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Solubility of Solid 1,4-Dimethoxybenzene in Supercritical Carbon Dioxide

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The solubility of solid 1,4-dimethoxybenzene in supercritical carbon dioxide was measured with a semiflow phase equilibrium apparatus over the temperature range from 313.15 K to 338.15 K and the pressure range from 200 bar to 280 bar. For each isotherm, the mole fraction solubilities of 1,4-dimethoxybenzene were represented by the Chrastil equation.

Introduction

Due to the easy separation of extracts from solvent after extraction and the avoidance of environmental pollution, the supercritical fluid (SCF) extraction method has been extensively investigated. Applications of SCF extraction have been demonstrated in the food, pharmaceutical, petroleum, petrochemical, and textile industries. The solubilities of many low-volatile liquid components in SCF have been reported in the literature. Unfortunately, few results have been reported for solids. This is probably due to the difficulties of such measurements, since channeling and caking take place easily while the supercritical fluid passes through an equilibrium cell loaded with solid solute. Thus, particular care must be taken to load the chemical uniformly in the equilibrium cell.

1,4-Dimethoxybenzene (melting point, 329.25 K) is used as a cosmetics' flavoring, as a fixative in perfumes, dyes, and resin intermediates, and as a weathering agent in paints and plastics. In this study, the solubility of this solid compound in supercritical carbon dioxide was measured over the temperature range from 313.15 K to 338.15 K and the pressure range from 200 bar to 280 bar. The experimental data were represented by the empirical Chrastil equation.

Experimental Work

Experimental Materials. 1,4-Dimethoxybenzene, purchased from Tokyo Chem. Inc., was analytical reagent grade with a purity of +99%. This solid was dried in a vacuum oven at 353 K for >48 h to purge dissolved gases and moisture. The liquefied carbon dioxide was purchased from Sanfu Chem. Co. with a purity of +99.8%. All chemicals were used directly without further purification.

Apparatus. The main equilibrium cell and the accessory components for the present study are illustrated schematically in Figure 1. The water bath temperature was controlled to within ±0.1 K. Temperatures were read with a quartz thermometer (Hart Scientific Microthermo, Model 1502) with an accuracy of ±0.02 K. The measuring range of the gas flow meter (Ritter Co., Model TG1) is 2−120 L/h, the finest division is 10 mL, and the accuracy is 0.2%.

Before an experiment, leakage from any connection and valve must be carefully examined and prevented. Liquid carbon dioxide is compressed by a positive-displacement liquid pump (Thermo Separation Products, Series 105686) from a cylinder. The impurities and trace of water in the compressed carbon dioxide are removed with a gas purifier consisting of a 25 cm long cylinder packed with 5 Å and 2 μm molecular sieves at both ends. The desired pressure is adjusted with a back-pressure regulator (Tescom Company, series 26-1700). For safety reasons, the apparatus is equipped with a check valve (Swagelok Comp.) and a safety valve (High Pressure Equip Inc.). The compressed liquid carbon dioxide was pumped through a preheating coil submerged in a temperature-controlled water bath with ±0.2 K accuracy before entering the equilibrium cell, which was submerged in the same water bath. The equilibrium cell (Keystone Scientific Company) is 30 cm long with a 1.4 cm inside-diameter and reducer−adapter couplings at each end. Approximately 18 g of 1,4-dimethoxybenzene solid was carefully introduced into the cell in three equally spaced sections separated by 0.2 cm stainless steel balls to prevent channeling. The line connecting the equilibrium cell and the sampling section (a cold trap) was wrapped with heating tape to prevent deposition of solute in the pipeline. The cold trap, which was directly attached to a metering valve, was weighed with an electronic balance (Ohaus Analytycal Plus Co.) with an accuracy of ±0.1 mg before an experimental run. The carbon dioxide flow rate was increased very slowly from the beginning to avoid caking until it was adjusted to approximately 1 L/min and run about 1 h to extract enough quantity of chemical for weighing. The amount of carbon dioxide was measured volumetrically at room temperature (about 298.15 K) and atmospheric pressure with a wet test meter (Ritter company, Model TG1) with a finest division of 0.01 L. During experiments, the molar volume of carbon dioxide needed to be calculated, since room temperature and atmospheric pressure varied every day. The cold trap was weighed again after it was dismantled from the apparatus to determine the mass of the extracted chemical. Three runs were carried out to determine one experimental point. We began our experiment at 313.15 K and 100 bar. Unfortunately, the solubility of 1,4-dimethoxybenzene at these conditions is too small to be accurately measured. Thus, we made the initial experimental pressure 200 bar.

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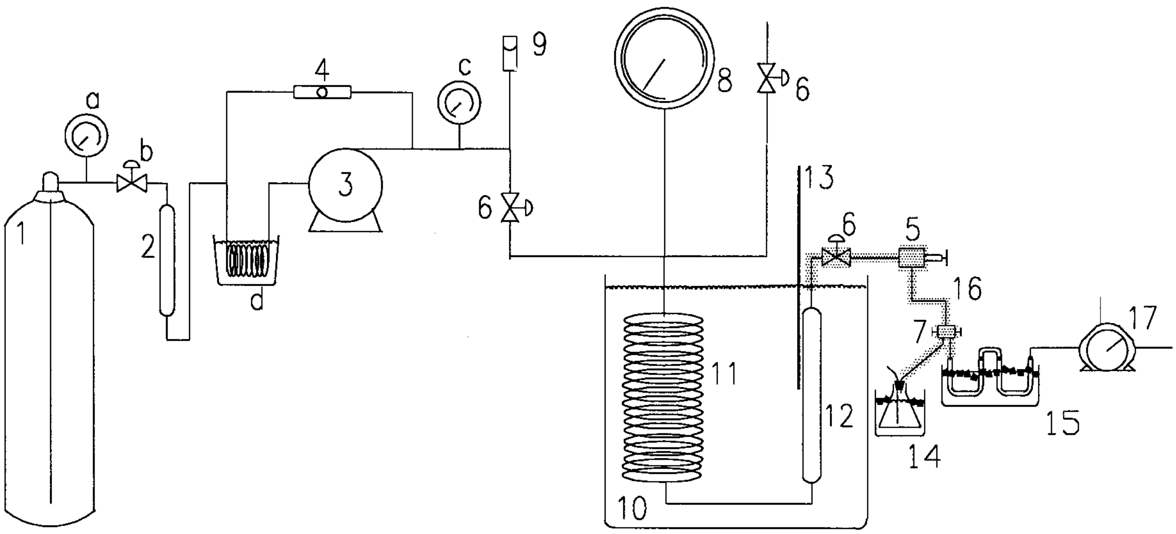

Figure 1. Experimental apparatus: 1, CO_2 cylinder; 2, CO_2 gas filter; 3, metering pump; 4, backpressure valve; 5, metering valve; 6, needle valve; 7, three-way valve; 8, pressure gauge; 9, safety valve; 10, water bath; 11, preheater; 12, equilibrium cell; 13, thermometer; 14, 15, ice—water bath; 16, wraped pipeline; 17, gas flowmeter.

Table 1. Solubilities of Naphthalene in Supercritical Carbon Dioxide at 328.15 K

	10^2y_2		
P/bar	Tsekhanskaya et al.	Kurnik et al.	this work
125	1.42	1.40	1.53
162	3.00	2.92	2.99
197	3.99	4.01	3.91
253	4.85	4.79	4.84
AAD(%)[a]	2.4%	3.6%	

[a] AAD(%) (average absolute deviation percent) =

$$\frac{1}{N}\sum_{i=1}^{N}|(y_2^{\mathrm{exp}} - y_2^{\mathrm{lit.}})/y_2^{\mathrm{exp}}|_i \times 100\%.$$

Table 2. Solubility of 1,4-Dimethoxybenzene in Supercritical Carbon Dioxide

T/K	P/bar	10^5y_2	T/K	P/bar	10^5y_2
313.15	200	4.74	328.15	200	6.14
	220	5.79		220	8.44
	240	6.13		240	10.6
	260	6.34		260	12.1
				280	13.2
338.15	200	10.2			
	220	13.9			
	240	15.4			
	260	17.2			
	280	18.5			

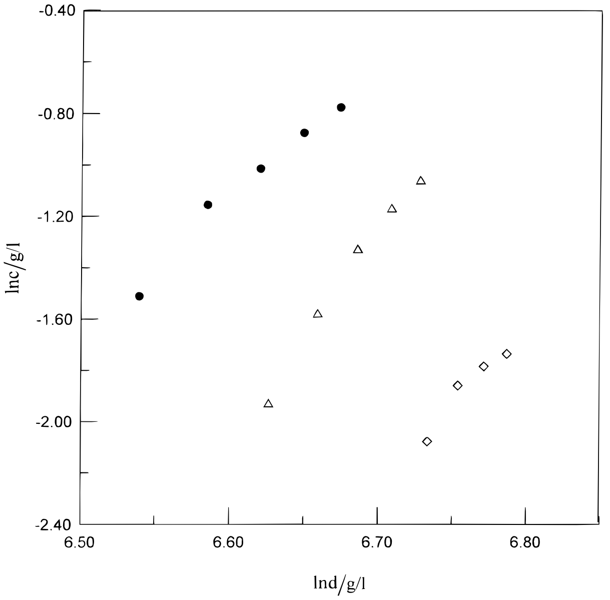

Figure 2. Experimental values of 1,4-dimethoxybenzene in supercritical carbon dioxide at different temperatures: ◇, T = 313.15 K; △, T = 328.15 K; ●, T = 338.15 K.

Before experiments were conducted, this apparatus was tested by making measurements of the solubilities of naphthalene at 328.15 K and different pressures. The measured solubilities of naphthalene in supercritical carbon dioxide are compared in Table 1 with those of Tsekhanskaya et al. (1964) and Kurnik et al. (1981). The average absolute deviation percentages (AAD(%)) of the present experimental data from those of the above two sources are 2.4% and 3.6%, respectively.

Experimental Results

The solubilities of 1,4-dimethoxybenzene were measured from 313.15 K to 338.15 K and from 200 bar to 280 bar. During the experiment, we experienced some difficulties in maintaining the carbon dioxide flow rate at the desired value, particularly at higher pressure. However, these difficulties were overcome through careful loading of the chemical and delicate control of the carbon dioxide flow rate. The experimental solubilities of 1,4-dimethoxybenzene in carbon dioxide are given in Table 2 and also plotted in Figures 2 and 3. The solubility of the solute increases with increasing pressure and temperature. Retrograde solubility (cross overpressure) behavior does not occur for the present system in the experimental range.

Data Correlation

The empirical model of Chrastil (1982) was employed to correlate the present experimental data. Chrastil assumed that a coupling effect would occur between solute and solvent molecules, and it is viewed as a chemical reaction. The final Chrastil formula is expressed as

$$c = d^k \exp(a/T + b) \tag{1}$$

where c is the concentration of solute and d is the density

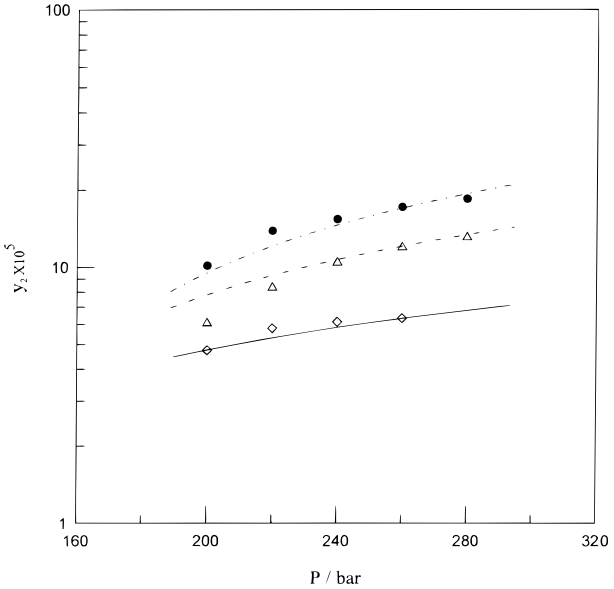

Figure 3. Correlation of solubility data by the Chrastil equation with the parameters $a = -7270.0$, $b = -21.1612$, and $k = 6.2826$: ◇, T = 313.15 K; △, T = 328.15 K; ●, T = 338.15 K; —, by the Chrastil equation at T = 313.15 K; — — —, by the Chrastil equation at T = 328.15 K; — • —, by the Chrastil equation at T = 338.15 K.

Table 3. Correlation of Carbon Dioxide (1) + 1,4-Dimethoxybenzene (2) by the Chrastil Equation with Parameters $a = -7270.0$/K, $b = -21.1612$, and $k = 6.2826$

T/K	P/bar	$10^5y_2^{\mathrm{exp}}$	$10^5y_2^{\mathrm{cal}}$
313.15	200	4.74	4.77
	220	5.79	5.31
	240	6.13	5.82
	260	6.34	6.32
328.15	200	6.14	6.82
	220	8.44	9.31
	240	10.55	10.57
	260	12.08	12.06
	280	13.22	13.39
338.15	200	10.16	9.53
	220	13.86	12.10
	240	15.40	14.53
	260	17.18	16.98
	280	18.50	19.37
			AAD(%)^a = 6.0%

^{a} $\mathrm{AAD}(\%) = \frac{1}{N}\sum_{i=1}^{N}|(y_2^{\mathrm{exp}} - y_2^{\mathrm{lit.}})/y_2^{\mathrm{exp}}|_i \times 100\%.$

of solvent, both in units of g/L. a, b, and k are the parameters to be determined from data correlation. The above equation can also be rewritten as

$$\ln c = a/T + k \ln d + b \tag{2}$$

In this study, two methods had been used to correlate the experimental data based on eq 1. In the first method, all the experimental data were used simultaneously to determine the parameters by the original Chrastil's equation (eq 1). The correlation results were given in Table 3 and also in Figure 3. The parameters are $a/K = -7270.0$, $b = -21.1612$, and $k = 6.2826$, and the AAD(%) for the solute concentration is 6.0%. In the second method, eq 2 was used, and the terms a/T and b were grouped together. At present, a has units of K, and b is unitless. Three sets of parameters were obtained for three different temperatures, as given in Table 4 and Figure 4. The average absolute deviation percentages of the three temperatures, 313.15 K, 328.15 K, and 338.15 K, were 1.8%, 3.5%, and 3.3% respectively. It is obvious that the correlation results of the second method are better than those of the first method.

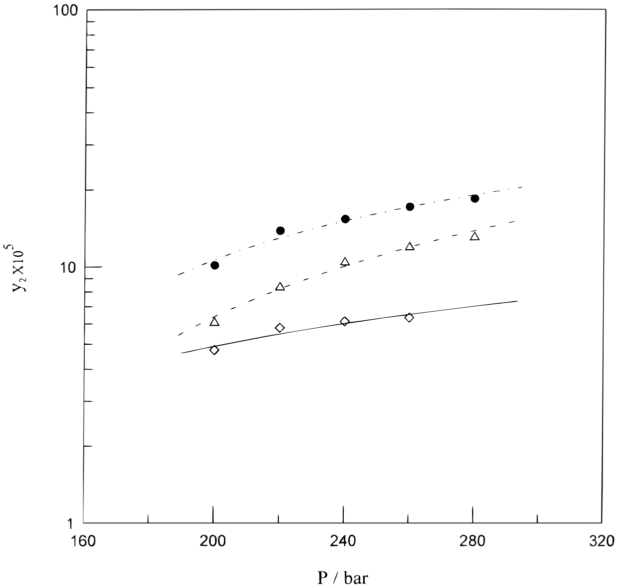

Figure 4. Correlation of solubility data by the Chrastil equation with parameters determined at individual temperature: ◇, T = 313.15 K; △, T = 328.15 K; ●, T = 338.15 K; —, by the Chrastil equation at T = 313.15 K; — — —, by the Chrastil equation at T = 328.15 K; — • —, by the Chrastil equation at T = 338.15 K.

Table 4. Correlation of Carbon Dioxide (1) + 1,4-Dimethoxybenzene (2) by the Chrastil Equation with Temperature Dependent Parameters

T/K	P/bar	$10^5y_2^{\mathrm{exp}}$	$10^5y_2^{\mathrm{cal}}$
$k = 6.3135$, $(a/\mathrm{K} + b) = -44.5516$			
313.15	200	4.74	4.91
	220	5.79	5.49
	240	6.13	6.03
	260	6.34	6.52
			AAD(%)^a = 1.8%
$k = 8.6019$, $(a/\mathrm{K} + b) = -58.8848$			
	200	6.14	6.41
	220	8.44	8.23
	240	10.55	10.07
	260	12.09	11.94
	280	13.22	13.86
			AAD(%)^a = 3.5%
$k = 5.3252$, $(a/\mathrm{K} + b) = -36.2841$			
	200	10.16	10.69
	220	13.86	13.00
	240	15.40	15.14
	260	17.18	17.16
	280	19.50	19.12
			AAD(%)^a = 3.3%

^{a} $\mathrm{AAD}(\%) = \frac{1}{N}\sum_{i=1}^{N}|(y_2^{\mathrm{exp}} - y_2^{\mathrm{lit.}})/y_2^{\mathrm{exp}}|_i \times 100\%.$

Conclusion

In this study, the solubility of 1,4-dimethoxybenzene in supercritical carbon dioxide was measured for the temperature range from 313.15 K to 338.15 K and the pressure range from 200 bar to 280 bar. The experimental data were correlated by the empirical equation of Chrastil (1982). Two different considerations were made for data correlation, and we obtained better results with the second method.

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