility enhancement is 6.0 % > 3.0 % > 0 %.

The modified Chrastil equation[9] including the influence of cosolvent on the solute solubility was depicted by eq 4 and used to correlate the experimental solubility data.

$$\ln S' = k \ln \rho + \gamma \ln m + a/T + b \tag{4}$$

where *S*' is the solubility of the solute containing acetone (g·L^{-1}); *m* is the concentration of cosolvent (g·L^{-1}); γ is the association number of cosolvent; and the meanings of other symbols are the same as those in eq 1. When the temperature *T* is kept constant, eq 4 can also be written as

$$\ln S' = k \ln \rho + \gamma \ln m + b' \quad (5)$$

where $b' = a/T + b$.

These constants can be estimated from experimental solubility data in SC CO_2 with different concentrations of cosolovent. The parameters of eq 5 and the average absolute relative deviation are listed as follows:

$k = 1.824$, $\gamma = 0.2117$, $b' = 24.19$, AARD = 3.54 %

To study the influence of the temperature on the solubility enhancement, we investigated the solubility of *p*-aminobenzenesulfonamide from $T = (308.15$ to $328.15)$ K with the mole percent of 6.0 % acetone cosolvent. The experimental results are shown in Table 3 and Figure 4. From Table 3, we can conclude that *e* decreases with increasing temperature.

Solubility data in SC CO_2 with the mole percent of 6.0 % acetone cosolvent were also correlated by the modified Chrastil eq 4. When the concentration of colsolvent *m* is kept constant, eq 4 can also be written as

$$\ln S' = k \ln \rho + a/T + b'' \quad (6)$$

where $b'' = \gamma \ln m + b$.

As a result, the values of *k*, *a*, and *b*″ are 1.157, −2998.70, and −10.74, respectively. The average absolute relative deviation (AARD) of eq 6 was 4.55 %.

Conclusions

The solubilities of *p*-aminobenzenesulfonamide in both pure and modified SC CO_2 are studied at (308.15, 318.15, and 328.15) K and over the pressure range from (11.0 to 21.0) MPa.

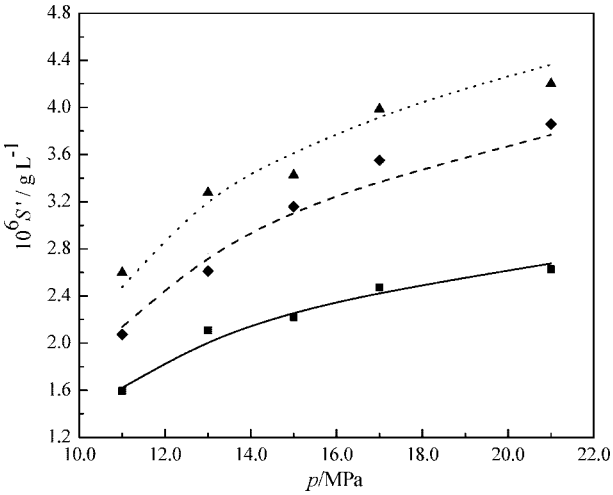

Figure 3. Comparison of experimental solubility data of *p*-aminobenzenesulfonamide and results correlated by the modified Chrastil equation in SC CO_2 with different concentrations of cosolvent at 318.15 K. ▲, exptl, ····, calcd at 6.0 %; ◆, exptl, - - -, calcd at 3.0 %; ■, exptl, —, calcd at 0 %.

Table 3. Solubility of *p*-Aminobenzenesulfonamide in SCCO$_2$with the Mole Percent of 6.0 % Cosolvent

	$S' \cdot 10^6$/g·L^{-1}		
p/MPa	308.15 K	318.15 K	328.15 K
11.0	2.5307	2.5972	2.6372
13.0	2.7529	3.2755	3.7584
15.0	3.0343	3.4251	3.9669
17.0	3.2750	3.9865	4.4691
21.0	3.4422	4.2012	5.0784
e	1.82	1.59	1.53

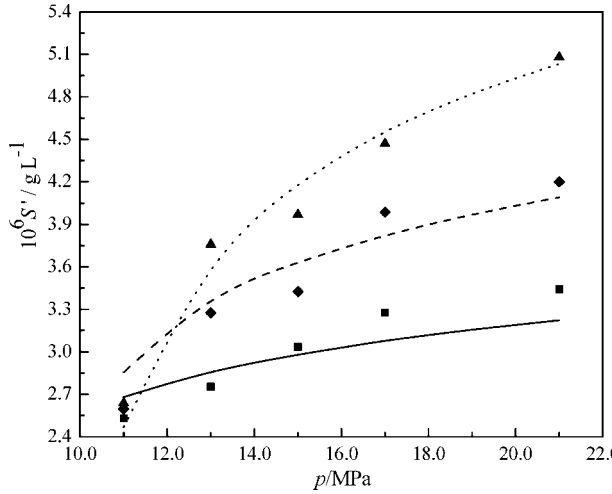

Figure 4. Comparison of experimental solubility data of *p*-aminobenzenesulfonamide and results correlated by the modified Chrastil equation in SC CO_2 with the mole percent of 6.0 % acetone cosolvent. ▲, exptl, ····, calcd at 328.15 K; ◆, exptl, - - - -, calcd at 318.15 K; ■, exptl, —, calcd at 308.15 K.

The solubility enhancement is 1.82 for 308.15 K, 1.59 for 318.15 K, and 1.53 for 328.15 K in the SC CO_2 with the mole percent of 6.0 % acetone system, and the concentration influence of acetone cosolvent on the solubility enhancement is 6.0 % > 3.0 % > 0 % at 318.15 K. The experimental data are correlated by the Chrastil and the modified Chrastil equation, and the overall deviation between the experimental data and correlated results is less than 4.55 % under all kinds of conditions in this work.

Literature Cited

(1) Ernesto, R.; Iolanda, D. M. Supercritical fluid extraction and fractionation of natural matter. *J. Supercrit. Fluids* **2006**, *38*, 146–166.
(2) Lan, D. W.; Adlard E. R.; Michael C.; Colin F. P. *Encyclopedia of separation science*; Academic Press: MI, 2000; pp 3094−3101.
(3) Byrappa, K.; Ohara, S.; Adschiri, T. Nanoparticles synthesis using supercritical fluid technology-towards biomedical applications. *Adv. Drug Delivery Rev.* **2008**, *60*, 299–327.
(4) Ram, B. Gupta, J.-J. S. *Solubility in supercritical carbon dioxide*; CRC Press: Cleveland, **2006**; pp 19−833.
(5) Jin, J. S.; Zhang, Z. T.; Li, Q. S.; Li, Y.; Yu, E. P. Solubility of propyl p-hydroxybenzoate in supercritical carbon dioxide with and without a cosolvent. *J. Chem. Eng. Data* **2005**, *50*, 801–803.
(6) Tian, G. H.; Jin, J. S.; Zhang, Z. T.; Guo, J. J. Solubility of mixed solids in supercritical carbon dioxide. *Fluid Phase Equilib.* **2007**, *251*, 47–51.
(7) Zhang, Z. T.; Li, W. M.; Jin, J. S.; Tian, G. H. Solubility of p-methylbenzene sulfonic acid in pure and modified supercritical carbon dioxide. *J. Chem. Eng. Data* **2008**, *52*, 600–602.
(8) Chrastil, J. Solubility of solids and liquids in Supercritical gases. *J. Phys. Chem.* **1982**, *86*, 3016–3021.
(9) González, J. C.; Vieytes, M. R.; Botana, A. M.; Vieites, J. M.; Botana, L. M. Modified mass action law-based model to correlate the solubility of solids and liquids in entrained supercritical carbon dioxide. *J. Chromatogr. A* **2001**, *910*, 119–125.

Received for review September 19, 2008. Accepted November 5, 2008. This work was financially supported by the National Natural Science Foundation of China (#20776006), the National High Tech Program ("863" Plan, #2006AA030203), and the Young Scholars Fund of Beijing University of Chemical Technology (NO: QN0607).

JE800700R