

# Solubilities of 3,4-Xylenol and Naphthalene + 2,5-Xylenol in Supercritical Carbon Dioxide at 35 °C

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The solubilities of 3,4-xylenol and naphthalene + 2,5-xylenol in supercritical carbon dioxide were measured by a flow-type apparatus at 35 °C over pressure ranges of 8.2–26.2 and 8.5–26.2 MPa, respectively. The solubilities were correlated by a three-constant cubic equation of state with two characteristic parameters.

## Introduction

Separation methods for coal-derived components have received considerable attention recently (1) for use as the raw materials of fine chemicals. Supercritical fluid extraction is showing promise as one of the new separation methods (2). The solubility data and an accurate correlation method are needed for the design of a supercritical fluid extraction process. In previous works (3, 4), the researchers measured the solubilities of naphthalene, 2,5-xylenol, and 2,6-xylenol. In the present work, solubilities of 3,4-xylenol and naphthalene + 2,5-xylenol in supercritical carbon dioxide were obtained and 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 (3, 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 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  $\pm 0.1$  °C. 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 mL, 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 mL, 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  $\pm 0.3\%$ ). 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 0.5–1.0 g of solute was trapped, and the flow rate of carbon dioxide was adjusted to be 1–4 cm<sup>3</sup> s<sup>-1</sup>. The volume of carbon dioxide was measured by a wet gas meter. Then, any small amount of solute in the expansion valve was

Table I. Solubilities of 3,4-Xylenol (2) in Supercritical Carbon Dioxide at 35 °C

<i>p</i> /MPa	10 <sup>3</sup> <i>y</i> <sub>2</sub>	<i>p</i> /MPa	10 <sup>3</sup> <i>y</i> <sub>2</sub>	<i>p</i> /MPa	10 <sup>3</sup> <i>y</i> <sub>2</sub>
8.2	2.34	18.5	7.68	23.3	8.65
11.2	5.12	20.4	8.19	26.2	9.10
16.3	7.19				

Table II. Solubilities of Naphthalene (2) + 2,5-Xylenol (3) in Supercritical Carbon Dioxide at 35 °C

<i>p</i> /MPa	10 <sup>2</sup> <i>y</i> <sub>2</sub>	10 <sup>2</sup> <i>y</i> <sub>3</sub>	<i>p</i> /MPa	10 <sup>2</sup> <i>y</i> <sub>2</sub>	10 <sup>2</sup> <i>y</i> <sub>3</sub>
8.5	1.65	1.21	18.4	3.12	2.41
11.1	2.26	1.74	22.3	3.09	2.43
14.2	2.76	2.13	26.2	3.21	2.49

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-3BF) was used for analyzing the concentrations of trapped solutes.

**Materials.** Reagent-grade naphthalene (supplied by Nakarai Chemicals, Ltd.) and 2,5-xylenol and 3,4-xylenol (supplied by Tokyo Kasei Co., Ltd.) were used without further purification. Gas chromatographic analysis indicated that their purities were more than 99.9%, 99%, and 99%, respectively. High-purity CO<sub>2</sub> (more than 99.9%, Setetu Kagaku Co., Ltd.) was used as received.

Before measuring the solubilities of mixed solids (naphthalene + 2,5-xylenol) in supercritical carbon dioxide, the solid-liquid equilibrium temperatures were measured for the binary system of naphthalene + 2,5-xylenol under atmospheric pressure by a differential scanning calorimeter (Seiko Instruments Inc., DSC-20). The results obtained are shown in Figure 1. This figure shows that the present system is a simple eutectic mixture and the eutectic temperature (324.1 K) is higher than the experimental temperature of solubilities. The 50 mol % mixture was adopted here for measuring solubilities.

## Results and Discussion

Experimental solubilities of 3,4-xylenol and naphthalene + 2,5-xylenol in supercritical carbon dioxide at 35 °C up to 26.2 MPa are given in Tables I and II. The solubility measurements were carried out under several flow rates at given pressures as shown in Figure 2. As illustrated, solubilities obtained are independent of flow rate. This shows that they were determined under equilibrium conditions. The values listed in Tables I and II are given by an arithmetic average of several data points at each pressure. In a previous work (3), the solubilities of naphthalene in supercritical carbon dioxide were measured by the same apparatus and were compared with literature values to check the reliability of the apparatus and experimental procedure. According to the result and the reproducibility of the solubility data obtained in this work, the accuracy of the solubility of 3,4-xylenol is considered to be within 3% and 1% in the pressure range below 10 MPa and above 10 MPa, respectively. That of naphthalene + 2,5-xylenol is considered to be within 3% in the all pressure ranges.

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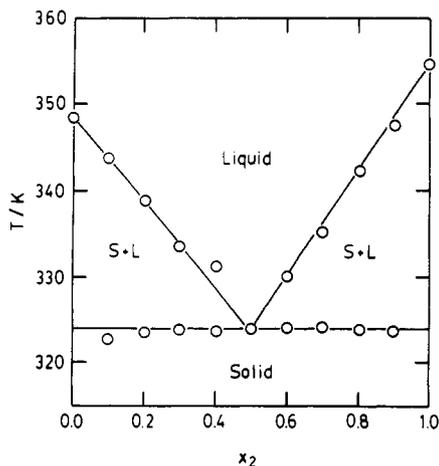


Figure 1. Solid-liquid equilibria of the naphthalene (2) + 2,5-xylene (3) system under atmospheric pressure: (O) experimental data; (—) smoothed line.

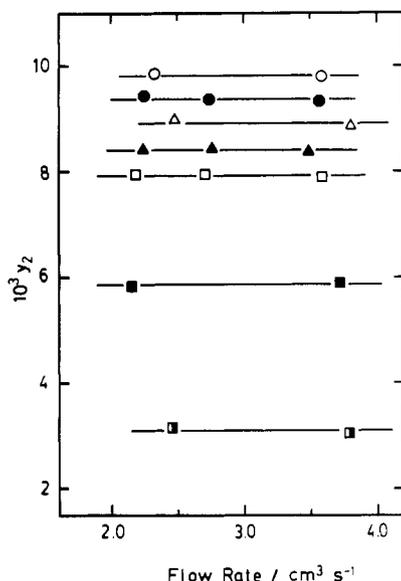


Figure 2. Relationship between solubility of 3,4-xylene (2) in supercritical carbon dioxide and flow rate of carbon dioxide: (O) 26.2 MPa; (●) 23.3 MPa; (Δ) 20.4 MPa; (▲) 18.5 MPa; (□) 16.3 MPa; (■) 11.2 MPa; (▣) 6.2 MPa.

It is noted that the solubilities of naphthalene and 2,5-xylene in ternary systems were about 100% up compared with those in binary systems (4, 7).

### Correlation

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

$$y_i = \frac{p_i^{\text{satn}}}{p} \frac{1}{\phi_i^{\text{G}}} \exp \left\{ \frac{v_i^{\text{S}}(p - p_i^{\text{satn}})}{RT} \right\} \quad (1)$$

where  $p$  denotes the equilibrium pressure,  $T$  is the equilibrium temperature,  $p_i^{\text{satn}}$  and  $v_i^{\text{S}}$  are the saturation vapor pressure and the solid-state molar volume of solute, respectively. The values of  $p_i^{\text{satn}}$  and  $v_i^{\text{S}}$  can be obtained from the properties of the pure component. The fugacity coefficient of solute in pressurized gaseous phase  $\phi_i^{\text{G}}$  is usually evaluated by adopting an equation of state.

To evaluate  $\phi_i^{\text{G}}$ , the following cubic equation of state proposed by Yu et al. (5, 6) was adopted:

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

Table III. Critical Temperature  $T_c$ , Critical Pressure  $p_c$ , Acentric Factor  $\omega$ , Solid Molar Volume  $v^{\text{S}}$ , and Saturation Vapor Pressure  $p^{\text{satn}}$

compound	$T_c/\text{K}$	$p_c/\text{MPa}$	$\omega$	$10^3 v^{\text{S}}/(\text{m}^3 \text{mol}^{-1})$	$p^{\text{satn}}(35^\circ\text{C})/\text{Pa}$
CO <sub>2</sub>	304.2	7.38	0.225		
naphthalene	748.4	40.0	0.302	0.1119	29.17
2,5-xylene	706.9	48.0	0.569	0.1257	12.15
3,4-xylene	729.8 <sup>b</sup>	48.95 <sup>b</sup>	0.576 <sup>c</sup>	0.1243 <sup>d</sup>	5.686 <sup>e</sup>

<sup>a</sup> Reference 9 except 3,4-xylene. <sup>b</sup> Reference 10. <sup>c</sup> Given as an average value obtained from two vapor pressure equations in ref 11. <sup>d</sup> Reference 12. <sup>e</sup> Reference 13.

Table IV. Values of Characteristic Parameters for Supercritical Carbon Dioxide (1) + Solute (2) and Supercritical Carbon Dioxide (1) + Naphthalene (2) + 2,5-Xylene (3) Systems

solute	$k_{ij}$	$l_{ij}$
naphthalene <sup>a</sup>	0.056	-0.096
2,5-xylene <sup>a</sup>	-0.104	-0.517
3,4-xylene <sup>a</sup>	-0.055	-0.413
naphthalene + 2,5-xylene <sup>b</sup>	-0.480	-1.000

<sup>a</sup>  $i = 1, j = 2$ . <sup>b</sup>  $i = 2, j = 3$ .

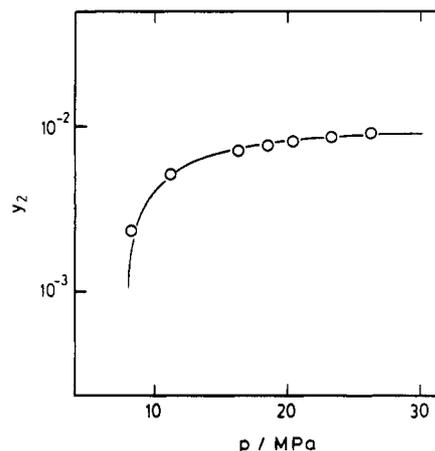


Figure 3. Solubility of 3,4-xylene (2) in supercritical carbon dioxide at 35 °C: (O) experimental data; (—) calculated line.

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  $\omega$ . To apply eq 2 to a binary or a ternary mixture, the following mixing rules for the constants  $a$ ,  $b$ , and  $c$  were used:

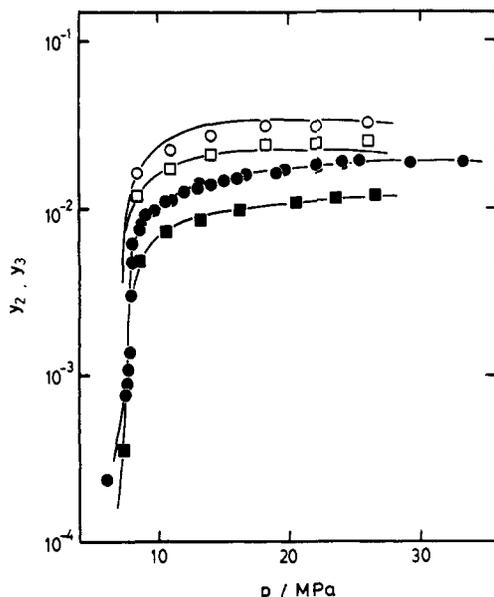
$$a = \sum_i \sum_j y_i y_j a_{ij} \quad a_{ij} = (1 - k_{ij})(a_i a_j)^{0.5} \quad (3)$$

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

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

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  $\phi_i^{\text{G}}$  can be thermodynamically derived (3, 8). As discussed previously (8), 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 solubilities of high-boiling compounds in supercritical fluids are quite small.

The experimental solubilities of 3,4-xylene and naphthalene + 2,5-xylene were correlated by using the properties of pure components listed in Table III. The values of  $k_{12}$  and  $l_{12}$  were determined by fitting calculated results to the experimental data of each carbon dioxide + single solute system. On the other hand, those of solute-solute interactions ( $k_{23}$ ,  $l_{23}$ ) were deter-



**Figure 4.** Solubility of naphthalene (2) and 2,5-xylene (3) in supercritical carbon dioxide at 35 °C: (O), (□) experimental solubilities of naphthalene and 2,5-xylene, respectively; (●) data of the supercritical carbon dioxide + naphthalene binary system from Tsakhanskaya et al. (7); (■) data of the supercritical carbon dioxide + 2,5-xylene binary system from Iwai et al. (4); (—) calculated line.

mined from the experimental data of the ternary system. The values of interaction parameters determined are listed in Table IV. As shown in Figure 3, the experimental results for 3,4-xylene are correlated within 5%. Experimental results for naphthalene + 2,5-xylene were correlated within 8%, as illustrated in Figure 4.

#### Glossary

$a, b, c$	parameters of eq 2
$k_{ij}, l_j$	characteristic parameters between unlike molecules $i$ and $j$
$p$	pressure
$p_c$	critical pressure
$p^{sat}$	saturation vapor pressure

$R$	gas constant
$T$	temperature
$T_c$	critical temperature
$v$	molar volume
$v^s$	solid-state molar volume
$x$	solid-phase mole fraction
$y$	solubility (gas-phase mole fraction)
$\phi^g$	gas-phase fugacity coefficient
$\omega$	Pitzer's acentric factor

#### Subscripts

$i, j$	components $i$ and $j$
1	carbon dioxide
2, 3	solutes 2 and 3

Registry No. CO<sub>2</sub>, 124-38-9; 3,4-xylene, 95-65-8; 2,5-xylene, 95-87-4; naphthalene, 91-20-3.

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## Excess Molar Enthalpies and Excess Molar Volumes of 1,2,4-Trimethylbenzene + Cyclic Ethers at 298.15 K

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Excess molar enthalpies and excess molar volumes of the binary systems 1,2,4-trimethylbenzene + oxane, + 1,4-dioxane, + oxolane, or + 1,3-dioxolane have been measured with an LKB microcalorimeter and an Anton Paar density meter, respectively. Results were correlated by polynomial equations of the type  $X^E = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k$ . The results are interpreted in terms of molecular interactions.

#### Introduction

The present paper forms the final part of the program to measure excess properties for several binary mixtures containing some methyl-substituted benzene compounds as a common component + some cyclic ethers. The binary mixtures studied in the present work include 1,2,4-trimethylbenzene + four cyclic ethers, oxane, 1,4-dioxane, oxolane, or 1,3-dioxolane.