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Solubility relationships for disperse dyes in supercritical carbon dioxide

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Abstract

The solubility of ten disperse dyes in supercritical carbon dioxide (SC-CO_2) was measured using a modified Suprex PrepMaster SFE apparatus and Varian Cary 3E UV–Visible spectrophotometer. These measurements were made over a pressure range of 200–400 atm, at 50–100°C. The results were combined with relevant solubility data from previous studies, and were used to develop correlations between disperse dye structures and SC-CO_2 solubility. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Disperse dyes; Solubility; Supercritical fluid; Polyester; Carbon dioxide; Dyeing

1. Introduction

Previous papers have presented the characteristics of a supercritical fluid and the advantages of SC-CO_2, over water, as a medium for dyeing polyester [1,2]. Among other advantages, SC-CO_2 eliminates colored wastewater and high drying-energy costs associated with aqueous polyester dyeing, making SC-CO_2 a potentially attractive alternative.

SC-CO_2 solubility is one of the most important parameters for dye selection and also for process temperature and pressure optimization. In order for this technology to have utility for industrial dye application, dye solubility must be sufficiently high at conditions that can be maintained in commercial dyeing machinery.

It is known that dye properties such as melting point, molecular weight, heat and entropy of fusion do not correlate with SC-CO_2 solubility [3,4]. In the present study, the SC-CO_2 solubility of 20 dyes was measured, and the results were used to identify structural factors that increase or decrease disperse dye solubility. It was invisaged that the results could be used in designing and screening dye candidates for SC-CO_2 dyeing of polyester, or in selecting compatible dyes for color matching, without exhaustive solubility testing of dyestuff inventories.

2. Experimental

Solubilities were measured using a modified Suprex PrepMaster apparatus to equilibrate the dye with SC-CO_2. A Varian Cary 3E UV–Visible spectrophotometer was used to determine the quantity of dye dissolved. The heats of fusion and melting points were determined on a Perkin–Elmer DSC-7 differential scanning calorimeter.

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The experimental procedure used to obtain solubility data is identical to the method used by Marlowe to determine solubility values as mole fraction of dye [3]. These values were obtained for six different SC-CO_2 densities. Two of the SC-CO_2 densities used for the ten additional dyes studied here are not common to the original dye candidates studied by Marlowe, so those values are not available for the first ten dyes. These are designated by an N/A in Tables 1 and 2, which means that the data are not available. The original dyes were all received and tested in presscake form, as were six of the ten additional dyes reported in this study. However, four of the ten colorant materials used in this work were received in commercial form with dispersing agents and diluents present. Isolation of colorants from commercial formulations employed the method described below.

2.1. Procedure for colorant purification

All colorants used in this study were either presscake materials (16 of the 20 materials studied) or colorants that were separated from diluents. To produce the latter, we vigorously stirred water (300 ml) at 65°C as commercial dye (20 g) dispersed in water (100 ml) was added. NaCl (5 g) was added at 10 min intervals, until the dispersion was saturated with NaCl. The dye dispersion was stirred with heating until it broke. The mixture was allowed to cool, with stirring, to room temperature and precipitated colorant was isolated using vacuum filtration. The solid was rinsed thoroughly with water to remove final traces of salt and other water-soluble contaminants.

3. Results and discussion

Table 1 contains a summary of the SC-CO_2 solubility data that was collected on the 20 disperse dyes employed in this study.

Table 2 provides a ranking of the 20 dyes studied, in order of decreasing solubility, along with some physical properties of the dyes. The best correlation is between SC-CO_2 solubility and molecular weight, which has a Pearson's Correlation Coefficient of 0.02 and an F statistic of less

Table 1
SC-CO_2 disperse dye solubility

	Solubility (mol fraction of dye)					
	350 atm, 100°C	350 atm, 50°C	300 atm, 100°C	300 atm, 50°C	200 atm, 100°C	200 atm, 50°C
Yellow 42	N/A	N/A	N/A	1.90E-5	N/A	1.60E-5
Blue 165:1	N/A	N/A	1.19E-6	6.54E-7	1.36E-7	2.48E-7
Red 167	N/A	N/A	1.14E-5	1.33E-5	9.70E-7	4.63E-6
Blue 77	N/A	N/A	8.73E-5	1.29E-4	1.50E-5	5.38E-5
Blue 118	N/A	N/A	3.55E-6	2.45E-6	3.63E-7	8.40E-7
Violet 91	N/A	N/A	5.99E-6	5.85E-6	3.30E-7	1.20E-6
Blue 102	N/A	N/A	1.90E-6	5.15E-7	1.90E-6	3.71E-7
Red 324	N/A	N/A	4.42E-6	2.60E-6	4.70E-7	1.41E-6
Yellow 86	N/A	N/A	1.06E-4	9.04E-5	2.43E-5	7.92E-5
Blue 60S	N/A	N/A	2.35E-6	9.30E-7	3.10E-7	4.10E-7
Blue 3	3.63E-5	9.56E-6	2.50E-5	1.25E-5	4.05E-6	4.71E-6
Red 30	3.03E-5	4.25E-6	2.04E-5	7.88E-6	1.64E-5	4.34E-5
Yellow 108	3.84E-5	8.12E-6	3.35E-6	3.70E-6	1.06E-6	8.37E-6
Orange 30	3.70E-5	7.25E-5	1.79E-5	3.04E-5	1.75E-6	6.38E-6
Brown 22	3.66E-5	1.54E-5	5.70E-5	1.17E-5	1.88E-5	1.59E-5
Red 137	7.42E-6	2.08E-6	1.07E-5	2.69E-6	2.75E-6	1.10E-5
Black 9	5.46E-6	2.40E-6	1.18E-5	1.53E-5	4.67E-6	1.40E-5
Blue 79:1	4.19E-5	4.75E-5	1.04E-4	2.25E-5	1.24E-5	1.87E-5
Red W-4BS	1.54E-5	5.73E-6	5.05E-6	1.61E-5	5.80E-7	1.96E-6
Blue 27	4.51E-6	1.24E-5	3.06E-6	7.95E-6	1.66E-7	8.19E-6

Table 2
Features of disperse dyes studied, in decreasing order of solubility

	Molecular weight (g/mol)	Melting point (°C)	Heat of fusion (J/g)	Dye class
1 Blue 77	377	226	29.74	Anthraquinone
2 Yellow 86	365	124	86.40	Nitrodiphenylmine
3 Blue 79:1	625	144	76.61	Azo
4 Orange 30	448	109	48.86	Azo
5 Brown 22	399	N/A	N/A	Azo
6 Yellow 108	429	171	22.91	Azo
7 Red 30	365	151	29.08	Azo
8 Blue 3	276	142	51.34	Anthraquinone
9 Red 167	506	137	65.41	Azo
10 Yellow 42	369	157	85.27	Nitrodiphenylmine
11 Violet 91	516	147	61.48	Azo
12 Red 324	426	170	30.88	Azo
13 Red W-4BS	469	186	46.03	Azo
14 Black 9	300	152	95.61	Azo
15 Blue 27	420	N/A	N/A	Anthraquinone
16 Red 137	430	125	36.22	Azo
17 Blue 118	346	239	37.66	Anthraquinone
18 Blue 60S	379	195	68.32	Anthraquinone
19 Blue 102	353	115	24.57	Azo
20 Blue 165:1	427	204	88.15	Azo

Table 3
Thermodynamic data for the dyes used in this study

Dye name and rank	Melting point (K)	Molar heat of fusion (kcal/mol)	Melting entropy (cal/mol K)
1 Blue 77	499	11.2	22.5
2 Yellow 86	397	31.4	79.4
3 Blue 79:1	417	47.9	114.8
4 Orange 30	382	21.9	57.3
5 Brown 22	–	–	–
6 Yellow 108	444	9.8	22.1
7 Red 30	424	10.6	25.0
8 Blue 3	415	14.2	34.1
9 Red 167	410	33.1	80.7
10 Yellow 42	430	31.5	73.2
11 Violet 91	420	31.8	75.5
12 Red 324	443	13.2	29.7
13 Red W-4BS	459	21.6	47.0
14 Black 9	425	28.7	67.5
15 Blue 27	–	–	–
16 Red 137	398	15.6	39.1
17 Blue 118	512	13.0	25.5
18 Blue 60S	468	25.9	55.3
19 Blue 102	388	8.7	22.4
20 Blue 165:1	477	37.6	78.9

than 0.5. Melting point, molar heat of fusion, and entropy of fusion show little correlation with solubility (Table 2). Similarly, a comparison of thermal data between pairs of similar molecules does not give a useful correlation that accounts for solubility differences. These data are shown in Table 3.

While one might expect solid state dye binding energy to provide an indicator of ease or difficulty of solubility, we found that thermal analysis was not a reliable indicator of SC-CO_2 solubility. In fact, dye structure is the only factor that correlated consistently with SC-CO_2 solubility. We observed that higher polarity generally led to lower SC-CO_2 solubility. Disperse dyes designed for aqueous applications have polar auxochromes to provide the necessary water solubility characteristics. In most cases, these groups suppress SC-CO_2 solubility.

While the dependence of solubility on temperature and pressure may appear very complex at first glance, solubility behavior for substances in SC-CO_2 typically follow the pattern as shown in Fig. 1 for benzoic acid [5]. The crossover points for inversion of benzoic acid solubility with changing temperature are charcateristic features in solubility–pressure plots. Solubility inversion points arise from temperature-induced density changes at constant pressure. Of course, the pressure scale and solubility enhancement will vary from solute to solute. By examining the temperature and pressure dependence of SC-CO_2 solubility, one can ascertain the experimental pressure data range for a given various dye. With these points in mind, a number of points can be made concerning the dyes in the present study.

In the 50–100°C temperature range and at pressures of 200–300 atm, C I Disperse Red 137, Yellow 108, Red 30 and Blue 27 have lower solubility at higher pressures and constant temperature. Disperse Blue 27 lies near a crossover and the minimum.

Dyes in which solubility is higher at lower temperature include C I Disperse Red 167, Blue 77,

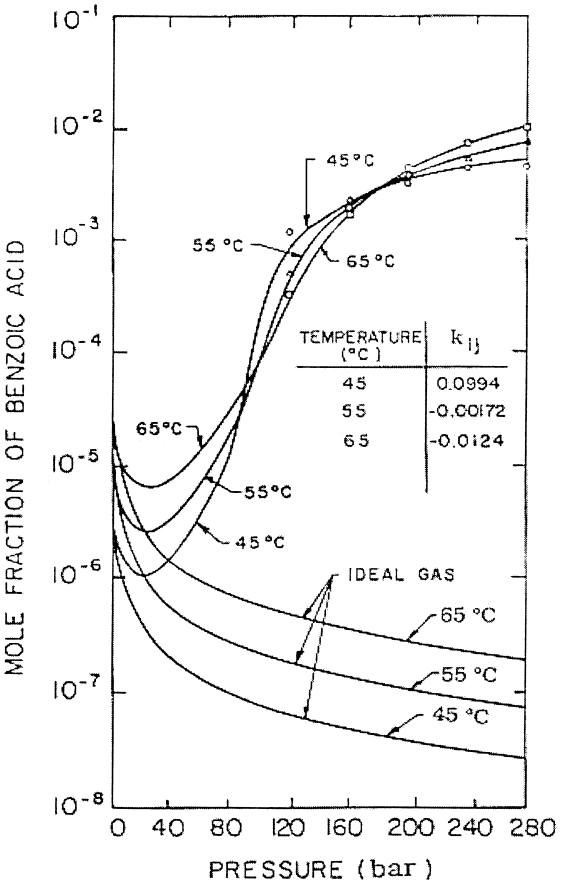


Fig. 1. Qualitative behavior of benzoic acid in SC-CO_2.

Orange 30, and Black 9. For these dyes, solubility increases with decreasing temperature at constant pressure. In addition, these dyes are always more soluble at higher pressure regardless of the temperature, but in this case solubility is greater at higher temperatures.

For C I Disperse Yellow 86, Blue 60, Blue 3, Brown 22, Blue 165:1, Violet 91, Blue 118, Red 324, and Blue 79, changing the temperature either increases or decreases solubility, but increasing the pressure always increases solubility. In fact, for these dyes there are pressures in the 200–300 atm range for which solubility is independent of temperature.

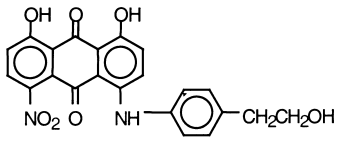
Finally, Blue 102 is always more soluble at higher temperature, and its solubility increases with increasing pressure. Changes in its solubility, as a function of pressure, are greater at lower temperatures.

3.1. Solubility–structure relationships

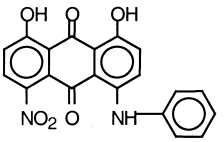
Anthraquinone disperse dyes CI Disperse Blue 27 and CI Disperse Blue 77 have similar structures, differing only in the presence of a hydroxyethyl group in the anilino moiety of CI Disperse Blue 27. Since SC-CO_2 is non-polar, the polar hydroxyethyl group lowers the solubility of CI Disperse Blue 27 in SC-CO_2, as shown in Table 4.

CI Disperse Blue 118 is also similar to CI Disperse Blue 77. In this case, the structural difference is an amino group in place of a nitro group. The amino group reduces SC-CO_2 solubility, as shown in Table 5.

Table 4
Comparison of SC-CO_2 solubility (mole fraction of dye) for Blue 27 and Blue 77



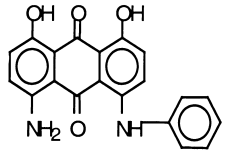
CI Disperse Blue 27



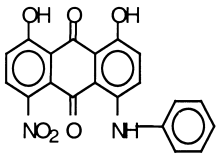
CI Disperse Blue 77

Dye name	$P=350$ atm $T=100°C$	$P=350$ atm $T=50°C$	$P=300$ atm $T=100°C$	$P=300$ atm $T=50°C$	$P=200$ atm $T=100°C$	$P=200$ atm $T=50°C$
Blue 27	4.51E-6	1.24E-5	3.06E-6	7.95E-6	1.66E-7	8.19E-6
Blue 77	–	–	8.73E-5	1.29E-4	1.50E-5	5.38E-5

Table 5
Comparison of SC-CO_2 solubility (mole fraction of dye) for Blue 118 and Blue 77



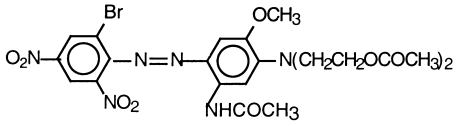
Cl Disperse Blue 118



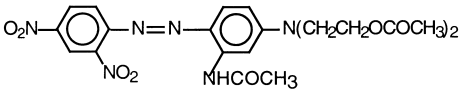
Cl Disperse Blue 77

Dye name	$P=400$ atm $T=100°C$	$P=400$ atm $T=50°C$	$P=300$ atm $T=100°C$	$P=300$ atm $T=50°C$	$P=200$ atm $T=100°C$	$P=200$ atm $T=50°C$
Blue 118	7.57E-6	3.41E-6	3.55E-6	2.45E-6	3.63E-7	8.40E-7
Blue 77	2.27E-4	2.32E-4	8.73E-5	1.29E-4	1.50E-5	5.38E-5

Table 6
Comparison of SC-CO_2 solubility (mole fraction of dye) for Blue 79:1 and Violet 91



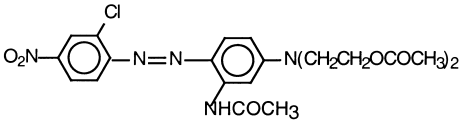
Disperse Blue 79:1



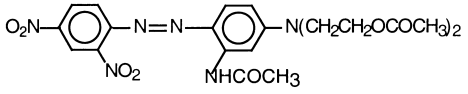
Disperse Violet 91

Dye name	$P=350$ atm $T=100°C$	$P=350$ atm $T=50°C$	$P=300$ atm $T=100°C$	$P=300$ atm $T=50°C$	$P=200$ atm $T=100°C$	$P=200$ atm $T=50°C$
Blue 79:1	4.19E-5	4.75E-5	1.04E-4	2.25E-5	1.24E-5	1.87E-5
Violet 91	NA	NA	5.99E-6	5.85E-6	3.30E-7	1.20E-6

Table 7
Comparison of SC-CO_2 solubility (mole fraction of dye) for Red 167 and Violet 91



Disperse Red 167



Disperse Violet 91

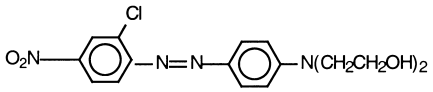
Dye name	$P=400$ atm $T=100°C$	$P=400$ atm $T=50°C$	$P=300$ atm $T=100°C$	$P=300$ atm $T=50°C$	$P=200$ atm $T=100°C$	$P=200$ atm $T=50°C$
Red 167	3.40E-5	2.22E-5	1.14E-5	1.33E-5	9.70E-7	4.63E-6
Violet 91	2.10E-5	9.24E-6	5.99E-6	5.85E-6	3.30E-7	1.20E-6

CI Disperse Violet 91 and CI Disperse Blue 79:1 are azo dyes with similar structures. CI Disperse Blue 79:1 contains bromo group in the diazo component and a methoxy group in the coupler. Although CI Disperse Blue 79:1 is a larger molecule, it is more soluble than CI Disperse Violet 91 (Table 6). These results and data on CI Disperse Red 167 and CI Disperse Brown 22 suggest that presence of halogens in disperse dye molecules enhances solubility.

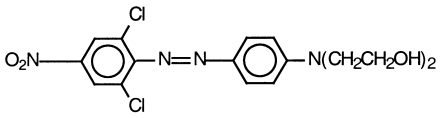
CI Disperse Red 167 is also structurally similar to CI Disperse Violet 91, but has a chloro group ortho to the azo bond in its diazo component (Table 7). This makes the solubility of CI Disperse Red 167 higher than that of CI Disperse Violet 91. However, the differences in solubility are not as significant as observed in other cases.

CI Disperse Brown 22 and CI Disperse Red 30 differ in the number of chloro groups in the diazo component (Table 8). CI Disperse Brown 22 has

Table 8
Comparison of SC-CO_2 solubility (mole fraction of dye) for Red 30 and Brown 22



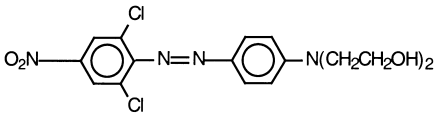
Disperse Red 30



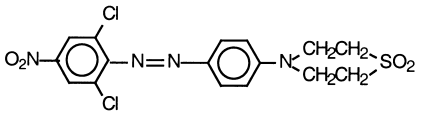
Disperse Brown 22

Dye name	$P=350$ atm $T=100°C$	$P=350$ atm $T=50°C$	$P=300$ atm $T=100°C$	$P=300$ atm $T=50°C$	$P=200$ atm $T=100°C$	$P=200$ atm $T=50°C$
Red 30	3.03E-5	4.25E-6	2.04E-5	7.88E-6	1.64E-5	4.34E-5
Brown 22	3.66E-5	1.54E-5	5.70E-5	1.17E-5	1.88E-5	1.59E-5

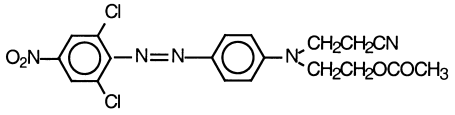
Table 9
Comparison of SC-CO_2 solubility (mole fraction of dye) for Orange 30, Yellow 108 and Brown 22.



Disperse Brown 22



Disperse Yellow 108



Disperse Orange 30

Dye name	$P=350$ atm $T=100°C$	$P=350$ atm $T=50°C$	$P=300$ atm $T=100°C$	$P=300$ atm $T=50°C$	$P=200$ atm $T=100°C$	$P=200$ atm $T=50°C$
Brown 22	3.66E-5	1.54E-5	5.70E-5	1.17E-5	1.88E-5	1.59E-5
Orange 30	3.70E-5	7.25E-5	1.79E-5	3.04E-5	1.75E-6	6.38E-6
Yellow 108	3.84E-5	8.12E-6	3.35E-6	3.70E-6	1.06E-6	8.37E-6

slightly higher solubility than CI Disperse Red 30. This suggests that the additional chloro group has a beneficial affect on the SC-CO_2 solubility.

In all previous cases, the differences in dye structures involved in the ring substituents. In contrast, CI Disperse Brown 22, CI Disperse Yellow 108, and CI Disperse Orange 30 have the same ring substituents but differ in the nature of their pendant side chains. CI Disperse Brown 22 is the most soluble dye molecule of the group with Orange 30 being second, and CI Disperse Yellow 108 the least soluble in SC-CO_2. Although the hydroxyethyl groups are very polar, the polarity of these groups may be mitigated in part by the presence of inter- or intra-molecular hydrogen bonding. While the CI Disperse Orange 30 pendant chains are polar, the individual end groups interact more readily with CO_2 than the pendant groups of CI Disperse Yellow 108. Also, the SO_2 residue on CI Disperse Yellow 108 is highly polar, giving this dye the lowest solubility of the three (Table 9).

4. Conclusions

For the 20 dyes examined in this study, SC-CO_2 solubility differences between pairs of dyes of similar molecular structure correlate with molecular structure. Specifically, solubility is influenced by the polarity of the dye molecule, leading to either increased solubility for less polar molecules and decreased solubility for more polar molecules. Dyes with amino or halo groups substituents are more soluble than those with nitro groups in the same ring positions.

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