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The Dyeing of Silk with Heterocyclic Disperse Azo-Dyes

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ABSTRACT

Studies on the dyeing behaviour on silk of some heterocyclic disperse dyes have been carried out. All dyes gave good coloration and good wet and light fastness properties. The results suggest that the dyeing of silk with selected disperse dyes can be promising for practical uses.

1 INTRODUCTION

Like wool, silk is a natural protein fibre. Peculiar features of silk fabrics are lustre, drape and softness. In order to maintain these properties, silk is treated with extreme care throughout all the wet processing stages. Because of the chemical similarity, silk is usually dyed with the typical dye classes used for the dyeing of wool, viz. acid dyes, metal complex dyes and reactive dyes. As regards acid dyes, they are usually applied on silk at 80°C in the presence of acetic acid and Glauber's salt.[1] Several authors[2–4] indicate that in the dyeing of wool with acid dyes, Coulombic forces between cationic sites (NH_3^+) of the wool and the dye anions play a very small part in the bonding of the dye to the fibre. The highest contribution is in fact made by polar forces (hydrogen bonds) and non-polar forces exerted between the hydrophobic regions of the dye and of the fibre.

In view of the structural analogies with wool, the silk–dye binding mechanism must be essentially the same. Moreover, owing to the remarkable reduction of basic and acid lateral groups in the proteic chain

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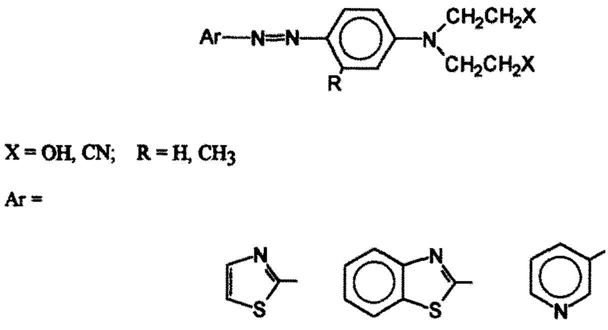

1

$X = OH, CN$; $R = H, CH_3$

Ar =

Fig. 1.

and to the minor number of hydroxylic groups, silk is more hydrophobic than wool and therefore should be dyed more easily than wool with hydrophobic dyes.

Up to now there does not appear to have been any attempt to investigate the behaviour of disperse dyes on this fibre. The aim of this work is therefore to study the dyeing properties on silk of a series of heterocyclic disperse dyes having the general formula 1 (Fig. 1).

2 EXPERIMENTAL

2.1 Materials

Commercial silk fabric, of weight $75\,g\,m^{-2}$ was used. The dyes were prepared according to the previously reported methods.[5,6] Purification was performed by crystallisation until constant melting point. Purity was checked by elemental analysis and thin layer chromatography. Characterisation data of the dyes are reported in Table 1.

2.2 Dyeings and fastness determinations

The dyeings were carried out in a thermostatted bath at 100:1 liquor ratio. Dye-baths were prepared by mixing an acetone solution of the dye with a solution of the dispersing agent (Setamol WS Bayer 1 g $litre^{-1}$). The acetone was then removed by boiling and distilled water was added to the required volume. The dyeings were carried out adjusting the pH of the dye liquor to 5 with a sodium acetate buffer. In order to ensure that equilibrium was reached, dyeing was continued for 12 h. After dyeing, the fibres were rinsed with Triton solution (0·5 g $litre^{-1}$), running water, distilled water and then dried.

The dye affinities were determined by means of the equation

$$-\Delta\mu^{\circ} = RT \ln C_f/C_s$$

TABLE 1
Characterization Data of the Dyes

Dye No.	*Ar*	*R*	*X*	λ_{max}[a] *(nm)*	*log* ε	λ_{max}[b] *(nm)*	*log* ε	*M.p.* (°*C*)
1	TZ	H	OH	483	4·58	496	4·58	172
2	TZ	H	CN	438	4·51	468	4·50	162
3	TZ	CH_3	OH	493	4·56	506	4·59	148
4	TZ	CH_3	CN	447	4·49	480	4·40	160
5	BTZ	H	OH	503	4·69	518	4·70	215
6	BTZ	H	CN	472	4·60	490	4·63	221
7	BTZ	CH_3	OH	514	4·72	528	4·72	186
8	BTZ	CH_3	CN	483	4·56	490	4·63	211
9	PY	H	OH	425	4·47	444	4·22	135
10	PY	H	CN	400	4·24	414	4·10	169
11	PY	CH_3	OH	429	4·45	448	4·44	99
12	PY	CH_3	CN	406	4·40	422	4·48	136

TZ, 2-thiazolyl; BTZ, 2-benzothiazolyl; PY, 3-pyridyl.
[a] In acetone.
[b] In *N*,*N*-dimethylformamide.

where C_f and C_s are the dye concentration in fibre (mol kg^{-1}) and in solution (mol litre^{-1}). The dye concentration on the fibre was determined spectrophotometrically after extraction with *N*,*N*-dimethylformamide of the dye from a known weight of dyed material. The wet and light fastnesses were assessed according to the ISO standard procedures.[7]

3 RESULTS AND DISCUSSION

3.1 Dye affinity

Inspection of Table 2 reveals a substantial increase in dye affinity as the dye hydrophobicity increases. Substitution of the hydrogen in the benzene ring with the methyl group in fact increases all the affinity values, whilst on replacing the hydroxy groups in the coupling component with cyano groups the affinity increases for all dyes except the benzothiazole derivatives. Another interesting observation is the effect of dye structure on substantivity. In general, the dye affinity increases as the conjugation increases, according to the following sequence: pyridine < thiazole < benzothiazole. These observations seem to be consistent with the mechanism of disperse dyeing as a partition of the dyes between a polar

TABLE 2
Affinity Values of the Dyes

Dye	$-\Delta\mu^\circ$ ($kJ\,mol^{-1}$)			$-\Delta H^\circ$ ($kJ\,mol^{-1}$)	$-\Delta S^\circ$ ($J\,mol^{-1}\,K^{-1}$)	$-\Delta\mu^{\circ a}$ ($kJ\,mol^{-1}$)
	60°C	*70°C*	*80°C*			
1	10·24	9·35	8·44	40·24	90·1	10·55
2	10·91	9·87	9·11	40·90	90·3	10·81
3	11·48	10·61	9·96	36·87	76·3	12·05
4	11·68	10·83	10·21	36·23	73·8	10·95
5	10·97	10·06	9·35	37·99	81·2	16·66
6	10·42	9·57	8·83	36·97	79·7	15·42
7	15·26	14·19	13·50	44·62	88·3	20·28
8	11·78	11·08	10·34	35·76	72·0	13·83
9	8·29	7·54	7·07	28·65	61·2	8·84
10	8·68	8·27	7·91	21·48	38·5	8·90
11	9·91	9·57	9·13	21·14	33·9	10·53
12	12·31	12·07	11·61	23·96	34·9	10·01

[a] On nylon at 80°C.

phase (water) and a less polar fibre.[8] However, the observation that the benzothiazole based dyes containing hydroxyl groups in the coupling component have higher affinity than the analogues with the cyano groups, the general good substantivity of hydroxylated dyes, and the fact that C_f values for these dyes are higher than those for cyano dyes, seems to suggest that the dye–fibre bonding is due to specific interactions (hydrogen bonds between dye and silk fibre) rather than to non-polar hydrophobic interactions. On the other hand, this fact is in agreement with studies on the adsorption of organic substances by wool and silk, which have shown that proton donors have higher substantivity than proton acceptors.[9–11]

Most likely, in the attachment of disperse dyes to silk all these interactions are operative, and it is the molecular structure of the dye that determines which of these forces will play the major role. In all cases, as indicated by the increase in affinity with dye conjugation, a planar structure, and then a close approach of the dye to the fibre is essential in order for the dye to be substantive.

In Table 2 are also reported the affinity values at 80°C for nylon. The dye affinities for silk are in general lower than for nylon. The affinity decrease is marked for the most hydrophobic dyes (benzothiazoles), the other dyes having affinity values for silk close to those for nylon. This shows that a high hydrophobicity is not imperative in order for the dye to be substantive to silk.

The effect of temperature on dyeing was estimated by plotting the $\Delta\mu^\circ/T$

TABLE 3
Colour Properties of the Dyes

Dye	x	y	Y (%)	λ_D (*nm*)	p (%)	L^* (%)	a^*	b^*
1	0·512	0·329	15·23	609	57·7	45·95	44·84	27·30
2	0·536	0·404	27·61	590	84·5	59·53	34·60	65·16
3	0·555	0·307	9·91	625	62·8	37·78	52·22	25·59
4	0·543	0·383	23·84	595	82·9	55·92	40·27	56·53
5	0·553	0·277	7·82	492[a]	61·3	33·59	57·03	16·80
6	0·461	0·356	31·99	594	51·7	63·33	33·13	33·09
7	0·528	0·271	4·71	493[a]	60·0	25·89	46·29	10·40
8	0·512	0·359	25·39	598	65·9	57·49	41·93	41·54
9	0·496	0·419	38·83	587	75·0	68·62	23·69	64·70
10	0·461	0·452	46·86	579	76·6	74·10	5·06	70·56
11	0·532	0·396	27·54	592	78·8	59·47	36·08	60·49
12	0·509	0·437	41·14	584	86·4	70·27	21·99	78·53

[a] Complementary wavelength.

values against $1/T$. The slope of the line gives the standard heat of dyeing (ΔH°) while the intercept on the y axis gives the entropy change (ΔS°) in the dyeing process. An increase in temperature lowers the dye affinity for silk and, as expected, the ΔH° values are negative. Since the adsorption process of dye is one in which the dye undergoes a transition from a state of random distribution in solution to a state of more ordered arrangement in the fibre, the entropy decreases. Because entropy values are a function of the number of bonds that the dye can form, they increase with the increase of ΔH° values (Table 2).

3.2 Colour properties

The dyes colour silk in deep shades from yellow to red (Table 3). As to the effect of the structure of the diazotable amine on the colour, replacement in the dye molecule of the pyridine ring with the thiazole or benzothiazole ring, causes a general bathochromic shift of the λ_D. The dominant wavelength depends also on the structure of the coupling component. A bathochromic shift is in fact observed on replacing the cyano groups in the N-alkyl chains with hydroxyl groups or by introducing a methyl group into the phenyl ring. Looking at the dominant wavelength with reference to the fibre used, we note that the λ_D values for silk are higher than those found for the same dyes applied on acetate or nylon fibres.[5,6] The purity values are approximately equivalent to those found for nylon and acetate, and are in general higher for

TABLE 4
Fastness Properties of the Dyes

Dye	*Washing*		*Perspiration*	*Dry cleaning*[a]		*Light*
	40°C	*50°C*				
1	4–5	4–5	5	5	5	3–4
2	5	4–5	5	5	5	4
3	5	5	5	5	5	3–4
4	5	5	5	5	5	4
5	5	4–5	5	4–5	4–5	3–4
6	5	4–5	5	5	5	4
7	5	5	5	4–5	5	3–4
8	5	4–5	5	5	5	4
9	4	3–4	5	5	5	4
10	5	4	5	5	5	5
11	4–5	3–4	5	5	5	4–5
12	5	4	5	5	5	5

[a] The first row of figures refers to staining of solvent, the second to change of colour of specimen.

cyano dyes than for the dyes having hydroxyl groups. Lightness of colours has the same trend of purity values.

3.3 Fastness properties

All dyes exhibited good build-up and levelling properties. Wet fastness data are given in Table 4. In general these values are equivalent to those found for acetate but wholly better than those for nylon.[5,6] The cyano substituted dyes, probably because of their poorer migration properties, have generally higher fastness than the hydroxylated analogues. However if we consider the dye size and the specific fibre used (silk is usually tested to washing to 40°C), all values must be regarded as good.

The fastness to dry cleaning and to perspiration are very good for all dyes. Since silk fabrics are usually subjected to dry cleaning rather than to aqueous washing, this is of importance.

Light fastness ranges from moderate to good and the values are equivalent to those for nylon fibres. The observed higher fastness of cyano containing dyes with respect to the hydroxylated analogous, can be explained in terms of the reduction of the electron density at the azo group due to the inductive effect exerted by the cyano group. From considerations of the particular kind of fibre and its end-use, the fastness to light can be regarded as quite good.

4 CONCLUSION

This paper shows that some disperse dyes, usually utilised for colouring cellulose acetate and nylon, can also be used on silk. With these dyes, the dyeing of silk can be performed at temperatures as low as 60 or 70°C without changing the properties which make this fibre unique, viz. handle, drape and softness. The wet and light fastnesses are better than those of acid dyes of the same molecular weight, and in general show good values. If the end-use of the fibre is taken into consideration, the fastness of the dyes can be regarded as very good.

The results suggest that the dyeing of silk with selected disperse dyes can be promising for practical uses, chiefly on account of the facility and cheapness of the dye synthesis, the ease of application and the overall versatility of their use.

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