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Solubility of Disperse Anthraquinone and Azo Dyes in Supercritical Carbon Dioxide at 313.15 to 393.15 K and from 10 to 25 MPa

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The solubility of disperse dyes in supercritical CO_2 was measured for three anthraquinone dyes (i.e., Celliton fast blue B, 1-amino-2-methylanthraquinone, and 1-(methylamino)anthraquinone) and two azo dyes (i.e., disperse red 1 and 4-[4-(phenylazo)phenylazo]-*o*-cresol). Measurement was carried out at 313.15 K, 353.15 K, and 393.15 K and (10, 15, 20, and 25) MPa in an autoclave-type phase equilibrium apparatus. The data were modeled by a semiempirical correlation. For all the dyes, the solubility increased with increasing density of supercritical CO_2. The anthraquinone dyes show higher solubility than the azo dyes.

Introduction

Conventionally the dispersed wet dyeing method has been widely used in coloring synthetic textiles such as poly(ethylene terephthalate)s. However, this process has intrinsic environmental problems such as water pollution due to the inevitable use of an excess amount of water and the discharge of various chemical additives (Kim, 1994). In recent years, a new concept of supercritical fluid dyeing (SFD) has been actively tested as a possible replacement of the traditional wet dyeing process (Saus et al., 1993; Gebert et al., 1994; Knittel et al., 1993; Özcan et al., 1997).

If the dry-SFD is applicable to synthetic textiles, the environmental problems arising in relation to the wet dyeing processes can be significantly mitigated. However, necessary phase equilibrium data for systems of dye substances and supercritical fluids are lacking in the literature for reliable SFD process design. To provide the phase equilibrium properties in conjunction with the SFD, the effect of supercritical conditions on the solubility of disperse dyes in supercritical CO_2 was measured. The reliability of the experimental apparatus was confirmed by measuring solubility of cholesterol in CO_2 and by comparing the data with those reported in the literature (Wong et al., 1985). The measured solubility data were correlated by a semiempirical equation (Bartle et al., 1991).

Experimental Section

Reagents. Sample dye compounds, e.g., disperse blue 14 (commercial name, Celliton fast blue B, 97.9%), disperse orange 11 (1-amino-2-methylanthraquinone, 95%), 1-(methylamino)anthraquinone (98.0%), disperse red 1 (95%), and disperse yellow 7 (4-[4-(phenylazo)phenylazo]-*o*-cresol, 95%) were purchased from Aldrich Chemicals, United States. These solutes are used directly without further purification. The chemical structure of the dye samples is shown in Figure 1. CO_2 (99.9%) was purchased from Seoul Gas Co. (Seoul, Korea).

SFD Apparatus. An autoclave-type high-pressure and high-temperature apparatus was used, and the schematic diagram is shown in Figure 2. The internal volume of the stainless steel 316 equilibrium cell was 60 cm^3. The cell was immersed in a heating mantle, and the apparatus was designed to be operated safely up to 473.15 K and 40 MPa. To minimize pressure disturbances, a reservoir tank (1 L) was installed in front of the preheater. Pressure at the cell was maintained by a gas booster (HASKEL 75/15, United States) and measured by a Heise pressure gauge (HEISE MM-43776, United States) within the uncertainty range ±0.05 MPa. The equilibrium temperature was controlled by a PID controller (DX9, Hanyoung Co., Korea) within the ±1.0 K range. The error range of measured temperatures was within ±0.1 K, which was confirmed by a standard high-precision thermometer (Witeg, Germany).

The CO_2 was preheated before flowing into the cell. The temperature was measured at the inlet, at the outlet, and inside the cell. The flow rate of effluent from the cell was controlled and measured by a mass flow meter/controller (Bronkhorst Hi-Tec, AK Ruurlo, Netherlands). The flow rates adopted in the experiment were in the range of (120−180) mL/min, and the accuracy of the flow meter was within ±1% of full scale range. To assist intimate contact of CO_2 and the powder dye, the sample dye was thinly held on each inside of multilayer-packed filter papers in the equilibrium cell. The equilibrated effluent was passed through a two-step acetone trap where the dissolved dye was separated from CO_2. After each experimental run, the whole line of the apparatus was rinsed by methanol, chloroform, and acetone, respectively, and dried. The residual solvents in the separated solute were completely removed by a rotary vacuum evaporator. For each sample solute, the experiment was repeated three to five times and averaged.

Spectroscopic Analysis. Since all the sample dyes have a coloring pattern and unique maximum frequency, λ_{max}, the amount of each solute was analyzed by a UV−visible recording spectrophotometer (UV-240, Shimadzu, Japan). The calibration curve for each solute was constructed within an uncertainty range of ±0.5%.

Correlation of the Solubility

The results from the present study were correlated by a simple semiempirical equation (Bartle et al., 1991; Özcan

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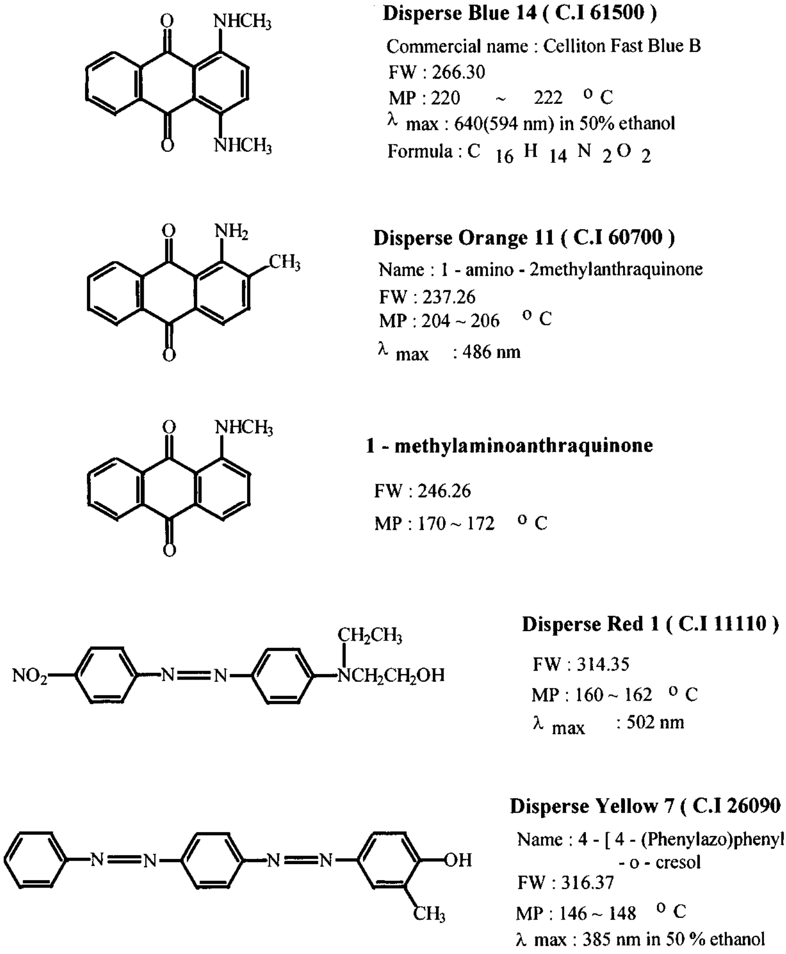

Disperse Blue 14 (C.I 61500)

Commercial name : Celliton Fast Blue B
FW : 266.30
MP : 220 ~ 222 °C
λ max : 640(594 nm) in 50% ethanol
Formula : $C_{16}H_{14}N_2O_2$

Disperse Orange 11 (C.I 60700)

Name : 1 - amino - 2methylanthraquinone
FW : 237.26
MP : 204 ~ 206 °C
λ max : 486 nm

1 - methylaminoanthraquinone

FW : 246.26
MP : 170 ~ 172 °C

Disperse Red 1 (C.I 11110)

FW : 314.35
MP : 160 ~ 162 °C
λ max : 502 nm

Disperse Yellow 7 (C.I 26090)

Name : 4 - [4 - (Phenylazo)phenylazo] - o - cresol
FW : 316.37
MP : 146 ~ 148 °C
λ max : 385 nm in 50 % ethanol

Figure 1. Chemical structure of disperse dyes tested.

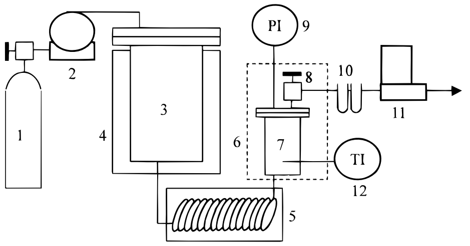

Figure 2. Schematic diagram of flow-type experimental equilibrium apparatus: 1, CO_2 tank; 2, gas booster; 3, reservoir; 4, heating mantle; 5, preheater; 6, temperature controller; 7, equilibrium cell; 8. metering valve; 9, pressure indicator; 10, cold trap; 11, mass flow meter; 12, temperature indicator.

et al., 1997). The model equation is given in eq 1

$$\ln\left(\frac{y_2 p}{p_{\mathrm{ref}}}\right) = A + c(\rho - \rho_{\mathrm{ref}}) \qquad (1)$$

where y_2 is the mole fraction solubility, p is the pressure, A and c are constants, p_{ref} is a standard pressure of 1 bar, ρ is the density of the solution, and ρ_{ref} is a reference density for which a value of 700 kg m^{-3} was used for calculations. The reason for using ρ_{ref} is to make the value of A much less sensitive to experimental error in the data and to avoid the large variations caused by extrapolation to zero density. A is given by

$$A = a + (b/T) \qquad (2)$$

where T is the absolute temperature. Combining eqs 1 and 2, the model equation becomes

$$\ln\left(\frac{y_2 p}{p_{\mathrm{ref}}}\right) = a + \frac{b}{T} + c(\rho - \rho_{\mathrm{ref}}) \qquad (3)$$

From the experimental data, each isotherm was fitted using eq 1 to obtain values A and c. The values c were then averaged for each dye, and values given in Table 2 were obtained. Afterward, the isotherms were refitted to obtain new values of A using the averaged values of c. These values were plotted against $1/T$ for each dye, and values a and b were obtained from eq 2, which are also given in Table 2.

Results and Discussion

To determine reliability of the apparatus used in this work with others, the solubility of cholesterol in CO_2 was measured over a wide range of temperatures and pressures and compared with literature data (Wong et al., 1985). A comparison is shown in Figure 3. We concluded that the data measured in this study are agree reasonably well with the literature solubility data within percent relative standard deviation (AAD) ±5%.

The measured averaged solubility, $\langle y_2 \rangle$, and the percent relative deviation (RSD%) of the measured solubility of sample dyes in supercritical CO_2 at temperatures (313.15, 353.15, and 393.15) K and pressures (10, 15, 20, and 25) MPa are summarized in Table 1. The solubility in general increases with increase in the temperature and the pressure of CO_2. Also, the low molecular weight anthraquinone dyes (i.e., disperse orange, blue and 1-(methylamino)-

Table 1. Measured Average Mole Fraction Solubility, $\langle y_2 \rangle$, of Disperse Dyes in Supercritical Carbon Dioxide

		$10^7 \langle y_2 \rangle$ [RSD%[a]]		
name	p/MPa	T/K = 313.15	353.15	393.15
disperse orange 11	10	10.78 [0.5]	3.64 [25.0]	11.67 [19.6]
	15	31.87 [14.6]	24.57 [4.1]	48.05 [1.1]
	20	70.23 [10.6]	87.13 [4.6]	134.35 [4.5]
	25	82.02 [5.1]	181.35 [8.8]	360.28 [4.0]
1-(methylamino)-anthraquinone	10	16.6 [18.1]	3.83 [9.1]	28.02 [14.2]
	15	59.62 [8.2]	13.89 [12.3]	56.5 [8.6]
	20	100.86 [8.0]	196.05 [14.4]	354.57 [8.8]
	25	155.8 [5.9]	350.01 [8.1]	951.61 [2.7]
disperse blue 14	10	2.34 [6.8]	0.79 [20.2]	3.48 [5.1]
	15	7.97 [15.1]	4.61 [21.6]	10.09 [12.1]
	20	13.39 [6.3]	21.11 [7.1]	31.57 [5.7]
	25	18.24 [4.9]	32.15 [1.8]	77.24 [4.2]
disperse red 1	10	0.81 [19.2]	0.45 [24.5]	2.36 [12.7]
	15	3.41 [2.3]	2.12 [12.1]	10.2 [17.6]
	20	6.44 [16.6]	14.33 [7.5]	51.81 [8.6]
	25	8.25 [19.1]	31.8 [6.7]	161.9 [3.0]
disperse yellow 7	10	3.99 [9.5]	1.21 [4.9]	4.79 [0.4]
	15	9.36 [9.4]	3.33 [8.4]	13.35 [7.9]
	20	29.71 [7.2]	47.06 [5.5]	88.40 [0.8]
	25	40.75 [2.1]	96.44 [4.7]	201.85 [1.0]

[a] RSD%: percent of relative standard deviation. RSD% = SD/$\langle y_2 \rangle \times 100$, where SD $= [(1/N)\sum_{i=1}^{N}(y_{2,i} - \langle y_2 \rangle)^2]^{0.5}$ and $\langle y_2 \rangle$ denotes average mole fraction.

Table 2. Best-Fit Parameters Used in the Calculation of Solubilities from Eq 3

name	A	b/K^{-1}	$10^2 c$/kg m^{-3}	AAD%[a]
disperse orange 11	18.70	−8451.4	1.21	21.5
1-(methylamino)-anthraquinone	21.80	−9257.2	1.22	9.2
disperse blue 14	15.63	−7919.3	1.08	18.5
disperse red 1	23.98	−10840.3	1.21	22.8
disperse yellow 7	20.54	−9333.1	1.25	17.3

[a] AAD% $= (1/N)[\sum_{i=1}^{N}|\{\langle y_{2,i} \rangle - y_{2,i}^{\text{cal}}\}/\langle y_{2,i} \rangle| \times 100]$, where the superscript "cal" denotes calculated mole fraction solubility.

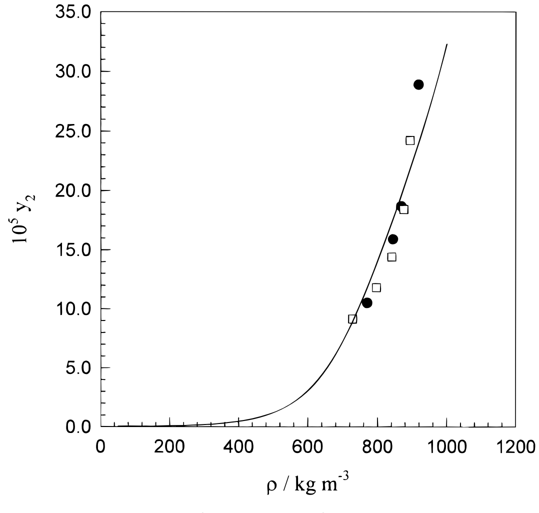

Figure 3. Comparison of solubility of cholesterol in supercritical CO_2 measured in this work with literature data: (●) data obtained in this work, (□) data reported by Wong et al., (1985).

anthraquinone) showed higher solubility than the azo dyes (i.e., disperse red and yellow). Among anthraquinone dyes, the low molecular weight dyes (i.e., disperse orange and 1-(methylamino)anthraquinone) were more soluble than the disperse blue. The correlated results by eqs 1 and 3 and absolute percent of fitting errors for each sample dye at the three isotherms are summarized in Table 2.

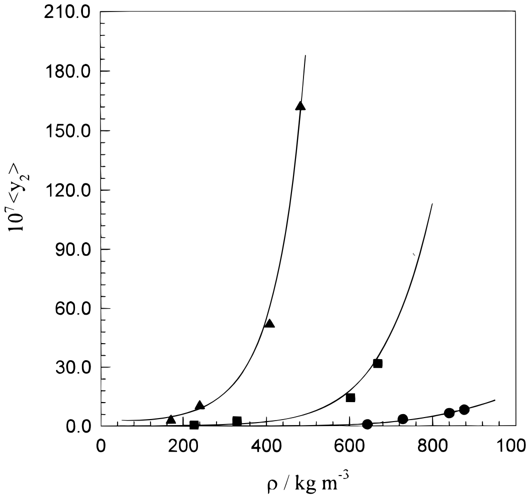

Figure 4. Solubiliy in mole fraction, y, for disperse blue 14 in supercritical CO_2. The graph shows the comparison of predicted curves (lines) and experimental points plotted versus density, ρ, of the average solubility, $\langle y_2 \rangle$: (●) 313.15 K; (■) 353.15 K; (▲) 393.15 K.

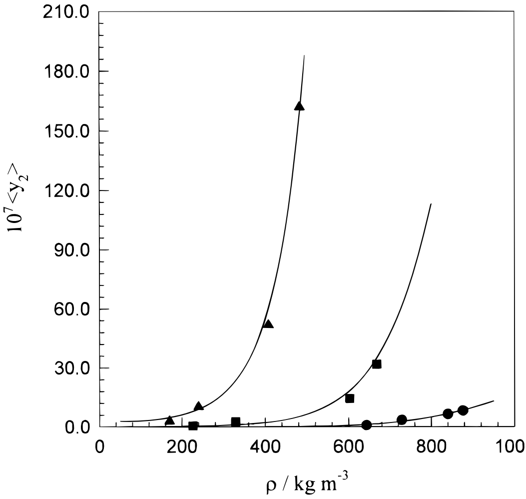

Figure 5. Solubiliy in mole fraction, y, for disperse red 1 in supercritical CO_2. The graph shows the comparison of predicted curves (lines) and experimental points plotted versus density, ρ, of the average solubility, $\langle y_2 \rangle$: (●) 313.15 K; (■) 353.15 K; (▲) 393.15 K.

Finally, calculated solubilities were compared with experimental values in Figures 4 and 5, using eq 3. The fraction solubility for disperse blue 14 is shown in Figure 4 for the disperse anthraquinone dyes. Among the azo dyes, the measured and calculated solubility of disperse red 1 is shown in Figure 5. Agreement between the calculated and experimental values for both dyes is good. Therefore, solubilities can be calculated at equilibrium condition. This type of empirical correlation should not be used for extrapolation outside the experimental conditions. However, it is simple and useful for evaluating the effect of equilibrium condition on the solubility.

Since we cannot find similar data in the experimental ranges we adopted so far in the literature (Özcan et al., 1997), we have not compared the data obtained in this work with other data sources in the figures. Instead, we performed measurements at least three times for each temperature and pressure in order to provide reliable data.

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