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Solubility of Propyl *p*-Hydroxybenzoate in Supercritical Carbon Dioxide with and without a Cosolvent

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The solid solubility of propyl *p*-hydroxybenzoate was measured for the first time in supercritical carbon dioxide at temperatures of (308.15, 318.15 and 328.15) K and pressures from (8.0 to 23.0) MPa. The influence of cosolvents—cyclohexane, cyclohexane + acetone (molar ratio 1:1), and acetone—was studied at a mole fraction of 0.035. The data were obtained by using a flow-type phase equilibrium apparatus, which was further tested by measuring the solubility of benzoic acid in compressed CO_2. The measured solubilities in supercritical CO_2 without and with cosolvents were correlated using the Chrastil equation and the modified Chrastil equation, respectively.

Introduction

Recently, a great deal of research has been carried out in the field of supercritical fluid (SCF) technology because of the superior properties of SCFs, including the ability to vary solvent density and properties by changing either the pressure or temperature, the lower viscosity of an SCF compared to that of a liquid, and the diffusivity value of an SCF that is intermediate between that of a gas and a liquid. CO_2 has been one of the most commonly used gases because it is inert, nontoxic, nonflammable, and easy to handle and obtain. However, CO_2 has limitations due to its lack of polarity and association capacity. It has been found that the addition of a small amount of organic solvent to an SCF can dramatically affect its solvent power, and many papers have been published on this topic.[1−4] However, nearly all papers consider only one cosolvent in a system. In some cases, a mixed cosolvent can be more effective than pure ones. By using a binary mixture as a cosolvent, the solubility of stearic acid[5] and benzoic acid[6] had been determined in supercritical carbon dioxide.

Propyl *p*-hydroxybenzoate (melting point 370.2 K) is used as an antiseptic of foodstuffs, cosmetics, and medicament. In this study, the solubility of propyl *p*-hydroxybenzoate was measured in supercritical CO_2 at (308.15, 318.15, and 328.15) K over the pressure range of (8.0 to 23.0) MPa without and with a cosolvent concentration of 3.5 mol % cyclohexane, cyclohexane + acetone (molar ratio 1:1), or acetone. The results were correlated by the Chrastil equation[7] and the modified Chrastil equation,[8] respectively. This work can also provide the basis for a future study on the specific interaction of solute and cosolvent and how to select a suitable cosolvent.

Experimental Section

Materials. Propyl *p*-hydroxybenzoate of purity better than 99.0% was purchased from the Beijing Chemical Regent Factory. Cyclohexane and acetone were obtained from the Beijing Experimental Chemical Factory, and each had a purity of more than 99.5%. High-purity carbon dioxide (more than 99.9% pure) was supplied from the Beijing Tianhao Chemical Factory. All chemicals were used without further purification.

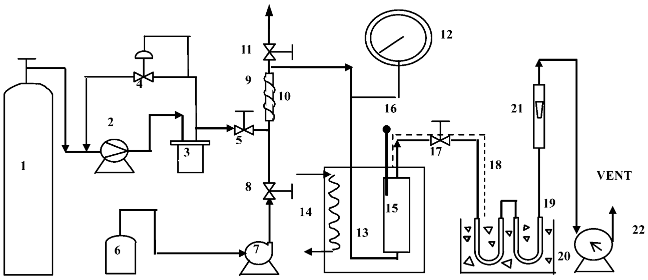

Figure 1. Schematic diagram of the experimental apparatus: (1) CO_2 cylinder, (2) syringe pump, (3) buffer, (4) back-pressure valve, (5) pressure regulating valve, (6) cosolvent vessel, (7) high-pressure pump, (8) cosolvent metering valve, (9) mixer, (10) electric coil, (11) safety valve, (12) pressure gauge, (13) constant-temperature stirred water bath, (14) heater, (15) equilibrium cell, (16) thermometer, (17) decompression sampling valve, (18) wrapped with heating coil, (19) U-shaped tube, (20) ice−water bath, (21) rotated flow meter, (22) wet gas flow meter.

Apparatus and Procedure. A flow-type apparatus was used to determine the solubility of propyl *p*-hydroxybenzoate in supercritical CO_2 with and without a cosolvent. The experimental apparatus was described in detail previously.[9] A schematic diagram of the experimental apparatus is shown in Figure 1. A major part is a high-pressure equilibrium cell that was made of stainless steel with an inner diameter of 21 mm and a length of 270 mm, with glass wool and a porous frit at either end. The maximum working pressure and temperature of the cell are 100 MPa and 623 K. The cell was immersed in a constant-temperature stirred water bath (Chongqing Yinhe Experimental Instrument Corporation, model CS-530) that maintained a constant temperature to within ±0.01 K. The temperature and pressure in the cell were measured using an internal platinum resistance thermometer at the top of the space above the solute (Beijing Chaoyang Automatic Instrument Factory, model XMT) and a calibrated pressure gauge (Heise, model CTUSA). The accuracy of the temperature measurement is ±0.1 K, and that for pressure is ±0.05 MPa. CO_2 was pressurized by a syringe pump (Nova, model 5542121), whereas the cosolvent was compressed by a high-pressure pump (Beijing Weixing Factory, model LB-

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10C). The concentration of the cosolvent was controlled by regulating the high-pressure gauge pump, accurate to ±0.01 mL·min^{-1}.

Before each run, the desired amount of solid, about (30 to 50) g, was distributed into three to five layers, and the equilibrium cell was packed with glass wool to avoid channeling and physical entrainment of undissolved solute into the saturated supercritical fluid stream. Then, low-pressure carbon dioxide was carefully passed through the cell at a low flow rate to remove the air trapped inside. Afterward, carbon dioxide and the cosolvent from the vessel were compressed into a mixer, which was heated by an electric coil, and they were transferred into the equilibrium cell from the bottom to a desired pressure and temperature. In the equilibrium cell, the solvent and solute reached equilibrium through mass transfer after about 30 min. Then, the saturated carbon dioxide flowed from the top of the cell through a decompression valve wrapped with a coiled heater into two weighed U-type tubes that were immersed in an ice−water bath. The two U-type tubes were partially packed with glass wool to catch the small particles of solute in the expanded gas stream. After vacuum drying, the solid solute collected in the U-type tubes was weighed by a single-pan balance with an accuracy of ±0.1 mg (Beijing Optical Instrument Factory, model DT-100). The total volume of carbon dioxide was measured by a calibrated wet-gas flow meter (Changchun Instrument Factory, model LML-2) with an accuracy of ±0.01 L at room temperature and atmospheric pressure during the experiment.

To ensure the accuracy of the experimental solubility data, we typically carried out three experiments in our research. The first step was to determine a suitable flow rate of CO_2. A wide flow-rate range was tested, and the results show that the solubility did not change in the range of (0.4 to 1.0) L·min^{-1}. Therefore, a flow rate of 0.6 was adopted in this work. The second step was to determine the equilibrium time. At a suitable CO_2 flow rate, the solubility of propyl *p*-hydroxybenzoate was measured after 20, 30, 40, 50, and 60 min. The results showed that after 30 min the solubilities were nearly invariable, which shows that the system had reached equilibrium. Therefore, all of the data were measured after 30 min. The third step was to test the reproducibility of the experimental data. Each experimental data point was measured more than three times and was found to have a deviation of less than ±5%.

Results and Discussion

The reliability of the flow-type apparatus used has been tested in our previous work,[6,9] which was further confirmed by measuring the solubility of benzoic acid in supercritical carbon dioxide at 328.15 K and at pressures of (8.0 to 23.0) MPa. None of the propyl *p*-hydroxybenzoate solubility data in supercritical CO_2 has been published. As shown in Figure 2, the solubilities obtained in this work are in good agreement with published values.[10,11] This illustrates that the apparatus employed in this work is reliable.

The solubility of propyl *p*-hydroxybenzoate was measured in supercritical carbon dioxide at (308.15, 318.15, and 328.15) K and pressures from (8.0 to 23.0) MPa. The cosolvents used were cyclohexane, cyclohexane + acetone (molar ratio 1:1), and acetone at a concentration of 3.5 mol %. The experimental results are tabulated in Tables 1 and 2 in terms of the mole fraction of the solute (y_2). The cosolvent effect in Table 2 is the result of the solubility of the solute in CO_2 with the cosolvent divided by that in pure CO_2. It can be seen that the cosolvent effect follows the order cyclohexane < cyclohexane + acetone < acetone.

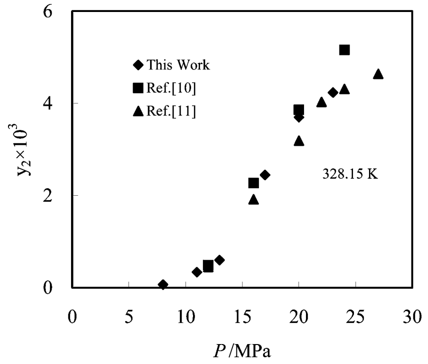

Figure 2. Comparison of the solubilities of benzoic acid in supercritical CO_2 measured in this work with those of refs 10 and 11.

Table 1. Solubility of Propyl *p*-Hydroxybenzoate in Pure Supercritical Carbon Dioxide

	T/K					
	308.15		318.15		328.15	
P/MPa	ρ_{CO_2}/g·L^{-1}	$y_2 \times 10^4$	ρ_{CO_2}/g·L^{-1}	$y_2 \times 10^4$	ρ_{CO_2}/g·L^{-1}	$y_2 \times 10^4$
8.0	422.21	0.3461	240.87	0.2335	203.48	0.0378
11.0	744.36	0.6595	604.25	0.6242	415.72	0.7004
13.0	786.10	0.7592	694.15	1.3320	572.16	1.6064
17.0	838.69	1.0059	775.99	2.6708	704.08	4.4370
20.0	866.44	1.9504	813.28	3.3589	754.98	5.3255
23.0	888.95	2.6990	841.85	4.0853	791.50	6.1751

Table 2. Solubility of Propyl *p*-Hydroxybenzoate in Supercritical Carbon Dioxide with a Cosolvent at a Concentration of 3.5 mol % ($y_2 \times 10^4$)

	308.15 K		
P/MPa	cyclohexane	cyclohexane + acetone	acetone
8.0	0.4405	0.4367	0.4472
11.0	1.4983	3.2538	4.0538
13.0	1.6149	6.0511	7.2101
17.0	1.9176	9.1679	10.6505
20.0	2.4504	10.1896	13.1172
23.0	3.4228	11.6134	14.1332
cosolvent effect[a]	1.68	5.47	6.58

[a] The cosolvent effect is the average value of the solubility of a solute in CO_2 with a cosolvent divided by that in pure CO_2 at 308.15 K.

Solubility data in supercritical carbon dioxide without and with a cosolvent was correlated by the Chrastil equation and the modified Chrastil equation that includes the influence of the cosolvent on solute solubility, given by

$$s_1 = \rho^{k_1} m^{\gamma_1} e^{(a_1/T + b_1)} \tag{1}$$

where ρ is the density of CO_2 (g·L^{-1}) and was obtained from the equation proposed by Angus et al.[12] and is listed in Table 1. Also, m is the concentration of the cosolvent (g·L^{-1}), T is the temperature in K, k_1 and γ_1 are the association numbers of CO_2 and the cosolvent, respectively. a_1 and b_1 are parameters. s_1 is the solubility of the solute (g·L^{-1}) and can be calculated from

$$s_1 = \frac{\rho M_2 y_2}{M_1(1 - y_2)}$$

where ρ is the density of supercritical CO_2 (g·L^{-1}), y_2 is the molar fraction of the solute, and M_1 and M_2 are the molecular weight of CO_2 and the solute, respectively.

The good agreement of the results calculated by the Chrastil equation with the experimental data in pure CO_2

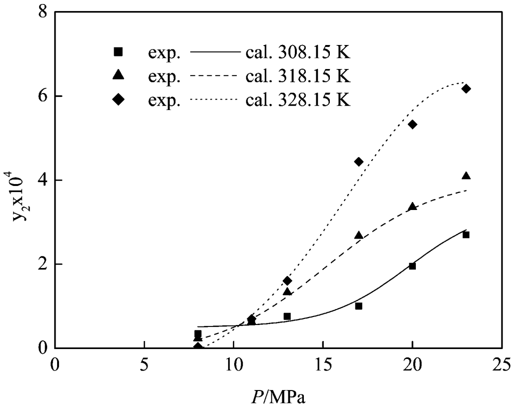

Figure 3. Correlation of the experimental solubility data of propyl p-hydroxybenzoate in pure CO_2 by the Chrastil equation.

Table 3. Results Correlated by the Modified Chrastil Equation for Each System with a Cosolvent at 308.15 K

	parameters of the modified Chrastil equation				
cosolvent	κ_1	γ_1	a_1/K	b_1	AARDy/%[a]
cyclohexane	0.42	3.66	−1336	−8.06	5.45
cyclohexane + acetone	5.81	0.42	−6823	−14.22	3.48
acetone	6.43	12.06	2995	−9.70	4.00

[a] AARDy = $^1/_N\sum_{i=1}^{N} |(y_2^{\text{exptl}} - y_2^{\text{calcd}})/y_2^{\text{exptl}}|_i \times 100$.

is illustrated in Figure 3. The absolute value of the average relative deviation (AARDy) was 4.49%, with the resulting correlation depicted as

$$s_1 = \rho^{3.90} e^{\{(-6665/T) - 5.27\}}$$

From Figure 3, we can see that the crossover pressure of this system is about 11.0 MPa. Beyond the crossover pressure point, solubilities increase with increases in both the pressure and the temperature, and below the crossover pressure point, solubilities increase with increasing pressure and decrease with increasing temperature.

With different cosolvents, the parameters for the modified Chrastil equation are listed in Table 3. The correlated results are shown in Table 3 and Figure 4, which illustrate that good agreement with the experimental data was obtained. From Figure 4, it can be seen that the solubility of the solute increases with increasing pressure in the system; however, the solubility rises more rapidly with acetone than with the other cosolvents. The reason is that polar acetone has a stronger ability to associate with the solute than does nonpolar cyclohexane. The mixed cosolvent, cyclohexane + acetone, has a cosolvent capability between that of acetone and cyclohexane.

Conclusions

The solubility of propyl p-hydroxybenzoate in supercritical CO_2 with and without a cosolvent was measured in the temperature range from (308.15 to 328.15) K and the pressure range from (8.0 to 23.0) MPa. The crossover pressure of the system was found to be about 11.0 MPa. The effects of the cosolvents (cyclohexane, cyclohexane + acetone (molar ratio 1:1), and acetone) are 1.68, 5.47, and 6.58, respectively. The experimental data were correlated by the Chrastil equation and the modified Chrastil equation. The absolute values of the average relative deviation of the mole fraction of the solute y_2 are 4.49%, 5.45%, 3.48%, and 4.00% for pure CO_2 and cyclohexane or cyclohexane + acetone or acetone as a cosolvent, respectively.

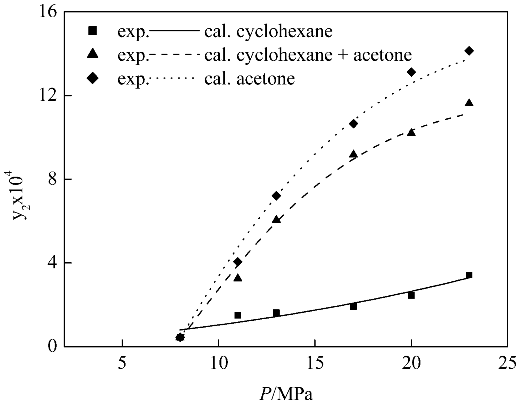

Figure 4. Experimental and calculated solublities of propyl p-hydroxybenzoate in supercritical CO_2 with a cosolvent by the modified Chrastil equation at 308.15 K.

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