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Solubilities of Azobenzene, *p*-Hydroxyazobenzene, and *p*-Dimethylaminoazobenzene in Supercritical Carbon Dioxide

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The solubilities of azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene which were suitable for dyeing from supercritical carbon dioxide (SC-CO_2) were measured at 308.2 K and 318.2 K over the pressure range from 9.1 MPa to 25.3 MPa by a flow type apparatus. The solubilities were determined from the mass of solute trapped by decompression and the volume of released CO_2. Solubility data were correlated by a solution model based on the regular solution concept.

Introduction

Recently the textile industry has put significant effort into its social obligation to reduce large amounts of solvent waste discharged to the environment in its dyeing process (Saus et al.[1]). Because of this environmental task, supercritical fluid dyeing has been attracting much attention as an environmentally benign procedure. Carbon dioxide (CO_2), which is inexpensive, essentially nontoxic, and nonflammable, has easily accessible critical conditions, that is, $T_c = 31$ °C and $P_c = 7.37$ MPa. In some cases, it may be utilized as an environmentally benign solvent substitute for hydrocarbons, chlorofluorocarbons, and other organics.[2−8] To aid design and optimization of the textile dyeing in supercritical carbon dioxide (SC-CO_2), solubilities of dyes are needed. Although studies have been made on solubilities of many compounds in SC-CO_2,[8−11] little is known about azobenzene derivatives which are generally used as dye chromogen in the textile industry.

In this work, the solubilities of azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene in SC-CO_2 at 308.2 K and 318.2 K over the pressure range from 9.1 MPa to 25.3 MPa were measured by a flow type apparatus. The solubilities of these substances were correlated by a solution model based on the regular solution concept proposed by Ziger and Eckert.[12]

Experimental Section

Apparatus and Procedures. A flow type apparatus was used to measure the solubilities of azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene in supercritical carbon dioxide (SC-CO_2). A detailed description of the apparatus and operating procedures is given in our previous paper.[10] The liquefied CO_2 leaving a gas cylinder was passed through a cooling unit to prevent vaporization of CO_2 from warming up and was directed to a compressor which was capable of a delivery pressure up to about 60 MPa and delivery rates up to 5.2 mL·min^{-1} (liquefied CO_2 basis). A back-pressure regulator was used to maintain a constant pressure with the pressure control accuracy of ±0.1 MPa. The equilibrium pressure was measured by a Bourdon gauge calibrated against a strain pressure gauge (accuracy ±0.3%). CO_2 passed through a preheating coil and then entered in two equilibrium cells containing azobenzene, *p*-hydroxyazobenzene, or *p*-dimethylaminoazobenzene. The cells were constructed from 316 Stainless Steel, and the inner diameter, height, and volume were 30 mm, 30 cm, and 210 cm^3, respectively. The solid component was packed in the second cell with glass beads to prevent channeling, while the first cell was used as a buffer tank. These cells were attached to a preheating coil and submerged in a water bath controlled with a temperature control accuracy of ±0.1 K. The supercritical fluid (SCF) saturated with the solid component was decompressed through an expansion valve and introduced into a U-shaped glass tube cooled in an ice bath. Gaseous CO_2 and the solid component were separated in the tube. The amount of the trapped solid component was determined by mass. The solute collected in the tubes was weighed by a direct reading balance (Exact A−V; accuracy 0.1 mg). The volume of released CO_2 was measured by a wet-gas meter that was calibrated to an accuracy of ±0.4%. Usually 0.1−0.3 g of solute was trapped, and the flow rate of expanded CO_2 was adjusted to be 0.30−0.85 L·min^{-1} (gaseous CO_2 basis). A small amount of the solid remaining in the tube and the expansion valve were removed and trapped by using SC-CO_2 through a bypass line.

Materials. Azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene were purchased from Tokyo Kasei Kogyo Co. Ltd. These chemicals have the azobenzene group as chromogen. The chemical structures of these substances are shown in Figure 1. Estimated purities determined by gas chromatographic analysis were better than 98% for all substances. High-purity CO_2 (more than 99%, Fukuoka Sanso Co. Ltd.) was used as received.

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Table 1. Mole Fraction Solubilities, y_2, of Azobenzene, *p*-Hydroxyazobenzene, and *p*-Dimethylaminoazobenzene in SC-CO_2

azobenzene				*p*-hydroxyazobenzene				*p*-dimethylaminoazobenzene			
$T = 308.2$ K		$T = 318.2$ K		$T = 308.2$ K		$T = 318.2$ K		$T = 308.2$ K		$T = 318.2$ K	
p/MPa	10^3y_2	p/MPa	10^3y_2	p/MPa	10^3y_2	p/MPa	10^3y_2	p/MPa	10^4y_2	p/MPa	10^4y_2
9.1	3.64	9.1	2.99	9.1	2.57	9.1	1.83	9.1	4.37	9.1	3.22
10.1	4.06	10.1	5.13	10.1	2.75	10.1	3.29	10.1	4.67	10.1	5.37
15.2	5.04	15.2	8.24	15.2	3.45	15.2	5.16	15.2	7.24	15.2	10.3
20.3	5.54	20.3	9.26	20.3	3.54	20.3	5.93	20.3	8.29	20.3	12.3
25.3	5.98	25.3	9.84	25.3	3.95	25.3	6.36	25.3	9.05	24.5	12.5

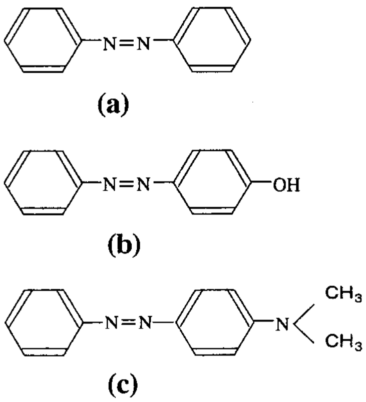

Figure 1. Chemical structures of azobenzene (a), *p*-hydroxyazobenzene (b), and *p*-dimethylaminoazobenzene (c).

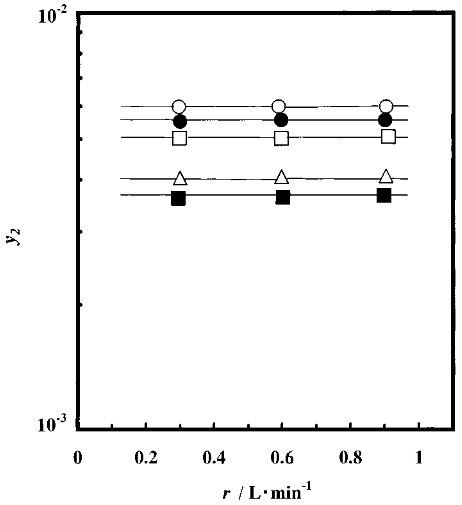

Figure 2. Relationship between the mole fraction solubility of azobenzene in SC-CO_2 at 308.2 K over the pressure range from 9.1 MPa to 25.3 MPa and the flow rate of expanded CO_2: (■) 9.1 MPa; (△) 10.2 MPa; (□) 15.2 MPa; (●) 20.3 MPa; (○) 25.3 MPa.

Results and Discussion

The measurements were carried out for several flow rates of CO_2 at known pressures, as shown in Figure 2, where r is the flow rate (gaseous CO_2 basis). The solubilities of azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene were independent of the flow rate of expanded CO_2, where the condition of CO_2 is standard state temperature and pressure. Similar results were obtained for flavone and 3-hydroxyflavone.[10] This shows that the solubilities of azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene were measured under equilibrium conditions in the flow type apparatus. The reproducibility of these solubilities was within ±4.0% when the pressure was varied from 9.1 MPa to 25.3 MPa. The experimental values listed in Table 1 were obtained from an arithmetic average of several measurements at each pressure. Experimental data of azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene at 308.2 K and 318.2 K are given in Figures 3−5. Just above the critical pressure of CO_2, the solubilities of azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene drastically increase because of a rapid increase in density with pressure. For pressures above 10 MPa, the solubility increases with increasing temperature because the decrease in CO_2 density cannot overcome the increase in vapor pressure. The solubility of azobenzene that has the smallest molecular mass is the largest. For these sub-

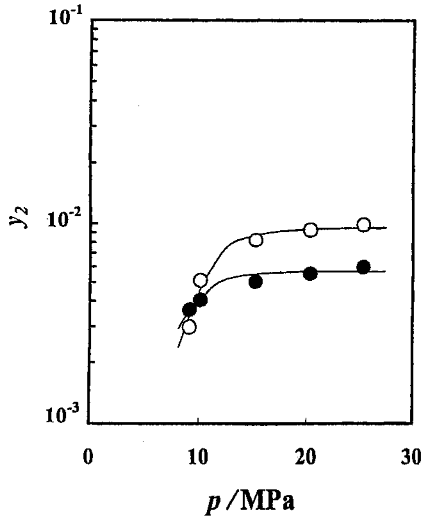

Figure 3. Mole fraction solubilities of azobenzene in SC-CO_2: (●) experimental data at 308.2 K; (○) experimental data at 318.2 K; (—) calculated results.

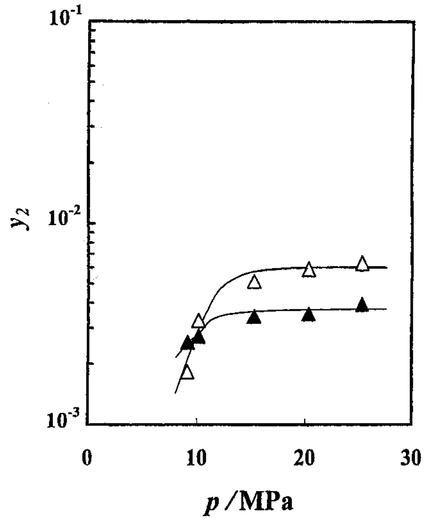

Figure 4. Mole fraction solubilities of *p*-hydroxyazobenzene in SC-CO_2: (▲) experimental data at 308.2 K; (△) experimental data at 318.2 K; (—) calculated results.

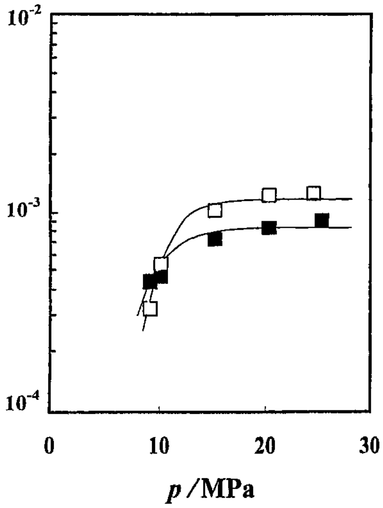

Figure 5. Mole fraction solubilities of *p*-dimethylaminoazobenzene in SC-CO_2: (■) experimental data at 308.2 K; (△) experimental data at 318.2 K; (—) calculated results.

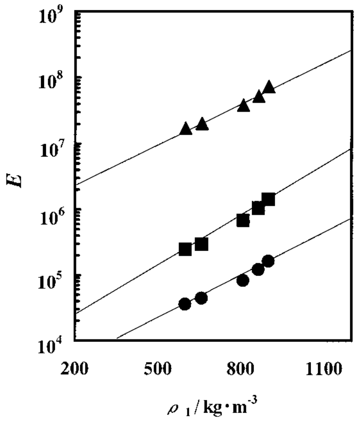

Figure 6. Relationship between the enhancement factor *E* and the density of pure CO_2 ρ_1: (●) azobenzene at 308.2 K; (▲) *p*-hydroxyazobenzene at 308.2 K; (■) *p*-dimethylaminoazobenzene at 308.2 K; (—) results calculated by eq 1.

Table 2. Coefficients in Eq 1

solute	*T*/K	*A*	10^3B/m^3 kg^{-1}
azobenzene	308.2	7.515	4.873
	318.2	7.831	4.349
p-hydroxyazobenzene	308.2	13.81	4.655
	318.2	13.50	4.417
p-dimethylaminoazobenzene	308.2	8.854	5.813
	318.2	9.230	4.853

stances, the solubility increases with a decrease in the molecular mass.

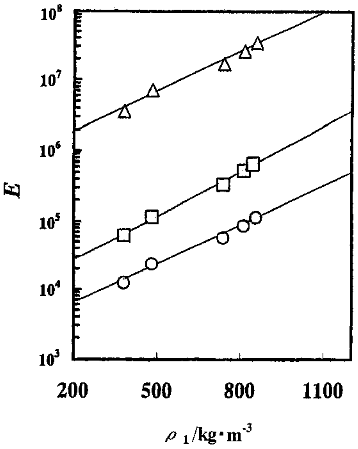

Figure 7. Relationship between the enhancement factor *E* and the density of pure CO_2 ρ_1: (○) azobenzene at 318.2 K; (△) *p*-hydroxyazobenzene at 308.2 K; (□) *p*-dimethylaminoazobenzene at 318.2 K; (—) results calculated by eq 1.

To confirm the reliability of the experimental data, the enhancement factor, $E = py_2/p_2^{sat}$,[13] was plotted against the density of pure CO_2, ρ_1, where y_2 is the solubility of the solid component in the SCF and *p* is the equilibrium pressure. The saturated vapor pressure, p_2^{sat}, was calculated by the Lee–Kesler equation, where the critical temperature, T_c, and critical pressure, P_c, were obtained by Lydersen's method.[14] The density of CO_2 was calculated by the equation of state of Angus et al.[15] As shown in Figures 6 and 7, it was observed that the logarithm of the enhancement factor, ln *E*, was a linear function of the solvent density, ρ_1, for each component. However, despite the fact that the solubility of *p*-hydroxyazobenzene in SC-CO_2 is higher than that of *p*-dimethylaminoazobenzene, the enhancement factor of *p*-hydroxyazobenzene is higher than that of *p*-dimethylaminoazobenzene. This may be caused by the estimated standard vapor pressure. The calculated saturated vapor pressure of *p*-hydroxyazobenzene, which has a hydroxyl group, is lower than that of *p*-dimethylaminoazobenzene, which has a dimethyl group. Similar results have been reported for naphthol and dimethylnaphthalene.[16] The relationship between the enhancement factor and the density of CO_2 can be represented by the following equation:

$$\ln E = A + B\rho_1 \qquad (1)$$

where the coefficients *A* and *B* are given in Table 2.

Correlation

Some methods for correlating and estimating the solubilities of solutes in supercritical carbon dioxide have been available.[17-19] To confirm the reliability of measured solubility data, we used a basic solution model. Ziger and Eckert[12] have assumed that the solubility of the solid component in SCF is expressed by a solution model based on the regular solution concept:

$$\ln E = \eta\left[\frac{v_2^{S}(2\delta_1\delta_2 - \delta_1^{2})}{RT} - \ln\left(1 + \frac{\delta_1^{2}}{p}\right)\right] + \nu \qquad (2)$$

Table 3. Physical Properties of Azobenzene, *p*-Hydroxyazobenzene, and *p*-Dimethylaminoazobenzene

					10^7p_2sat/Pa	
substance	T_c/K	P_c/MPa	$10^4v_2^s$/m^3 mol^{-1}	δ_2/MPa$^{1/2}$	*T* = 308.2 K	*T* = 318.2 K
azobenzene	792.9[a]	2.576[a]	1.020[b]	23.91[c]	9.228[d]	22.22[d]
p-hydroxyazobenzene	877.2[a]	3.015[a]	1.065[b]	27.27[c]	0.01355[d]	0.04647[d]
p-dimethylaminoazobenzene	839.8[a]	2.106[a]	1.312[b]	22.94[c]	0.1592[d]	0.4728[d]

[a] Estimated by the Lydersen method. [b] Estimated by the relation $v_2^s = 1.5V_w$, where V_w is given by the Bondi method. [c] Estimated by the Fedors method. [d] Estimated by the Lee–Kesler equation.

Table 4. Optimized Values of η and ν in Eq 2 and Deviations

substance	T/K	η	ν	$100\sigma^a$
azobenzene	308.2	1.005	7.691	5.02
	318.2	0.9747	7.783	7.08
p-hydroxyazobenzene	308.2	0.7997	13.94	6.23
	318.2	0.8171	13.46	8.42
p-dimethylaminoazobenzene	308.2	0.9784	8.982	6.22
	318.2	0.8058	9.470	8.84

[a] $\sigma = (1/N)\Sigma^N|y_{\mathrm{exp}} - y_{\mathrm{calc}}|/y_{\mathrm{exp}}$, where N is the number of data.

where T is the absolute temperature, R is the universal gas constant, δ_1 is the solubility parameter of SC-CO_2 calculated by the method proposed by Giddings et al.,[20] p is the experimental pressure, δ_2 is the solubility parameter of the solid component calculated by Fedors' method,[21] v_2^s is the molar volume of the solid component, and η and ν are the parameters defined by eq 2, respectively. v_2^s is nearly proportion to the hard-core van der Waals volume, V_w, which was obtained by the method of Bondi.[22] As shown by Yamamoto et al.,[16] we assumed that the proportionality constant, $K = v_2^s/V_w$, was about 1.5. So the v_2^s values for azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene were calculated with their values of V_w and $K = 1.5$. The physical properties of azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene are shown in Table 3. The values of η and ν can be calculated by using a generalized linear least-squares approach. They are listed in Table 4. The logarithm of the enhancement factor has been correlated well by the regular solution model. The solubilities of azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene in SC-CO_2 can also be well represented, as shown in Figures 3−5.

Conclusion

The solubilities of azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene in SC-CO_2 were measured by using a flow type apparatus at 308.2 K and 318.2 K over the pressure range from 9.1 MPa to 25.3 MPa. Furthermore, the solubilities of these substances in SC-CO_2 have been correlated by using a solution model based on the regular solution concept. It was shown that the solubilities of these substances could be correlated with fairly good accuracy.

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