

# Solubility of Disperse Dyes in Supercritical Carbon Dioxide

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The solubilities of eight disperse dyes, suitable for dyeing from a supercritical medium, have been measured in supercritical carbon dioxide. For two of the dyes, 3-(1*H*-benzimidazol-2-yl)-7-(diethylamino)chromen-2-one (C.I. Disperse Yellow 82, DY82) and 1-((4-aminophenyl)azo)-2-naphthol, studies have been made at 80 °C and 100 °C between 200 bar and 350 bar. The results were correlated using a semi-empirical equation. The remaining six dyes were studied at 200 bar and 80 °C, to investigate trends of solubility with molecular properties.

## Introduction

The textile industry uses large amounts of water in their dyeing processes, emitting organic compounds into the environment (Saus et al., 1993). Due to this environmental problem, a dyeing process for polyester fibers was developed by Saus et al. (1992), in which supercritical carbon dioxide is used as the transfer medium.

Supercritical carbon dioxide gives an option avoiding water discharge, it is low in cost, nontoxic, and nonflammable, and the carbon dioxide can be recycled. Also, when dyeing from an aqueous medium, reduction clearing is carried out to stabilize the color intensity, producing further water waste. Reduction clearing is not carried out following supercritical dyeing. Supercritical carbon dioxide also has other advantages. The application of the dye to the fabric can be controlled and a better quality of application achieved (Saus and GmbH, 1995; Clifford and Bartle, 1996). The dyes used in supercritical dyeing are the nonionic, so-called disperse dyes.

In this paper the solubilities of disperse dyes have been measured in supercritical carbon dioxide to assist with the design of the dyeing processes. Although the solubilities of many compounds have been measured in this medium (Bartle et al., 1991), no solubilities of disperse dyes have been published. The eight disperse dyes studied were 4-(*N*-phenylamino)-4'-nitroazobenzene (C.I. Disperse Orange 1, DO1), 4-amino-4'-nitroazobenzene (C.I. Disperse Orange 3, DO3), 4-[*N*-ethyl-*N*-(2-cyanoethyl)amino]-4'-nitroazobenzene (C.I. Disperse Orange 25, DO25), 4-[*N*-(2-acetoxyethyl)-*N*-(2-cyanoethyl)amino]-2',6'-dichloro-4'-nitroazobenzene (C.I. Disperse Orange 30, DO30), 2-(acetylamino)-4-(*N,N*-bis(acetoxyethyl)amino)-5-ethoxy-2',4',6'-trinitroazobenzene (C.I. Disperse Blue 79:1, DB79:1), 1-amino-4-hydroxy-2-phenoxy-9,10-anthracenedione (C.I. Disperse Red 60, DR60), 3-(1*H*-benzimidazol-2-yl)-7-(diethylamino)chromen-2-one (C.I. Disperse Yellow 82, DY82), and a specially synthesized dye 1-((4-aminophenyl)azo)-2-naphthol (APAN). The structures of these dyes are given in Table 1.

## Experimental Section

**Samples and Preparation.** Of the eight disperse dyes studied, seven are commercially available and one (APAN) was synthesized at the University of Leeds Colour Chemistry Department. Before solubility measurements were

performed, the commercially available dyes, except DY82, were purified and the water soluble impurities removed by recrystallization in acetone. APAN and DY82 were used directly. (Elemental analyses of the dyes used are given in Table 1. Oxygen analyses were obtained by difference. Errors in C, H, N, and Cl were  $\pm 0.3\%$  and in O were around  $\pm 0.6\%$ .)

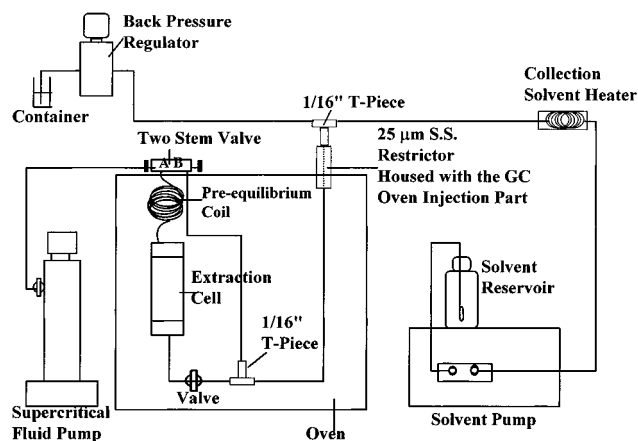
**Apparatus.** The solubility measurements of the dyes were carried out on a modified SFE system (Burford et al., 1996), which can be seen in Figure 1, consisting of a CO<sub>2</sub> pump (ISCO 260D syringe pump), solvent-trapping system, and an extraction cell (Keystone, 10.4 mL). The dye was loaded into the extraction cell and mixed (1:1) with glass beads (Alltech Association, 100/120). Carbon dioxide was flowed through the cell at a rate of 0.5 cm<sup>3</sup> min<sup>-1</sup>, which was measured as liquid CO<sub>2</sub> at the pump. Solubilities were measured dynamically at 80 °C and 100 °C, between 200 bar and 350 bar for APAN and DY82 and at 200 bar and 80 °C for the other dyes. The accuracy of the temperature was  $\pm 1$  deg; the accuracy of the pressure measurement was  $\pm 2\%$  of the full scale of the pump, and errors in flow rate were  $\pm 0.5\%$ . Initially, some experiments were made at different flow rates to verify that equilibrium was being reached in the cell. It was found that the solubility obtained was the same at flow rates of both 0.25 cm<sup>3</sup> min<sup>-1</sup> and 0.5 cm<sup>3</sup> min<sup>-1</sup>. A flow rate of 0.5 cm<sup>3</sup> min<sup>-1</sup> was therefore used. Dynamic extractions were performed for consecutive 15 min periods, and the dye was trapped in chloroform at the outlet of the back-pressure regulator (Go Inc. BP66). The dye chloroform content was analyzed by a UV/vis spectrophotometer (PYE Unicam SP8-500). The solubility of the dye in supercritical carbon dioxide was then calculated in terms of mole fraction by using the calculated densities (Duschek et al., 1990) of the supercritical fluid in the pump and the volume of supercritical carbon dioxide used during each collection and displayed at the pump. Measurements were made in quadruplicate.

## Results and Discussion

**Survey of the Solubility Made in Constant Conditions.** The solubility measurements on eight dyes in supercritical carbon dioxide, made at 200 bar and at 80 °C, show how the solubility changes with molecular structure. The results also are given in Table 2 with their

**Table 1. Structure of Dyes and Their Elemental Analysis Results**

Dyes	Structures	Elemental Analyses Results (Mass %)	
APAN		by calculation	73.0% C, 4.9% H, 6.2% O, 15.9% N
		by analysis	71.1% C, 4.2% H, 10.1% O, 14.6% N
DO30		by calculation	50.7% C, 3.8% H, 14.2% O, 15.5% N, 15.8% Cl
		by analysis	51.1% C, 3.5% H, 14.5% O, 14.9% N, 15.9% Cl
DO3		by calculation	59.5% C, 4.1% H, 13.2% O, 23.1% N
		by analysis	60.4% C, 3.5% H, 13.9% O, 22.2% N
DR60		by calculation	72.5% C, 3.9% H, 19.3% O, 4.2% N
		by analysis	72.7% C, 3.5% H, 19.7% O, 4.1% N
DO1		by calculation	67.9% C, 4.4% H, 10.1% O, 17.6% N
		by analysis	68.3% C, 3.7% H, 10.9% O, 17.1% N
DO25		by calculation	63.2% C, 5.3% H, 9.9% O, 21.7% N
		by analysis	63.3% C, 4.2% H, 11.85% O, 20.6% N
DB79:1		by calculation	47.6% C, 4.5% H, 31.7% O, 16.2% N
		by analysis	44.8% C, 3.2% H, 38.8% O, 13.2% N
DY82		by calculation	72.1% C, 5.7% H, 9.7% O, 12.6% N
		by analysis	71.2% C, 5.1% H, 11.5% O, 12.2% N

**Figure 1.** Solubility measurement apparatus.**Table 2. Solubilities in Mole Fraction,  $x$ , for the Disperse Dyes at 200 bar and 80 °C in Supercritical Carbon Dioxide**

dyes	$M/g\ mol^{-1}$	$10^6x$	RSD%
APAN	263	12.8	3.3
DO30	450	5.70	8.2
DO3	242	3.99	7.8
DR60	331	3.76	4.6
DO1	318	2.91	3.8
DO25	323	1.31	4.6
DB79:1	605	1.13	6.0
DY82	333	0.60	5.2

percentage relative standard deviations. Also shown are the molar masses of the dyes, and it can be seen that, although there is a weak trend for lower solubilities with higher molar mass, there is not a strong correlation. One would also expect dyes with polar groups like aromatic,  $-OH$ , and  $-NH_2$  groups to be less soluble, but this does not appear to be the case for APAN and DR60. The likely

**Table 3. Solubilities in Mole Fraction,  $x$ , for DY82 in Supercritical Carbon Dioxide**

$P/bar$	$10^6x$	
	80 °C	100 °C
200	0.60	0.79
250	1.66	2.41
300	2.38	4.14

**Table 4. Solubilities in Mole Fraction,  $x$ , for APAN in Supercritical Carbon Dioxide**

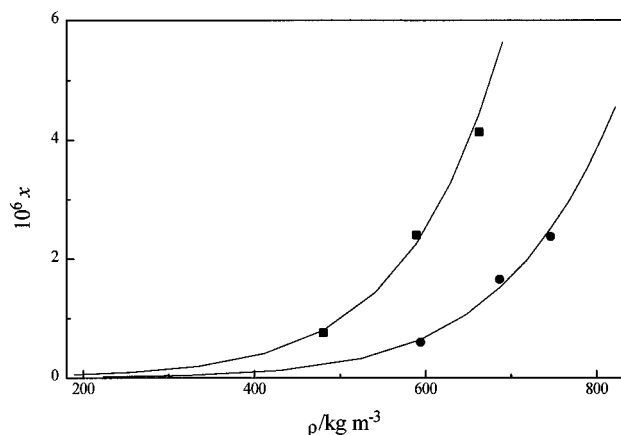
$P/bar$	$10^5x$	
	80 °C	100 °C
200	1.28	0.95
250	3.24	3.31
300	5.76	7.03
350	8.78	11.6

hydrazone structure of APAN probably accounts for its high solubility. It must be reluctantly concluded that it is difficult to predict dye solubilities from structure, as so many unquantifiable effects seem to be included.

**Solubility of DY82.** The measurements of the solubility of DY82 in supercritical carbon dioxide were made at three pressures at each of two temperatures to enable data correlation and are given in Table 3. The precision of the solubility measurements was determined by obtaining the percentage relative standard deviation; this varied from 0.7% to 5.2% in the worst case.

**Solubility of APAN.** Using the same procedure as for DY82, measurements for APAN in supercritical carbon dioxide were carried out at four pressures at each of two temperatures and are given in Table 4. For APAN the percentage relative standard deviation changed from 1.8% to 6.4% in the worst case.

**Correlation of the Solubility Data.** Although the prediction of solubility in supercritical fluids is difficult and



**Figure 2.** Solubility in mole fraction,  $x$ , for DY82. The graph shows the comparison of predicted curves (lines) and experimental points plotted versus density,  $\rho$ , of the solubility: (■) 100 °C; (●) 80 °C.

**Table 5. Parameters Used in the Calculation of Solubilities from Eq 3**

	$a$	$b/K^{-1}$	$c/kg\ m^{-3}$
DY82	21.12	-10190.79	0.0116
APAN	18.66	-8223.68	0.0130

not very accurate, a simple semi-empirical method (Bartle et al., 1991) was used for the correlation of the experimental data. The correlation equation is given in eq 1, where

$$\ln(xp/p_{ref}) = A + c(\rho - \rho_{ref}) \quad (1)$$

$x$  is the mole fraction solubility,  $p$  is the pressure,  $A$  and  $c$  are constants,  $p_{ref}$  is a standard pressure of 1 bar,  $\rho$  is the density of the solution, and  $\rho_{ref}$  is a reference density for which a value of 700 kg m<sup>-3</sup> was used for calculations. The reason for using  $\rho_{ref}$  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

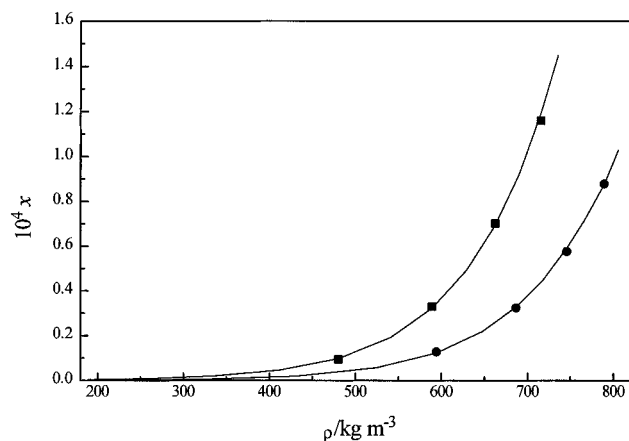
$$A = a + b/T \quad (2)$$

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

$$\ln(xp/p_{ref}) = a + b/T + c(\rho - \rho_{ref}) \quad (3)$$

From the experimental data, each isotherm was fitted using eq 1 to obtain values of  $A$  and  $c$ . The values  $c$  were then averaged for each dye, and values given in Table 5 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 for  $a$  and  $b$  were obtained from eq 2, which are also given in Table 5.

Finally, predicted solubilities were compared with experimental values in Figures 2 and 3, using eq 3. Agreement between the calculated and experimental values for both dyes is good. Therefore, solubilities can be confidently calculated at any temperature and pressure within the experimental range using eq 3 and the parameters of Table



**Figure 3.** Solubility in mole fraction,  $x$ , for APAN. The graph shows the comparison of predicted curves (lines) and experimental points plotted versus density,  $\rho$ , of the solubility: (■) 100 °C; (●) 80 °C.

5. Although only two temperatures were used in this correlation, previous work with data for a range of temperatures show that the correlation with temperature is valid (Bartle et al., 1991).

## Conclusions

The study of two dyes over a pressure and temperature range could be well fitted by a published empirical equation and showed the consistency of the results. No clear trend of solubility with the expected molecular properties of molar mass, polarity, and polarizability could be seen from the survey of solubilities of eight dyes at 200 bar and 80 °C.

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