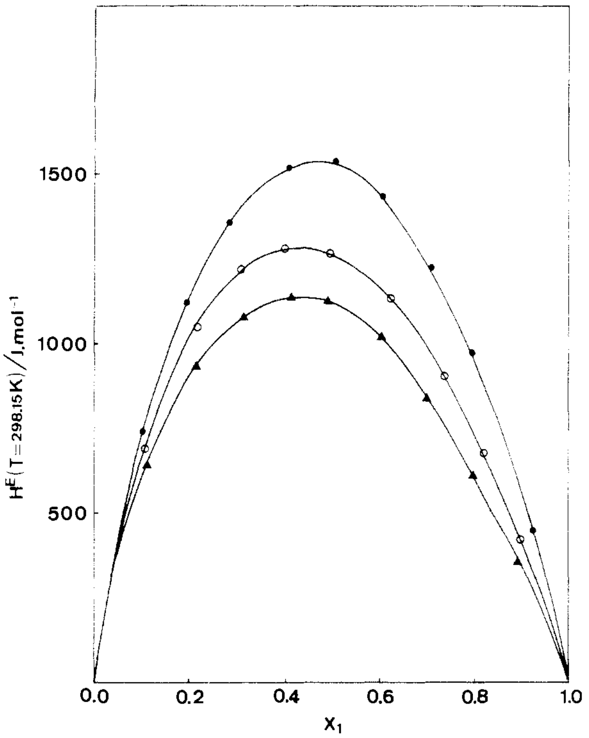

Figure 2. Experimental molar excess enthalpies, H^E, of alkanenitrile (1) + cyclohexane (2) mixtures at 298.15 K vs x_1, the mole fraction of alkanenitrile: ●, propanenitrile; ○, butanenitrile; ▲, pentanenitrile.

where x_1 is the mole fraction of alkanenitrile and x_2 the mole fraction of *n*-alkane or cyclohexane.

The values of the coefficients a_i and the standard deviations $\sigma(H^E)$,

$$\sigma(H^E) = [\sum(H^E_{sm} - H^E_{exp})/(N - n)]^{1/2} \qquad (2)$$

where N is the number of experimental points and n the number of coefficients a_i, were determined by a least-squares fit and are reported in Table I.

Our H^E measurements on propanenitrile or butanenitrile + hexane and butanenitrile + hexane agree to better than 3% with the data reported by McLure et al. (*13*).

Discussion

As shown in Figures 1 and 2, the values of H^E are large and positive; this behavior is mainly due to breaking of dipole–dipole interactions between the alkanenitrile molecules. Since the dipole moments (*17*) of the alkanenitriles are similar, it is the decreasing surface fraction of the CN group that determines the decrease of H^E with increasing number of $-CH_2-$ groups in the alkanenitriles.

A detailed interpretation of these results in terms of the DISQUAC group contribution model (*6*) will be presented separately.

Glossary

a_i	coefficients in eq 1
H^E	molar excess enthalpy, J mol^{-1}
n	number of coefficients a_i in eq 1
N	number of experimental points
T	temperature, K
x_i	mole fraction in liquid phase of component i (i = 1, alkanenitrile; i = 2, *n*-alkane or cyclohexane)
$\sigma(H^E)$	standard deviation, eq 2, J mol^{-1}

Subscripts

exp	experimental value
sm	smoothed value

Literature Cited

(1) Kehiaian, H. V. *Pure Appl. Chem.* **1985**, *57*, 15.
(2) Kehiaian, H. V.; Marongiu, B. *Fluid Phase Equilib.* **1985**, *21*, 197.
(3) Kehiaian, H. V.; Marongiu, B. *Fluid Phase Equilib.* **1986**, *27*, 445.
(4) Marongiu, B.; Dernini, S.; Polcaro, A. M. *J. Chem. Eng. Data* **1986**, *31*, 185.
(5) Marongiu, B.; Dernini, S.; Lepori, L.; Matteoli, E.; Kehiaian, H. V. *J. Chem. Eng. Data* **1988**, *33*, 118.
(6) Kehiaian, H. V.; Marongiu, B. *Fluid Phase Equilib.* **1988**, *40*, 23.
(7) McLure, I. A.; Trejo Rodriguez, A. T.; Ingham, P. A.; Steele, J. F. *Fluid Phase Equilib.* **1982**, *8*, 271.
(8) Vani, V.; Guha, S.; Gopal, E. S. R. *J. Chem. Phys.* **1986**, *84*, 3999.
(9) Lakhanpal, M. L.; Mandal, H. G.; Ahuja, S. C. *Indian J. Chem.* **1981**, *A20*, 1008.
(10) Palmer, D. A.; Smith, B. D. *J. Chem. Eng. Data* **1972**, *17*, 71.
(11) Amaya, K. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1278.
(12) Alessandrini, A.; Alessi, P.; Kikic, I. *Ann. Chim.* (*Rome*) **1980**, *70*, 293.
(13) McLure, I. A.; Trejo Rodriguez, A. *J. Chem. Thermodyn.* **1982**, *14*, 439. McLure, I. A. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1984**, 154-171.
(14) Valero, J.; Gracia, M.; Gutierrez Losa, C. *J. Chem. Thermodyn.* **1983**, *15*, 985; *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1984**, 172-179.
(15) Bares, D.; Soulie, M.; Metzger, J. *J. Chim. Phys.* **1973**, *70*, 1531.
(16) Marsh, K. N. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1973**, 2.
(17) Harrison, R. D. *Book of Data*; Nuffield Advanced Science; Longman Group: Harlow, Essex, England, 1984, p 110.

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Solubilities of 2,5- and 2,6-Xylenols in Supercritical Carbon Dioxide

Yoshio Iwai, Hiroshi Yamamoto, Yoshiyuki Tanaka, and Yasuhiko Arai*

Department of Chemical Engineering, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

The solubilities of 2,5- and 2,6-xylenols in supercritical carbon dioxide were measured by using a flow-type apparatus at 308.15 K up to 27 MPa. The appearance of a liquid phase was seen for the CO_2 + 2,6-xylenol system though the equilibrium temperature was lower than the melting point of 2,6-xylenol. The solubilities of 2,5-xylenol were correlated by a three-constant cubic equation of state with the 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. The supercritical fluid extraction is showing promise as a separation method (*2*). Solubility data of coal-derived components in supercritical fluids are very important as a fundamental knowledge. Correlation methods are also important in the design of a supercritical extraction pro-

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Table I. Experimental Solubilities of 2,5- and 2,6-Xylenol at 308.15 K

p, MPa	10^3y_2	ρ_1,[a] kg/m^3	$10^{-3}E$[b]
	2,5-Xylenol (mp = 75 °C)[c]		
7.4	0.365	255.5	0.223
8.7	4.88	648.3	3.476
10.7	7.37	731.3	6.460
13.4	8.57	789.9	9.474
16.4	9.80	831.2	13.24
20.7	10.7	873.3	18.28
23.7	11.3	896.5	21.97
26.7	11.6	916.3	25.41
	2,6-Xylenol (mp = 49 °C)[c]		
10.3	310[d]		
20.7	271[d]		

[a] Densities of carbon dioxide were calculated by using an equation of state proposed by Adachi et al. (*8*). [b] Enhancement factor was evaluated by using p_2^{sat} (35 °C), which is 12.145 Pa cited from Andon et al. (*9*). [c] Reference 10, p C-434. [d] Liquid phase must be coexisting.

cess. In the present work, solubilities of 2,5- and 2,6-xylenols in supercritical carbon dioxide were obtained and those of 2,5-xylenol were correlated by using a three-constant cubic equation of state (*3*, *4*) with two characteristic parameters.

Experimental Section

Equipment and Procedures. A flow-type apparatus was used to determine solubilities of solid-state xylenols in supercritical carbon dioxide. A detailed description of the equipment and operating procedures is given elsewhere (*5*). Solubilities were determined from the weight of the solute and the volume of carbon dioxide. 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. The amount of solute trapped was determined with a balance, and the volume of carbon dioxide was measured by a wet gas meter. The temperature of water bath containing a high-pressure equilibrium cell was controlled within ±0.1 °C, and the equilibrium pressure was measured by using a Bourdon gauge calibrated against a strain pressure gauge (accuracy ±0.3%). Usually, 0.5–1 g of solute was trapped, and the flow rate of carbon dioxide was adjusted to be 1–3 cm^3/s. Validation of the experimental procedure made by comparison with literature data for the solubility of naphthalene in carbon dioxide (*6*, *7*) is reported in ref 5.

Materials. Reagent-grade 2,5-xylenol (supplied by Tokyo Kasei Co., Ltd.) and 2,6-xylenol (supplied by Nakarai Chemicals, Ltd.) were used without further purification. Gas chromatographic analysis indicated that their purities were more than 99.0% and 99.9%, respectively. High-purity CO_2 (more than 99.9%, Seitetsu Kagaku Co., Ltd.) was used as received.

Results and Discussion

The experimental solubilities of 2,5- and 2,6-xylenols in supercritical carbon dioxide at 308.15 K up to 27 MPa are given in Table I. The solubility measurements were carried out under several flow rates at given pressures as shown in Figure 1. As illustrated, the solubilities obtained are independent of flow rates. This shows that they were determined under equilibrium conditions. The reproducibility of the solubilities is within 4% and 1% in the pressure range below 10 MPa and above 10 MPa, respectively. The values listed in Table I are given by an arithmetic average of several data points at each pressure.

As shown in Table I, the solubilities of 2,6-xylenol are much higher than those of 2,5-xylenol. Therefore, the solute packed in the high-pressure equilibrium cell was watched closely after the solubility measurements. The condition of the solid solute indicated that a liquid phase must be appearing under the high-pressure experimental condition. Therefore, the solubility measurement for 2,6-xylenol was not continued because liquid-phase compositions could not be determined by using the present apparatus.

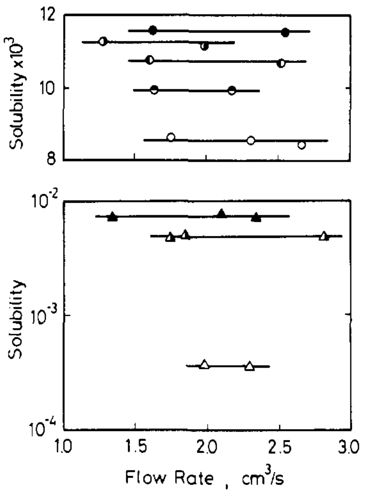

Figure 1. Relationship between solubilities (mole fraction) and flow rates: (●) 26.7 MPa; (◑) 23.7 MPa; (◐) 20.7 MPa; (◒) 16.4 MPa; (○) 13.4 MPa; (▲) 10.7 MPa; (◭) 8.7 MPa; (△) 7.4 MPa.

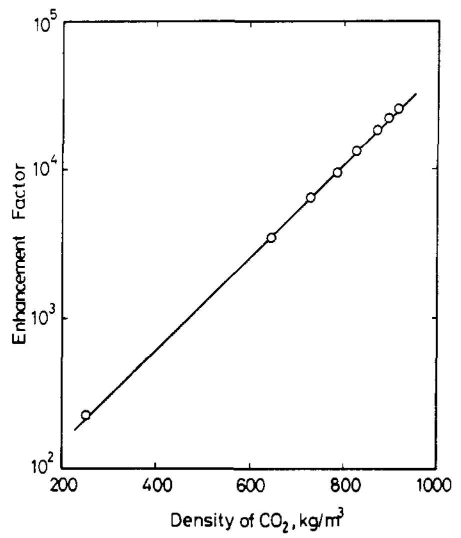

Figure 2. Relationship between enhancement factor and density of pure CO_2.

According to Schmitt et al. (*11*), the enhancement factor $E = py_2/p_2^{sat}$ was plotted against the density (ρ) of carbon dioxide. Figure 2 shows a good linear relationship between E and the ρ of CO_2. This indicates that the present solubility data seem to be consistent.

Correlation

For the correlation of the experimental results of 2,5-xylenol, we used the following expression:

$$y_2 = \frac{p_2^{sat}}{p}\frac{1}{\phi_2^G}\exp\left[\frac{v_2^S(p - p_2^{sat})}{RT}\right] \qquad (1)$$

where p and T respectively denote the equilibrium pressure and temperature, p_2^{sat} and v_2^S respectively are the saturation pressure and solid-state molar volume of solute, and ϕ_2^G means the

Table II. Physical Properties of CO_2 and 2,5-Xylenol

component	T_C, K	p_C, MPa	ω	$10^3 v^S$, m^3/mol	p^{sat}, Pa
CO_2	304.2[a]	7.38[a]	0.225[a]		
2,5-xylenol	706.9[b]	4.86[b]	0.565[c]	0.1257[d]	12.15[e]

[a] Reference 13. [b] Reference 14. [c] Given as an average value obtained from two vapor pressure equations in ref 15 (p 629, p 630) by definition. [d] Obtained from an averaged density of 2,4- 3,4-, and 3,5-xylenols given in ref 10 (p C-434, p C-435) because no density data for 2,5-xylenol are reported. [e] Reference 9.

vapor-phase fugacity coefficient of the solute. To evaluate ϕ_2^G, the following cubic equation of state proposed by Yu et al. (*3*, *4*) 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 by using the values of critical properties p_C and T_C and the Pitzer's acentric factor ω. Application of eq 2 to supercritical components and solid-state components was discussed in detail in a previous study (*12*). To apply eq 2 to a binary 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_2^G can be thermodynamically derived (*5*, *12*). As discussed previously (*12*), 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 2,5-xylenol were correlated by using the properties of pure components listed in Table II. The values of k_{ij} and l_{ij} were determined by fitting calculated results to experimental data. As shown in Figure 3, the present experimental results are correlated within 6.2%.

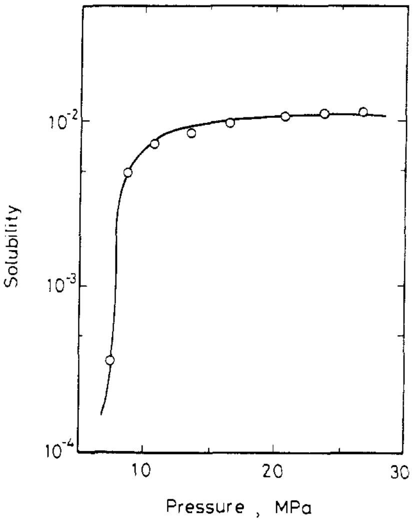

Figure 3. Solubilities (mole fraction) of 2,5-xylenol in supercritical CO_2 at 308.15 K: (O) experimental data; (—) calculated with $k_{ij} = -0.106$ and $l_{ij} = -0.518$.

Glossary

a	parameter of eq 2, m^6 Pa/mol^2
b	parameter of eq 2, m^3/mol
c	parameter of eq 2, m^3/mol
E	enhancement factor
k_{ij}	characteristic parameter between unlike molecules *i* and *j*
l_{ij}	characteristic parameter between unlike molecules *i* and *j*
p	pressure, Pa
p_C	critical pressure, Pa
p^{sat}	saturation pressure, Pa
R	gas constant, m^3 Pa/(mol K)
T	temperature, K
T_C	critical temperature, K
v	molar volume, m^3/mol
v^S	solid-state molar volume, m^3/mol
y	solubility (mole fraction)
ϕ^G	gas-phase fugacity coefficient
ω	Piter's acentric factor

Subscripts

i,*j*	components *i* and *j*
1	CO_2
2	2,5-xylenol or 2,6-xylenol

Registry No. CO_2, 124-38-9; 2,5-xylenol, 95-87-4; 2,6-xylenol, 576-26-1.

Literature Cited

(1) Yoshitomi, S.; Nobe, Y.; Ukegawa, K. *Nenryo Kyokaishi* **1988**, *67*, 2.
(2) Arai, Y.; Iwai, Y.; Yamamoto, H. *Nenryo Kyokaishi* **1988**, *67*, 822.
(3) Yu, J.-M.; Lu, B. C.-Y. *Fluid Phase Equilib.* **1987**, *34*, 1.
(4) Yu, J.-M.; Lu, B. C.-Y.; Iwai, Y. *Fluid Phase Equilib.* **1987**, *37*, 207.
(5) Iwai, Y.; Yamamoto, H.; Sohda, M.; Tanaka, Y.; Shimizu, T.; Arai, Y. *Mem. Fac. Eng., Kyushu Univ.* **1989**, *49*, 175.
(6) McHugh, M. A.; Paulaitis, M. E. *J. Chem. Eng. Data* **1980**, *25*, 326.
(7) Tsekhanskaya, Yu. V.; Iomtev, M. B.; Mushkina, E. V. *Russ. J. Phys. Chem.* **1964**, *38*, 1173.
(8) Adachi, Y.; Sugie, H.; Lu, B. C.-Y. *Fluid Phase Equilib.* **1986**, *28*, 119.
(9) Andon, R. J. L.; Biddiscombe, D. P.; Cox, J. D.; Handley, R.; Harrop, D.; Herrington, E. F. G.; Martin, J. F. *J. Chem. Soc.* **1960**, 5246.
(10) Weast, R. C., Melvin, J. A., Eds. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1982.
(11) Schmitt, W. J.; Reid, R. C. *Supercritical Fluid Technology*; Penninger, et al., Eds.; Elsevier: Amsterdam, 1985; p 123.
(12) Iwai, Y.; Lu, B. C.-Y.; Yamamoto, H.; Arai, Y. *Kagaku Kogaku Ronbunshu* **1989**, *15*, 676.
(13) Reid, R. D.; Prausnitz, J. M.; Sherwood, K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.
(14) Simmrock, K. H.; Janowsky, R.; Ohnsorge, A. *Critical Data of Pure Substances*; Chemical Data Series; DECHEMA: Frankfurt/Main, FRG, 1986; Vol. II, Part 2, p 614.
(15) Boublik, T.; Fried, V.; Hala, E. *The Vapour Pressures of Pure Substances*; Phys. Science Data 17; Elsevier: Amsterdam, 1984.

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