Solubility Measurement of Disperse Dyes in Supercritical Carbon Dioxide

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The solubility of disperse dyes, CI disperse red 60 and CI disperse orange 3 in supercritical carbon dioxide have been measured at temperatures from 323.7 K to 413.7 K and pressures from 100 bar to 300 bar, using a flow-type equilibrium cell. The solubility data are correlated with an expanded liquid model which needs no critical properties of dyes, as well as an empirical equation.

Introduction

Conventional dyeing of polyester fabrics requires a large amount of water and also discharges much wastewater. Various kinds of dispersing agents and surfactants lead to contamination. It is difficult to treat wastewater with such additives by conventional biological processes. To solve this problem, an alternative technique of dyeing with supercritical fluids has been developed by many investigators (Saus et al., 1993; Gebert et al., 1994; Chang et al., 1996). Recently, dyeing technology in supercritical carbon dioxide has applied to dyeing of fabrics. This process needs no water, no auxiliary agents such as surfactants and dispersing agents, and no drying facilities of fabrics. For industrialization of this supercritical dyeing process, solubility data for dyes in supercritical carbon dioxide are required. Bae and Her (1996), Haarhaus et al. (1995), Swidersky et al. (1996), Özcan et al. (1997), and Joung et al. (1998) have reported solubility data of dyes in supercritical carbon dioxide.

In this study, we measured the solubility of disperse dyes in supercritical carbon dioxide at the temperatures 323.7 K, 353.7 K, 383.7 K, and 413.7 K between 100 bar and 300 bar of pressure. The results were correlated to a model that considered the supercritcal fluid as an expanded liquid as well as an empirical model, ultimately in order to offer them to the process design of supercritical dyeing.

Experimental Section

Apparatus. The solubility measurement of dyes was carried out using a flow-type cylindrical equilibrium cell that is shown in Figure 1. The apparatus consists of three main sections: the compression, equilibrium, and expansion parts. The equilibrium cell (300 mm long by 17 mm i.d.) is packed alternatively with glass wool, glass beads of 2 mm diameter, and dyestuff in series. The glass beads are employed to make a uniform flow distribution of the supercritical fluid, and the glass wool is to prevent the dye from being entrained in the fluid. The overall height of the bed is about 150 mm. The total mass of dyestuff is 5 to 7 g per bed. The pressure in the equilibrium vessel is measured by a Heise pressure gauge (3D Instrument) and is regulated within ±0.4 bar by a back-pressure regulator. The temperature of the vessel is controlled to ±0.5 K by a temperature controller. A metering valve is used to keep

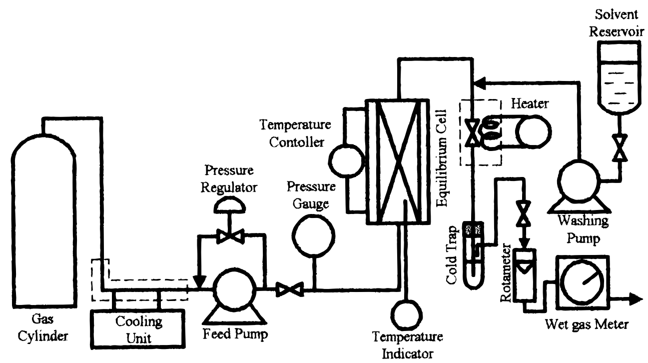

Figure 1. Schematic diagram of experimental apparatus.

the pressure and flow rate of the fluid at the desired values. The valve is heated to prevent it from clogging with dry ice. The expanded carbon dioxide flows through a trap that is filled with chlorobenzene. Two flowmeters, a rotameter and a wet gas meter, are placed at the downstream of the trap to measure the flow rate. The flow rate is controlled within about 150 mL(STP)/min, with which flow rate was assured the saturation of dyes in the supercritical conditions (Bae and Her, 1996). A UV spectrometer (Shimadzu, UV-160A) is utilized to analyze the concentration of dyestuffs dissolved in chlorobenzene solution, by scanning the wavelengths from 400 nm to 800 nm to obtain a specific absorbency peak of the individual dye in the solvent.

Materials. The dyestuffs did not contain any additives such as dispersing agents and surfactants. They were obtained from LG Chemical Co. and used without further treatment. The molecular structures and physical properties of disperse dyes are shown in Table 1. The carbon dioxide was 99.8% in purity, and chlorobenzene as a special grade reagent was used without further purification.

Results and Discussion

The solubility of disperse dyes in carbon dioxide at supercritical conditions of 323.7 K, 353.7 K, 383.7 K, and 413.7 K between 100 bar and 300 bar is summarized as shown in Table 1.

The dye solubility in supercritical carbon dioxide is correlated to the empirical method proposed by Özcan et al. (1997). The relation is given by eq 1

$$\ln(y_2 p/p_{ref}) = a + b/T + c(\rho - \rho_{ref}) \qquad (1)$$

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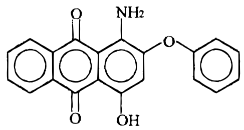
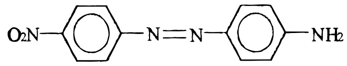
Table 1. Molecular Structure and Physical Property of Disperse Dyes

dyestuff	structure	MW	T_m/K	Δh_f/kJ mol^{-1}	v_2[a]/cm^3 mol^{-1}	U_2[a]/kJ mol^{-1}
CI disperse red 60		331	459.2	22.56	388.9	147.57
CI disperse orange 3		242	481.0	14.20	188.0	80.58

[a] Obtained by group contribution method proposed by Fedors (1974a, 1974b).

Table 2. Experimental Solubility (y_2) of Dyes in Supercritical Carbon Dioxide

T = 323.7 K		T = 353.7 K		T = 383.7 K		T = 413.7 K	
p/bar	$10^6 y_2$	p/bar	$10^6 y_2$	p/bar	$10^6 y_2$	p/bar	$10^6 y_2$
CI Disperse Red 60							
102.9	2.112	101.5	0.778	101.5	0.229	101.5	0.138
155.3	7.555	153.6	5.170	153.8	2.187	156.5	1.721
200.3	12.657	204.7	9.808	205.8	9.776	208.6	7.072
251.3	16.675	252.3	20.214	254.7	19.172	252.3	18.682
305.7	21.253	305.6	29.531	300.3	29.935	301.8	37.506
CI Disperse Orange 3							
101.3	1.518	103.3	0.094	103.4	0.125	103.7	0.453
149.8	6.983	154.2	2.564	150.4	4.239	148.1	4.399
205.8	13.656	203.9	9.918	198.5	10.691	203.0	10.861
247.5	20.755	247.8	18.219	250.6	19.108	251.3	20.783
305.0	16.342	304.7	27.517	301.6	32.243	310.6	92.435

where y_2 is the mole fraction of dye, p is the pressure, a, b, and c are constants, p_{ref} is a standard pressure of 1 bar, ρ_{ref} is a reference density for which a value of 700 kg m^{-3} was used for calculations, and T is the absolute temperature.

From the experimental data, each isotherm is fitted to obtain values of a, b, and c using eq 1. Their values are listed in Table 2 for each isotherm. The predicted solubility of individual dyes using eq 1 is compared with the experimental values as depicted in Figures 2 and 3. The agreement between the calculated and experimental solubility of disperse dyes is fairly good.

Moreover, we used a theoretical method known as the expanded liquid model where the supercritical fluid phase was treated as an expanded liquid. Using an equilibrium relation between the solid and liquid state for the dyes, the solubility of dyestuff (y_2) can be evaluated in eq 2.

$$y_2 = \frac{1}{\gamma_2^\infty}\left(\frac{f_2^{os}}{f_2^{ol}}\right) \quad (2)$$

The fugacity ratio, f_2^{os}/f_2^{ol} can be expressed as follows (Prausnitz, 1969; Kramer and Thodos, 1988):

$$\ln\frac{f_2^{os}}{f_2^{ol}} = \frac{\Delta h_2^{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right) - \frac{1}{RT}\int_{T_m}^{T}\Delta C_p\, dT + \frac{1}{R}\int_{T_m}^{T}\frac{\Delta C_p}{T}\, dT + \int_{p_2^{sat}}^{p}\frac{\Delta v_2}{RT}\, dP \quad (3)$$

Equation 3 can calculate this from the basic physical properties such as enthalpy of fusion (Δh_2^{fus}) and melting point (T_m), neglecting the last three terms of right side of eq 3. In eq 2, the infinite activity coefficient (γ_2^∞) is expressed by the regular solution model coupled with the

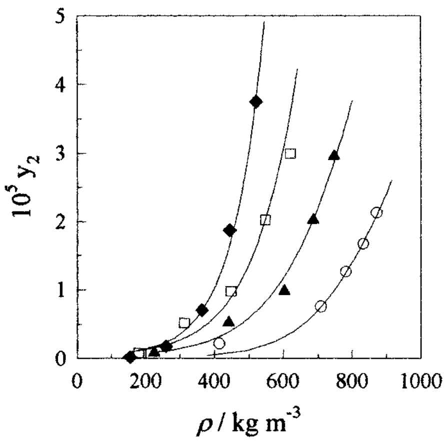


Figure 2. Solubility of CI disperse red 60 vs density of carbon dioxide: (○) 323.7 K; (▲) 353.7 K; (□) 383.7 K; (◆) 413.7 K; (lines) calculated by eq 1.

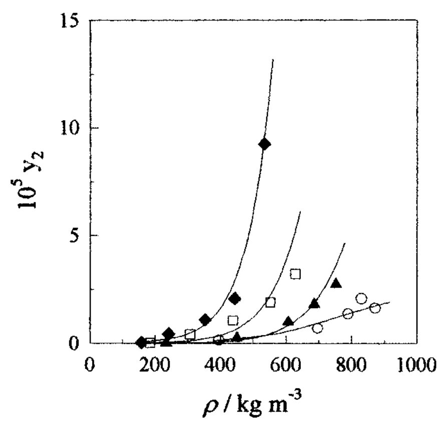


Figure 3. Solubility of CI disperse orange 3 vs density of carbon dioxide: (○) 323.7 K; (▲) 353.7 K; (□) 383.7 K; (◆) 413.7 K; (lines) calculated by eq 1.

Flory–Huggins theory (Kramer and Thodos, 1988a, 1988b, 1989; Iwai et al., 1992, 1993),

$$\ln \gamma^\infty = \frac{\nu_2}{RT}[(\delta_{d1} - \delta_{d2})^2 + \tau_2{}^2 - \beta_{12}] + 1 - \frac{\nu_2}{\nu_1} + \ln\frac{\nu_2}{\nu_1} \quad (4)$$

where δ_{d1} is the solubility parameter of carbon dioxide, which is calculated by the method of Giddings et al. (1969) and Allada (1984); $\tau_2{}^2$ expressing the polar and hydrogen bonding contribution is taken as zero in this work. ν_1 and ν_2 are molar volumes of carbon dioxide and subcooled liquid state of solid, respectively. ν_1 is calculated by an equation of state (Huang et al., 1985). ν_2 and δ_{d2} are obtained from group contribution proposed by Fedors (1974a, 1974b). The regressed binary interaction parameter, β_{12}, is found to be

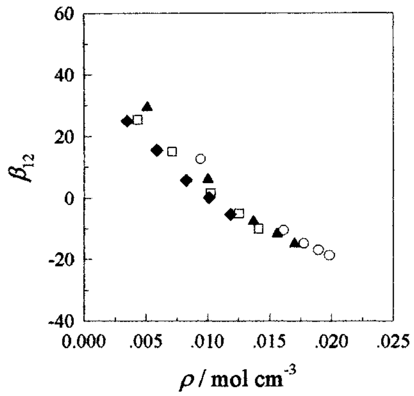


Figure 4. β_{12} vs density of carbon dioxide for carbon dioxide + CI disperse red 60 system: (○) 323.7 K; (▲) 353.7 K; (□) 383.7 K; (◆) 413.7 K.

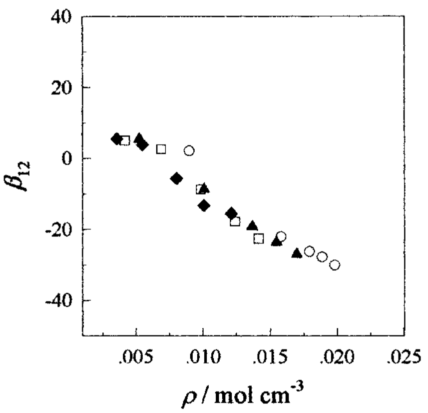


Figure 5. β_{12} vs density of carbon dioxide for carbon dioxide + CI disperse orange 3 system: (○) 323.7 K; (▲) 353.7 K; (□) 383.7 K; (◆) 413.7 K.

Table 3. Parameters in Eq 1

dye	T/K	a	b/K^{-1}	c/kg m^{-3}
CI disperse red 60	323.7	−3.745	−889.54	0.0072
	353.7	−3.078	−735.88	0.0088
	383.7	−2.351	−519.31	0.0103
	413.7	−1.067	−441.34	0.0131
CI disperse orange 3	323.7	−3.271	−1058.94	0.0076
	353.7	−2.580	−912.48	0.0129
	383.7	−1.567	−601.40	0.0137
	413.7	−0.459	−189.89	0.0156

Table 4. Parameter in Eq 5 and AAD%

		parameter			
dye	T/**K**	a_0	a_1	a_2	AAD%[a]
CI disperse red 60	323.7	64.17	−6642.5	124256	39.0
	353.7	62.30	−7234.9	158410	35.9
	383.7	42.19	−5023.7	73509	27.8
	413.7	41.43	−4965.6	85498	26.0
CI disperse orange 3	323.7	93.99	−7083.3	144196	20.8
	353.7	23.29	−3551.8	33755	16.4
	383.7	10.95	−672.4	−125613	27.6
	413.7	16.88	−2851.8	6294	30.4

[a] AAD% = $\{\Sigma|y_2^{\text{expl}} - y_2^{\text{cald}}|\}/y_2^{\text{expl}} \times 100$/no. of data.

almost independent of the temperature and strongly dependent on the density of carbon dioxide. The results are depicted in Figures 4 and 5. The parameter β_{12} is correlated to the density of carbon dioxide.

$$\beta_{12} = a_0 + a_1\rho + a_2\rho^2 \qquad (5)$$

The parameters, a_0, a_1, and a_2 in eq 5 are summarized in Table 3.

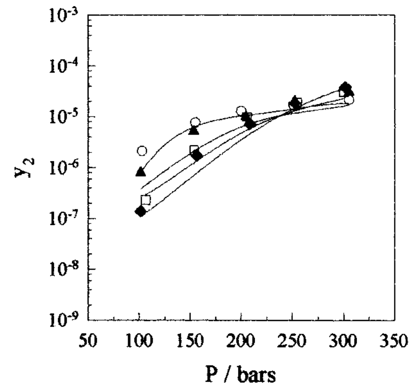


Figure 6. Solubility of CI disperse red 60 in supercritical carbon dioxide: (○) 323.7 K; (▲) 353.7 K; (□) 383.7 K; (◆) 413.7 K; (lines) calculated by eqs 2−5.

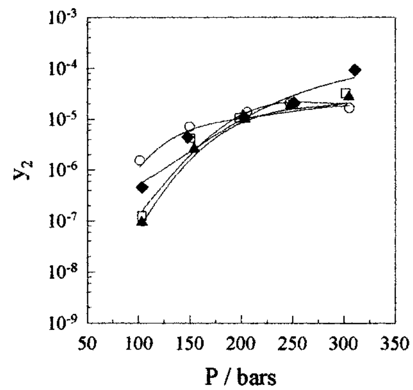


Figure 7. Solubility of CI disperse orange 3 in supercritical carbon dioxide: (○) 323.7 K; (▲) 353.7 K; (□) 383.7 K; (◆) 413.7 K; (lines) calculated by eqs 2−5.

The solubility of dye in carbon dioxide can be evaluated using eqs 2−5. Comparison between the experimental and the calculated solubility is expressed as AAD% in Table 4 and shown in Figures 6 and 7. The calculated results are in good agreement with the experimental one, although the solubility of dyes shows very small value of 10^{-7}−10^{-5} mole fraction.

Conclusions

The solubility of dyestuffs, CI disperse red 60 and orange 3, in supercritical carbon dioxide has been measured in the temperature range 323 K to 413 K and pressure range of 100 bar to 300 bar, using a flow-type equilibrium cell. It is shown that the solubility of dyes in supercritical carbon dioxide can be correlated to the expanded liquid model as well as the empirical method, with fairly good accuracy. It is worth noting that the expanded liquid model can be applied to the systems containing high-molecular solids such as dyes for which critical properties are not available.

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