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Studies on New Reactive Dyes Having Two Vinyl Sulfone Groups. Part I: Synthesis and Application Properties

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ABSTRACT

Three novel reactive dyes having two vinyl sulfone fiber-reactive groups were synthesized and their application properties studied. Dye 1 having two m-(β-*sulfatoethyl-sulfonyl)aniline moities possesses excellent dyeing properties with a fixation value above 90%. The dyeing method of the new reactive dyes was improved by the amount and mode of added alkali (Na_3PO_4). When the dyes are taken up at 40°C, and the dyeing temperature then raised to 60°C after the first addition of Na_3PO_4 the dyeing results were more satisfactory.* © *1998 Elsevier Science Ltd*

Keywords: reactive dye, synthesis, application properties, vinyl sulfone-type, bifunctionality, exhaustion value, fixation value.

INTRODUCTION

It is necessary to raise the fixation yields of reactive dyes and the bifunctionality built into such dyes has been suggested to be an efficient method for improving the application properties of such dyes. In studying reactive dyes with two reactive groups we have found that:

(a) for the heterobifunctional C.I. Reactive Red 240, having a VS (vinylsulphonyl or its precursor) and an MCT (monochlorotriazinyl) group, kinetic studies showed the rate of alkaline hydrolysis of the VS group was 3–4 times faster than that of the MCT group under equivalent

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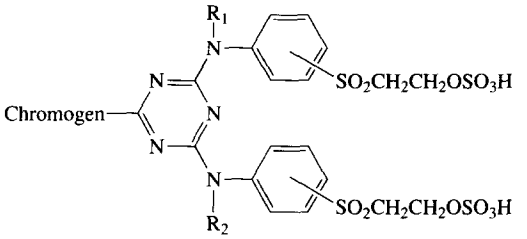
conditions. The different reactivity indicates that the two reactive groups in one molecule cannot reach their respective highest fixation simultaneously [1].

(b) the homobifunctional C.I. Reactive Red 120, having two MCT groups reacts with cellulose at temperatures above 80°C.

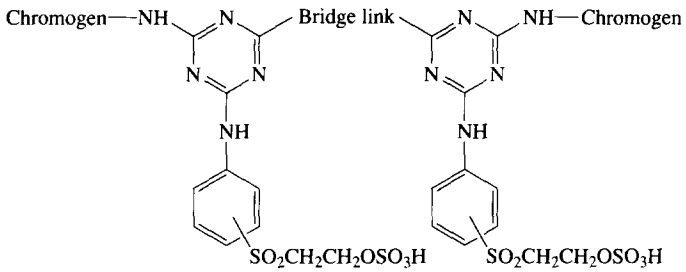
(c) Another type of homobifunctional reactive dye having two VS groups has been reported [2]. The two VS groups are linked with one chromogen by an s-triazine moiety, and the general structure may be depicted by Formula 1.



I

where R_1 and R_2 are H or an alkyl group.

In this present paper, new reactive dyes of general Formula 2 were synthesized.



II

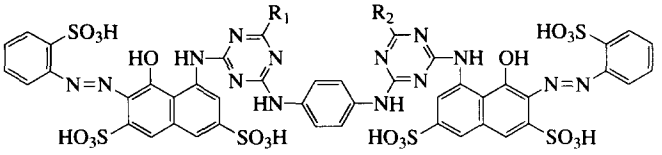
The objectives of the investigation were to: enhance substantivity by enlarging dye molecule with a linear structural configuration; introduce bifunctionality; and to reduce the cost of introducing the VS groups, relative to dyes I, through one chromogen combining with one VS group.

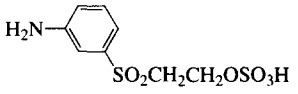
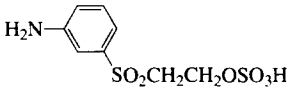
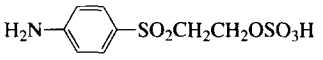
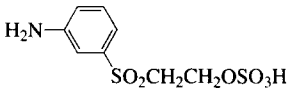
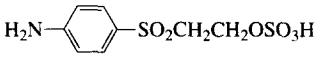
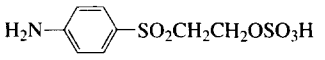
SYNTHESIS OF NEW REACTIVE DYES HAVING TWO VINYL SULFONE-TYPE FIBER-REACTIVE GROUPS

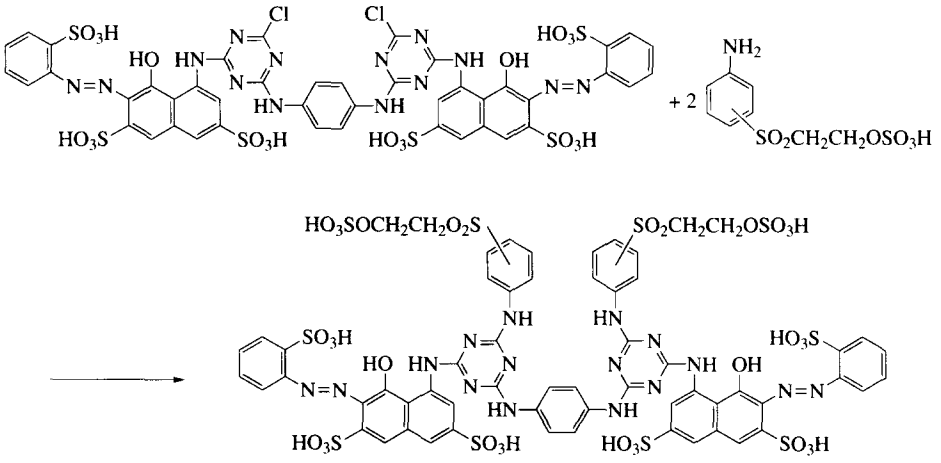
Three dyes having two vinyl sulfone-type fiber-reactive groups were synthesized and their structures are as shown in Table 1.

Dyes 1 and 3 were synthesized following the route shown in Scheme 1.

TABLE 1
Structure of Novel Reactive Dyes Synthesized



Dye no.	*R_1*	*R_2*
1		
2		
3		



Scheme 1

Method of production:

An aqueous solution of C.I. Reactive Red 120 was synthesized by known methods [3]. To this 2 mol equiv. of *m*- or *p*-(*β*-sulfatoethyl-sulfonyl)aniline was added and the mixture stirred at 20°C for 30 min 15% aqueous sodium carbonate solution was added to adjust the pH to 5.5, the mixture then

refluxed for one hour, cooled to 25°C, adjusted to pH 6.0 and sufficient sodium chloride was then added to give a concentration of 150 g l^{-1}. After stirring for one hour the liquor was filtered and the product dried at 80–85°C.

Dye 2 was synthesized according to the following method: To the aqueous solution of C.I. Reactive Red 120 prepared as above [3], a 1 mol equiv. of *m*-(*β*-sulfatoethyl-sulfonyl)aniline was added, the pH adjusted to 5.5 and the liquor refluxed for one hour, and then cooled to 25°C. A 1 mol equiv. of *p*-(*β*-sulfatoethyl-sulfonyl)aniline was then added, the pH adjusted to 4.0 and the liquor refluxed for 2.5 h. After cooling to 25°C, pH was adjusted to 6.0, and sufficient sodium chloride added to give a concentration of 150 g l^{-1}; the mixture was stirred for 1 h, then filtered and the product dried at 80–85°C.

APPLICATION PROPERTIES OF THE NEW REACTIVE DYES

Materials

Special-grade reagents or their equivalent, and water purified by ion exchange, were used for the dyeing tests. Scoured and bleached unmercerized cotton yarn was obtained from Shanghai No.8 Dyestuffs & Chemicals Works.

Measurements

Visible absorption spectra were recorded on a Shimadzu UV/Visible spectrophotometer model UV-260, using water as solvent. Dyeing tests were carried out on a High-temp. & High-pres. Laboratory Dyeing Machine model RJ-100, (Shanghai No. 11 Dyestuffs & Chemicals Works).

Dyeing

Each solution (200 ml) was prepared at 20–30°C with dye, Na_2SO_4 (12 g) and water, in which the dye concentration was 0.5 g $dm.^{-3}$ The temperature of each dyebath was raised to 60°C, and cotton (10 g) was immersed in the dyebath for 30 min with stirring to permit primary exhaustion. Na_3PO_4 (1.2 g) was then added and dyeing was continued for a further 45 min at 60°C to permit secondary exhaustion. After dyeing, the cotton was washed in 200 ml boiling water, to which detergent LS (sodium 2-methoxy-5-oleoylaminobenzenesulfonate, Shanghai Assistants Factory) had been added to give a concentration of 1 g dm^{-3}, to remove unfixed (hydrolyzed) dye, and dried.

Measurements were made spectrophotometrically on the residual dyebath solution after secondary exhaustion and washing. Exhaustion (EV) and fixation values (FV) were determined respectively, all of which were based on the amount of dye used.

RESULTS AND DISCUSSION

Relationships between reactive groups and dyeing properties

On the basis of the dyeing procedures as in Dyeing section, relationships between the reactive groups and dyeing properties were determined (Table 2). The FV of dye 1 with two *m*-(β-sulfatoethyl-sulfonyl)aniline was the highest, that of the dye 2 with one *m*-(β-sulfatoethyl-sulfonyl)aniline and one *p*-(β-sulfatoethyl-sulfonyl)aniline was inferior to it, and that of dye 3 with two *p*-(β-sulfatoethyl-sulfonyl)aniline was the most inferior.

Dying properties in relation to the amount and the mode of added Na_3PO_4

Since there are two vinylsulfonyl groups in the dyes, the amount and the mode of adding alkali will affect the dyeing behavior of the dyes. The results are shown in Tables 3 and 4. A suitable concentration of Na_3PO_4 is between 1.2 and 1.6 g dm^{-3}, and Na_3PO_4 is preferably added twice at 15 min intervals. The dyeing method was according to that in Dyeing section, except for the different amounts and different mode of addition of Na_3PO_4. The dyeing processes pertinent to Tables 3 and 4 are shown in Schemes 2 and 3, respectively.

Temperature dependence of fixation for dye 1

Figure 1 shows the temperature dependence of fixation for dye 1, observed under exhaust dyeing conditions between 40 and 80°C. Dye 1 is characteristically insensitive to temperatures of 50–80°C.

TABLE 2
Relationships Between Reactive Groups and Dyeing Properties

Dye no.	*EV(%)*[a]	*FV(%)*[b]	*Rel. FV(%)*[c]
1	96.01	87.18	90.80
2	92.18	76.34	82.82
3	92.74	74.54	80.38

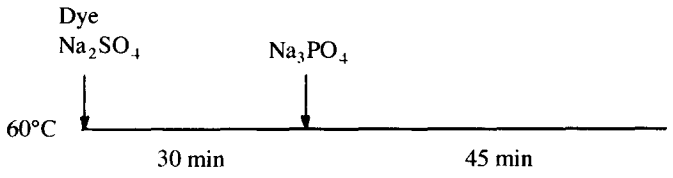
[a]Exhaustion value, which indicates portion of dye absorbed on (or fixed to) cellulose during the dyeing process.
[b]Fixation value, which indicates portion of dye forming one or two covalent bonds with cellulose.
[c]Relative fixation value, which indicates FV/EV.

TABLE 3
Dyeing Properties in Relation to the Amount of Na_3PO_4

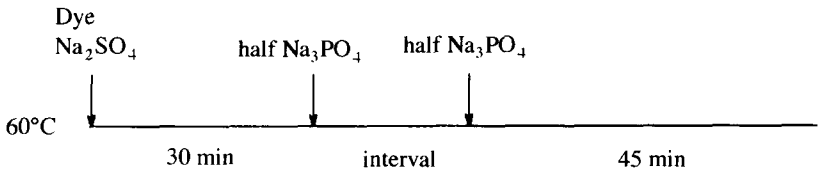
Amount of Na_3PO_4 (g)	*EV(%)*	*FV(%)*	*Rel. FV(%)*
0.8	94.96	82.97	87.37
1.0	96.05	85.79	89.32
1.2	96.01	87.18	90.80
1.4	96.41	87.28	90.53
1.6	96.37	87.50	90.80
1.8	96.26	86.51	89.87
2.0	95.96	84.98	88.56

TABLE 4
Dyeing Properties in Relation to the Mode of Adding Na_3PO_4

Interval of two times (min)	*EV(%)*	*FV(%)*	*Rel. FV(%)*
0	96.37	87.50	90.80
5	96.56	88.59	91.75
10	97.00	89.40	92.16
15	97.79	90.13	92.17
20	96.93	89.08	91.90



Scheme 2



Scheme 3

Dyeing curve of dye 1

The dyeing curve of dye 1 is shown in Fig. 2. The rate of up-take and fixation for dye 1 are very high, which is a disadvantage for the application of the dye. Improved results were obtained as shown in Fig. 3, when the dye is taken up at 40°C, and after the first addition of half the Na_3PO_4, the temperature is raised to 60°C, and then the other half of the Na_3PO_4 added.

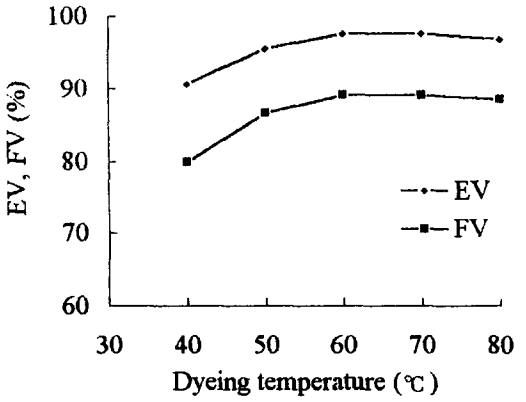


Fig. 1. Temperature dependence of exhaustion and fixation for dye 1.

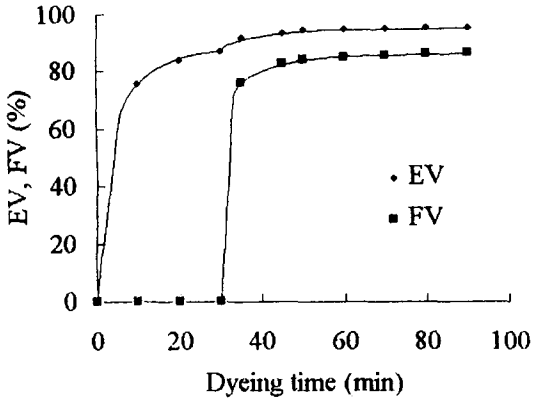


Fig. 2. Dyeing curve of dye 1.

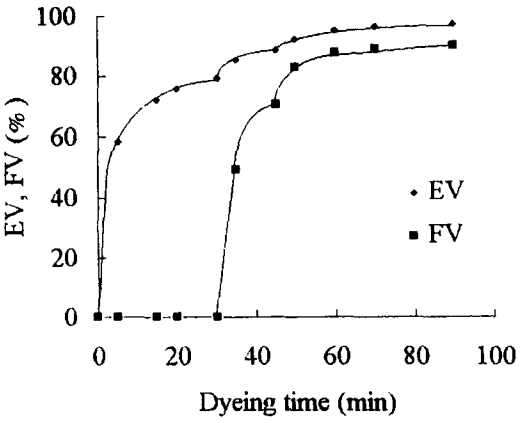


Fig. 3. Improved dyeing curve of dye 1.

CONCLUSION

Three new reactive dyes having two vinyl sulfone-type fiber-reactive groups have been synthesized and their application properties studied. It was found that the highest fixation yield was obtained when the two reactive groups were from *m*-(*β*-sulfatoethyl-sulfonyl)aniline. The dyeing method of the dyes was improved by the amount and the mode of adding alkali (Na_3PO_4). When Na_3PO_4 (1.2–1.6 g) was added twice at 15 min intervals, and the dyes taken up at 40°C, and after the first addition of Na_3PO_4 the dyeing temperature was raised to 60°C, the dyeing results were more satisfactory, with a fixation value above 90%.

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