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Thermodynamic Affinity of Acid Dyes on Silk*

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ABSTRACT

The dyeing mechanism of silk with acid dyes is likely to be similar to that of wool and is therefore subject to the same type of uncertainty of interpretation. For wool, two models have been postulated: the model of Gilbert and Rideal, and that of Donnan. In this first approach, for the study of sorption isotherms and for the determination of thermodynamic affinity, we utilized the Gilbert–Rideal model, based on the formulation of a site mechanism. The apparent saturation values S, calculated from the sorption isotherms, showed good agreement with the content of the amino groups of silk fibroin determined experimentally, which supported the proposed site mechanism. A relation was found between thermodynamic affinity values and conjugation in the dye molecules.

INTRODUCTION

Because of its hydrophilic nature and amphoteric properties, silk is one of the most easily dyeable fibres; many dyes used on cotton and wool give good results with silk. Silk, as well as wool, potentially contains not only negatively charged groups (COO^-) but also positively charged ones (NH_3^+). This fact, together with the empirical observation that, in certain conditions

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* Dedicated to the memory of Professor Angelo Mangini (1905–1988).

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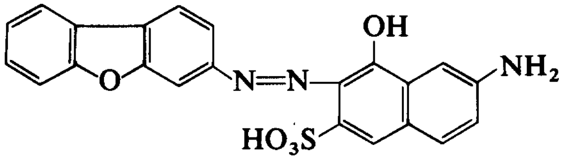
of application, the fibre shows a tendency to become apparently saturated with acid dyes, leads to the formulation of a site dyeing mechanism. Two models have been postulated for wool: the Gilbert–Rideal model,[1] based on the hypothesis that the adsorbed anions are localized on specific sites, and the Donnan model,[2] where it is assumed that the adsorbed anions are distributed between an internal and an external phase.

In order to afford a contribution to the dyeing mechanism of silk with acid dyes and to attempt an interpretation of the affinity of the dyes as a function of their molecular structure, we have synthesized a series of acid dyes based on a heterocyclic nucleus, and having the formulae shown below, and

Dye

I



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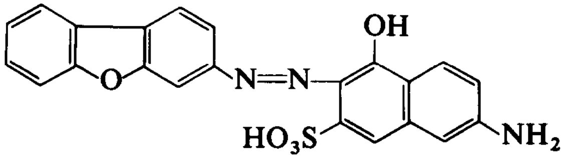

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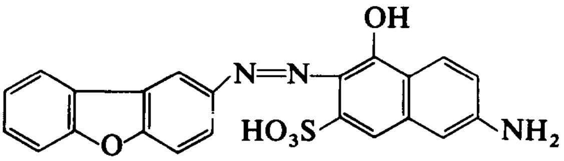

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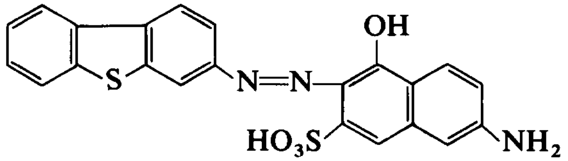

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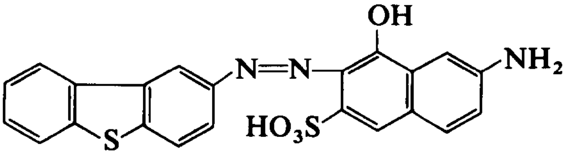

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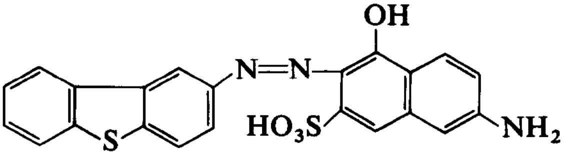

determined the thermodynamic affinity of the dyes by means of sorption isotherms at equilibrium.

Since the chemical characteristics of silk are essentially similar to those of wool, for the determination of thermodynamical affinity in this first approach we have adapted the Gilbert–Rideal model to silk dyeing, hypothesizing that the dye anion can be associated with the protonated amino groups of the fibre according to the reaction:

$$-NH_3^+ + D^- \rightleftarrows —NH_3D$$

when the equilibrium is reached:

$$\frac{[—NH_3^+][D^-]}{[—NH_3D]} = K_D \tag{1}$$

An analogous equation can be written for $—COO^-$ and H^+ at equilibrium. Multiplying the two equations, eqn (2) is obtained:

$$\frac{[H^+][—COO^-]}{[—COOH]} \cdot \frac{[D^-][—NH_3^+]}{[—NH_3D]} = K_{HD} \tag{2}$$

where K_{HD} is a constant.

The thermodynamic affinity of an acid dye for the fibre is therefore[3]

$$-\Delta\mu^\circ = RT \ln \frac{\theta_H}{1-\theta_H} \frac{\theta_D}{1-\theta_D} - RT \ln [H_s][D_s] \tag{3}$$

where θ_H is the fraction of hydrogen ions in the undissociated state and $(1-\theta_H)$ that in the dissociated state; θ_D is the fraction of positive sites occupied by the dye anions and $(1-\theta_D)$ by the remaining sites; and $[H_s]$ and $[D_s]$ are the amount of hydrogen ions and dye anions respectively in the bath.

EXPERIMENTAL

Materials

A degummed silk twill fabric made with 23 dtex 3-ply raw yarn was used for the dyeing. Degumming of the fabric was carried out with 7 g/litre olive oil–soap solution, in two treatments of 30 min each at 95°C; the liquor ratio was 1:50. A degumming loss of 24·5% was obtained. The following fabric characteristics were determined.

Intrinsic viscosity

After LiBr solubilization according to norm SNV 195595-68[4] (undamaged silk fibre: $[\eta] > 0{\cdot}6$, the value obtained was 0·692 dl/g.

Tensile strength

According to norm UNI 1932-86.

			Weft	*Warp*
Breaking load		g	152	159
	CV	%	5·42	5·33
Tenacity		g/dtex	2·77	2·90
Elongation at rupture		%	10·6	10·1
	CV	%	8·16	5·80

Determination of primary amino groups

The determination of the primary amino groups was carried out by reaction with ninhydrin according to the method proposed by Knott *et al.* for wool[5] using a 2×10^{-3}M leucine reference solution. The samples were left in the reaction liquor at 98°C for 45 min. As the amount of primary amino groups in silk fibroin is lower than in wool, each test was conducted on 20 mg of material. The value obtained was 55 mmol/kg of protein.

Determination of the carboxylic groups in silk

A method reported in the literature[6] for wool was adapted to silk fibroin. The fabric was washed to the isoelectric point according to the indications contained in norm SNV 195595-68 for the determination of viscosity. Special care was given during the final scouring with distilled water to obtain total elimination of any acetate buffer residue. The silk was then placed in a solution containing HCl (0·1N) and KCl (1N) and stirred for 40 min. Aliquots of the resultant solution were titrated under a nitrogen atmosphere with 0·1N NaOH using a Mettler DL 40GP automatic titrator. The value obtained was 182 mmol/kg of protein.

Dyes

Dyes **I–VI** were prepared by diazotization of 3-aminodibenzofuran, 2-aminodibenzofuran, 3-aminodibenzothiophene or 2-aminodibenzothiophene and subsequent coupling in a weakly basic environment (pH = 8) with J acid (7-amino-4-hydroxy-2-naphthalenesulphonic acid) and γ acid (6-amino-4-hydroxy-2-naphthalenesulphonic acid) respectively, according to the previously reported method.[7] Purification was carried out by the method of Rose.[8] Purity was checked by thin layer chromatography.

TABLE 1
Spectroscopic Data

Dye	λ_{max} (*nm*, H_2O)	*log* ε	λ_{max} (*nm*, *DMF*)	*log* ε
I	496	4·55	422	4·27
II	499	4·46	491	4·57
III	489	4·40	483	4·45
IV	497	3·93	494	4·18
V	498	4·08	496	4·09
VI	495	4·42	486	4·46

Sorption isotherms

Equilibrium sorption was attained in a refluxed thermostatted bath (85 ± 0·1°C) with a liquor ratio of about 1:200, and pH = 4·5 (obtained by an acetic acid and sodium acetate buffer). The time necessary to reach equilibrium dyeing was between 6 and 10 h, depending on the dye. The amount of dye adsorbed by the fibre at equilibrium was determined spectrophotometrically after extraction with N,N-dimethylformamide. The concentration of the dye in the bath was calculated by taking into account the initial concentration of the dye in solution, the concentration of the dye on the fibre and the weight of the fibre. All the dyes examined were stable under the application conditions.

The visible absorption maxima and absorptivities were recorded on a Hitachi U-3200 from solutions both in water and in N,N-dimethylformamide (Table 1).

RESULTS AND DISCUSSION

Referring to wool, Gilbert and Rideal have assumed that the number of sites for the adsorption of dye ions is equal to the number of sites on the fibre to which the hydrogen ions can bind. This approximation can be made for wool but not for silk fibroin, which contains significantly fewer amino groups than carboxylic acid groups. We have determined experimentally the content of carboxylic acid groups and amino groups in the fibre (182 and 55 mmol/kg respectively). If the excess of carboxylic acid groups is a_1 and the saturation value is S, eqn (3) may be written as[9]

$$-\Delta\mu = -RT \ln K_{HD} = RT \ln \frac{[H_f] + a_1}{S - [H_f]} \frac{[D_f]}{S - [D_f]} - RT \ln [H_s][D_s] \quad (4)$$

where $[H_f]$ and $[D_f]$ are the concentrations of hydrogen ions and dye anions taken up by the fibre respectively.

Equation (4) is in fact the same as that derived by the Donnan approach, in the absence of salt. For electrical neutrality $[D_f] = [H_f]$, which is correct for adsorption of pure dye acid; eqn (4) gives

$$\frac{\{[D_f]([D_f]+a_1)\}^{1/2}}{\{[H_s][D_s]\}^{1/2}} = \frac{S-[D_f]}{K_{HD}^{1/2}} \tag{5}$$

Equation (5) can be written according to (6):

$$\frac{\{[D_f]([D_f]+a_1)\}^{1/2}}{\{[H_s][D_s]\}^{1/2}} = \frac{S}{K_{HD}^{1/2}} - \frac{[D_f]}{K_{HD}^{1/2}} \tag{6}$$

By plotting $\{[D_f]([D_f]+a_1)\}^{1/2}/\{[H_s][D_s]\}^{1/2}$ against $[D_f]$, a straight line is obtained. The intercept with the ordinate axis gives the value $S/K_{HD}^{1/2}$, while the intercept at the abscissa gives S and the slope of the line is $1/K_{HD}^{1/2}$.

The equilibrium isotherms are given in Figs 1 and 2 for the six examined dyes, while the related linear relationships are shown in Fig. 3. From the latter, the apparent saturation values S of the fibre, together with the values of K_{HD}, were calculated and are reported in Table 2. The saturation values thus calculated show good agreement with the experimentally determined amino group content of the fibre (55 mmol/kg of fibre). On the basis of this finding, the site mechanism proposed by us for the acid dyeing of silk can be considered valid.

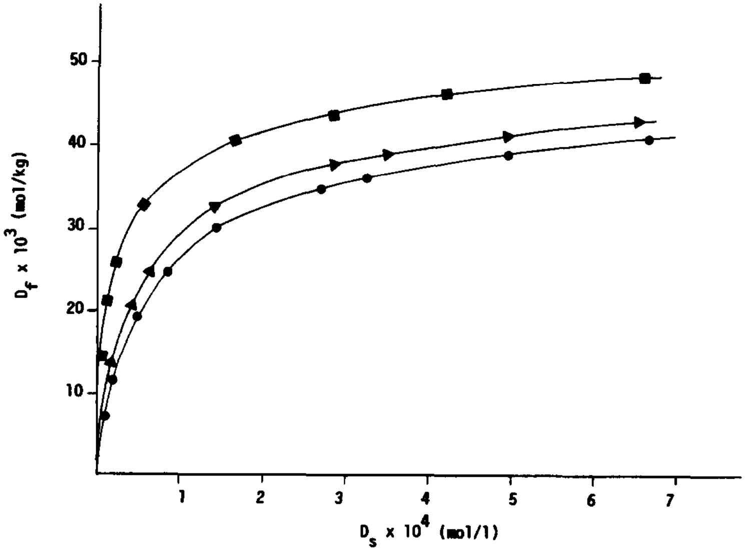

Fig. 1. Adsorption isotherms of dibenzofuran dyes at pH 4·5 and 85°C. ▶, dye I; ■, dye II; ●, dye III.

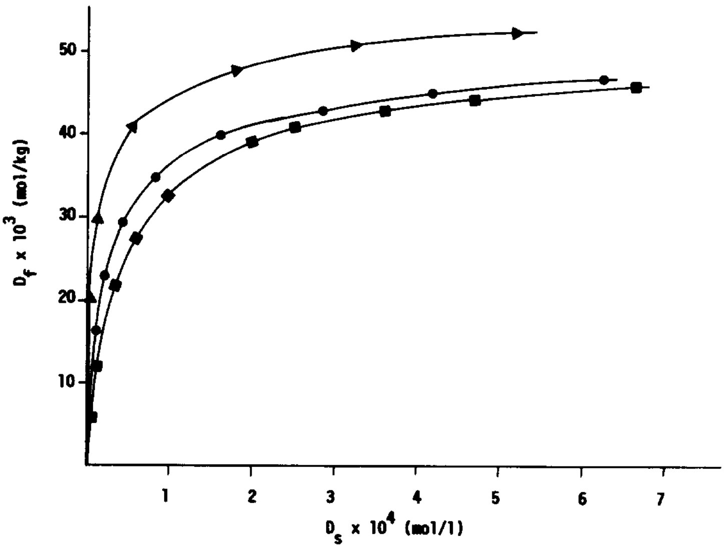

Fig. 2. Adsorption isotherms of dibenzothiophene dyes at pH 4·5 and 85°C. ■, dye IV; ●, dye V; ▶, dye VI.

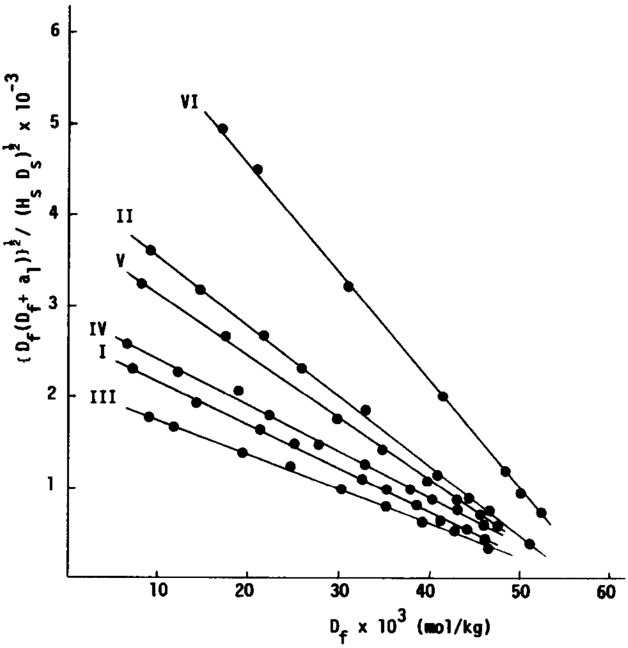

Fig. 3. Equilibrium adsorption isotherms according to eqn (7) for the six dyes examined at pH 4·5 and 85°C ($r \geq 0{\cdot}998$).

TABLE 2

K_{HD}, Affinity and Apparent Saturation Values of Monobasic Acid Dyes for Silk at 85°C and pH = 4·5

Dye	K_{HD} *10^{10}*	*S* (*mmol/kg*)	$\Delta\mu^\circ$ (*kcal/mol*)
I	4·26 ± 0·21	54·72 ± 1·58	15·36 ± 0·05
II	1·73 ± 0·05	56·51 ± 1·00	16·00 ± 0·03
III	6·77 ± 0·06	56·06 ± 0·30	15·03 ± 0·03
IV	4·00 ± 0·02	58·46 ± 0·15	15·40 ± 0·02
V	2·17 ± 0·11	56·39 ± 1·17	15·84 ± 0·05
VI	0·72 ± 0·01	57·41 ± 0·17	16·62 ± 0·02

From the K_{HD} values obtained from the adsorption isotherms at a constant pH, the affinity of dyes **I**–**VI** was calculated and the values are reported in Table 2.

From an examination of these values it can be concluded that, besides the remarkable affinity of the dibenzofuran and dibenzothiophene nuclei for silk, there is also a relation between conjugation in the dye molecule and dye affinity to the fibre. The series of dyes derived from dibenzothiophene show greater affinity. In fact the adsorption spectrum of dibenzothiophene is analogous to that of dibenzofuran,[10] but it is shifted towards the red (Table 1). The greater affinity of the dibenzothiophene dyes compared to the dibenzofuran derivatives, can be explained if the concept of valence shell expansion of sulphur[11] with possible involvement of the 3d orbital is not excluded. As regards the two series of dyes, there is an apparent contradiction in affinity values. In the dibenzofuran series, the 3-substituted dyes show higher affinity, while in the dibenzothiophene series, the higher affinity is shown by the 2-substituted dyes. An explanation can be sought in the contribution of the two heteroatoms to the resonance system. In the case of dibenzofuran, especially on nitration, there is a balance between activation of the 2- and 3-position,[12] with a slight prevalence at the 3-position. This could explain the greater affinity of dye **I** with respect to **III**. In the case of dibenzothiophene, the essential contribution of the sulphur atom to the resonance system is the greater charge density at the 2-position.[13] A comparison between the two couplers, J acid and γ acid, indicates that the dyes obtained by coupling with J acid (**II** and **VI**) show a greater affinity to silk fibroin than those obtained from γ acid (**I** and **V** respectively).

This could be due to the greater extension of the conjugation between the azo group and the amino group.

The results obtained seem to confirm the hypothesis of a relation between conjugation in the dye molecule and affinity of the dye for silk fibroin, i.e. affinity increases with increasing conjugation.

ACKNOWLEDGEMENT

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