Solubilities of Solid Benzoic Acid, Phenanthrene, and 2,3-Dimethylhexane in Supercritical Carbon Dioxide

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The solubilities of solid benzoic acid, phenanthrene, and 2,3-dimethylhexane in supercritical carbon dioxide were measured with a semiflow phase equilibrium apparatus at the temperatures 318.15 K and 328.15 K and the pressure range from 120 bar to 240 bar. The experimental results show that crossover pressures exist for these three solid solutes. For each isotherm, the mole fraction solubilities of these solutes were correlated satisfactorily with the equation of Adachi and Lu.

Introduction

The supercritical fluid (SCF) extraction method has been extensively studied by many researchers because it allows the easy separation of extracts from solvent with minimal environmental pollution. In practical applications, it has been widely applied to food, pharmaceutical, petroleum, petrochemical, textile, and environmental industries. In processes, it has been used for close-boiling-point and azeotropic mixture separations, crystallization, extraction of solid and liquid solutes, and isomerization reactions.

The extensive experimental data of solubilities of low-volatile liquid compounds in SCF can be found in the literature. Unfortunately, few solid compounds have been studied. This is probably because the attainment of solid−SCF equilibrium is more difficult than that of liquid−SCF equilibrium, since channeling and caking takes place in the solid bed when the SCF passes through the equilibrium cell. Besides, the solubility of a solid in a SCF is always so small that an accurate mass determination is difficult.

Benzoic acid (melting point, 394.4 K) is used as a cosmetic flavoring, perfume intermediate, dye intermediate, and preservative. Phenanthrene (melting point 373.5 K) is used as a dye intermediate, medicine additive, and explosive stabilizer. 2,3-Dimethylhexane (melting point 389.3 K) is used as a speciality chemical.

Experimental Work

Experimental Materials. Benzoic acid, phenanthrene, and 2,3-dimethylhexane were purchased from Showa Chem. Inc. (Japan) and Tokyo Kasei Kogyo Ltd. (Japan), respectively. All chemicals are analytical reagent grade with a purity of +99% as guaranteed by the supplier. The liquefied carbon dioxide was from Kee Chang Gas Co. (Taiwan) with a purity of +99.5%. All chemicals were used directly without further purification but were dried in a vacuum oven more than 48 h to purge possibly dissolved gases and moisture.

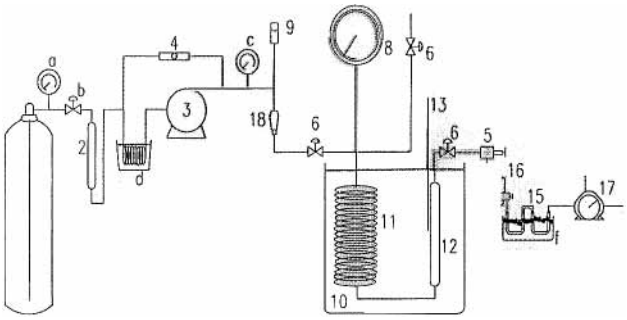

Figure 1. Experimental apparatus: 1, CO_2 cylinder; 2, CO_2 gas filter; 3, metering pump; 4, back-pressure valve; 5, metering valve; 6, needle valve; 7, three-way valve; 8, pressure gauge; 9, safety valve; 10, water bath; 11, preheater; 12, equilibrium cell; 13, thermometer; 14, 15, ice−water bath; 16,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

Apparatus and Procedure. The apparatus for the present study consisted of an equilibrium cell and the accessories, similar to that previously described by Lee et al.[1] with a minor modification of the cell as illustrated schematically in Figure 1. The water bath temperature was controlled at the desired temperature to within ±0.1 K. The cell temperatures were read with a quartz thermometer (Hart Scientific Microthermo Co., Model 1502) with an uncertainty of ±0.02 K. The gas flow rate was measured with a gas flow meter (Ritter Co., Model TG1) with the measuring range from 2 to 120 L/h and the finest division of 10 mL. The uncertainty of the pressure measurement is 0.2%.

After the apparatus was set up, all the connections and valves were carefully examined for any leakage. A positive-

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displacement liquid pump (Thermo Separation Products, Series 105686) was used to compress carbon dioxide from an upside down gas cylinder to ensure that only the liquid carbon dioxide was pumped. After the gas cylinder, there is a gas purifier consisting of a 25 cm long cylinder packed with 5 Å and 2 μm molecular sieves at both ends connected to remove the possible impurities and trace water. The desired pressure was adjusted with a back-pressure regulator (Tescom Company, Series 26-1700). A check valve (Swagelok Company) and a safety valve (High-Pressure Equip Inc.) were installed for safety considerations. The compressed liquid carbon dioxide was pumped through a preheating coil before it entered the equilibrium cell. Both coil and cell were submerged in the same water bath. The equilibrium cell (Keystone Scientific Company) was 50 mL in volume, 32 cm in length, and 1.4 cm in inside diameter. The solid solute was ground to a powder, dried, and then carefully introduced into the cell in several uniform layers separated by a layer consisting of 0.2 cm inside-diameter stainless steel balls. Packing the solid solute and stainless steel balls was an important step regarding the successful sampling. Improper packing would cause channeling inside the equilibrium cell. The line connecting the equilibrium cell and the cold trap (sampling section) was wrapped with heating tape to prevent the deposition of extracted solute in the pipeline. Before an experimental run, the cold trap, which was directly connected to a metering valve, was weighed with an electronic balance (Ohaus Analytical Plus Co.) with an uncertainty of ±0.1 mg. The carbon dioxide flow rate was increased very slowly from the beginning to prevent caking and finally adjusted to a very low amount (about 0.1 L·min^{-1} for the present experiment) to attain equilibrium. About 1.5 h was required to extract enough quantity of solute for weighing; then the cold trap was detached from the apparatus and weighed to determine the mass of the extracted solute. The amount of carbon dioxide was measured volumetrically with a wet test meter (Ritter Company, Model TG1) with a finest division of 0.01 L at room temperature and atmospheric pressure. The molar volume of carbon dioxide was calculated on the basis of the daily room temperature (about 289.15 K) and atmospheric pressure during the experiment. Due to the experimental difficulty, five runs were carried out, and the unreliable data (no more than two in each experiment) were discarded, to determine an experimental point. The present experiments were conducted from 120 bar to 270 bar and at the temperatures 318.15 K and 328.15 K.

Experimental Results

The solubilities of benzoic acid, phenanthrene, and 2,3-dimethylhexane in supercritical carbon dioxide were measured at 318.15 K and 328.15 K and from 120 bar to 270 bar. At the beginning of the experiment, the channeling and caking that happened in our previous study[1] were encountered again. Actually, the experimental failure was due to the nonuniform solute loading and the abruptly increasing carbon dioxide flow rate. Thus, through very carefully reloading of the chemicals and the delicate adjustment of the carbon dioxide flow rate, the difficulties were overcome.

The experimental solubilities of benzoic acid in supercritical carbon dioxide are given in Table 1 and also plotted in Figure 2. It is obvious that the solubility increases with increasing pressure at constant temperature. Benzoic acid has a lower solubility at 328.15 K than at 318.15 K for a pressure approximately lower than 160 bar. Thus, there exists the retrograde solubility (crossover pressure) for this compound at approximately 160 bar. The experimental solubilities of phenanthrene were given in Table 2 and also plotted in Figure 3. The solubility increases with increasing pressure at constant temperature. A crossover pressure exists at approximately 150 bar. The experimental solubilities of 2,3-dimethylhexane were given in Table 3 and also plotted in Figure 4. Similar to the cases of benzoic acid and phenanthrene, the solubility of 2,3-dimethylhexane increases with increasing pressure at constant temperature and a crossover pressure at approximately 135 bar was located. It is observed that 2,3-dimethylhexane has the largest solubility among these three chemicals and it tends to reach a constant value after about 240 bar, as shown in Table 3 and Figure 4. Due to the existence of retrograde solubility, the better extraction pressure should be lower at low temperature and higher at high temperature.

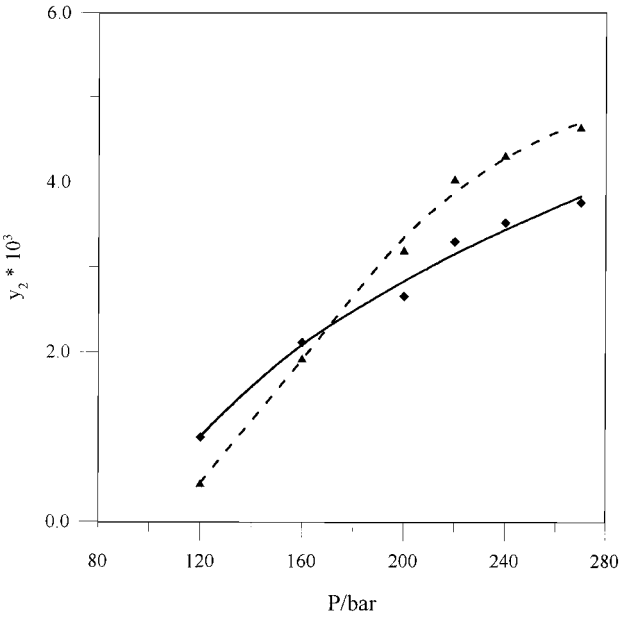

Figure 2. Experimental solubility data and correlation of benzoic acid in supercritical carbon dioxide by the modified Adachi and Lu equation: ◆, experimental; —, correlated at $T = 318.15$ K; ▲, experimental; - - -, correlated at $T = 328.15$ K.

Table 1. Correlation of Carbon Dioxide (1) + Benzoic Acid (2) by the Adachi and Lu Equation with Temperature Dependent Parameters

T/K	P/bar	$10^3 y_2^{exp}$	$10^3 y_2^{cal}$
$e_1 = 13.3497$, $e_2 = -0.0019$, $e_3 = 4.5093 \times 10^{-7}$, $(a/T + b) = -79.0521$			
318.15	120	0.987	0.988
	160	2.110	2.078
	200	2.650	2.825
	220	3.290	3.144
	240	3.510	3.428
	270	3.750	3.822
			AAD(%)[a] = 2.82%
$e_1 = -43.8379$, $e_2 = 0.0216$, $e_3 = -9.1791 \times 10^{-6}$, $(a/T + b) = 219.1066$			
328.15	120	0.451	0.451
	160	1.920	1.905
	200	3.190	3.336
	220	4.030	3.867
	240	4.310	4.277
	270	4.640	4.697
			AAD(%)[a] = 1.91%

[a] AAD(%) = $1/N\sum_{t=1}^{N}|(y_2^{exp} - y_2^{cal})/y_2^{exp}| \times 100\%$.

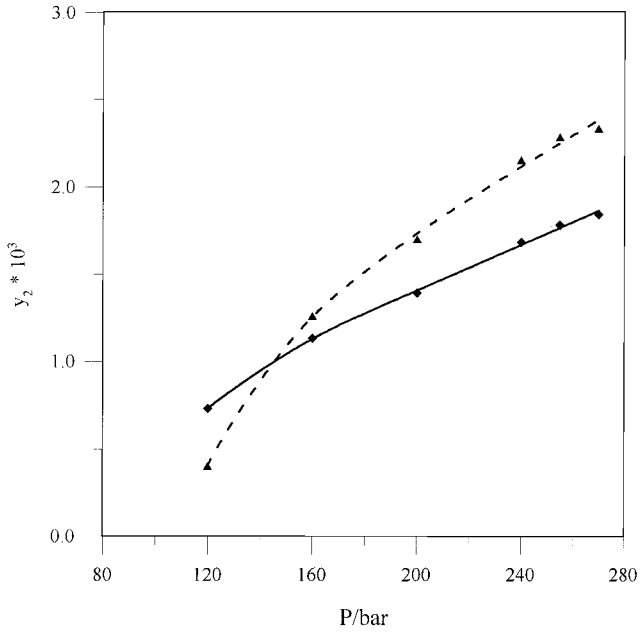

Figure 3. Experimental solubility data and correlation of phenanthrene in supercritical carbon dioxide by the modified Adachi and Lu equation: ◆, experimental; —, correlated at $T = 318.15$ K; ▲, experimental; - - -, at $T = 328.15$ K.

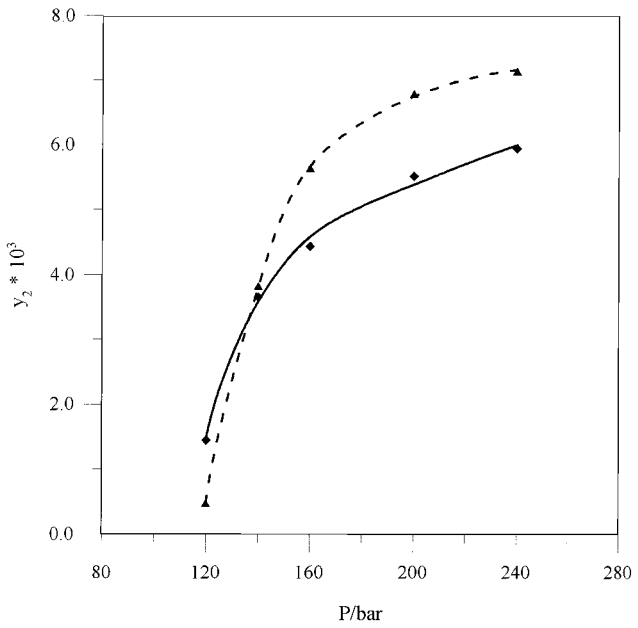

Figure 4. Experimental solubility data and correlation of 2,3-dimethylhexane in supercritical carbon dioxide by the modified Adachi and Lu equation: ◆, experimental; —, correlated at $T = 318.15$ K; ▲, experimental; - - -, at $T = 328.15$ K.

Table 2. Correlation of Carbon Dioxide (1) + Phenanthrene (2) by Adachi and Lu's Equation with Temperature Dependent Parameters

T/K	P/bar	$10^3 y_2^{exp}$	$10^3 y_2^{cal}$
$e_1 = 24.5325$, $e_2 = -0.0083$, $e_3 = 3.3602 \times 10^{-6}$, $(a/T + b) = -132.5850$			
318.15	120	0.732	0.732
	160	1.130	1.126
	200	1.390	1.405
	240	1.680	1.666
	255	1.780	1.763
	270	1.840	1.860
			AAD(%)[a] = 0.74%
$e_1 = 20.4263$, $e_2 = -0.0064$, $e_3 = 2.5410 \times 10^{-6}$, $(a/T + b) = -111.2971$			
328.15	120	0.404	0.404
	160	1.260	1.254
	200	1.700	1.731
	240	2.150	2.112
	255	2.280	2.246
	270	2.330	2.377
			AAD(%)[a] = 1.27%

[a] AAD(%) = $1/N\sum_{t=1}^{N}|(y_2^{exp} - y_2^{cal})/y_2^{exp}| \times 100\%$.

Table 3. Correlation of Carbon Dioxide (1) + 2,3-Dimethylhexane (2) by Adachi and Lu's Equation with Temperature Dependent Parameters

T/K	P/bar	$10^3 y_2^{exp}$	$10^3 y_2^{cal}$
$e_1 = 306.3824$, $e_2 = -0.1033$, $e_3 = 3.6094 \times 10^{-5}$, $(a/T + b) = -1647.53$			
318.15	120	1.440	1.443
	140	3.650	3.576
	160	4.430	4.580
	200	5.510	5.378
	240	5.930	5.980
			AAD(%)[a] = 1.79%
$e_1 = 105.5223$, $e_2 = -0.0370$, $e_3 = 1.3493 \times 10^{-5}$, $(a/T + b) = -562.4857$			
328.15	120	0.475	0.475
	140	3.820	3.807
	160	5.630	5.669
	200	6.780	6.739
	240	7.130	7.148
			AAD(%)[a] = 0.39%

[a] AAD(%) = $1/N\sum_{t=1}^{N}|(y_2^{exp} - y_2^{cal})/y_2^{exp}| \times 100\%$.

Experimental Data Correlation

For the experimental data correlation, the empirical model of Adachi and Lu,[2] which is a modification of the original Chrastil equation,[3] was used. Chrastil assumed that a coupling effect would occur between solute and solvent molecules when solute was extracted by supercritical carbon dioxide, and it was considered as a pseudo-chemical reaction. The final form of the Chrastil equation is expressed as

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

where c is the concentration of solute and d is the density of solvent, both in units of grams per liter. The parameters a, b, and k are to be determined from experimental data correlation.

When the Chrastil method was applied to benzoic acid and phenanthrene, the AAD(%)'s were 3.34% and 2.33%, respectively. While for 2,3-dimethylhexane, the AAD(%) was larger than 25%. These correlation results were not satisfactory. Thus, the method of Adachi and Lu[2] was applied for better correlation results.

Adachi and Lu[2] considered the parameter k in the Chrastil equation as a serial function of the density of solvent and expressed as

$$k = e_1 + e_2 d + e_3 d^2 \tag{2}$$

After eq 3 was substituted into eq 2, the modified Chrastil equation became an equation containing five parameters

$$\ln c = (e_1 + e_2 d + e_3 d^2) \ln d + a/T + b \tag{3}$$

In our previous work,[1] the correlation was done either using all experimental data of different temperatures and pressures at one time or grouping the a/T and b terms together (a is in units of kelvin and b is unitless) for each

temperature data set. For the present systems, the better correlation results were obtained by the later consideration. Thus, the Adachi and Lu equation was modified by grouping the a/T and b terms together and reduced to an equation of four parameters.

In the above equation, the density of carbon dioxide, d, at the operating conditions was calculated by the equation of Huang et al.[4] Then the concentration of solution, c, in carbon dioxide was calculated by the equation

$$c = \frac{dM_2y_2}{M_1(1 - y_2)} \tag{4}$$

where M_1 and M_2 are the molecular weights of solvent and solute, respectively.

The correlation results and the parameters of benzoic acid were given in Table 1 and plotted in Figure 2. The AAD(%) of 318.15 K was 2.82%, and that of 328.15 K is 1.91%. The correlation results and the parameters of phenanthrene were given in Table 2 and Figure 3. The AAD(%)'s were 0.74% and 1.27% for 318.1 K and 328.15 K, respectively. The correlation results for 2,3-dimethylhexane along with parameters were reported in Table 3 and plotted in Figure 4. The AAD(%) for 318.15 K is 1.79%, and that for 328.15 K is 0.39%.

Conclusion

In this study, the experimental solubilities of three solid compounds, benzoic acid, phenanthrene, and 2,3-dimethylhexane in supercritical carbon dioxide were measured at 318.5 K and 328.15 K and pressure ranges from 120 bar to 270 bar. The experimental results showed that the solubilities of these chemicals increase with increasing pressure. It is observed that all three chemicals exhibit the feature of retrograde solubility at different pressures. The experimental solubility data were satisfactorily correlated by the modified equation of Adachi and Lu.

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