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Solubilities of 2,6- and 2,7-Dimethylnaphthalenes in Supercritical Carbon Dioxide

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The solubilities of 2,6-dimethylnaphthalene and 2,7-dimethylnaphthalene at 308.2 and 328.2 K and the solubilities of the binary mixture at 308.2 and 318.2 K in supercritical carbon dioxide were measured by a flow-type apparatus. The pressure range of measurement was about 8–25 MPa. The solubilities were correlated by a three-constant cubic equation of state with two characteristic parameters.

Introduction

Separation methods for coal liquefaction products have received considerable attention recently for use as the raw materials of fine chemicals. Supercritical fluid extraction is showing promise as one of the new separation methods (*1*). However, the solubility data in supercritical fluid are limited, and thermodynamic analysis of solubility behavior has not been fully advanced. In previous works (*2–4*), the solubilities of naphthalene and isomeric xylenols in supercritical carbon dioxide were measured. In the present work, solubilities of 2,6-dimethylnaphthalene (2,6-DMN), 2,7-dimethylnaphthalene (2,7-DMN), and the binary mixture in supercritical carbon dioxide were measured and crossover pressures were found. The solubility data were correlated by using a three-constant cubic equation of state (*5, 6*) with two characteristic parameters.

Experimental Section

Equipment and Procedures. A flow-type apparatus was used to determine solubilities of solid-state solute in supercritical carbon dioxide. A detailed description of the equipment and operating procedures is given elsewhere (*2–4*). From a cylinder, carbon dioxide was supplied and was liquefied through a cooling unit. The liquefied carbon dioxide was sent to a preheater by a high-pressure liquid chromatography pump. When carbon dioxide passed through the preheater, it became a supercritical fluid. Then supercritical carbon dioxide entered into a preequilibrium cell and an equilibrium cell. The preheater, preequilibrium cell, and equilibrium cell were immersed into a water bath which was controlled within ±0.1 K. The preequilibrium cell was equipped to obtain sufficient equilibrium conditions. It was made of SUS 316, and its inner diameter, height, and volume were 30 mm, 150 mm, and about 100 cm^3, respectively. Solid solute was packed into the cell. The equilibrium cell was made of SUS 304, and its inner diameter, height, and volume were 30 mm, 170 mm, and about 120 cm^3, respectively. Solid solute was packed into the equilibrium cell with glass beads to prevent channeling. When supercritical carbon dioxide passed through the preequilibrium cell and equilibrium cell, supercritical carbon dioxide was in contact with solid solute under equilibrium pressure. The equilibrium pressure was measured by a Bourdon gauge calibrated against a strain pressure gauge (accuracy ±0.3%). The supercritical carbon dioxide containing solute was decompressed through an expansion valve and then introduced into a U-shaped glass tube in which gaseous carbon dioxide and solid solute were separated. Usually 0.2–0.5 g of solute was trapped, and the flow rate of carbon dioxide was adjusted to be 1.5–5.0 cm^3·s^{-1}. The volume of carbon dioxide was measured by a wet gas meter. Then, any small amount of solute in the expansion valve was removed and trapped by using pure carbon dioxide gas. The amount of solute trapped was determined with a balance. Solubilities were determined from the weight of the solute and the volume of carbon dioxide. In the case of measuring solubilities of mixed solids, a gas chromatograph with a flame ionization detector (Shimadzu Co. GC-8A) was used for analyzing the composition of trapped solutes.

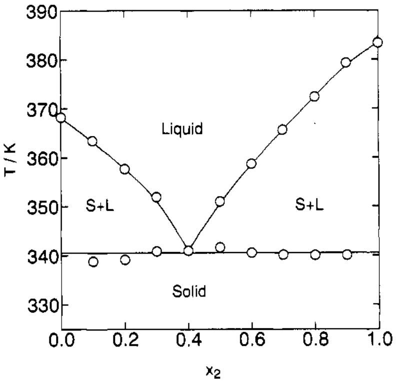

Figure 1. Solid–liquid equilibria of the 2,6-dimethylnaphthalene (2) + 2,7-dimethylnaphthalene (3) system under atmospheric pressure: (○) experimental data; (—) smoothed line. x_2 is the mole fraction of 2,6-DMN.

Materials. Reagent-grade 2,6-DMN and 2,7-DMN (supplied by Wako Pure Chem. Ind., Ltd.) were used. Gas chromatographic analysis indicated that their purities were more than 99% and 98%, respectively. After impurity components were extracted with supercritical CO$_2$ by the

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Table I. Solubilities of 2,6-Dimethylnaphthalene (2) and 2,7-Dimethylnaphthalene (3) in Supercritical CO_2 (1)[a]

CO_2 (1) + 2,6-dimethylnaphthalene (2)				CO_2 (1) + 2,7-dimethylnaphthalene (3)			
T = 308.2 K		T = 328.2 K		T = 308.2 K		T = 328.2 K	
p/MPa	10^3y_2	p/MPa	10^3y_2	p/MPa	10^3y_3	p/MPa	10^3y_3
7.9	1.07	10.0	0.509	8.8	2.68	10.0	0.745
9.1	1.95	10.9	1.07	10.7	3.51	11.0	1.75
12.1	2.66	12.1	2.01	15.0	4.72	14.9	6.64
14.6	3.06	12.7	2.70	20.0	5.29	19.8	10.1
				24.2	5.74	24.9	11.9

CO_2 (1) + 2,6-dimethylnaphthalene (2) + 2,7-dimethylnaphthalene (3)					
T = 308.2 K			T = 318.2 K		
p/MPa	10^3y_2	10^3y_3	p/MPa	10^3y_2	10^3y_3
9.0	2.20	3.22	9.0	0.475	0.682
9.9	2.64	3.82	10.0	1.91	2.73
12.0	3.12	4.55	12.0	3.69	5.31
14.8	3.77	5.47	14.9	5.15	7.42
19.8	4.24	6.17	19.8	6.63	9.55
24.6	4.37	6.38	24.7	7.26	10.5

[a] The reproducibility of the solubilities is within 5% and 1% in the pressure range below 10 MPa and above 10 MPa, respectively.

apparatus, the remaining component was used for measurement of solubilities. High-purity CO_2 (more than 99.9%, Sumitomo Seika Co.) was used as received.

Before measuring the solubilities of the mixed solid (2,6-DMN + 2,7-DMN) in supercritical carbon dioxide, the solid–liquid equilibrium temperatures of the mixture were measured under atmospheric pressure by a differential scanning calorimeter (Rigaku Co., Ltd., DSC8230B). The results obtained are shown in Figure 1. This figure shows that the present system is a simple eutectic mixture and the eutectic temperature (340.2 K) is higher than the experimental temperature. The 50 mol % mixture was adopted here for measuring solubilities.

Results and Discussion

The solubility measurements were carried out under several flow rates of carbon dioxide (1.5–5.0 $cm^3 \cdot s^{-1}$) at given pressures. Solubilities obtained were independent of the flow rate. Thus, they were determined under equilibrium conditions. The values are given by an arithmetic average of several data points at each pressure. Experimental solubilities of 2,6-DMN and 2,7-DMN at 308.2 and 328.2 K and those of the binary mixture (50 mol %) at 308.2 and 318.2 K are given in Table I. The solubilities of 2,6-DMN measured in this work are in good agreement with the experimental results of Kurnik et al. (*7*) as shown in Figure 2. The reproducibility of the solubilities is within 5% and 1% in the pressure range below 10 MPa and above 10 MPa, respectively.

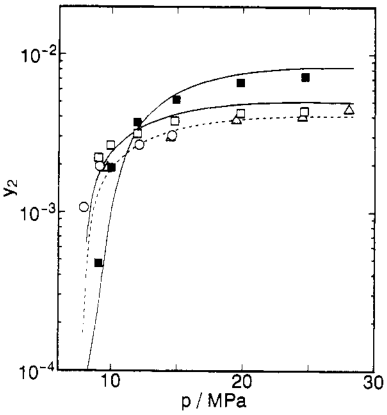

Figure 2. Solubilities of 2,6-dimethylnaphthalene (2) in supercritical carbon dioxide (1): (○) experimental data at 308.2 K for the CO_2 (1) + 2,6-DMN (2) system; (△) data of Kurnik et al. (*7*) at 308.2 K; (□, ■) experimental data at 308.2 and 318.2 K for the CO_2 (1) + 2,6-DMN (2) + 2,7-DMN (3) system, respectively; (- - -, —) calculated results with parameters determined by data fitting listed in Table III.

The accurate solubilities of the mixture at 328.2 K could not be measured because the liquid phase appeared in the equilibrium cell under the high-pressure experimental condition though the eutectic temperature of the mixture under the atmospheric pressure is 340.2 K.

The crossover pressures of 2,6-DMN and 2,7-DMN are very close. Also, the crossover pressures in the mixed solid system are very close as shown in Figures 2 and 3. Therefore it is very difficult to separate the isomeric mixture by the retrograde crystallization (*8*).

Calculation

The following fundamental equation can be used to calculate the solubilities of high-boiling compounds in supercritical fluid:

$$y_i = \frac{p_i^{\text{sat}}}{p} \frac{1}{\phi_i^{\text{G}}} \exp\left[\frac{v_i^{\text{S}}(p - p_i^{\text{sat}})}{RT}\right] \qquad (1)$$

where p denotes the equilibrium pressure, T is the equilibrium temperature, and p_i^{sat} and v_i^{S} are the saturation vapor pressure

Table II. Physical Properties

substance	T_C/K	p_C/MPa	ω	$10^3v^S/(m^3 \cdot mol^{-1})$	p^{sat}[f]/Pa 308.2 K	p^{sat}[f]/Pa 318.2 K	p^{sat}[f]/Pa 328.2 K
CO_2	304.2[a]	7.37[a]	0.225[a]				
2,6-dimethylnaphthalene	770.6[b]	2.91[b]	0.420[c]	0.1368[d]	1.222	3.448	9.130
2,7-dimethylnaphthalene	771.0[b]	2.91[b]	0.420[c]	0.1368[e]	1.690	4.736	12.46

[a] Reference 10. [b] Estimated by the Lydersen method (*10*). [c] Estimated by the Edmister method (*10*). [d] Reference 11. [e] Assumed to be the same value as that of 2,6-dimethylnaphthalene. [f] Extrapolated data of ref 12.

Table III. Values of Characteristic Parameters and Deviations

system	T/K	calculated by eqs 3–9 k_{ij}	calculated by eqs 3–9 l_{ij}	calculated by eqs 3–9 100σ[a]	fitting the experimental data k_{ij}	fitting the experimental data l_{ij}	fitting the experimental data 100σ[a]
CO_2 (1) + 2,6-dimethylnaphthalene (2)	308.2	0.117	0.007	16.43	0.117	0.008	16.28
	318.2	0.113	0.007	7.00	0.107[b]	−0.003[b]	5.39
	328.2	0.110	0.007	19.23	0.044	−0.130	7.39
CO_2 (1) + 2,7-dimethylnaphthalene (3)	308.2	0.118	0.007	10.44	0.087	−0.058	7.48
	318.2	0.114	0.007		0.050[c]	−0.129[c]	
	328.2	0.110	0.007	22.88	0.013	−0.199	5.52

[a] $\sigma = (1/N)\sum|y_{\text{exp}} - y_{\text{calc}}|/y_{\text{exp}}$, where N is the number of data. [b] Obtained by the data of Kurnik et al. (*7*). [c] Interpolation of parameters between 308.2 and 328.2 K.

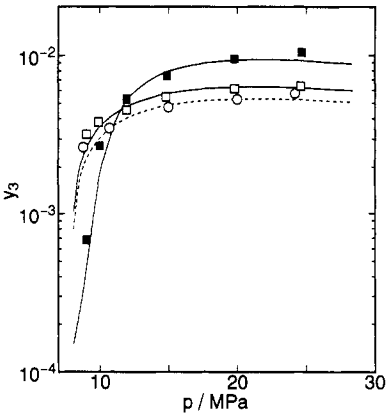

Figure 3. Solubilities of 2,7-dimethylnaphthalene (3) in supercritical carbon dioxide (1): (○) experimental data at 308.2 K for the CO_2 (1) + 2,7-DMN (3) system; (□, ■) experimental data at 308.2 and 318.2 K for the CO_2 (1) + 2,6-DMN (2) + 2,7-DMN (3) system, respectively; (- - -, —) calculated results with parameters determined by data fitting listed in Table III.

and solid-state molar volume of solute, respectively. The values of p_i^{sat} and v_i^S can be obtained from the properties of the pure component. The fugacity coefficient of solute in the pressurized gas phase ϕ_i^G is usually evaluated by adopting an equation of state.

To evaluate ϕ_i^G, the following cubic equation of state proposed by Yu et al. (*5*, *6*) was adopted:

$$p = \frac{RT}{v-b} - \frac{a}{v(v+c) + b(3v+c)} \qquad (2)$$

where a, b, and c are pure component parameters that can be calculated with the critical properties p_C and T_C and Pitzer's acentric factor ω. To apply eq 2 to a binary or a ternary mixture, the following mixing rules for the constants a, b, and c were used:

$$a = \sum_i \sum_j y_i y_j a_{ij}, \quad a_{ij} = (1 - k_{ij})(a_i a_j)^{0.5} \qquad (3)$$

$$b = \sum_i \sum_j y_i y_j b_{ij}, \quad b_{ij} = (1 - l_{ij})(b_i + b_j)/2 \qquad (4)$$

$$c = \sum_i \sum_j y_i y_j c_{ij}, \quad c_{ij} = (1 - l_{ij})(c_i + c_j)/2 \qquad (5)$$

where k_{ij} and l_{ij} denote the characteristic parameters between unlike molecules i and j. When eqs 2–5 are utilized, the fugacity coefficient ϕ_i^G can be thermodynamically derived (*2*, *9*). As discussed previously (*9*), the conventional mixing rules with k_{ij} and l_{ij} introduced into both attraction and size terms give a better correlation than the local composition mixing rules, because the solubilites of high-boiling compounds in supercritical fluids are quite small.

The solubilities were calculated by using the properties of pure components listed in Table II. In the previous papers (*13*, *14*), it was found that the binary interaction parameters could be correlated with pure component properties as follows.

The parameter $b_{1j}/(\mathrm{m^3 \cdot mol^{-1}})$ can be correlated by the following equation for many CO_2 (1) + solid solute (j) systems:

$$b_{1j} = 3.097 \times 10^{-5} + 4.388 \times 10^{-5}(v_j^S/v_{C,1}) \qquad (6)$$

where $v_{C,1}$ is the critical molar volume of CO_2 (9.40×10^{-5} $\mathrm{m^3 \cdot mol^{-1}}$) (*10*). The binary interaction parameter l_{1j} can be calculated from eqs 4 and 6. It was assumed that l_{1j} was independent of temperature.

The binary parameter k_{1j} contained in attraction term $a_{1j}/(\mathrm{J \cdot m^3 \cdot mol^{-2}})$ can be expressed approximately as follows:

$$k_{1j} = k_{1j}(308) - 3.656 \times 10^{-4}(T/K - 308) \qquad (7)$$

where $k_{1j}(308)$ is the k_{1j} at 308 K and T is the absolute temperature. The parameter a_{1j} at 308 K, $a_{1j}(308)$, can be correlated by the following equation:

$$a_{1j}(308) = a_{1j}^{NP}(308) + a_{1j}^{PH}(308) \qquad (8)$$

where $a_{1j}^{NP}(308)$ is the contribution of the dispersion nonpolar force and $a_{1j}^{PH}(308)$ is the contribution of polar and hydrogen-bonding forces. $a_{1j}^{NP}(308)$ can be correlated by

$$a_{1j}^{NP}(308) = 1.0659\{C_n(v_j^S \times 10^3)^{2/3}\}^{0.5184} \qquad (9)$$

where C_n is the number of atoms except for hydrogen in the solid molecule and $v_j^S/(\mathrm{m^3 \cdot mol^{-1}})$ is the molar volume of the solid. In the present systems, $a_{1j}^{PH}(308)$ is zero. For a binary system, a_{1j} can be calculated by eqs 3 and 7–9. The calculated interaction parameters are listed in Table III. The calculated results of solubilities are fairly good for binary systems. To calculate the ternary system CO_2 (1) + 2,6-DMN (2) + 2,7-DMN (3), the parameters k_{23} and l_{23} were set to zero. The absolute average deviation in calculated results for the ternary system at 308.2 K was 13.9%, and that at 318.2 K was 34.9%.

To give better representation for the experimental data, the binary parameters were recalculated to fit the experimental data. The determined parameters are listed in Table III. As shown in Figures 2 and 3 and Table III, the experimental results were correlated well for the binary systems. To calculate the solubilities for the ternary system at 318.2 K, the binary interaction parameters at 318.2 K are necessary. The binary interaction parameters of the CO_2 (1) + 2,6-DMN (2) system at 318.2 K were determined using the solubility data of Kurnik et al. (*7*). Those of the CO_2 (1) + 2,7-DMN (3) system at 318.2 K were estimated by the interpolation between 308.2 and 328.2 K. The values of interaction parameters thus determined are also listed in Table III. The parameters k_{23} and l_{23} were set to zero. The absolute average deviation in calculated results for the ternary system at 308.2 K was 19.0%, and that at 318.2 K was 9.82% as illustrated in Figures 2 and 3.

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