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Solubility of Troeger's Base in Supercritical Carbon Dioxide

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The solubility of Troeger's base in supercritical carbon dioxide over the pressure range 8 to 19 MPa and from 308 to 328 K was measured using a flow system. Models based on chemical association, which did not require the critical parameters of the solute, were used to correlate the experimental data.

Introduction

Application of supercritical fluid technology has been widely studied in the past few decades because of the advantages of supercritical fluids over conventional liquid solvents. Supercritical fluid extraction (SFE) and supercritical fluid chromatography (SFC) require dissolution and transport of the product as solute. Therefore, the solubilities of the solutes are basic data.

Troeger's base (TB, see Figure 1), is a classical racemate, and its chirality is solely due to a very high inversion barrier around the nitrogen atoms. Work done during the past decade has shown that TB and its analogues could be used as chiral solvating agents, as DNA-binding ligands, and for the construction of biomimetic molecular receptors and clathrate hosts (Bag, 1995). To separate TB racemate by supercritical chromatography, its solubility in supercritical carbon dioxide (SC-CO_2) becomes important. In this work, the solubility of TB in SC-CO_2 was determined in the pressure range from 8 to 19 MPa at 308, 318, and 328 K.

Many models for the correlation of solubility in supercritical fluid have been presented, including equation of state (EOS) and chemical association (Tan et al., 1989). Compared with the model derived from chemical association, the EOS model requires critical parameters of the solute. This restricts its application. When the critical parameters of the solute are unknown, the model based on chemical association is better. Two chemical association models are tested with data of this work and from the literature with satisfactory results.

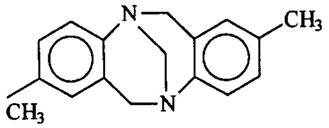

Figure 1. Structure of Troeger's base.

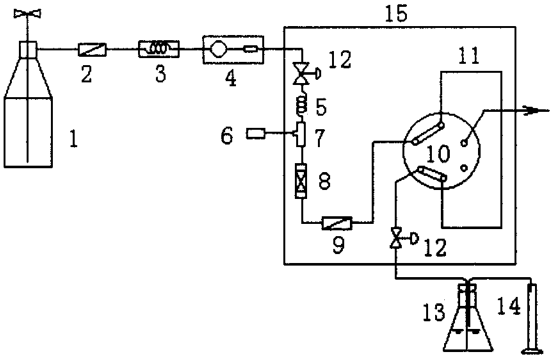

Figure 2. Schematic diagram of the flow-type apparatus: 1, CO_2 cylinder; 2, fliter (2 μm); 3, cooling bath; 4, CO_2 pump; 5, heat exchanger; 6, pressure transducer; 7, T-union; 8, saturator; 9, filter (0.5 μm); 10, sampling valve; 11, injection loop; 12, heated valve; 13, Erlenmeyer flask; 14, graduated cylinder; 15, thermostat.

Experimental Section

Equipment and Operation. A flow-type apparatus (Figure 2) was built for solubility determination of TB in supercritical carbon dioxide. The pure liquefied CO_2 was cooled with a cooling bath, and then it was pressurized above its critical pressure with an HPLC pump. The fluid flowed through a heat exchanger (stainless steel tubing), where the solvent was heated to the temperature of the thermostat (controlled within ±0.1 K), before it reached the saturator. The saturator was a commercially available empty HPLC column (50 mm × 4.6 mm) with sintered stainless steel frits of 0.5 μm at both ends. The column was packed with 80 to 100 mesh diameter glass beads for the solute to be distributed on and to avoid potential blockage of the frits. Before operation, sufficient solute was placed at the solvent entrance end of the saturator. At the exit of the saturator a pressure transducer was used to monitor the equilibrium pressure of the system. The pressure of the system was maintained with a heated valve, and the pressure variation was controlled within ±0.15 MPa. The system used a sampling valve of a 20 μL injection loop to obtain the sample. To check the state of equilibrium (saturation), the flow rate through the saturator was changed periodically. If the variation of the measured solubility was within the range of the estimated uncertainty while the flow rate was doubled, the system was considered to be at equilibrium.

The concentration of the solute was determined by liquid chromatography. The flow rate was maintained constant at about 5 to 10 mL/min of fluid expanded to atmospheric pressure. Determination of the solubility was made in ascending steps of pressure, since decreasing the pressure often led to plugging of the injection loop or the heated valve due to precipitation of the solute.

The system was designed for safe operation in the pressure range from 0.1 to 40 MPa and at temperatures from 0 to 80 °C.

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Table 1. Solubility of Naphthalene (1) in CO_2 at 328 K

P/MPa	$10^3 y_1{}^a$	$\rho^b(CO_2)$/mol·L^{-1}
7.0	0.598	3.71
10.0	3.82	7.46
12.5	15.3	12.39
16.2	32.1	15.65

[a] y_1 is the mole fraction of the solute in the supercritical fluid. [b] The density of pure CO_2 was calculated using the equation of state of Huang et al. (1985).

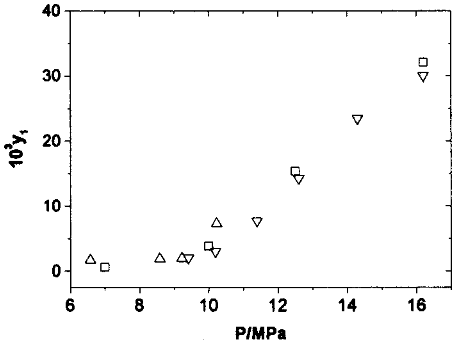

Figure 3. Solubility data of naphthalene in SC-CO_2 at 328 K versus pressure from this work compared to data from the literature: □, this work; △, from Hansen and Brunl; ▽, from Tsekhanskaya.

Table 2. Solubility of Troeger's Base (1) in SC-CO_2

T/K	*P*/MPa	$10^4 y_1$	$\rho_s{}^a$/mol·L^{-1}
308	8.0	1.51	10.07
	10.0	3.04	16.28
	13.0	5.01	17.92
	16.0	6.25	18.83
	19.0	7.08	19.50
318	8.0	0.454	5.51
	10.0	1.35	11.47
	13.0	4.13	15.83
	16.0	5.51	17.32
	19.0	6.44	18.26
328	8.0	0.313	4.63
	10.0	0.488	7.46
	13.0	2.77	13.07
	16.0	5.64	15.53
	19.0	8.00	16.855

[a] Density of pure SC-CO_2.

Materials. Pure carbon dioxide with a stated purity of 99.99% was used. Naphthalene with a purity > 99% and a racemic mixture of Troeger's base with the purity 98% were used without further purification. Acetone, methanol, and so forth were of analytically pure grade.

Results and Discussion

Validation of the Apparatus. Naphthalene was used to test the apparatus. The solubility of naphthalene in supercritical carbon dioxide was measured at 328 K (Table 1) and compared to the data from Tsekhanskaya et al. (1964) and Hansen and Bruno (1993). As shown in Figure 3, the agreement is good in the range of experimental pressure.

Solubility of Troeger's Base in SC-CO_2. The solubility of Troeger's base in SC-CO_2 was determined by means of the method described in the Experimental Section. The results are shown in Table 2.

The reproducibility of most of the data was within 3%, besides the data at low densities. This indicated that the sampling procedure was consistent.

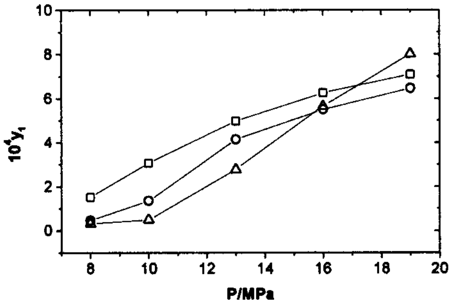

Figure 4. Solubility of Troeger's base in SC-CO_2: □, 308 K; ○, 318 K; △, 328 K.

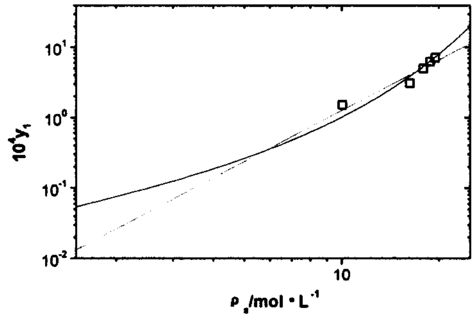

Figure 5. Relationship between y_1 and ρ_s at 308 K: □, experiment; —, Tan; — — —, Chrasil.

The solubility isotherms are shown in Figure 4, which indicates that the solubility of TB in SC-CO_2 changes with temperature and pressure. In the low-pressure range, solubility increases with temperature. However, solubility does not increase monotonically in the higher-pressure range. When the pressure > 16 MPa, the isotherm of 328 K crosses over other isotherms of lower temperature. This is similar to the results of some systems (McHugh et al., 1986); that is, the solubility increases dramatically near the upper critical end point. So far the mechanism has not been well explained.

The plots of the logarithm of y against the logarithm of r_s show a nearly linear relationship in the high-density region, but in the low-density region the experimental data do not fit the linear relationship well (Figure 5). So it was unsuitable to use the classical relationship between the mole fraction and the density to correlate these data.

Data Correlation

Two models based on the concept of chemical association were used for the correlation of the experimental results: Chrastil's equation and Tan's equation.

Most of the models describing the solubility of a solid in a supercritical fluid were based on thermodynamic considerations. In 1982, using the idea of solvent association, Chrastil proposed a model to correlate the solubility of a solute in a SCF (Chrastil, 1982):

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

where c is the concentration of a solute in a fluid, ρ is the density of the fluid, n is an association number, and a and b are equation parameters.

As the density in the near critical region is small, the association interaction between the molecules is weak. In the meantime the contribution of physical interaction between molecules is more significant. Therefore, the error of Chrastil's equation would be large. Thus, recently, the combination of physical and association effect has been studied (Tan Fei et al., 1989; Long et al., 1988). According

Table 3. Regression Analysis of Eq 1 for Troeger's Base in SC-CO_2

Parameter Fitting	
parameter	value
b	−17.509 25
n	3.399 52
a	−1335.125 99

Model

$c = \rho^{3.39952}\exp(-1335.12599/T - 17.50925)$; AAD%^{a} = 19.75

[a] AAD% = $(100/15)\Sigma|y_{\mathrm{exp},i} - y_{\mathrm{cal},i}|/y_{\mathrm{exp},i}$; $i = 1-15$.

Table 4. Regression Analysis of Eq 5 for Troeger's Base in SC-CO_2

Parameter Fitting	
parameter	value
H_4	−11.148 84
H_1	0.881 68
H_2	0.003 32
H_3	−1357.828 85

Model

$\ln y = 0.88168\ln(\rho T) + 0.00332\rho - 1357.82885/T - 1.14884$; AAD% = 14.91

to these studies, in a system of SCF and solute, the solute molecule (A) evaporates into the fluid phase by the interaction of the fluid and then reacts with the fluid molecule (B) to form the solvating complex AB_k.

The reaction at equilibrium is expressed as

$$A + nB \Leftrightarrow AB_n \qquad (2)$$

The equilibrium constant (k) of the reaction could be written as

$$k = \hat{f}_3/[\hat{f}_2(\hat{f}_1)^n] \qquad (3)$$

where the subscript 1 denotes B, 2 denotes A, and 3 denotes AB_n, and $\hat{f}_i$ is the fugacity of component i.

By putting the expressions for the fugacities into the above equation, the following equation is obtained (Tan et al., 1989):

$$y/(1-y)^n = \left\{k\hat{\varphi}_1^n f_2^* \exp\left[\frac{V_2}{RT}(P - P_2^*)\right]/\hat{\varphi}_3\right\}P^{n-1} \qquad (4)$$

where y is the concentration of a solute in a fluid in mole fraction, $\hat{\varphi}_i$ is the fugacity coefficient of component i, V_2 is the molar volume of pure component 2 in the condensed state, and $*$ denotes the pure state.

From eq 4, no association takes place when $n = 0$; in this case, the equation reduces to the equation derived by an equation of state. If the SCF is taken as an ideal gas, the equation reduces to Chrastil's equation, which only takes into account the association effect. When $n \neq 0$ and $y \ll 1$, the following equation could be derived:

$$\ln y = H_1\ln(\rho T) + H_2\rho + H_3/T + H_4 \qquad (5)$$

where H_1 is the association number and H_2 to H_4 are equation parameters.

Both thermodynamics and association were synthetically considered in Tan's equation.

By linear least-squares fitting, The experimental data were correlated by eqs 1 and 4. The results are presented in Figure 5 and Tables 3 and 4. It can be seen that the average absolute error (AAD%) of eq 5 is smaller than that of eq 1. Thus, Tan's equation is more suitable to describe the solubility of TB in SC-CO_2. That means both physical and association effects should be considered.

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