J. Chem. Eng. Data **1999,** *44,* 985−989

Solubility of C. I. Disperse Red 60 and C. I. Disperse Blue 60 in Supercritical Carbon Dioxide

Hwan-Do Sung and Jae-Jin Shim*

School of Chemical Engineering and Technology, Yeungnam University, 214−1 Tae-dong,
Kyongsan City, Kyongbuk 712-749, South Korea

Solubility of two disperse dyes (C. I. Disperse Red 60 and C. I. Disperse Blue 60) in supercritical carbon dioxide was measured at pressures up to 35 MPa and temperatures between 313 K and 423 K in a closed-loop equilibrium apparatus equipped with a magnetic pump. The solubility increased with pressure at the same temperature. Solubility isotherms were straight and parallel to each other when the logarithm of solubility was plotted versus density of the fluid, whereas the slope of each isotherm decreased with increasing temperature when it was plotted versus the logarithm of density. The experimental data were successfully correlated using two semiempirical equations.

Introduction

As an application of polymer impregnation in supercritical fluids (Shim and Johnston, 1989), the supercritical fluid dyeing (SFD) process has recently received significant attention and has been under development in several countries such as Germany (Saus et al., 1993) and South Korea (Chang et al., 1996). It is a novel and environmentally friendly technique that may replace the pollution-generating and energy-consuming conventional wet-dyeing process. Since the dyeing industry uses water as a dyeing medium and a lot of dispersing agents and surfactants to overcome the inherent hydrophobicity of the textile and the dye, it discharges a lot of hard-to-destroy (very little biodegradable) wastewater. To reduce the environmental pollution problem, supercritical carbon dioxide is considered as a potential alternative dyeing medium to water as it is inherently nontoxic and does not require any dispersing agents and surfactants in the dyeing process. Furthermore, a lot of energy (roughly 50%) can be saved in the SFD process, as it requires neither the washing step nor the drying step, whereas the conventional wet-dyeing process requires both steps (Saus et al., 1993).

To develop and design the SFD process a lot of basic dye-solubility data are necessary. However, only a limited number of studies on the dye solubility have been reported so far (Bae and Her, 1996; Haarhaus et al., 1995; Swidersky et al., 1996; Shim and Sung, 1997; Özcan et al., 1997; Kautz et al., 1998; Tuma and Schneider, 1998). Disperse dyes for dyeing polyester textiles are divided into two groups: azo and anthraquinone derivatives. In this study the solubility of the two anthraquinone derivative disperse dyes in supercritical carbon dioxide have been measured over a wide range of pressure and temperature. In a manner different from other studies, a closed-loop equilibrium apparatus circulating with a magnetic pump was used to get equilibrium solubility accurately in a short time. The experimental data were correlated with two simple semiempirical equations. The behavior of the solubility isotherms was analyzed and discussed. Solubility enhancement by a cosolvent, ethyl alcohol or acetone, was also measured in the same apparatus and reported separately (Shim and Sung, 1997; Muthukumaran et al., 1999).

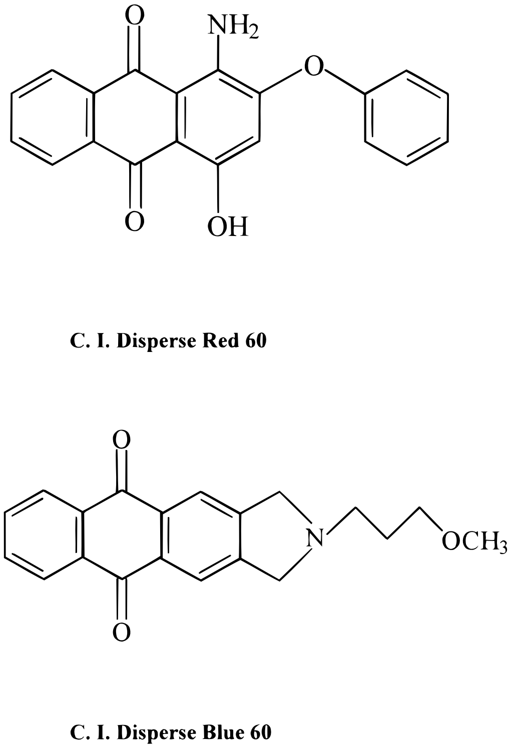

Figure 1. Molecular structures of C. I. Disperse Red 60 and C. I. Disperse Blue 60 dyes.

Experimental Section

Materials. C. I. Disperse Red 60 and C. I. Disperse Blue 60 dyes (Figure 1) containing neither dispersing agents nor surfactants were obtained from LG Chemical. Carbon dioxide (purity 99%) in a siphon-installed cylinder was obtained from Taedong Oxygen. These materials were used without further purification.

Experimental Equipment. A closed-loop (batch) equilibrium apparatus was placed in a constant-temperature

---

* Corresponding author. Tel: +82-53-810-2587; fax: +82-53-814-8790; e-mail: jjshim@ynucc.yeungnam.ac.kr.

10.1021/je990018t CCC: $18.00

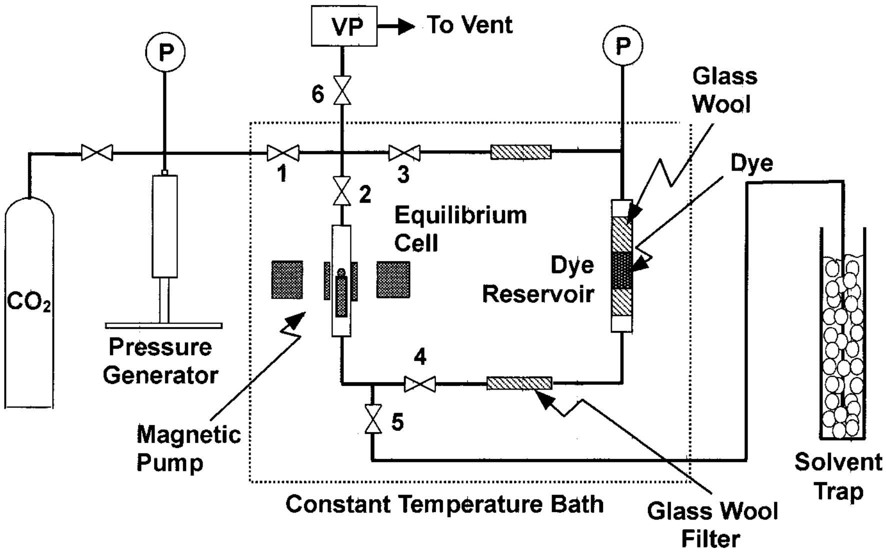

Figure 2. Schematic diagram of the closed-loop equilibrium solubility apparatus. VP, vacuum pump; P, pressure transducer.

air bath that was controlled within ±1 K (Figure 2). A high-pressure magnetic pump consisting of a small cylinder with a piston inside and a concentric coil outside was used to circulate the fluid in the system (the dye reservoir and the equilibrium cell) by moving the piston up and down continuously. A small amount of dye was placed in the dye reservoir and both ends were plugged with glass wool to prevent the dye powder from being entrained to the equilibrium cell. Two additional filters packed with glass wool were placed on both sides of the dye reservoir to block the possible dye−powder entrainment. These filters were cleaned after each series of measurement. Sensotec TJE pressure transducer and Sensotec GM signal conditioner/indicator were installed and calibrated to read the pressure to ±0.01 MPa.

Experimental Procedures. After evacuating the entire system using a rotary vacuum pump with all the valves open except for valves 1 and 5, liquid carbon dioxide was delivered from the cylinder to the system at a desired pressure by a manual syringe pump (High-Pressure Equipment). After closing valve 6, carbon dioxide in the closed-loop equilibrium system was circulated with a magnetic pump for about 2 h until the equilibrium solubility was attained. Valves 3 and 4 were then closed. By opening valve 5, the fluid mixture (CO_2−dye) was slowly released from the equilibrium cell into the ethyl alcohol trap to strip off the dye in the fluid mixture. Dye powder precipitated on the wall of the equilibrium cell was also recovered in the ethyl alcohol that was pumped into the cell from the top of valve 6. These solutions were then mixed together to analyze the concentration of the dye by a UV/visible spectrophotometer (Perkin-Elmer Lambda 40). The dye concentration in the equilibrium cell was calculated from the amount of carbon dioxide (see *Results and Discussion* for details) and the amount of dye that was measured above. To minimize error in the next measurement, the ethyl alcohol remaining in the cell was completely removed by flushing with air, followed by dissolving it out with supercritical carbon dioxide four or five times. Equilibrium solubility at different temperatures and pressures were also measured in the same way.

Results and Discussion

Solubility Measurement in a Batch Apparatus. There are two methods used to measure solubility: the flow method and the batch method. Most researchers have preferred the former because the results are not strongly influenced by a small leakage from the vessel and the operation is relatively easy (Bae and Her, 1996; Özcan et al., 1997; Fat'hi et al., 1998). Nevertheless, the latter was adopted in this study because a complete equilibrium can be achieved and thus more accurate solubility data may be obtained by the continuous circulation of the fluid mixture in the closed-loop apparatus with a magnetic pump. Consumption of dye and carbon dioxide could also be minimized. A similar method was used in Schneider's group (Haarhaus et al., 1995; Swidersky et al., 1996; Kautz et al.; 1998, Tuma and Schneider, 1998). They measured solubility spectroscopically in a static cell agitated with a magnetic stirrer. These two batch methods require accurate measurement of the volume and pressure in the equilibrium cell. The volume of the equilibrium cell was obtained from the pressure difference before and after the expansion of helium into the reference vessel of a known volume. The amount of supercritical carbon dioxide in the equilibrium cell was estimated from the accurate density that was calculated by a computer program (CO2PAC) based on the Wagner and Schmidt equation of state (Ely, 1986). The amount of dye in the fluid in the equilibrium cell was calculated from the dye concentration in the washing ethyl alcohol, which was measured by the UV/visible spectrophotometer. Therefrom the solubility of dye was estimated.

Although it took about 90 min to reach the solubility equilibrium, we maintained the circulation longer (150 min) before measuring the dye solubility to ensure complete equilibrium. If a small amount of the washing ethyl alcohol remains in the equilibrium cell, the solubility in the next measurement could be greatly increased because of the enhancing effect of ethyl alcohol. We carefully determined the number of flushing operations necessary to remove completely the remaining ethyl alcohol. The alcohol was stripped off by a single flush with carbon dioxide at 313.15 K and 24.5 MPa. However, we repeated flushing three times at the end of each solubility measurement to ensure the complete removal of ethyl alcohol. Experimental uncertainties were less than ±4% including all the errors from measurements and calculations.

Correlation of Experimental Solubility Data. The solubilities of the two disperse dyes increased with pressure at constant temperatures. Although the solubility iso-

Table 1. Solubilities of C. I. Disperse Red 60 Dye in Supercritical Carbon Dioxide

pressure (MPa)	density ($\mathrm{mol{\cdot}L^{-1}}$)	solubility ($y_2 \times 10^6$)	pressure (MPa)	density ($\mathrm{mol{\cdot}L^{-1}}$)	solubility ($y_2 \times 10^6$)
	313.15 K			333.15 K	
9.85	14.04	1.61	12.20	10.25	0.82
10.41	14.92	1.92	12.62	10.95	1.66
11.34	15.85	2.55	15.83	14.38	4.14
11.99	16.32	3.28	18.05	15.65	6.47
15.95	18.06	5.46	21.05	16.81	9.80
18.81	18.83	7.41	24.88	17.86	13.91
24.23	19.88	9.59	28.31	18.57	17.79
27.51	20.37	12.39	30.71	18.99	20.52
32.83	20.82	14.13			
	363.15 K			393.15 K	
12.10	6.10	0.72	14.55	6.13	2.33
14.92	8.39	2.64	18.18	8.38	6.95
18.11	10.90	5.92	21.48	9.88	13.58
18.36	11.08	4.96	24.66	11.36	22.75
20.06	12.16	8.93	26.45	12.08	32.30
20.18	12.24	7.20	27.29	12.39	38.02
23.08	13.70	14.35	28.55	12.84	42.08
24.29	14.19	15.04	32.30	13.98	68.98
27.99	15.44	27.79	32.84	14.13	68.03
30.96	16.21	36.09	33.54	14.31	72.47
32.28	16.53	41.38			
	423.15 K				
11.44	3.86	2.03			
13.69	4.78	4.40			
16.70	6.04	7.15			
20.09	7.49	15.40			
25.89	9.82	49.78			
29.17	10.92	85.03			
32.23	11.87	129.92			

Table 2. Solubilities of C. I. Disperse Blue 60 Dye in Supercritical Carbon Dioxide

pressure (MPa)	density ($\mathrm{mol{\cdot}L^{-1}}$)	solubility ($y_2 \times 10^6$)	pressure (MPa)	density ($\mathrm{mol{\cdot}L^{-1}}$)	solubility ($y_2 \times 10^6$)
	313.15 K			333.15 K	
16.78	18.31	1.04	18.36	15.79	1.38
19.56	19.00	1.33	19.09	16.10	1.54
24.03	19.85	1.67	21.33	16.90	1.91
24.94	19.99	1.76	21.97	17.10	2.39
27.22	20.33	2.09	24.21	17.70	2.75
32.41	20.98	2.27	24.39	17.74	2.77
32.88	21.03	2.30	28.04	18.52	3.39
			30.84	19.05	3.65
	363.15 K			393.15 K	
20.41	12.37	1.74	19.41	8.81	1.75
22.18	13.29	2.18	21.60	9.95	2.93
25.25	14.55	3.34	22.40	10.34	3.37
26.43	14.96	3.93	23.29	10.75	3.69
27.96	15.43	4.57	23.90	11.03	4.48
31.89	16.44	6.94	24.14	11.13	4.21
32.66	16.61	7.53	28.00	12.65	7.65
			28.24	12.73	7.64
	423.15 K		30.12	13.34	10.48
			31.07	13.63	11.48
15.08	5.40	2.46	32.62	14.07	14.03
16.70	6.06	3.66	33.76	14.37	16.39
20.21	7.54	5.88			
23.07	8.71	8.14			
24.73	9.35	10.10			
24.96	9.44	10.69			
25.17	9.52	11.08			
27.39	10.32	15.70			
29.77	11.12	21.33			
31.95	11.79	29.04			
34.20	12.41	38.67			

therms intersected each other in the pressure plot, making the plot complex, they appeared as simple straight lines that are parallel each other in the semilogarithmic density plot (logarithm of solubility versus fluid density). Kumar and Johnston (1988), Shim and Johnston (1991), and Bae and Her (1997) have reported the same behavior in the density plots of solubility of solids and of the distribution coefficient of solids. Bartle et al. (1991) and Özcan et al. (1997) derived an empirical equation correlating a modified enhancement factor (yP/P_{ref}) with fluid density. Their correlation includes a term to correct the effect of temperature on the modified enhancement factor. Fat'hi et al. (1998) derived a semiempirical equation correlating logarithm of solute concentration with logarithm of density from the theory of Chrastil (1982). Their equation is almost the same form as that of Özcan et al.

Kumar and Johnston (1988) showed near-linear behavior for both the semilog and the log−log relation between solubility and density. In this study we modified Kumar and Johnston's equations into similar forms to those of Fat'hi et al. and Özcan et al. because solubility is generally preferred to concentration in the thermodynamic analysis and is simpler than modified enhancement factor. These modified equations are

$$\ln y = A + B/T + C\rho \tag{1}$$

$$\ln y = A' + B'/T + C' \ln \rho \tag{2}$$

where y is the mole fraction (solubility) of dye in the fluid, T is the absolute temperature (K), ρ is the molar density of fluid ($\mathrm{mol{\cdot}L^{-1}}$), and A, B, C, A', B', and C' are constants.

Solubilities of C. I. Disperse Red 60 and C. I. Disperse Blue 60 dyes are shown in Tables 1 and 2 and Figures 3−5. The larger solubility of the former might be because it is more polar than the latter and because it can form hydrogen bonds with CO_2. The latter does not have any ability to form hydrogen bonds. A minor contribution was from its smaller molecular weight. In the semilog plots we obtained near-linear parallel solubility isotherms, whereas in the log−log plot the solubility isotherms were linear but their slopes were decreasing with temperature. Therefore, we introduced the following function of temperature for constant C':

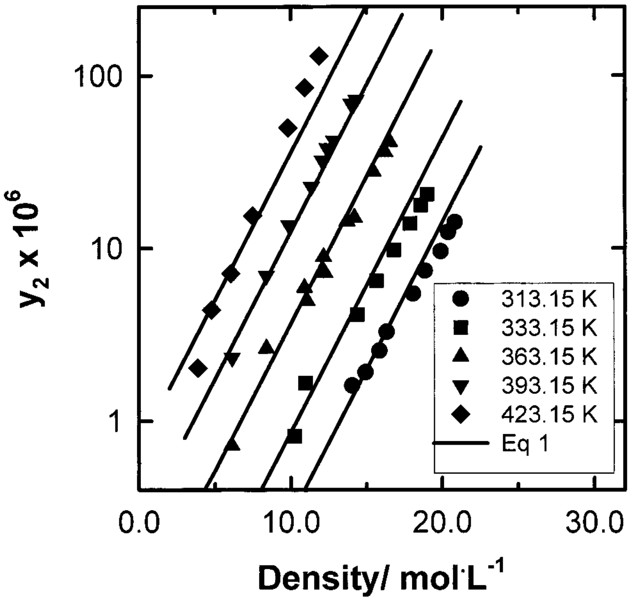

Figure 3. Linear parallel solubility isotherms for C. I. Disperse Red 60 dye in supercritical carbon dioxide. Lines are those correlated with eq 1.

$$C' = c + d/T \tag{3}$$

where c and d are constants. Combining eqs 2 and 3, we

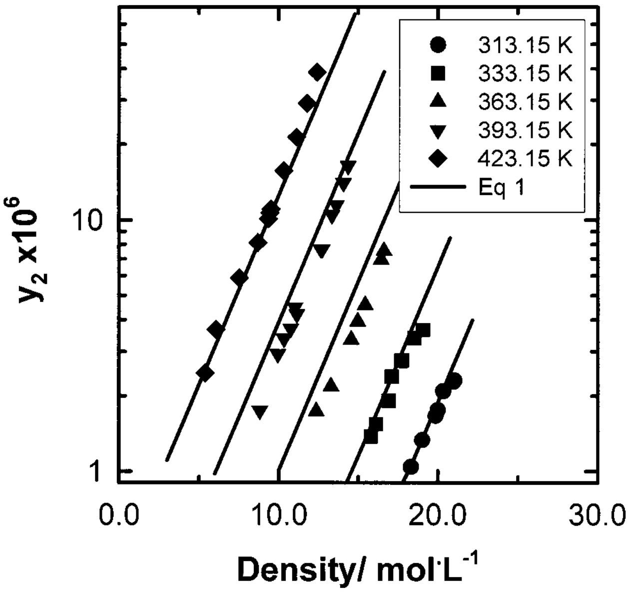

Figure 4. Linear parallel solubility isotherms for C. I. Disperse Blue 60 dye in supercritical carbon dioxide. Lines are those correlated with eq 1.

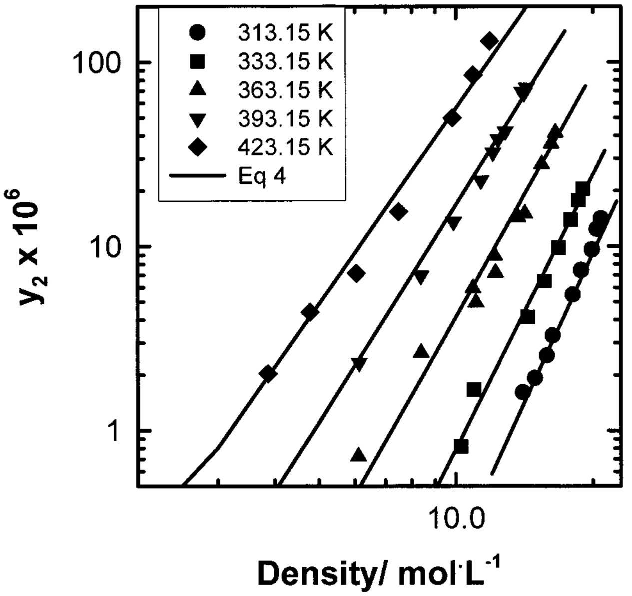

Figure 5. Solubility isotherms of C. I. Disperse Red 60 dye with varying slopes with temperature in supercritical carbon dioxide. Lines are those correlated with eq 4.

developed a new empirical equation

$$\ln y = a + b/T + (c + d/T)\ln \rho \tag{4}$$

where a and b are constants. Figures 3–5 show that eqs 1 and 4 can fit the experimental data well. The constants in these equations were obtained from the lines that best describe the experimental data (Table 3).

The experimental solubilities of the disperse dyes were described a little better by the semilogarithmic solubility–density relation (eq 1) than the log–log relation (eq 4). As discussed in Kumar and Johnston (1988), the ratios of the partial molar volumes of anthraquinone derivative disperse dyes in supercritical carbon dioxide and the isothermal compressibility of the fluid (κ) must not be a constant but a function of temperature as in eq 3. Figures 3 and 4 show that the slopes of the solubility isotherms are the same for all temperatures in the semilog plots, whereas in the log–log plot they vary with temperature (Figure 5). The same is true for C. I. Disperse Blue 60. The ratio of the partial molar volume and the product of density and the compressibility must be a constant. The semilog relation with three constants is obviously simpler than the log–log relation with four constants. However, either equation, the semilog or the log–log, can be used to predict solubility of the disperse dyes within or near the experimental conditions of this work.

Table 3. Constants in Eqs 1 and 4 Correlating the Solubility of Disperse Dyes with Fluid Density

	C. I. Disperse Red 60	C. I. Disperse Blue 60
constants in eq 1	$A = 13.439$	$A = 15.9414$
	$B = -5837.2$	$B = -6453.7$
	$C = 0.39236$	$C = 0.3465$
constants in eq 4	$a = 24.045$	$a = 31.8450$
	$b = -1188.89$	$b = -1409.72$
	$c = -4.1631$	$c = -11.5162$
	$d = 5199.27$	$d = 8011.4$

Conclusions

Solubility of C. I. Disperse Red 60 and C. I. Disperse Blue 60 dyes was measured in a close-loop (batch) equilibrium apparatus equipped with a magnetic pump. The resulting solubility isotherms for disperse dyes showed linear behavior at pressures between 9 MPa and 35 MPa and temperatures between 313 K and 413 K when they were plotted versus density of fluid (i.e., a semilog plot) or versus the logarithm of density (i.e., a log–log plot). In the former the solubility isotherms were parallel to each other, whereas in the latter their slopes decreased with increasing temperature. Two empirical equations fit experimental solubility data well, showing good consistency. The semilog equation with three constants is simpler and therefore easier to use than the log–log equation with four constants. However, we can predict solubility of disperse dyes at any temperature and pressure using any one of the two semiempirical relation.

Acknowledgment

We thank LG Chemical for the disperse dye samples.

Literature Cited

Bae, H.-K.; Her, B.-K. Solubility of Disperse Dyes in Supercritical Carbon Dioxide. *Hwahak Konghak* **1996**, *34*, 379–382.

Bartle, K. D.; Clifford, A. A.; Jafar, S. A. Solubilities of Solids and Liquids of Low Volatility in Supercritical Carbon Dioxide. *J. Phys. Chem. Ref. Data* **1991**, *20*, 713–757.

Chang, K.-H.; Bae, H.-K.; Shim, J.-J. Dyeing of PET Textile Fibers and Films in Supercritical Carbon Dioxide. *Korean J. Chem. Eng.* **1996**, *13*, 310–316.

Chrastil, J. Solubility of Solids and Liquids in Supercritical Gases. *J. Phys. Chem.* **1982**, *86*, 3016–3021.

Ely, J. F. CO2PAC: A Computer Program to Calculate Physical Properties of Pure CO_2; National Institute of Science and Technology: Boulder, CO, 1986.

Fat'hi, M. R.; Yamini, Y.; Sharghi, H.; Shamsipur, M. Solubilities of Some 1,4-Dihydroxy-9,10-anthraquinone Derivatives in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1998**, *43*, 400–402.

Haarhaus, U.; Swidersky, P.; Schneider, G. M. High-Pressure Investigation on the Solubility of Dispersion Dyestuffs in Supercritical Gases by VIS/NIR–Spectroscopy. Part I. *J. Supercrit. Fluids* **1995**, *8*, 100–106.

Kautz, C. B.; Wagner, B.; Schneider, G. M. High-Pressure Solubility of 1,4-Bis-(*n*-alkylamino)-9,10-anthraquinones in Near- and Supercritical Carbon Dioxide. *J. Supercrit. Fluids* **1998**, *13*, 43–47.

Kumar, S. K.; Johnston, K. P. Modeling the Solubility of Solids in Supercritical Fluids with Density as the Independent Variable. *J. Supercrit. Fluids* **1988**, *1*, 15–22.

Muthukumaran, P.; Gupta, R. B.; Sung, H.-D.; Shim, J.-J.; Bae, H. K. Dye Solubility in Supercritical Carbon Dioxide. Effect of Hydrogen Bonding with Cosolvents. *Korean J. Chem. Eng.* **1999**, 16, 111–117.

Özcan, A. S.; Clifford, A. A.; Bartle, K. D.; Lewis, D. M. Solubility of Disperse Dyes in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1997**, *42*, 590−592.

Saus, W.; Knittel, D.; Schollmeyer, E. Dyeing of Textiles in Supercritical Carbon Dioxide. *Text. Res. J*. **1993**, *63*, 135−142.

Shim, J.-J.; Johnston, K. P. Phase Equilibria, Partial Molar Enthalpies, and Partial Molar Volumes Determined by Supercritical Fluid Chromatography. *J. Phys. Chem*. **1991**, *95*, 353−360.

Shim, J.-J.; Johnston, K. P. Adjustable Solute Distribution Between Polymers and Supercritical Fluids. *AIChE J*. **1989**, *35*, 1097−1106.

Shim, J.-J.; Sung, H.-D. Effect of Cosolvents on the Dye Solubility in Supercritical Carbon Dioxide. *Proceedings of the 4th International Symposium on Supercritical Fluids*, 1997; pp 467−470.

Swidersky, P.; Tuma, D.; Schneider, G. M. High-Pressure Investigation on the Solubility of Anthraquinone Dyestuffs in Supercritical Gases by VIS−Spectroscopy. Part II. *J. Supercrit. Fluids* **1996**, *9*, 12−18.

Tuma, D.; Schneider, G. M. High-Pressure Solubility of Disperse Dyes in Near- and Supercritical Fluids: Measurements up to 100 MPa by a Static Method. *J. Supercrit. Fluids* **1998**, *13*, 37−42.

Received for review January 18, 1999. Accepted June 1, 1999. This research was supported by the Yeungnam University Research Grants in 1996 and was partially supported by the Dongil Foundation for a Culture-Scholar Grant in 1997.

JE990018T