Solubility of *p*-Methylbenzene Sulfonic Acid in Pure and Modified Supercritical Carbon Dioxide

Ze-ting Zhang, Wen-ming Li, Jun-su Jin,* and Guo-hua Tian

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

The solubilities of *p*-methylbenzene sulfonic acid in supercritical carbon dioxide were determined at (308, 318, and 328) K and in the pressure range from (8 to 21) MPa. The effects of cosolvents (ethyl acetate, ethyl acetate + ethanol (molar ratio 1:1), ethanol, and acetone) on the solubility of *p*-methylbenzene sulfonic acid were studied at a concentration of 1.5 mol %. The measured solubilities in supercritical carbon dioxide in the absence and presence of cosolvents were correlated using the Chrastil and modified Chrastil equation with good results, respectively.

Introduction

As a new separation technique, supercritical fluid extraction (SFE) has received much interest in the past thirty years. This is attributed to the unique advantage offered by the SFE process, such as high mass-transfer rate and low operating temperature. Among the solvents used as supercritical fluid (SCF), supercritical carbon dioxide (SC CO_2) is particularly appealing for practical applications since it is nontoxic, inflammable, and relatively inexpensive. With the development of SFE, people have come to know that the solubility of a strong polar organic compound in a nonpolar SCF can be greatly increased by a polar cosolvent.[1–7] The introduction of cosolvent is an effective method to broaden the application of SCF.

p-Methylbenzene sulfonic acid is widely used as an intermediate in dye, pesticide, and pharmaceutical industries, and its applications can also be found in plastic products, pigment, and cleaner, etc. However, until now its solubility data in SC CO_2 can not be found in the literature. As is known, the solubilities of solids or liquids in supercritical fluids are a very important consideration in developing any SFE process. Additionally, the prediction of solution properties of solutes with various functional groups in SCF is our long-term objective, and the group contribution of sulfonic group to the solubility is what we are interested in. Taking these aspects into account, the solubilities of *p*-methylbenzene sulfonic acid in SC CO_2 are measured in a flow type apparatus at (308, 318, and 328) K over the pressure range of (8 to 21) MPa without and with a cosolvent concentration of 1.5 mol % ethyl acetate, ethyl acetate + ethanol (molar ratio 1:1), ethanol, or acetone. The influences of different cosolvents on the solubility have also been investigated. The measured solubility data are correlated using the Chrastil and modified Chrastil equation.

Experimental Section

Materials. Carbon dioxide was supplied by the Beijing Analytical Instrument Factory with a minimum purity of 99.9 %. Ethanol, ethyl acetate, acetone, and *p*-methylbenzene sulfonic acid were purchased from Beijing Chemical Reagent Factory with a minimum purity of more than 99.7 %, 99.5 %, 99.5 %, and 99.6 %, respectively. All chemicals were used directly without further purification.

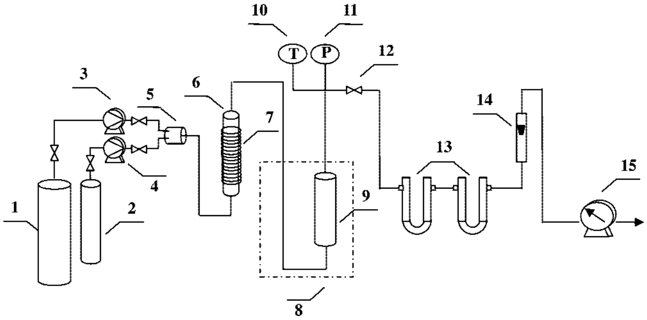

Figure 1. Schematic diagram of the apparatus for solubility measurement: 1, CO_2 cylinder; 2, cosolvent vessel; 3, syringe pump; 4, high-pressure pump; 5, mixer; 6, preheater; 7, heating coil; 8, constant-temperature water bath; 9, equilibrium cell; 10, resistance thermometer; 11, pressure meter; 12, decompression valve; 13, U-type tube; 14, rotated flow meter; 15, wet-gas flow meter.

Equipment and Procedure. Figure 1 shows the schematic diagram of the apparatus assembled in our laboratory to perform solubility measurements, and the experimental apparatus has been described in detail in our previous work,[8,9] The 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 using an internal platinum resistance thermometer (Beijing Chaoyang Automatic Instrument Factory, model, XMT) and a calibrated pressure meter (Heise, Newtown CONN). The accuracy 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 was maintained constant within ± 0.5 K by a temperature controller. CO_2 was pressurized by a syringe pump (Nova, model 5542121), while the cosolvent was compressed by a high-pressure pump (Beijing Weixing Factory, model LB-10C). The concentration of the cosolvent was controlled by regulating the high-pressure gauge pump, accurate to ± 0.01 $mL\cdot min^{-1}$. After the CO_2 and cosolvents were mixed in a vessel heated by the electricity coil, they were put into the equilibrium cell, which was loaded by solid solute of about (40 to 50) g from the bottom at a desired pressure and temperature. In the

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

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Table 1. Solubility of *p*-Methylbenzene Sulfonic Acid in Pure SC CO_2

	T(K)					
	308		318		328	
P/MPa	ρ/g·L^{-1}	$10^5 y_2$	ρ/g·L^{-1}	$10^5 y_2$	ρ/g·L^{-1}	$10^5 y_2$
8	419.09	2.57	241.05	2.09	203.64	2.00
11	743.95	4.12	603.15	3.99	414.90	3.72
13	785.70	4.28	693.65	5.18	571.33	5.79
17	838.09	4.81	775.53	5.88	703.82	6.60
21	873.67	5.06	822.91	6.21	767.88	7.38

Table 2. Solubility of *p*-Methylbenzene Sulfonic Acid ($10^5 y_2$) in the Modified SC CO_2 at 308 K and 1.5 mol % Cosolvent

	T = 308 K			
P/MPa	ethyl acetate	ethyl acetate + ethanol	ethanol	acetone
8	4.28	4.20	3.27	3.17
11	5.70	5.18	4.46	4.37
13	5.93	5.41	4.64	4.48
17	6.29	5.65	5.01	4.90
21	6.66	5.89	5.25	5.11
E	1.41	1.30	1.10	1.07

equilibrium cell, the solvents and the solute reached equilibrium after 30 min. Then the saturated CO_2 flowed from the top of the cell through a decompression valve wrapped with a heating coil into two U-type tubes in turn. The solid solute *p*-methylbenzene sulfonic acid collected in the U-type tube was determined by a model 2100 Unico UV–vis spectrophotometer at $\lambda_{max} = 228$ nm. The total volume of CO_2 released during the experiment was determined by the calibrated wet gas flow meter (Changchun Instrument Factory, model LML-2) with an accuracy of ± 0.01 L at room temperature and atmospheric pressure.

To ensure the reliability of the experimental data, each measurement was carried out more than five times, and the deviation was less than ± 5 %. Through experiment, it is found that when the flow rate of CO_2 was in the range of (0.3 to 1.0) L·min^{-1}, the variation in solubility of *p*-methylbenzene sulfonic acid was negligible. Therefore, the flow rate of 0.6 L·min^{-1} is adopted in this work. The equilibrium time needed for *p*-methylbenzene sulfonic acid was found to be less than 30 min. Therefore, all the data listed in this work were measured after 30 min.

Results and Discussions

Solubility of Solid in Pure SC CO_2. The solubility of *p*-methylbenzene sulfonic acid in pure SC CO_2 is listed in Table 1, and the typical behavior of the solubility is shown in Figure 2. As Figure 2 has shown, the solubilities are changed markedly by pressure at a given temperature and usually increase with increasing pressure. However, the temperature dependence of solubilities differs in the low-pressure (P < 10.5 MPa) and high-pressure (P > 12.2 MPa) regions. This is the so-called retrograde solubility (crossover pressure at about (10.5 to 12.2) MPa). Below the crossover pressure point, solubilities increase with increasing pressure and decrease with the increase of temperature; beyond the crossover pressure point, solubilities increase with the increase of both pressure and temperature. The different effects of temperature on the solubilities are due to the influence of temperature on the density of the SCF, the vapor pressure of the solute, and the molecular interaction between solute and solvent.

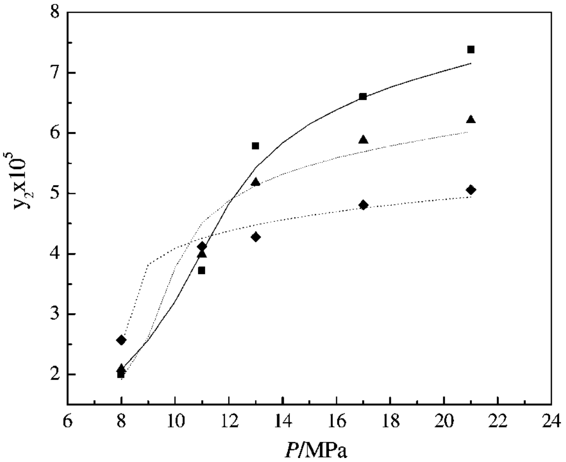

Figure 2. Comparison of experimental solubility data of *p*-methylbenzene sulfonic acid and results correlated by the Chrastil equation in pure SC CO_2 ■, exptl; —, calcd at 328 K; ▲, exptl; - -, calcd at 318 K; ◆, exptl; ··, calcd at 308 K.

The solubilities in pure SC CO_2 were correlated using the density-based equation proposed by Chrastil[10]

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

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

$$s = \frac{\rho M_2 y_2}{M_1(1 - y_2)} \tag{2}$$

where ρ is the density of SC CO_2; y_2 is the molar fraction of the solute; and M_1 and M_2 are the molecular weights of CO_2 and the solute, respectively.

As a result, the solubility of *p*-methylbenzene sulfonic acid in SC CO_2 is expressed as follows

$$\ln s = 1.93 \ln \rho - 2462.66/T - 6.85 \tag{3}$$

The average absolute relative deviation (AARDy) is 4.23 %.

Solubility of Solid in Modified SC CO_2. To compare the solubility enhancement effect of different cosolvents, here a factor E was defined as the ratio of the solubility obtained with cosolvent, $y_2(P, T, y_3)$, to that obtained without cosolvents at the same temperature and pressure, $y_2(P, T, y_3 = 0)$

$$E = \frac{y_2(P, T, y_3)}{y_2(P, T, y_3 = 0)} \tag{4}$$

Here, y_3 is the cosolvent concentration.

In this work, the solubility enhancement effects of ethyl acetate, ethyl acetate + ethanol (equal molar ratio), ethanol, and acetone are investigated. The experimental results are presented in Table 2. At the temperature of 308 K and the cosolvent concentration of 1.5 mol %, as Figure 3 has shown, the order of the solubility enhancement effect is ethyl acetate > ethyl acetate + ethanol (equal molar ratio) > ethanol > acetone. Obviously the enhancement effect of mixed ethyl acetate and ethanol is between their respective enhancement effects.

Solubility data in SC CO_2 with cosolvents were correlated by the modified Chrastil equation,[11] which includes the influence of cosolvents on the solute solubility and is depicted as

$$\ln s = k \ln \rho + \gamma \ln m + a/T + b \tag{5}$$

where m is the concentration of cosolvent (g·L^{-1}); γ is the association number of cosolvent; and the meanings of other

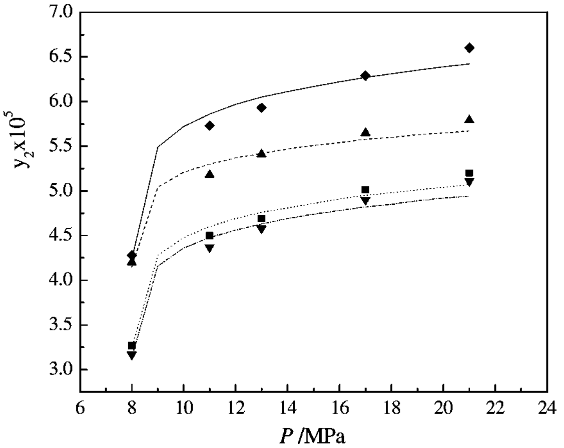

Figure 3. Comparison of experimental solubility data of *p*-methylbenzene sulfonic acid and results correlated by the modified Chrastil equation at 308 K. ◆, exptl; —, calcd, ethyl acetate; ▲, exptl; --, calcd, ethyl acetate + ethanol; ■, exptl; ··, calcd, ethanol; ▼, exptl; — - — calcd, acetone.

Table 3. Parameters of the Modified Chrastil Equation

	parameters		
cosolvent	*k*	*b′*	AARD*y* %[a]
ethyl acetate	1.56	−12.11	2.72
ethyl acetate + ethanol	1.43	−11.33	2.01
ethanol	1.61	−12.67	2.48
acetone	1.62	−12.74	2.18

[a] AARD*y* % $= 1/N \sum_{i=1}^{N} |y_2^{\mathrm{exptl}} - y_2^{\mathrm{calcd}} / y_2^{\mathrm{exptl}}| \cdot 100\ \%$ N = number of datum points; y_2^{exptl} = experimental results; y_2^{calcd} = calculated results.

symbols are the same as those in eq 1. When the concentration of colsolvent *m* and the temperature *T* are kept constant, eq 5 can also be written as

$$\ln s = k \ln \rho + b' \tag{6}$$

where $b' = \gamma \ln m + a/T + b$.

With different cosolvents, the parameters and the values of AARD*y* % for the modified Chrastil equation are listed in Table 3. From Figure 3, it can be seen that satisfactory agreement was obtained between experimental data and calculated results correlated by the modified Chrastil equation.

Conclusions

The solubilities of *p*-methylbenzene sulfonic acid in both pure and modified SC CO_2 are studied at (308, 318, and 328) K and over the pressure range from (8 to 21) MPa. The crossover pressure of the solute + SC CO_2 system is close to (10.5 to 12.2) MPa. At the temperature of 308 K and the cosolvent concentration of 1.5 mol %, the order of the solubility enhancement effect is ethyl acetate > ethyl acetate + ethanol (equal molar ratio) > ethanol > acetone. 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 4.30 % under all kinds of conditions in this work.

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