

Dispersant-free Dyeing of Polyester with Temporarily Solubilized Azo Disperse Dyes from Indole Derivatives

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Abstract: Temporarily solubilized azo disperse dyes based on 1,2-substituted indoles were synthesized and characterized. Dispersant-free dyeing of polyester by using the synthesized dyes has been investigated. The colour yields of the dyes on the polyester fabric were found to be highly dependent on the dyeing pH, optimum results being obtained at pH 5. The dyes exhibited good to excellent fastness properties on polyester while lightfastness was moderate.

Keywords: Temporarily solubilized disperse dyes, Polyester, Dispersant-free dyeing

Introduction

Temporarily solubilized disperse dyes were first synthesized in 1922[1,2]. These dyes, such as those of the Ionamine range, contained *N*-methylsulfonic acid group that gave temporary solubility to the dye molecules. They are hydrolyzed in the dyebath during dyeing to form insoluble species that are adsorbed onto the surface of the hydrophobic fiber, and diffuse into it.

Disperse dyes containing β -sulfatoethylsulfonyl group also have temporary solubility. The terminal sodium sulfonate group confers sufficient water solubility at room temperature so that no milling process is needed during manufacturing of dye, and the dyebath can be prepared without dispersing agents. During the dyeing process, the water-soluble dyes are converted into the insoluble vinylsulfone derivatives that have substantivity to the hydrophobic polyester. In an effort to overcome some of the environmental problems associated with the use of dispersing agents, we synthesized some temporarily solubilized azo disperse dyes containing β -sulfatoethylsulfonyl group, measured the conversion rates of the soluble dyes into insoluble derivatives using HPLC, and examined the feasibility of dispersant-free polyester dyeing [3,4]. These dyes showed moderate to good fastness properties on polyester fabric. We also reported the application of these dyes for one-bath dyeing of polyester/cotton blend fabric[5,6].

Recently, we have attempted to synthesize a range of temporarily solubilized disperse dyes which have a wider variety of color. Thus, for the yellow shades, aromatic heterocyclic compounds such as pyridone[7] and indole were used as coupling components.

In this study, three temporarily solubilized disperse dyes were prepared by coupling the diazonium salt of aminophenyl-4-(β -sulfatoethylsulfone) with 1,2-substituted indoles. Dispersant-free polyester dyeing with these dyes was performed using a

high temperature dyeing method. Dyeing and fastness properties of the dyes on polyester fabric were investigated.

Experimental

Materials and Chemicals

Scoured, woven polyester fabric (density, 113 \times 93 tpi; weight, 69 g/m²) was obtained from the Korea Apparel Testing and Research Institute. Aminophenyl-4-(β -sulfatoethyl sulfone) was supplied by Kyung-In Synthetic Co. and used as a diazo component. Indole (98 %), 2-phenylindole (95 %) and 1-methyl-2-phenylindole (99 %) were purchased from Aldrich and used as coupling components. All the other chemicals used were of laboratory grade.

Instrumentation

Melting points were recorded in capillary tubes on an Electrothermal 9100, Dong-Bo Chem. Co. and are uncorrected. ¹H-NMR spectra were recorded in DMSO-*d*₆ using a Jeol lambda series instrument at 300 MHz. Visible spectra were recorded in DMF in 1 cm quartz cells using a HP 8452A spectrophotometer. Mass spectra were recorded in fast atom bombardment ionization mode using Jeol JMS-AX505WA/HP 5890 Series II GC-Mass Spectrometer.

Synthesis of Temporarily Solubilized Dye

Aminophenyl-4-(β -sulfatoethylsulfone) (2.81 g, 0.01 mol) was diazotized with the same method mentioned in the previous work[7] using concentrated hydrochloric acid and sodium nitrite. The prepared diazonium salt solution was added to the corresponding coupling component (0.01 mol) dissolved in 80 ml of ethanol and the temperature was maintained at 0-5 °C. The solution was stirred for 2 hrs and allowed to reach room temperature. Sodium acetate solution (1 M) was added to adjust the pH between 4 and 5. After 50 g sodium chloride was added to the solution, the precipitate formed was filtered and dried in a vacuum oven at room temperature. To remove

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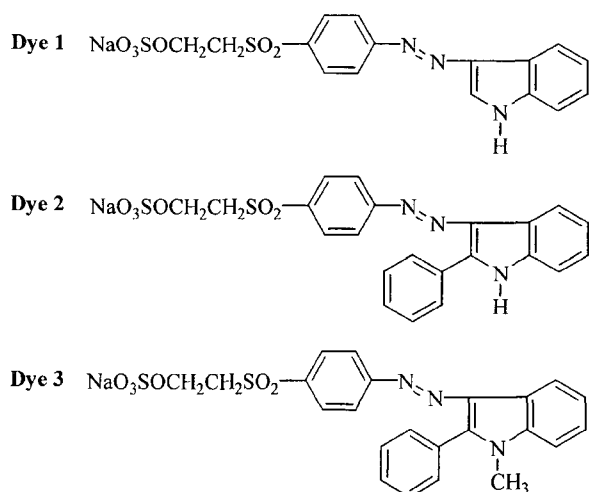


Figure 1. Structures of the temporarily solubilized disperse dyes synthesized in this study.

excess sodium chloride, 5 g of dried dye was dissolved in 100 ml dimethyl formamide (DMF). The solution was filtered and poured into 200 ml of dichloromethane. The precipitated dye 1-3 were filtered and dried. The structures of the synthesized dyes are shown in Figure 1.

Dyeing Procedure

Polyester fabrics were dyed in an Ahiba dyeing machine at a liquor ratio of 20:1. The dyebaths were prepared with the synthesized dyes 1-3 (0.5-3 % owf) and buffered as follows: at pH 4 and 5 with sodium acetate (0.05 M)/acetic acid, at pH 6, 7, and 8 with sodium dihydrogen phosphate (0.05 M)/disodium hydrogen phosphate and at pH 10 with sodium dihydrogen phosphate (0.05 M)/trisodium phosphate.

Dyeing was commenced at 70 °C. The dyebath temperature was raised at a rate of 1 °C/min to 130 °C, maintained at this temperature for 60 min, and rapidly cooled to 60 °C. The dyeings were rinsed and then reduction cleared in an aqueous solution of 2 g/l sodium hydroxide and 2 g/l sodium hydrosulphite at 80 °C for 30 min.

Colour Measurement

The colour parameters of the dyed fabrics were determined on a Macbeth coloureye 3000 spectrophotometer, under illuminant D₆₅ using the 10° standard observer with specular component excluded and UV component included.

Measurement of Exhaustion

The exhaustion of dye on the polyester fabric was measured by DMF extraction method (30 min at 150 °C). The absorbance of the solution extracted was determined using a HP 8452A UV/VIS spectrophotometer. The percentage exhaustion was calculated using equation (1):

$$\text{Exhaustion (\%)} = C_t/C_0 \times 100 \quad (1)$$

Where C_t is the amount of dye extracted from a dyed fabric at time t and C_0 is the amount of dye in the initial dyebath.

Fastness Determination

The dyed fabrics were subjected to wash (ISO 105-C06/ C1S:1994), light (AATCC Test Method 16-1998), sublimation (ISO 105-X11:1994) and rub (ISO 105-X12:2001) fastness tests after heat setting at 180 °C for 60 s. The shade change, together with staining of adjacent fabrics, was assessed according to appropriate SDC grey scale.

Results and Discussion

Dye Synthesis

For the synthesis of the temporarily solubilized azo disperse dyes, aminophenyl-4-(β -sulfatoethylsulfone) was used as a diazo component and 1,2-substituted indoles as coupling components. Aminophenyl-4-(β -sulfatoethylsulfone) was diazotized and the diazonium salt was coupled with indole derivatives to give temporarily solubilized azoindole dyes 1-3.

For dye 1 in which indole was used as a coupling component, the attack by the electrophilic diazonium ion can take place in many position of the indole ring[8]. Of the two rings of indole, the heterocyclic ring is very electron-rich, by comparison with a benzene ring, and the attack always takes place in the five-membered ring, except in special circumstances[9]. Of the three positions on the heterocyclic ring, attack at nitrogen would destroy the aromaticity of the five-membered ring, and produce a localized cation; both of the remaining positions can be attacked, but the β -position (3-position) is preferred by a considerable margin. The intermediate for attack at α -position (2-position) is stabilized but it cannot derive assistance from the nitrogen without disrupting the benzenoid resonance. The more stable intermediate from attack at 3-position has charge located adjacent to nitrogen and is able to derive the very considerable stabilization attendant upon interaction with its lone pair of electrons as shown in Figure 2. In the case of dyes 2 and 3, the attack should take place at 3-

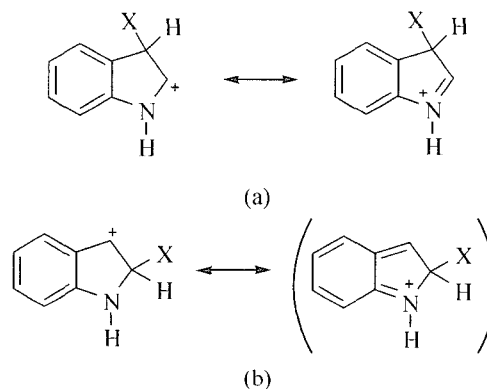


Figure 2. Electrophilic attack by the diazonium ion (X^+) at the β - or α -position of the indole; (a) β -attack, (b) α -attack.

Table 1. Yields and characterization data of the dyes 1-3

Dye	Yield (%)	M.P. (°C)	λ_{\max}^a (nm)	$^1\text{H-NMR}^b$ δ (ppm)	Mass (m/z)
1	62	165-167	394	3.65-3.70 (t, 2H, $-\text{CH}_2-\text{SO}_2$) 4.01-4.05 (t, 2H, $\text{O}-\text{CH}_2-$) 7.08-8.52 (m, 9H, aromatic protons) 12.41 (s, 1H, 1-position on indole ring)	432 (MH^+)
2	79	224-226	418	3.60-3.65 (t, 2H, $-\text{CH}_2-\text{SO}_2$) 4.02-4.05 (t, 2H, $\text{O}-\text{CH}_2-$) 7.35-8.56 (m, 13H, aromatic protons) 12.70 (s, 1H, 1-position on indole ring)	508 (MH^+)
3	82	186-188	410	3.64-3.69 (t, 2H, $-\text{CH}_2-\text{SO}_2$) 4.02-4.06 (t, 2H, $\text{O}-\text{CH}_2-$) 3.82 (s, 3H, $\text{N}-\text{CH}_3$) 7.42-8.54 (m, 13H, aromatic protons)	522 (MH^+)

^{a)}measured in DMF.

^{b)}measured in $\text{DMSO}-d_6$.

position because 2-position is substituted by a phenyl ring.

The dyes synthesized were characterized using NMR and Mass spectrometry. Yields and characterization data of the dyes are shown in Table 1. In the $^1\text{H-NMR}$ spectra, all spectra have two triplet peaks at 3.60-3.70 and 4.01-4.06 ppm attributed to the 4H ethyl protons in the sulfatoethylsulfonyl group. The peaks for $-\text{NH}$ protons of dyes 1 and 2 appear at 12.41 and 12.70 ppm respectively. The spectrum of dye 3 has a singlet peak at 3.82 ppm for 3H methyl protons. In the absorption spectra of dyes 1 and 2, dye 2 exhibited higher λ_{\max} value than dye 1. It can be explained by considering that phenyl substituent at 2-position of dye 2 is more electron donating group than hydrogen of dye 1.

Dispersant-free Dyeing of Polyester

As shown in a previous study, the dyeing properties of temporarily solubilized disperse dyes are highly dependent

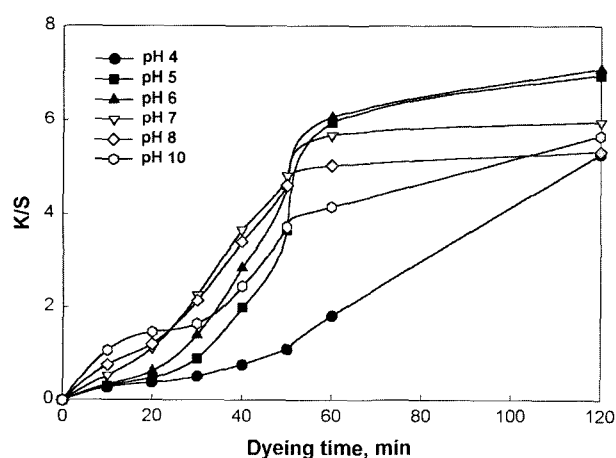


Figure 3. Effect of pH on the colour yield of dye 1 on polyester fabric (1 % owf, liquor ratio 20:1).

on pH values. Figure 3 shows the colour yield of dye 1 on polyester fabric at various pH values. A good colour yield was obtained at pH 5 and 6. At pH 4, colour yield was lower than that at pH 5 and 6 due to the low conversion rate of the soluble dye into the insoluble vinylsulfone form. However, the colour yield on polyester fabric increased continuously throughout the whole dyeing procedure, implying that the conversion of dye occurred steadily. The colour yields at pH 7, 8, and 10 were low and the dyed samples showed poor levelling since the rapid conversion of dye caused a collapse in the dyebath dispersion stability. This is why the colour yields at these pH conditions for first 30 min of dyeing were higher than those at other pH conditions. These results are well consistent with the previous results[4,7]. The percentage exhaustion values of the dyes 1-3 on the polyester fabric are shown in Table 2. For pH 5, Exhaustion values were slightly higher than those at pH 6.

Figure 4 shows the colour yields of the dyes on polyester fabrics dyed at pH 5. The dyeing rate seems to be related to the molecular weight of the dye; the high molecular weight of the dye lowers the dye diffusion rate. Thus the rate of dyeing was fast in the order of dyes 1, 2, and 3. However, the colour yields of dyes 2 and 3 increased continuously throughout the latter part of dyeing process whereas that of dye 1 increased slightly. This may be due to the more hydrophobic character of dye 2 and 3 induced from 2-phenyl group giving more substantivity to hydrophobic polyester than dye 1. Dye

Table 2. Exhaustion of dyes 1-3 on polyester at pH 5 and 6 (1 % owf)

pH	Exhaustion (%) of dye		
	1	2	3
5	67.8	82.7	75.4
6	66.4	82.3	71.8

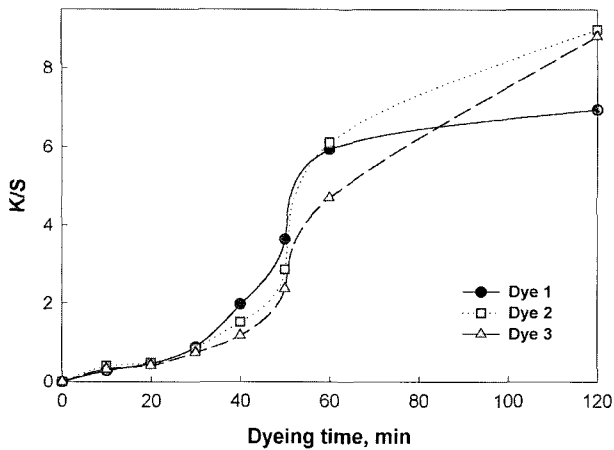


Figure 4. The colour yields of dyes 1-3 on polyester fabric (1 % owf, pH 5).

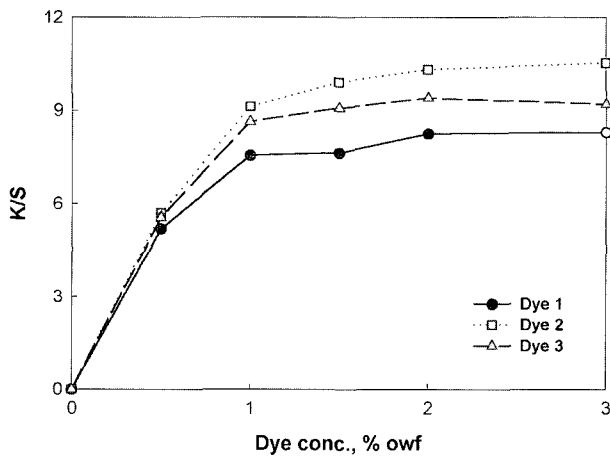


Figure 5. Build-up of dyes 1-3 on polyester fabric (pH 5, liquor ratio 20:1).

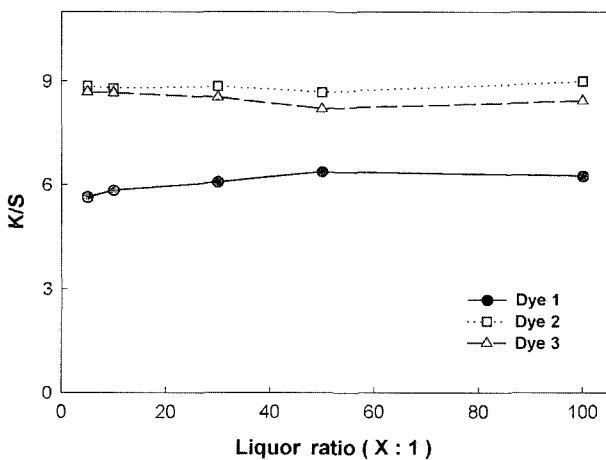


Figure 6. Effect of liquor ratio on colour yields of dyes 1-3 on polyester fabric (1 % owf, pH 5).

1 has low molecular weight giving the fast diffusion of the dye but has polar NH group causing the less substantivity to polyester and low final colour yield.

Figure 5 shows the build-up of dyes at pH 5. Dyes 1-3 exhibited good build-up on polyester and colour strength reached saturation at ca. 2.0 % owf. All of the dyes gave yellow hues. The colour yields of all the dyes were not dependent on the liquor ratio as shown in Figure 6.

Fastness Properties

All the dyeing for fastness test was carried out at pH 5, which was optimum pH condition. Table 3 shows the light and wash fastness results of dyes 1-3 on polyester fabric. Without regard to the dye concentrations used, the lightfastness of all dyes was moderate and washfastness was excellent. Table 4 shows the results of rubbing and sublimation fastness, which are all good to excellent.

Conclusions

Temporarily solubilized azo disperse dyes based on 1,2-substituted-indole derivatives were synthesized and dispersant-free polyester dyeing was examined. The dyes were prepared by common diazo-coupling reaction and polyester was

Table 3. The wash (ISO 105-C06/C1S) and light (AATCC 16-1998) fastness of dyes 1-3 on polyester fabric (heatsetting 180 °C, 60 s)

Dye	Dye conc. (owf)	Light	Wash		
			Change	Staining	
				Polyester	Cotton
1	1 %	3	5	5	5
	2 %	3	5	5	5
2	1 %	4	5	5	5
	2 %	4	5	5	5
3	1 %	4	5	5	5
	2 %	4	5	5	5

Table 4. The rubbing (ISO 105-X12) and sublimation (ISO 105-X11) fastness of dyes 1-3 on polyester fabric (heatsetting 180 °C, 60 s)

Dye	Dye conc. (owf)	Rubbing		Sublimation		
		Staining		Change	Staining	
		Dry	Wet		Polyester	Cotton
1	1 %	4/5	5	4/5	4/5	4/5
	2 %	4/5	4/5	4/5	4/5	4/5
2	1 %	5	5	4/5	4/5	4/5
	2 %	5	5	4/5	4/5	4/5
3	1 %	5	5	4/5	4/5	4/5
	2 %	5	5	4/5	4/5	4/5

successfully dyed with synthesized dyes without dispersing agent. Colour yield on polyester was highly dependent on dyeing pH and optimum result was obtained at pH 5. All the dyes gave yellow shade and the final colour yield of dye 1 was lower than those of dyes 2 and 3 possibly due to its lower substantivity to the hydrophobic polyester. The lightfastness of the dyes was moderate and all the other fastness results were good to excellent.

Acknowledgements

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