Relationships between the Solubility of C. I. Disperse Red 60 and Uptake on PET in Supercritical CO_2

Ping Bao*,†,‡ and Jinjin Dai†

National Engineering Research Center for Dyeing and Finishing of Textiles, Donghua University, Shanghai 200051, China, and School of Chemistry and Engineering, Qingdao University, Qingdao, China

The solubilities of C. I. disperse red 60 in supercritical CO_2 at temperatures of 353 K, 373 K, and 393 K and pressures from 11 MPa to 23 MPa were determined. The results showed that within the range of the experiments the solubilities remained at a magnitude of 10^{-6} mol dye/mol CO_2 and were increasing with increasing pressure or density at constant temperature. The equilibrium solubility data were successfully correlated using a semiempirical model. To reveal the relationships between dye solubility and its uptake on the fiber, we carried out dyeings of PET fiber in supercritical CO_2 at corresponding pressures and temperatures. The results showed that very high solubility was not beneficial for high dye uptake because the dyeing of PET in SC-CO_2 also obeyed the partition rule as in water.

1. Introduction

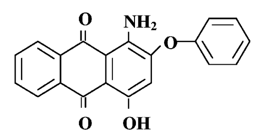
Conventional dyeing of textiles uses water as a solvent or a transport medium for the dyestuffs, which results in a high consumption of water and causes serious pollution. To reduce environmental pollution, supercritical fluid dyeing, which emerged at the end of the 20th century, has been attracting much attention as an environmentally benign process.[1] Carbon dioxide (CO_2), which is inexpensive, essentially nontoxic, and nonflammable, has easily accessible critical conditions (T_c = 31 °C and P_c = 7.37 MPa) and is the most popularly used solvent. The dyeing process in supercritical carbon dioxide (SC-CO_2) needs no water, no auxiliary agents such as surfactants and dispersing agents, no drying process, and no reduction clearing of fabrics.[2]

The solubility of dyes in SC-CO_2 is one of most important parameters for dye selection and also for process temperature and pressure optimization.[3] Research carried out by Ciba Specialty Chemicals Inc., Basel Switzerland, on the dye uptake of PET fiber dyed in SC-CO_2 with all kinds of disperse dyes on the market indicated that those disperse dyes with a higher degree of exhaustion in conventional aqueous dyeing did not give a higher degree of exhaustion in SC-CO_2 at all.[4] A set of disperse dyes especially suitable for supercritical fluid dyeing had been developed by Ciba for DTNW in Krefeld, Germany, but no detailed information was reported. Therefore, it is necessary for us to search for dyes for the dyeing of PET in SC-CO_2.

It is shown that the solubility of dyes in SC-CO_2 has an effect on the dyeing rate and dye uptake of PET fiber. Some studies on the determination of the dye solubility in SC-CO_2 had been reported,[5−10] and the experimental data were correlated with different empirical equations.[9,11−12] There are two methods for determining the dye solubility (e.g., the flow method and the batch method). Most researchers prefer the flow method because the results are not strongly influenced by small leakages from the vessel and the operation is relatively easy.[5,7−9,12] However, it is difficult to determine if the solution has reached complete equilibrium. The batch method was adopted in this study because complete equilibrium could be achieved in a shorter time, more accurate solubility data may be obtained with the apparatus, in which the fluid mixture was two-way circulated with a circulating pump, and the consumption of dye and carbon dioxide could also be minimized.

In this study, the solubility of C. I. disperse red 60 in SC-CO_2 was measured at temperatures from 353 K to 393 K and pressures from 11 MPa to 23 MPa in an apparatus that was successfully designed and constructed for the determination of the solubility of disperse dyes in SC-CO_2 in our laboratory. The dyeing of PET in SC-CO_2 was carried out under corresponding conditions, and the dye uptake was determined. The dye uptake of PET fiber and dye solubility in SC-CO_2 was correlated.

Table 1. Structure and Properties of Disperse Dye

Dyestuff	Molecular Structure	Molecular Weight	Tm/K
C.I. disperse red 60		331	460

2. Experimental Section

2.1. Measurement Solubility. C. I. disperse red 60 (1-amino-4-methoxy-2-phenoxy-9,10-anthraquinone), whose chemical structure and properties are shown in Table 1, was supplied by Hangzhou Jihua Chemical Company. The dye was used after purifying by recrystallization with acetone. The purity of the dye was checked by thin-layer chromatography, and the melting point of the dye was measured by a differential scanning calorimeter. The purity of CO_2 was 99.99%.

The apparatus we used in this work for determining the dye solubility in SC-CO_2, which was equipped with a constant-volume tube, is shown in Figure 1. The temperature was controlled to ±1 K by a temperature controller. The pressure was measured with an accuracy of ±1%. The

* Corresponding author. E-mail: baoping@mail.dhu.edu.cn. Tel: + 86-21-62373672.
† Donghua University.
‡ Qingdao University.

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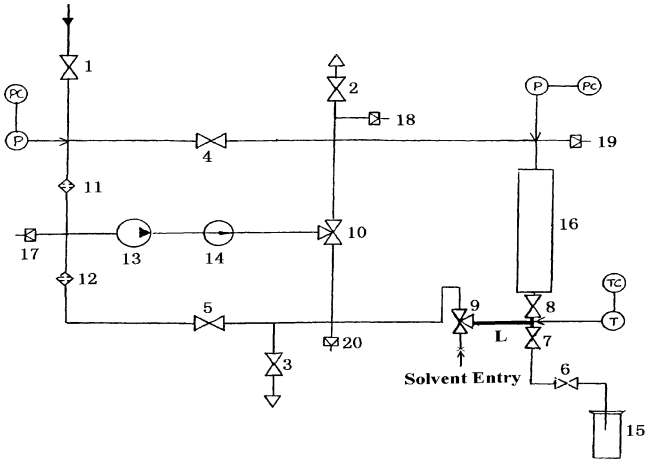

Figure 1. Schematic diagram of the experimental apparatus: (1, 2, 3) needle valve; (4, 5, 6, 7, 8) two-way valve; (9, 10) three-way valve; (11, 12) filter; (13) circulating pump; (14) mass flow meter; (15) solvent trap; (16) equilibrium cell; (17, 18, 19, 20) safety demolition flat; (L) constant-volume tube.

internal volume of the constant-volume tube (L) was 60 cm^3. A small amount of dye was placed in the equilibrium cell, and both ends were plugged alternatively with stainless steel beads of 4-mm diameter and glass wool. These were used to make a uniform flow distribution of the SC-CO_2 fluid. The two filters (11 and 12) mounted in the circulation line were used to prevent the dye powder from being entrained in the constant-volume tube. The flow direction of the SC-CO_2 fluid was controlled by valves 4, 5, and 10, and the flow rate was controlled by regulating the revolution of the circulating pump.

Liquid CO_2 was delivered from valve 1 to the system at a desired pressure, where it was heated to the desired temperature. By regulating valves 4, 5, and 10, the CO_2 in the equilibrium system was circulated with a circulating pump for a certain period of time until equilibrium solubility was attained. Valves 8 and 9 were then closed. By opening valves 6 and 7, the fluid mixture (CO_2−dye) was slowly released from the constant-volume tube into the acetone trap to strip off the dye in the fluid mixture. Dye powder that precipitated onto the wall of the constant-volume tube was also recovered in the acetone that was pumped into the tube from the top of valve 9. These solutions were then mixed together to analyze the concentration of the dye with a visible spectrophotometer. The dye concentration in the constant-volume tube was calculated from the volume of CO_2 and the amount of dye that was measured above. Measurements were made in triplicate. Experimental uncertainties were less than ±5% including all measurement and calculation errors.

2.2. Dyeing Process. The PET fabric (80 g/m^2, plain weave) was a commercial product purchased from Wujiang Textile Company in Jiangsu province. The dyeing of PET in SC-CO_2 was carried out in the pilot equipment, which was designed and constructed by our research team. The detailed operating procedures were described elsewhere.[13] The dye concentration on the fabric (measured as mg dye/g fiber) was determined according to GB/T 9337-2001. Approximately 0.1 g of dyed fabric (accurate to within 0.0001 g) was placed in a 50-mL flask filled with 3 mL of chlorobenzene and phenol (mass ratio 1:1) and boiled to make it dissolve completely. After cooling to room temperature, acetone was added with shaking to separate the PET out. The concentration of the dye in acetone was measured by the spectrophotometer at the maximum wavelength of the dye.

Table 2. Dye Concentrations, *y*, of C. I. Disperse Red 60 in SC-CO_2 at 393 K and 20 MPa at Different Dissolving Times, *t*

t/min	$y \times 10^6$
20	9.55
40	9.84
60	10.13
90	12.67
100	12.26
150	12.49

Table 3. Effects of Temperature, *T*, and Pressure, *P*, on the Solubilities, *y*, of C. I. Disperse Red 60 in SC-CO_2

	T = 353 K		T = 373 K		T = 393 K	
P	density		density		density	
MPa	$g{\cdot}cm^{-3\,a}$	$y \times 10^6$	$g{\cdot}cm^{-3\,a}$	$y \times 10^6$	$g{\cdot}cm^{-3\,a}$	$y \times 10^6$
11	0.260	7.09	0.216	6.66	0.189	6.53
14	0.387	7.39	0.304	7.75	0.255	8.58
17	0.506	8.21	0.396	8.65	0.330	9.78
20	0.594	8.91	0.480	10.74	0.440	12.67
23	0.656	9.71	0.550	12.36	0.466	15.20

[a] The density of SC-CO_2 was obtained from the *CRC Handbook of Basic Tables for Chemical Analysis*.[14]

3. Results and Discussion

3.1. Determination of the Solubility of the Dye. The concentrations of C. I. disperse red 60 in SC-CO_2 were measured over a wide range of dissolving times from 20 min to 150 min at 393 K and 20 MPa to determine the solubility of the dye. The results are shown in Table 2. It can be seen that the dye concentration increased as the time was extended from 20 min to 90 min, but there was no significant change after 90 min. This indicated that 90 min was enough for C. I. disperse red 60 to reach the dissolution equilibrium at 393 K and 20 MPa. To ensure the saturation of the dye in SC-CO_2 at temperatures and pressures of less than 393 K and 20 MPa, a dissolving time of 120 min was used.

3.2. Influences of Temperature and Pressure on Solubility. To elucidate the influences of temperature and pressure on the solubility of C. I. disperse red 60 in SC-CO_2, the solubilities were determined in the temperature range from (353 to 393) K and at pressures from (11 to 23) MPa and are shown in Table 3. The results showed that over the investigated conditions the solubility of C. I. disperse red 60 remained at a magnitude of 10^{-6} mol dye/mol CO_2. Figures 2 and 3 show the relationships of solubility−pressure and solubility−density. It can be seen from Figure 2 that the solubility increased as the pressure increased when the temperature was constant. A similar relationship held for the influence of the density (Figure 3).

Several investigations of the solubility of C. I. disperse red 60 in SC-CO_2 have been published.[5,11,15−17] Schneider et al.[17] measured the solubility of C. I. disperse red 60 in a cell agitated with a magnetic stirrer at temperatures from (303.1 to 322.5) K and pressures from (7.2 to 97.6) MPa. Özcan et al.,[5] however, had determined the solubility for the same dye at 20 MPa and 353.15 K and got a value of 3.76×10^{-6}mol dye/mol CO_2. Muthukumaran et al.[16] used a cosolvent, ethanol or acetone, to study the solubility of the same dye at temperatures from (313.15 to 333.15) K and pressures up to 34 MPa. Figure 4 shows a comparison of the solubilities of C. I. disperse red 60 in SC-CO_2 reported previously[11] with our experimental results. As shown in

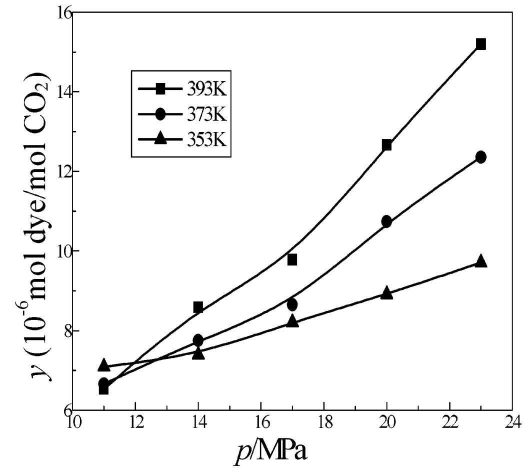

Figure 2. Solubility of C. I. disperse red 60, y, in SC-CO_2 as a function of pressure, p.

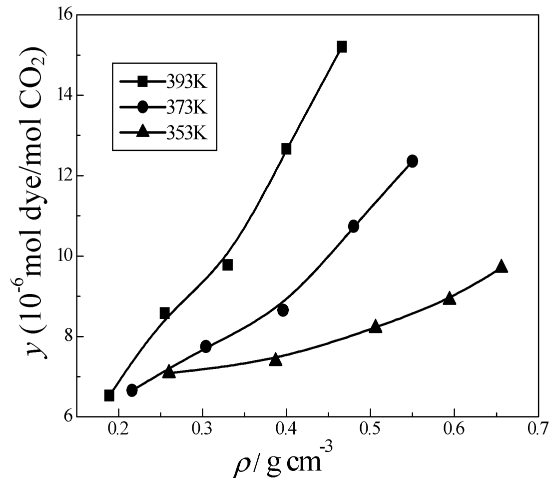

Figure 3. Solubility of C. I. disperse red 60, y, in SC-CO_2 as a function of density, ρ.

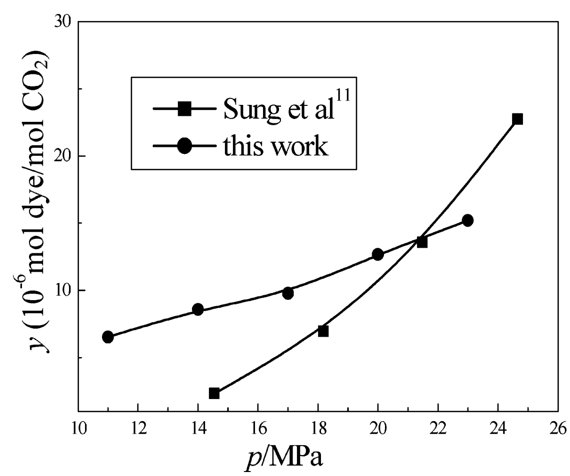

Figure 4. Comparison of the determined solubility of C. I. disperse red 60, y, in SC-CO_2 at 393 K with Sung's data.

Figure 4, when the pressures were lower than 22 MPa the solubilities measured in our laboratory were higher than those of Sung and Shim, but after that they were lower. This may be due to the fact that the dissolution of the dye in Sung's work had not reached complete equilibrium at lower pressures.

3.3. Mathematical Correlation of Solubility with Temperature and Pressure. The results from the present

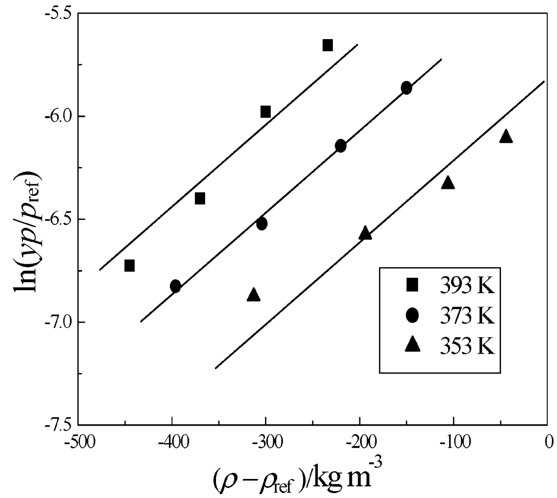

Figure 5. Plots of isotherms of $\ln(yp/p_{ref})$ versus density, $(\rho - \rho_{ref})$, for C. I. disperse red 60.

Table 4. Solubility Constants *a*, *b*, and *C* and AARD % Obtained from the Data Correlation Procedure

dye	a	b/K	C/kg^{-1} m^3	AARD %[a]
C. I. disperse red 60	3.74	−3370.33	0.00398	2.63−13.17

[a] AARD % = $100/N \times \{\sum (y^{exptl} - y^{calcd})/y^{calcd}\}$, where y^{exptl} and y^{calcd} are the experimental and calculated solubility data, respectively, and N is the number of data points.

study were mathematically correlated with a semiempirical equation proposed by Bartle et al.[18] The correlation equation was given in eq 1, where y is the mole fraction of dye, p is the pressure, p_{ref} is a standard pressure of 1 bar, ρ is the density of solution (taken as the density of pure carbon dioxide), ρ_{ref} is a reference density with a value of 700 kg m^{-3}, and A and C are constants.

$$\ln\left(\frac{yp}{p_{ref}}\right) = A + C(\rho - \rho_{ref}) \tag{1}$$

A is given by

$$A = a + \frac{b}{T} \tag{2}$$

where a and b are constants and T is the absolute temperature. Combining eqs 1 and 2, the correlation equation becomes

$$\ln\left(\frac{yp}{p_{ref}}\right) = a + \frac{b}{T} + C(\rho - \rho_{ref}) \tag{3}$$

In the first step, $\ln(yp/p_{ref})$ values were plotted against density (Figure 5), and the values were fit to a straight line by least-squares regression to estimate the C and A parameters. The values of C, obtained from the slopes of the corresponding plots, were then averaged for C. I. disperse red 60, and the value was listed in Table 4. Afterward, the isotherms were refit to obtain new values of A using the averaged value of C. The plot of A versus $^1/_T$ resulted in a straight line (Figure 6), and from the intercept and slope, the values of a and b were obtained. The resulting a and b values are also shown in Table 4. Finally, the values of a, b, and C were used to predict the solubility from eq 3. Figure 7 showed a comparison of the calculated solubilities with the experimental data. The coincidence between them can be seen, with absolute average relative

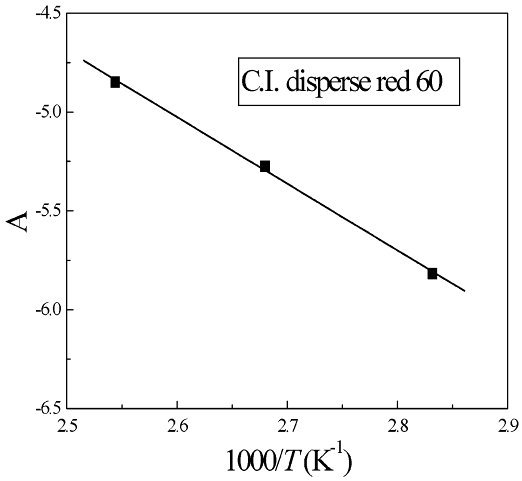

Figure 6. Plot of A as a function of ($^1/_T$).

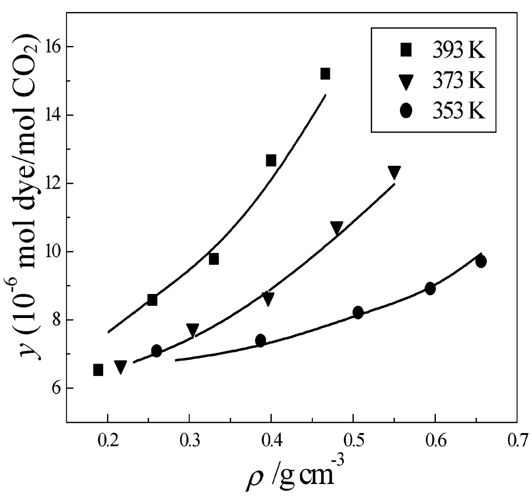

Figure 7. Comparisons of experimental (points) and calculated (lines) solubilities for C. I. disperse red 60 in SC-CO_2.

Table 5. Relation of Solubility, *y*, to the Dye Uptake of C. I. Disperse Red 60 in SC-CO_2 at Different Pressures, *P*

P / MPa	$y \times 10^6$	dye uptake[a] / mg dye/g fiber
14	8.58	5.23
17	9.78	5.45
20	12.67	10.53
23	15.20	6.78

[a] Dye concentration: 5% owf; flow rate of CO_2: 100 kg/h; dyeing: 2 h at 393 K.

deviations (AARD) in the range of 2.63% to 13.17% at different temperatures (Table 4).

3.4. Correlation of the Solubility of C. I. Disperse Red 60 with the Dye Uptake of PET. To reveal the relationships between dye solubility and its uptake on the fiber, dyeings of PET fiber in SC-CO_2 were carried out at corresponding pressures and temperatures, and the results are shown in Table 5 and Table 6. It was observed from Table 5 that the dye uptake of PET fiber increased before 20 MPa but decreased when the pressure was beyond 20 MPa, although the solubility of the dye showed a steady increase from (14 to 23) MPa. The result indicated that very high solubility was not beneficial for high dye uptake. This was also valid for the temperature dependence as shown in Table 6, from which it could be seen that the dye uptake of PET fiber dyed in SC-CO_2 at 20 MPa increased with increasing solubility before 393 K but did not change significantly after 393 K. As previously proven that the dyeing of PET in SC-CO_2 also obeyed the partition rule as in water,[19] very high solubility would cause more dye to remain in the medium.

Table 6. Relation of Solubility, *y*, to the Dye Uptake of C. I. Disperse Red 60 in SC-CO_2 at Different Temperatures, *T*

T / K	$y \times 10^6$	dye uptake[a] / mg dye/g fiber
373	10.78	4.15
383	12.00	8.50
393	12.67	10.53
403	14.17	10.40

[a] Dye concentration: 5% owf; flow rate of CO_2: 100 kg/h; dyeing: 2 h at 20 MPa.

4. Conclusions

The results obtained in this study indicate that within the range of the experiments the solubility of C. I. disperse red 60 remained at a magnitude of 10^{-6} mol dye/mol CO_2. The relationships of solubility−pressure showed that the solubility increased as the pressure increased when the temperature was constant. A similar relationship holds for the influence of the density. The measured solubilities were correlated using a semiempirical model. The calculated results showed satisfactory agreement with the experimental data. The dye uptake of PET fiber at 393 K increased before 20 MPa but decreased when the pressure was beyond 20 MPa, although the solubility of the dye showed a steady increase from (14 to 23) MPa. This meant that very high solubility was not beneficial for high dye uptake because the dyeing of PET in SC-CO_2 also obeyed the partition rule as in water. This was also valid for the temperature dependence.

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