Correlation between Thermodynamic Parameters and % Exhaustions of Some Carboxylated Reactive Dyes on Silk

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Abstract

Nine dyes having various functional groups were synthesized and applied on silk fabric. The equilibrium exhaustions %E of the dyes on silk were determined. From this the thermodynamic parameters such as partition coefficient K, and standard affinity, $\Delta\mu^{\theta}$ which is a driving force behind the dyeing process are determined. There is a strong correlation between the %E and the thermodynamic parameters values on one hand and effect of aftertreatment on the thermodynamic parameters on the other hand.

Keywords : exhaustion, aftertreatment, partition coefficient, standard affinities, thermodymanic parameters

1. Introduction

Silk fibres have long held the interest of man from the scientific, technological and aesthetic points of view. The importance of silk as a textile fibre lies in its luster, handle and draping qualities. In the early decades of synthetic dyes, silk was dyed mainly with cationic (basic) dyes and only later with anionic dyes, i.e. with acid and direct dyes. Acid tend to give dyeings of low depth on silk, and if very deep colours are required 'bronzing' occurs. They do not have the wide range of bright colours generally required for silk, so some old basic dyes are still sued for application on silk in spite of their low light fastness. The majority of dyeing with acid, basic and direct dyes are poor in wet fastness due to binding forces based on non-polar electrostatic, van der Waals and hydrogen bond interactions only. In order to improve the fastness properties of silk dyeing the application of reactive dyes would undoubtedly be attractive, as a wide range of brilliant colours with good wet and light fastness is potentially available.

The discovery of reactive dyes containing a carboxylic acid group as the dye/fibre reaction site was made by Burlington Industries Inc.[2] In 1978, these dyes were applied to cotton under acidic condition in the presence of a carbodiimide, to give dyeing of good resistance to alkaline washing[3]. The same group of dyes has been applied to wool with excellent fastness to alkaline washing[4]. Unfortunately very little work has been carried out on the carboxylated reactive dyeing of silk, especially using the carbodiimide as after treatment immediately after the exhaustion dyeing. The dye-fibre bond stabilities have never been investigated on silk.

The work described in this paper is an investigation on silk corresponding to those on cellulose, nylon and on wool. It is of interest for practical reasons whether reactive dyeing of silk with carboxylated dyes have high dye-fibre bond stabilities similar to those on wool (which would indicate that the fixation ratio is an important parameter influencing fastness properties), or similar to those on cotton, because of the significant percentage of bonds formed with hydroxyl groups.

We used nine different dyes for this investigation (see Figure 1) and determined exhaustion, fixation and dye-fibre bond stabilities of dyed silk after the after treatment with carbodiimide.

2.0 Experimental

2.1 Silk

Anaphe silk fibre obtained locally in Nigeria was used for dyeing. The fibre was degummed and bleached in 50 volume hydrogen peroxide at 90°C for 20 min at a liquor ratio of 20:1, then washed well in water at room temperature for 10 min and dried at room temperature.

2.2 Dye

The structure of the dyes used are given in Figure 1. They were prepared by diazotization of suitable amines and coupled to 2-naphthol, chromotropic acid, and J-Acid respectively using the available procedure.[5]

Three of the dyes contained carboxylic acid group (Dyes 1a, 2a, and 3a), three contained sulphonic acid group (Dyes 1b, 2b and 3b) while the other three (Dyes 1c, 2c and 3c) contained no substituent group in the diazo component. The dyes were recrystallized from suitable solvents until the molar extinction coefficients of all the dyes remain constant.

2.3 Dyeing

Dyestuff (40 mg) was dissolved in 50 ml of water at room temperature contained in a 150 ml quick-fit round-bottomed flask fitted with a reflux water condenser and standing on a heating mantle. The dyebath was set at the required pH (3.0) by the addition of dilute acetic acid. The material (1.0 g of silk fibre) was wetted out in warm water and the excess water squeezed out. The material was immersed in the dye liquor at 40°C for 15 min before the temperature was raised, over 20 min, to the boil. Dyeing was performed at the boil for a further 30 min. occasional gentle agitation of the dyeing arrangement was adopted throughout the dyeing cycle to promote uniform dye uptake.On the completion of the dyeing, the dyed sampled was taken out, rinsed in cold water, and dried at 60°C.

After the removal of the sample, the dyebath liquor was made up to standard volume and the optical density measured at the λ_{max} of each dyes. The initial optical density of the dyebath was taken before the commencement of dyeing. The percentage exhaustion of the dyes on the fibre (E) was calculated according to Equation 1:

$$E = \frac{A_d - A_b}{A_d} \times 100........(1)$$

Where A_d and A_b are the quantities of dye originally in the dyebath and of residual dye in the dyebath respectively using spectrophotometer. The results obtained are shown in Table 1.

2.4 Extraction of Unfixed Dye

The extraction solution used was 10% aqueous pyridine. The extraction was carried out in the glass tube with a stirrer. The dyed silk fibre was clipped to the stirrer and kept in the extraction solution for 30 min at 70 °C. Each piece was extracted until the extraction liquor became colourless. At the end of each extraction the solution was decanted and made up to a standard volume and its absorbance was measured spectrophotometrically. Fixation ratio (F) was calculated according to Equation 2.

$$F = \frac{A_d - A_b - A_o}{A_d - A_b} \times 100........(2)$$

Where A_o is the quantity of extractable dye. The results are given in Table 1.

2.5 Extent of Dyeing to Alkaline Washing

The stability of the dye/fibre bond to alkaline washing was tested by subjecting samples of the silk dyeings to the ISO 2 and 3 wash tests[6]. The results obtained with dyes 1-9 are summarized in Table 2.

3. Results and Discussion

3.1 Spectra Data

From the results summarized in Table 1, it can be seen that dyes obtained by coupling diazotized 4-aminobenzoic acid, sulphanilic acid and aniline to 2-naphthol absorb in the range 480nm to 488nm, thus the incorporation of carboxylic acid group in the parent dye (1c) to give (1a) has very little effect on the λ_{max} of the dyes. For example, dye (1c) absorbs at 480 nm and (1a) absorbs at 485 nm, a bathochromic shift of 5nm relative to dye (1c). similarly when the carboxylic acid group is substituted with sulphonic acid group as in dye (1b), the dye absorbs at 488 nm and this gives a bathochromic shift of 8nm relative to dye (1c).

Replacing the 2-naphthol with chromotropic acid gave dyes in (2) with λ_{max} in the range 500nm to 513 nm. Dyes in this series are more bathochromic than those in series (1) by about 20 nm – 23nm relative to each other.

Using J-acid as the coupling component gave dyes in (3) with λ_{max} similar to dyes in series (1). This means that the electron releasing effect of J-acid and 2-naphthol are similar.

3.2 Dyeing, Exhaustion, hydrolysis to alkaline washing and fixation

From the dyeing results in Table 1, it can be seen that exhaustion varies between 97 and 80% for the dyes used in this investigation. All the dyes gave very good exhaustion fibre penetration, the dyeing obtained also show very good levelness, with dyes having very high value of partition coefficient (K) and having high % exhaustion (E), just like the standard affinity ($\Delta\mu^{\theta}$).

The results of the wash fastness test summarized in Table 2 with most of the dyes having fastness rating of 1, indicating poor fastness to alkaline washing. This shows that the dyes are anchored to the fibre by mechanical retention and hydrogen bonding which are not strong enough to withstand the action of washing agents.

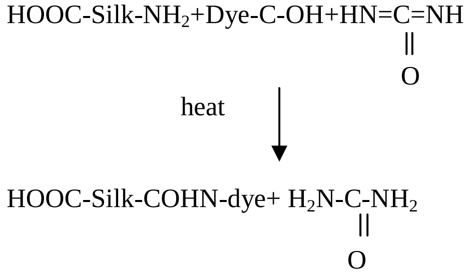
Similarly, the results of the fixation, carried out by subjecting all the dyeing to stripping with 10% aqueous pyridine summarized in Table 1, clearly show that there was less fixation of all the dyes under investigation on the silk fibre before the dyeing were aftertreated with carbodiimide. Infact most of the dyes were extracted in the first extraction solution and virtually none was left on the fibre after 30 min of extraction at 70°C.

However, when all the dyeing were aftertreated with dicyclohexylcarbodiimide, all the three dyes containing carboxylic acid group (i.e, dyes, 1a, 2a and 3a) show very strong resistance to 10% aqueous pyridine extraction and even after successive extraction with pyridine extraction and even after successive extraction with pyridine, more than 20% of the dyes are covalently bonded to the silk mores. All the other dyes without the carboxylic group are still very sensitive to pyridine extraction, showing apparently no fixation on the fibre.

The results of the wash fastness test conducted when the dyeing were aftertreated with carbodiimide also show very good fastness ratings for all the dyes with carboxylic acid group.

These results clearly show that carboxylated reactive dyes can be covalently bonded to silk fibre similar to those of wool and cotton fibres when aftertreated with carbodiimide.

Since wool and silk are built up from the same amino acids, (though, their physical and chemical structures are very different), the reaction scheme of carboxylated dyes with silk in the presence of cabrodiimide can be represented as shown in Scheme 1.



$$\mathrm{HOOC\text{-}Silk\text{-}NH_2{+}Dye\text{-}C\text{-}OH{+}HN{=}\underset{\overset{\|}{O}}{C}{=}NH} \xrightarrow{\text{heat}} \mathrm{HOOC\text{-}Silk\text{-}COHN\text{-}dye{+}\ H_2N\text{-}\underset{\overset{\|}{O}}{C}\text{-}NH_2}$$

Scheme 1

4. Conclusion

All the dyes used in this work have high equilibrium exhaustion for silk fibre. They however recorded poor wash fastness because of the small structure of the dyes. Likewise their fixation, which is a measure of the fibre-dye bond which is also weak. This shortcoming is overcome by having the dyed fabric treated with dicyclohexylcarbodiimide i.e. the fixation and wash fastness improved tremendously after applying the aftertreatment.

It meant that carboxylated reactions dyes can covalently bond to silk fibre when the dyed fibre is treated with carbodiimide, which is a major breakthrough since they already have high standard affinities for the fibre as recorded in Table 1.

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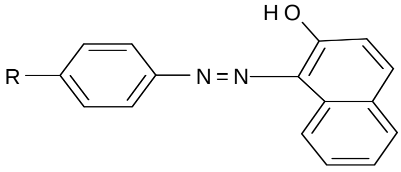
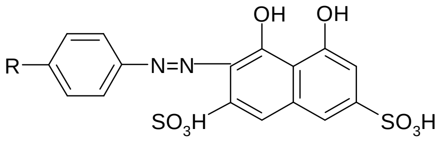
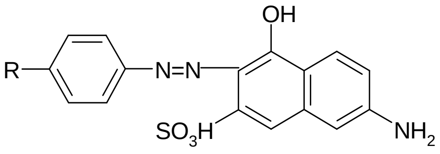


(1)



(2)



(3)

a. R = COOH
b. R = SO_3H
c. R = H

Figure 1 . Dyes used in the present study

Table 1: λmax, % Exhaustion, % Fixation and Thermodynamic Parameter value of the Dyes

Dye No.	**λ_{max}/min (water)**	**% Exhaustion**	**% Fixation**		**K**	**$\Delta\mu^0$**
			(a)	**(b)**	**$ltKg^{-1}$**	**$kJmol^{-1}$**
1a	485*	90	0.3	25	1350.0	22352.4
1b	488	92	0.6	2	1725.0	23112.6
1c	480*	85	0.7	2	850.0	20917.8
2a	513	97	0.2	23	4850.0	26318.4
2b	510	90	0.4	3	1350.0	22352.4
2c	500	96	0.3	2	3600.0	25394.1
3a	485	81	0.6	28	639.5	20235.4
3b	485	80	0.2	3	600.0	19837.7
3c	480	84	0.8	2	787.5	20680.9

(a) Before the Aftertreatment with carbodiimide
(b) After the Aftertreatment with carbodiimide
*** measured in acetone**

Table 2: Wash Fastness Rating of the Dyes

Dye No.		A		B	
		Change in shade	Staining of white	Change in shade	Staining of white
1a	ISO 2	1-2	5	5	5
	ISO 3	1	5	4-5	5
1b	ISO 2	1-2	4	2	5
	ISO 3	1	4	1-2	5
1c	ISO 2	1	4	2	5
	ISO 3	1	4	2	5
2a	ISO 2	1-2	4	4-5	5
	ISO 3	1	4	4	5
2b	ISO 2	1	4	2	5
	ISO 3	1	4	1-2	5
2c	ISO 2	1-2	4-5	2	5
	ISO 3	1	4-5	1-2	5
3a	ISO 2	1-2	5	4	5
	ISO 3	1	4-5	3-4	5
3b	ISO 2	1-2	5	2	5
	ISO 3	1	4-5	1-2	5
3c	ISO 2	1	4-5	2	5
	ISO 3	1	4-5	1-2	5

(a) Before the aftertreatment with carbodiimide
(b) After the treatment with carbodiimide

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