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Solubility of Disperse and Mordant Dyes in Supercritical CO_2

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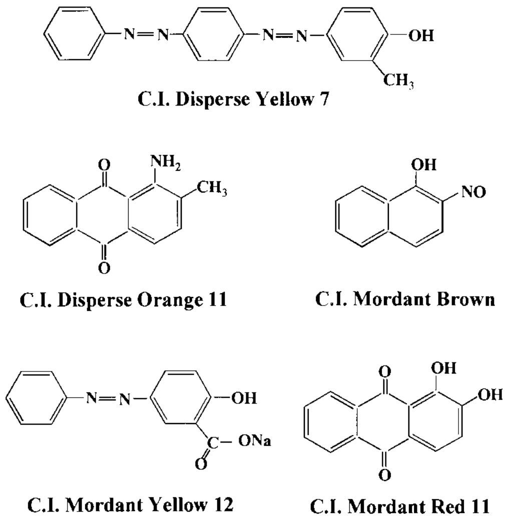
Waterless dyeing is the new approach in textile dyeing in order to reduce or eliminate effluent waste, and supercritical carbon dioxide is an alternative solvent being considered. The research focus has therefore been on determination of dyestuff solubilities in supercritical carbon dioxide. We have determined the solubilities of two disperse dyes (C. I. Disperse Yellow 7, C. I. Disperse Oranges 11) and three mordant dyes (C. I. Mordant Brown, C. I. Mordant Yellow 12, and C. I. Mordant Red 11) at 323−343 K and pressures in the range 132−195 bar. Mordant Brown had the highest solubility in the range $(1.2-5.1) \times 10^{-4}$ mole fraction whereas Mordant Yellow 12 had the lowest solubility in the range $(1.7-5.1) \times 10^{-7}$ mole fraction. The disperse dyes and Mordant Red had solubilities of the order 10^{-6} mole fraction.

Introduction

Since the early 1990s, "waterless dyeing" has been gaining increasing importance in the textile industry for environmental reasons. Supercritical carbon dioxide has been considered as an alternate solvent for the process. The pioneering studies were done at Deutsches Textilforschungszentrum Nord-West at Krefeld, Germany, initially on dyeing of synthetic fibers. Saus et al. (1993) reported on dyeing of poly(ethylene terephthalate) by disperse dyes. Gebert et al. (1994) extended supercritical dyeing to natural fibers, such as cotton and wool, by first treating the fiber with a swelling agent and using monoazo and anthraquinone disperse dyes. Knittel and Schollmeyer (1995) reported on dyeing of poly(ethylene terephthalate) and polypropylene with different dyes. Bach et al. (1996) investigated the pretreatment of poly(ethylene terephthalate) by a heat-setting process before dyeing in supercritical carbon dioxide.

Since most dyes were developed specifically for water base applications, they have been designed as water soluble dyes, with very limited solubility in supercritical carbon dioxide. Hence later studies concentrated on identifying supercritical carbon dioxide soluble dyes. Schneider and Schollmeyer (1996) investigated the solubilities of anthraquinone type disperse dyes and β-carotene (natural dye) in supercritical carbon dioxide. They reported that the solubilities increase more rapidly with increasing density at higher temperatures. Ozcan et al. (1997) have determined the solubilities of eight disperse dyes that have different structure and classes (azo, anthraquinone, imidazol) in supercritical carbon dioxide. They reported that there is no strong correlation between solubility, structure, and molecular weight. Recently Joung and You (1998) reported on the solubilities of disperse anthraquinone and azo dyes at 313−393 K and 10−25 MPa.


C.I. Disperse Yellow 7

C.I. Disperse Orange 11

C.I. Mordant Brown

C.I. Mordant Yellow 12

C.I. Mordant Red 11

Figure 1. Disperse and mordant dyes used.

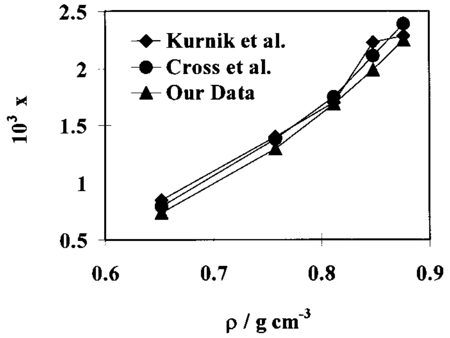


Figure 2. Mole fraction of phenantrene in supercritical carbon dioxide at 318.15 K.

In this study, the solubilities of two disperse and three mordant dyes have been determined at the pressure range 132−195 bar and at 323.15 K and 343.15 K. The pressure measurements had an uncertainty of ±3 bar, whereas the temperature determinations were within ±1 K. The dyes were C. I. Disperse Yellow 7 {4-[4-(phenylazo)phenylazo]-*o*-cresol}, C. I. Disperse Oranges 11 (1-amino-2-metanthraquinone), C. I. Mordant Brown (2-nitroso-1-naphthol), C. I. Mordant Yellow 12 [5-(4-aminophenylazo)salicylic acid sodium salt], and C. I. Mordant Red 11 (1,2-dihydroxanthraquinone); open structures are given in Figure 1. C. I. Disperse Yellow 7 and C. I. Mordant Yellow 12 are azo dyes, C. I. Disperse Orange 11 and C. I. Mordant Red 11

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Table 1. Solubility of Disperse and Mordant Dyes in Supercritical Carbon Dioxide

Disperse Yellow 7				Disperse Orange 11				Mordant Yellow 12				Mordant Red 11				Mordant Brown			
333.15 K		353.15 K		333.15 K		353.15 K		333.15 K		353.15 K		333.15 K		353.15 K		333.15 K		353.15 K	
P (bar)	$X \times 10^6$	*P* (bar)	$X \times 10^6$	*P* (bar)	$X \times 10^6$	*P* (bar)	$X \times 10^6$	*P* (bar)	$X \times 10^7$	*P* (bar)	$X \times 10^7$	*P* (bar)	$X \times 10^6$	*P* (bar)	$X \times 10^6$	*P* (bar)	$X \times 10^4$	*P* (bar)	$X \times 10^4$
132	1.68	132	1.32	132	1.71	132	0.925	132	3.17	133	1.66	132	2.66	133	1.76	132	2.20	134	1.29
152	2.07	152	1.90	152	2.39	152	1.73	154	3.50	154	2.60	155	3.91	154	3.16	155	3.17	154	2.56
172	2.48	172	2.62	172	3.21	172	3.00	175	4.38	175	3.71	176	5.19	175	5.16	175	4.23	176	4.16
193	2.92	193	3.48	193	4.16	193	4.88	198	4.87	189	5.13	189	6.28	192	6.56	195	4.80	195	5.15

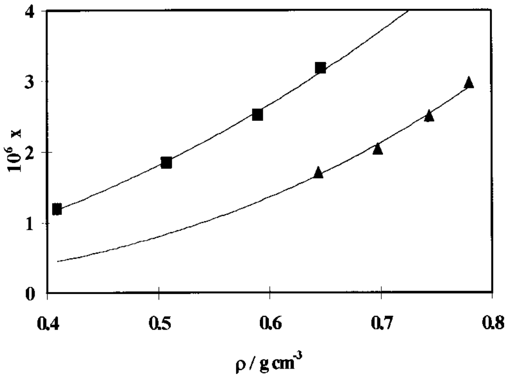

Figure 3. Mole fraction of C. I. Disperse Yellow 7 in SC−CO$_2$: (▲) 323.15 K, (■) 343.15 K.

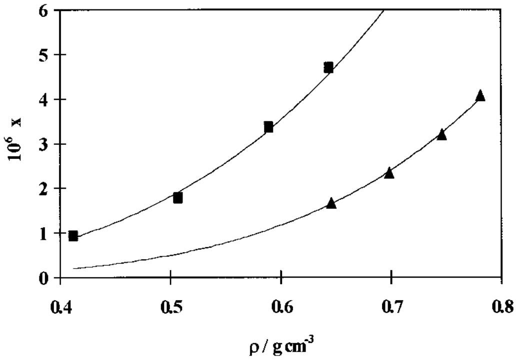

Figure 4. Mole fraction of C. I. Disperse Orange 11 in SC−CO$_2$: (▲) 323.15 K, (■) 343.15 K.

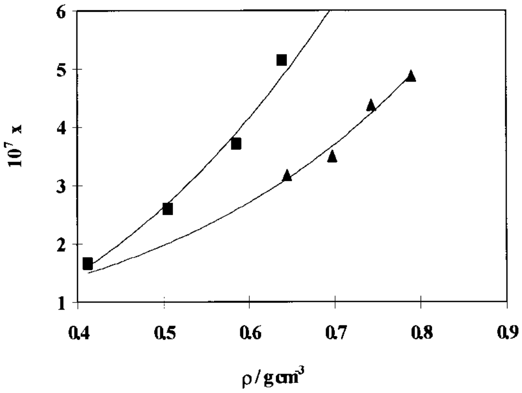

Figure 5. Mole fraction of C. I. Mordant Yellow 12 in SC−CO$_2$: (▲) 323.15 K, (■) 343.15 K.

are anthraquinone dyes, and C. I. Mordant Brown is a nitroso dye.

All dyes were purchased from Aldrich and purified before use by recrystallization. A flow type apparatus was used to measure the solubilities of the dyes. The apparatus used is similar to that used by Cross et al. (1996), and the details of the experimental technique are given elsewhere (Cross et al., 1996). The validity of the experimental technique was first determined by measuring phenantrene solubility in SC−CO$_2$. The current data are compared to the data by Kurnik et al. (1981) and Cross et al. (1996) in Figure 2. The reproducibility was in the range $\pm(0.01-0.24) \times 10^{-3}$ mole fraction. Although the results are systematically lower than those reported by Cross et al. (1996), they are within the error ranges. The equipment was not the same equipment used by Cross et al. (1996), but a very similar new setup, which may explain the systematic variation in the data.

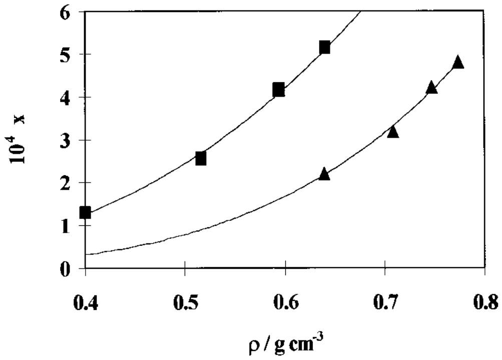

Figure 6. Mole fraction of C. I. Mordant Brown in SC−CO$_2$: (▲) 323.15 K, (■) 343.15 K.

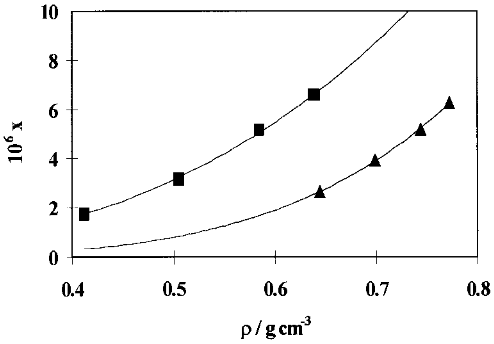

Figure 7. Mole fraction of C. I. Mordant Red 11 in SC−CO$_2$: (▲) 323.15 K, (■) 343.15 K.

Results and Discussion

The solubility measurements were carried out at 323.15 K and 343.15 K and 132−195 bar pressure, and the results are given in Table 1 and summarized in Figures 3−7. For all dyes it was observed that the solubility increases with temperature and with density, the increase with density being more pronounced at high temperatures. At a specified temperature and pressure, C. I. Mordant Brown has the highest solubility and C. I. Mordant Yellow has the lowest solubility. We believe that the high solubility of Mordant Brown is not only due to its small size compared to the other dyes but also due to forming an oxime structure through tautomerization (equilibrium between enol and carbonyl forms). This results in strong hydrogen bonding within the molecule rather than between molecules, hence fixing the size of the molecule. All of the other dyes contain −OH and $-NH_2$ groups, which enable hydrogen bonding between different molecules. Thus molecules associate and interect with each other and in effect behave as a large molecule, resulting in lower solubilities. Similar to our observations, Uchiyama et al. (1997) gave solubility of flavone and of 3-hydroxyflavone at 318.2 K and 25.3 MPa as 5.61×10^{-4} and 5.56×10^{-5}, respectively. The only difference between these compounds is the −OH group, which results in an order of decrease in solubility. This also suggests that hydrogen bonding between molecules results in decreased solubility. Lucas et al. (1998) studied solubilities of substituted phenols (by −Cl, $-CH_3$, $-OCH_3$, $-NO_2$, and −COOH) and showed that the carboxyl group results in the largest decrease in solubility, again indicative of hydrogen bonding between molecules.

The data are also consistent with the measurements of Joung and Yoo (1998). At a given density, the solubility values for Disperse Orange 11 and Disperse Yellow 7 they report at 313 K are lower than the solubility values we have at 323 K and the values they report at 353 K are higher than our values at 343 K.

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