日蚕雑 54(3), 181-185 (1985)
J. Seric. Sci. Jpn.

Reaction Mechanism of Reactive Dye with Silk

MIHOKO DOHMYO[1], YOSHIAKI SHIMIZU[1], and MITSUO KIMURA[2]*

1) *Shiga Prefectural Junior College, Hassaka-cho, Hikone, Shiga Prefecture 522*

2) *Faculty of Industrial Arts, Kyoto Technical University, Sakyo-ka Kyoto 606*

(Received December 1, 1984)

Studies were carried out to determine whether the adsorption of a reactive dye (vinylsulfonyl type) on the protonated amino group in the protein fiber played an important role in the reaction between the dye and the fiber. The effects of electrolyte and urea addition on the dyeing process were also examined.

The results obtained were as follows : Based on the difference in dyeability of acid dyes and reactive dye (vinylsulfonyl type of C. I. Reactive Blue 19) for silk at 60°C and 100°C, it was revealed that the reaction of the reactive dye with silk is not associated with the adsorption of the dye on the protonated amino group.

The addition of sodium sulfate in the dyebath promotes exhaustion and fixation, whereas urea depresses both processes.

The demand for reactive dyes has increased steadily (Kenmochi, 1981). These dyes have been studied from various angles. Recently reports were published on the mechanism of solvent dyeing (Chavan, 1976), solvent assisted dyeing (Giles and Iver, 1976), the increase in fixation by aftertreatment (Finnimore *et al.*, 1978) and light fastness (Kamel *et al.*, 1982).

The reaction mechanisms of reactive dyes with cellulose (Baumgarte and Feichtmayr, 1963) and protein fibers (Shore, 1968, 1969) have been considerably clarified. However, some aspects concerning the mechanism of reactive dyeing of protein fibers (notably in the case of silk) require further studies.

For the reaction of a reactive dye with a fiber, the dye must be adsorbed on the fiber. It has so far been considered that the dyes were adsorbed on the protonated amino group before the reaction with the protein fiber (Derbyshire and Tristram, 1965) takes place.

The purpose of the present report was to determine whether the above theory (that is, the necessity of adsorption of the dye on the protonated amino group for the reaction) could be validated and to analyse the effects of electrolyte and urea addition on process of reactive dyeing.

It is important to note that the dyeing conditions used in the current experiment were different from the practical conditions. Since the mechanism of the reaction of a reactive dye with silk was the main objective of this investigation.

Materials and Methods

Sample : Silk yarn was used after scouring by the method described in the previous paper (Shimizu, 1971).

This work was presented at the Annual Meeting of The Society of Fiber Science and Technology, Japan held in Tokyo on June 1-3, 1982.

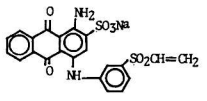
* Present Address : Mie University, Tsu City, Mie Prefecture 514

The reactive dye used was the vinylsulfonyl derivative (abbreviated as Vy) of C. I. Reactive Blue 19, which was synthesized from the commercial dye (the major component of this dye is a sulfatoethylsulfonyl type.) and purified by recrystallization in water. Five gram of Remazol Brilliant Blue R (Hoechst) dissolved in 100 ml of the buffer solution at pH 11 was stirred at 65°-75°C for 45 minutes. The precipitate was obtained by concentrating the solution, followed by cooling. The precipitate was purified by recrystallization in water.

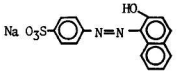
Acid dyes used for comparison are C. I. Acid Blue 25 (abbreviated as AS) and C. I. Acid Orange 7 which were purified by column chromatography and by the Robinson-Mills method, respectively.

The structure of the dyes used is as follows :

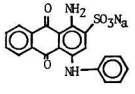
Vinylsulfonyl type of C. I. Reactive Blue 19



C. I. Acid Orange 7



C. I. Acid Blue 25



Dyeing : Dyeing was carried out under the following conditions :

{ Degummed silk yarn 1 g
{ Dye 2 % o. w. f. or 5 % o. w. f.

pH : 3-11 (Buffer solutions used are as follows in the total concentration of 0. 01 mol dm^{-3} ; pH 3 : $CH_3COONa+HCl$, pH 4-6 : $CH_3COOH+CH_3COONa$, pH 7-8 : $KH_2PO_4+Na_2B_4O_7$, pH 9-11 : $Na_2CO_3+NaHCO_3$), liquor : silk ratio ; 50 : 1, Temperature and Time : 20°C·72 hr, 60°C·24 hr, 100°C·2 hr

The exhaustion rate of the acid dye by silk in all cases and that of Vy in one instance (20°C, 72 hr) was determined by spectrophotometric analysis of the dye solutions using a Hitachi 100 -10 spectrophotometer. In the case of Vy, the dyed silk yarn was taken out of the apparatus after the prescribed time and then was treated four times with 50% urea solution containing 1% Nonypol® 80 (by boiling for three minutes) to extract the unfixed dye. The dyebath exhaustion rate was determined spectrophotometrically and the quantity of the fixed dye was calculated by subtracting the amount of unexhausted dye and extracted dye from the quantity of the dye originally in the bath. The differece in the quantities of the fixed dye determined by the above-mentioned method and the method previously reported (Shimizu, 1975)-colorimetry of the solution of dissolved dyed silk- was not significant.

The rates of exhaustion and fixation were defined as indicated below :

$$\text{Exhaustion}(\%)=E(\%)=\frac{D_0-Du}{D_0}\times 100 \quad (1)$$

$$\text{Fixation}(\%)=F(\%)=\frac{D_0-(De+Du)}{D_0}\times 100$$

$$=\frac{Df}{D_0}\times 100 \quad (2)$$

$$D_0=Du+De+Df \quad (3)$$

Where, D_0 : Ouantity of dye originally in the bath. Du : Ouantity of unexhausted dye in the bath. De : Ouantity of loosely bound, extractable dye on silk. Df : Ouantity of dye covalently bound to silk,

Results and Discussion

Affinity of Vy and AS for silk

Fig. 1 shows the relationship between the pH and the adsorbed amounts of Vy and AS on silk yarn (20°C, 72 hr).

No significant differences in the adsorbed amounts between the two dyes were observed in the region of pH 3-6. Thus it appears that the affinity of these dyes for silk was nearly equal.

Dyeability of Vy, AS and Acid Orange 7 for silk

Fig. 2 shows the effect of the dyebath pH on the E(%) in the dyeing process of silk with Vy, AS and Acid Orange 7 (60°C, 24 hr). F(%) at pH8 in Vy was also plotted in that figure.

The difference in E(%) between Vy and AS which was small at a lower pH, gradually increased with the increase of the dyebath pH. E(%) in Vy was approximately constant up to a pH of 8, and then decreased rapidly of a higher pH. On the other hand E(%) decreased more rapidly in Acid Orange 7 which shows a lower affinity for silk than AS. The behavior of Acid Orange 7 was the same at 100°C (refer to Fig. 3).

Fig. 3 shows the E(%) in silk dyed with AS (100°C, 2 hr) in the range of pH 3-11, and E(%) and F(%) in Vy under the same conditions.

E(%) of AS decreased rapidly with the increase in the pH value, whereas that of Vy was constant up to pH 8 and then decreased rapidly of a higher pH. E(%) of Vy in pH values above 6 went significantly beyond that of AS.

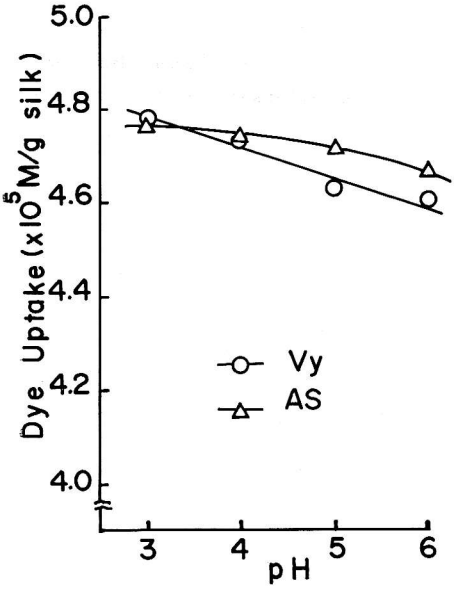


Fig. 1. Relationship between pH and the uptake of Vy and AS by silk (concentration of dye : 9.615×10^{-4} mol/l, 1.r.; 1,500 : 1)

E(%) of Vy was larger than that of AS at both 60°C and 100°C. When Vy and AS were adsorbed on the fiber by a binding mechanism

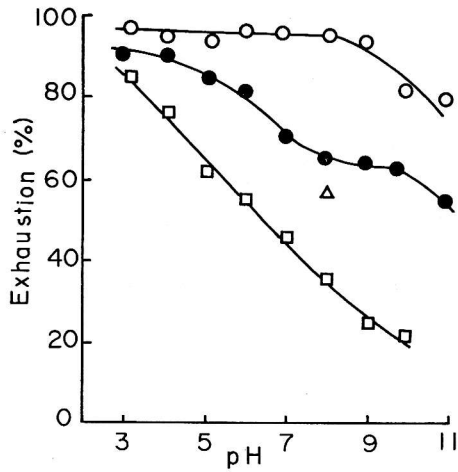


Fig. 2. Effect of pH on the exhaustion (%) of Vy, AS and Acid Orange 7 by silk (60°C, 24 hr).
○ : Vy △ : Vy (fixation)
● : AS □ : Acid Orange 7

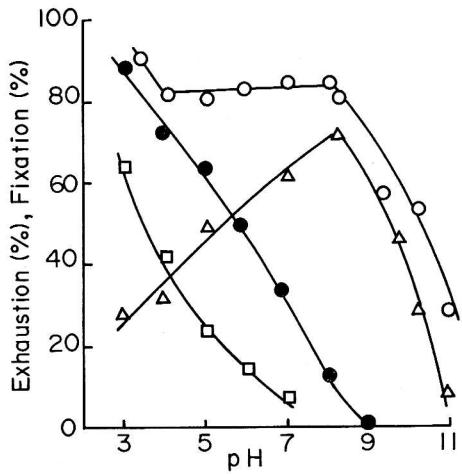


Fig. 3. Effect of pH on the exhaustion (%) and the fixation (%) in silk dyed with Vy, AS and Acid Orange 7 (100°C, 2 hr).
○ : Exhaustion of Vy, △ : Fixation of Vy, ● : Exhaustion of AS, □ : Exhaustion of Acid Orange 7

different from the covalent bond, E(%) of the two dyes in silk should have almost the same value, because the affinity of these dyes is almost equal. Hence the difference in E(%) appears to be related to the reaction (namely fixation) of Vy with silk.

Ether-type dye (Rys and Stamm, 1966) is not being considered in the present report since the experiments were carried out at a high temperature

Effect of electrolyte addition

At pH9 (100°C, 2 hr) AS was not exhausted by silk at all, whereas the E(%) of Vy was estimated to be 70%. This finding suggests that the reaction of Vy with silk does not require the adsorption of the dye on the protonated amino group, but only requires the penetration into the fiber of dyes whose energy exceed the potential barrier, in taking also account of the change in entropy. Thus it is anticipated that increases in the rates of exhaustion and fixation may occur after the addition of electrolyte in the bath, which reduces the electric potential or increases the apparent affity of Vy for silk. In the dyeing at pH 7 (5% dyeing, 100°C, 2 hr) the results of dyeing in the presence and absence of sodium sulfate are indicated in Table 1.

Table 1. Effect of sodium sulfate on the dyeing of silk with Vy(pH 7, 100°C, 2 hr).

Conc. of $Na_2SO_4 \cdot 10H_2O$(g/1)	Exhaustion (%)	Fixation (%)
0	84.5	61.7
100	94.8	72.5
300	97.8	65.0

By the addition of sodium sulfate, E(%) increased conspicuously while F(%) increased to some extent. The degree of increase in the fixation rate was smaller than that in the exhaustion rate presumably because Vy aggregates in the fiber. This phenomenon can be predicted from the fact that E(%) at a sodium sulfate concentration of 300 g/1 is higher than that at a sodium sulfate concentration of 100 g/1 but F(%) at the former concentration is lower than that at the latter concentration.

Effect of urea addition

When the solution containing urea is heated, pH increases due to the formation of ammonia as a result of the decomposition of urea (Asquith and Booth, 1970). Thus if the dyeing of silk with Vy is started in an acidic solution containing urea, the exhaustion rate is likely to increase and simultaneously the fixation is promoted as the pH increases during the dyeing process.

Table 2 shows results of dyeing in the presence and absence of urea at 100°C at an initial pH of 5.

Table 2. Effect of urea on the dyeing of silk with Vy at 100°C.

Conc. of urea(g/1)	Exhaustion (%)	Fixation (%)
0	69.5	47.7
50	56.6	34.9
300	32.1	28.5

This result differs from the expectation, presumably because the increase of the pH value in a shorter time (see, Fig. 4) leads to the decrease of the exhaustion rate* or because Vy reacts partly with urea (Kissa, 1969).

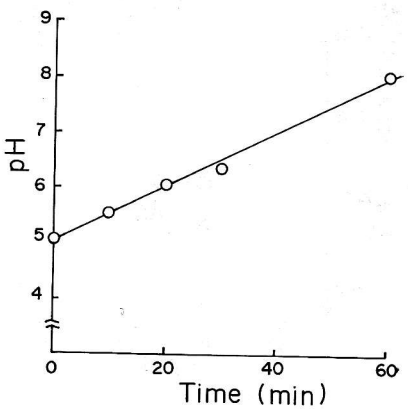


Fig. 4. Change in pH of the solution containing urea (50 g/1) at 100°C.

In a bath with an initial pH value of 5, dyeing was started at room temperature, allowed for 1hr at 60°C and followed for 1hr at 100°C. Then the values of E(%) and F(%) were 66.5 and 36.1 respectively.

As a result the addition of urea in the bath leads to the decrease of the exhaustion and fixation rates.

References

ASQUITH, R. S. and BOOTH, A. K. (1970) : J. Soc. Dyers Col., **86**, 393-398.

BAUMGARTE, U. and FEICHTMAYR, F. (1963) : Melliand Textilber., **44**, 163-168, 267-270, 600-605, 716-719.

CHAVAN, R. B. (1976) : J. Soc. Dyers Col., **92**, 59.

COCKETT, K. R. F., RATTEE, I. D. and STEVENS, C. B. (1969) : J. Soc. Dyers Col. **85**, 461-468.

DERBYSHIRE, A. N. and TRISTRAM, G. R. (1965) : J. Soc. Dyers Col. **81**, 584-591.

FINNIMORE, E., MEYER, U., and ZOLLINGER, H. (1978) : J. Soc. Dyers Col. **94**, 17-24.

GILES, C. H. and MC IVER, N. (1976) : Text. Res. J., **46**, 385-388.

KAMEL, M. HEBEISH, A. KAMEL, M.M. and MASHOOR R. A. (1982) : Am. Dyestuff Reptr., **71**, 34-35.

KENMOCHI, H. (1981) : Senshoku Kohgyo, **29**, 435-443.

KISSA. E. (1969) : Text. Res. J., **39**, 734-741.

RYS, P. and STAMM, O. A. (1966) : Helv. Chim. Acta **49**, 2287-2296.

SHIMIZU, Y. (1971) : Sen-i Gakkaishi, **27**, 540-543.

SHIMIZU, Y. (1975) : Sen-i Gakkaishi , **31**, T180-T185.

SHORE, J. (1968) : J. Soc. Dyers Col., **84**, 408-412, 413-422, 545-555.

SHORE, J. (1969) : J. Soc. Dyers Col., **85**, 14-22.

道明美保子・清水慶昭・木村光雄：絹に対する反応染料の反応機構

反応染料が蛋白繊維（ここでは絹）と反応するためのプロトン化アミノ基への染料の吸着の必要性の有無や反応染色における電解質の効果ならびに尿素の影響を調べた。

酸性染料（C. I. Acid Orange 7, Acid Blue 25）と反応染料（C. I. Reactive Blue 19 のビニルスルホン型）の 60°C および 100°C における染色性から推定すると，反応染料が絹と反応するにはプロトン化アミノ基への染料の吸着は必要ではない。

また，硫酸ナトリウムの添加が吸尽および固着の増加をもたらすのに対し，尿素はそれらの両方とも低下させる。

* In the dyeing of slk with acid dye a lowering of the exhaustion rate was observed (Cockett *et al.*, 1969).