

Reactive dyeing systems for wool fibres based on hetero-bifunctional reactive dyes

조호정, D.M. Lewis*

한국생산기술연구원, *Dept. of Colour Chemistry, University of Leeds, Leeds, UK

1. Introduction

Although fibre reactive dyes for wool were developed before those for cellulosic fibres, there are still limited ranges of fibre reactive dyes available for wool compared to those for cellulosic fibres. Since Fujioka and Abeta introduced the first mixed bifunctional reactive system in the early 1980s for cellulosic fibres [1], there has been some works on cotton and on silk [2-4]. Imada et al. also reported studies on dyeing cellulose/wool blends with hetero-bifunctional reactive dyes and suggested that these dyes are not only suitable for dyeing cellulose but also can be used for dyeing wool, synthetic polyamide fibres and their blends [5].

Six selected model dyes were prepared, and subsequently characterised by FTIR and HPCE analysis. Several dyeing properties were investigated. In the case of hetero-bifunctional dyes the arrangement of the two reactive groups was based on the study by Omura et al. [6].

2. Experimental

2.1. Preparation of Dyes

Dye I was prepared by coupling γ -acid, pre-condensed with cyanuric chloride, with diazotised aniline, followed by condensing with 1-amino-4- β -sulphatoethylsulphonyl-benzene. Dye II was prepared by coupling H-acid, pre-condensed with cyanuric chloride, with diazotised aniline-2-sulphonic acid, followed by condensing with 1-amino-4- β -sulphatoethylsulphonyl-benzene. Dye III was prepared by coupling H-acid, pre-condensed with cyanuric chloride, with diazotised aniline-2-sulphonic acid, followed by condensing with sulphanilic acid. Half of dye III was then sampled and dye IV was prepared by refluxing under alkaline conditions (pH 8~9) with sodium hydroxide

(10%w/w) for 6 hours. The corresponding vinylsulphone forms were prepared from aqueous solutions of dye I, II, adjusted to pH 8 with sodium carbonate and heated at 60~70°C until the pH stabilised. The resulting dyes were precipitated by the addition of sodium chloride. The precipitated dyes were filtered, washed with 10%w/w sodium chloride aqueous solution and dried at room temperature. The dye structures are shown in Figure 1.

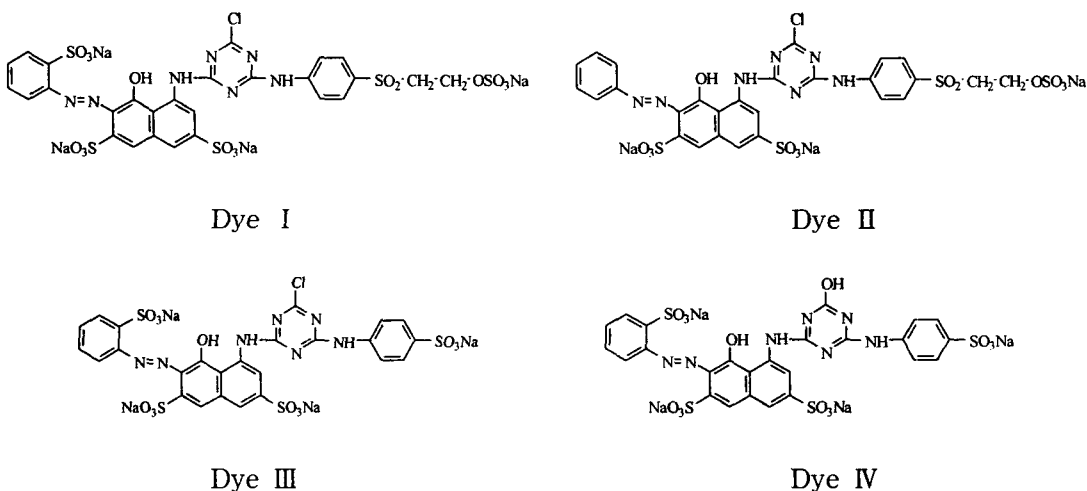


Figure 1 Dye Structures used in this Study

2.2. Analysis of the Dyes

HPCE(High-Performance Capillary Electrophoresis) analysis was carried out using a Dionex CSI capillary electrophoresis system, incorporating a silica capillary (50 μ m internal diameter, 60cm length). FTIR analyses were carried out using the Perkin Elmer 1740 Fourier Transform Infrared Spectrometer. Samples were prepared by mixing 1mg of the sample in 200mg of potassium bromide.

2.3. Application of the Dyes to Wool

All dyeings (3% o.w.f., pH 3~7.) were carried out on wool serge (2/2 twill) fabrics, using the Mathis Labomat IR dyeing machine (Werner Mathis AG, Switzerland). Albegal B (1% o.w.f.), an amphoteric surface active agent, was supplied by Ciba. In each case the wool sample was introduced into the dyebath and the bath raised to 100°C over 40 minutes and dyeing at this temperature continued for a further 60 minutes. The dyebath

pH in each case was controlled by the use of the McIlvaine buffer system. Buffered solutions covering the range of pH 3~7 were prepared using 0.2 M Na₂HPO₄ and 0.1 M citric acid. 20ml of each pH buffer solution was prepared and diluted with distilled water to 40ml. Liquor ratio was 20:1.

2.4. Microscopy Investigation

3% o.w.f. dyeings were produced using the prepared six dyes at pH 5 and 100°C on wool fibres. The wool fibres were introduced into the dyebath and the dyebath raised to the boil over 40 minutes, and dyeing at the boil continued for a further 60 minutes. Cross sections were viewed using an Olympus optical microscope. The magnification ratio was ×400.

3. Results and Discussion

3.1. Analysis of the Dyes

Capillary Electrophoresis (CE) Analysis

It was seen that the retention times of the sulphatoethylsulphone (SES hereafter) compounds such as dye I and II are longer than those of the vinylsulphone (VS hereafter) compounds such as dye I-1 and II-1, respectively, due to different number of sulphonate groups despite the slight change of molecular weight. In addition, the more sulphonate groups in a molecule, the lower the retention time for both SES and VS compounds. Also the retention time of dye II was nearly the same as that of dye III, due to similar molecular weight and the structures having the same number of sulphonate groups. CE analysis results are shown in Table 1 where MCT represents monochlorotriazine group (MCT hereafter).

Table 1 CE Analytical Data

Name	Functional Groups	Retention Time (min.)	% Purity
Dye I	MCT & SES	5.8	87.2
Dye I -1	MCT & VS (VS Form of Dye I)	4.2	71.5
Dye II	MCT & SES	9.9	84.1
Dye II -1	MCT & VS (VS Form of Dye II)	6.8	77.8
Dye III	MCT	9.8	86.8
Dye IV	× (Hydroxytriazine Form of Dye III)	11.0	75.8

FTIR Analysis

The selected FTIR spectra of dyes are shown in Figures 2. From the normalised spectra, it is difficult to assign the characteristic frequencies of SES and VS groups. Second derivative spectroscopy was therefore carried out.

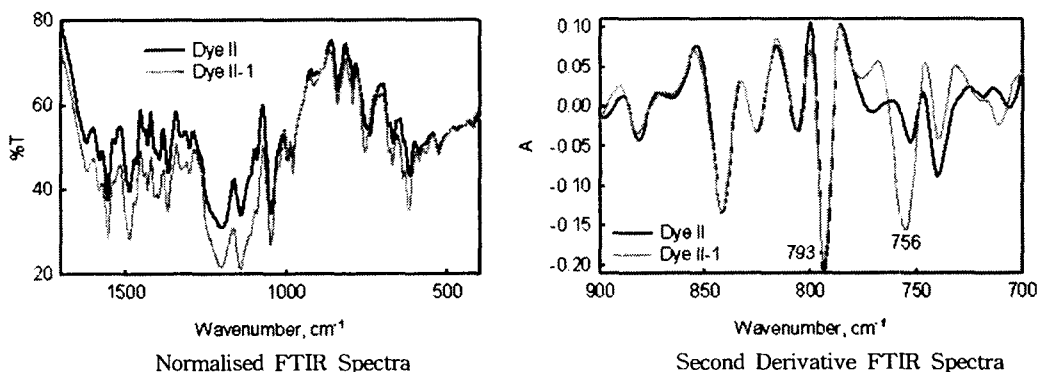


Figure 2 FTIR Spectra of Dye II and II-1

From the second derivative figure, it can be clearly seen that the characteristic frequency of the VS group of dye II-1 appears at 756cm^{-1} whereas dye II has a very weak peak in this region. Moreover the frequency of the C-Cl bond on triazine appears clearly for both dyes at 793cm^{-1} . In the case of dye III and IV, it was shown that only dye III shows a characteristic band for C-Cl bond on triazine at 793cm^{-1} whereas, in the case of dye IV, the frequency for the C-Cl bond had totally disappeared.

Application of the Dyes to Wool

Results show that all the synthesised dyes exhibited high substantivity for the wool at low pH values ($\%E > 90$ at pH 4). This is because all the dyes have sulphonate residues in the dye molecule and as such are comparable to acid dyes for wool. As the dyebath pH increased from 4~7 the overall positive potential of the wool fibre decreased, and thus all the dyes showed remarkably reduced exhaustion values ($\%E$) as the dyebath pH increased. Dye IV is considered to be an acid dye because it is non-reactive dye due to hydrolysed MCT group. Dye IV showed less than 20% exhaustion at pH 7, because there are few sites available for acid dye-fibre electrostatic interaction.

The fixation ($\%F$) of all dyes, except dye IV, increased as the dyebath pH increased, giving maximum values at pH 6~7. However, in the case of pre-activated VS dyes

(dyes I-1 and II-1), the fixation values of those dyes were remarkably improved especially at lower pH(≤ 5).

In the case of overall fixation efficiency (%T), VS dyes such as dye I-1 and II-1 showed greatly improved values over a wide pH range, especially at lower pH(≤ 5). This is because the SES dyes are able to covalently bond to the fibre above pH 5 due to their ability to β -eliminate to form the reactive VS form at these pH values.

The only difference between dye II and III is that dye III contains only a MCT group as functional group, whereas dye II contains both MCT and SES groups. It was clearly seen that the %F and %T values of dye II were significantly higher than those of dye III by about 15% over the whole pH range. This indicates that hetero-bifunctional reactive dyes show higher reactivity than mono-functional reactive dyes, whilst having similar chemical structure and molecular weight. In addition, hetero-bifunctional reactive dyes are less affected by the change of pH than mono-functional (MCT) reactive dyes.

Investigation of Migration Properties using Microscopy

Skitteriness was quantified by calculating the brightness of each image. The numerical values display statistical information about the grey-scale values (from darkest (0) to brightest (255)) of the pixels. Mean represents the average brightness value. Standard deviation (SD) represents how widely the values vary. These values, in fact, represent variability in lightness to indicate levelness problem. Pixels represent the total number of pixels in the image.

Table 2 Brightness Analysis Data of Dyed Fabrics

Name	Mean	Standard Deviation (SD)	Pixels
Dye I	109.40	41.35	179324
Dye I -1	110.85	47.19	180540
Dye II	110.28	49.24	179677
Dye II -1	111.52	53.47	179200
Dye III	110.60	46.77	181760
Dye IV	108.60	37.66	181050

It is shown in Table 2 that SES dyes, the dye I and II, diffused more evenly (lower SD

values) than VS dyes, the dye I-1 and II-1, respectively. It is also clear that dye IV shows the lowest SD values, indicating that this dye diffused more evenly than any other dyes.

4. Conclusions

Six model dyes having different functionality were synthesised. They were expected to show different wool dyeing behaviour. Pre-activated VS dyes show higher fixation efficiency values due to their higher reactivity compared with SES dyes. Also hetero-bifunctional reactive dyes are more efficiently able to bond to the wool fibre regardless of dyebath pH than mono-functional reactive dyes.

Microscopy results show that, in general, dyes containing a SES group in a molecule, diffused more evenly than dyes containing a pre-activated VS group in a molecule. It is also shown that dye containing more number of sulphonate groups shows reduced chances for level dyeing, producing more ring-dyed fibres. When comparing dyes containing different number of reactive groups, dyes containing more reactive groups of greater reactivity would have less time to migrate within the wool fibre because once the reactive groups react with a nucleophile it is impossible for it to diffuse within the wool fibre.

5. References

1. S Fujioka and S Abeta, *Dyes and Pigments*, 3 (1982) 281.
2. M Matsui, U Meyer and H Zollinger, *J.S.D.C.*, 104 (1988) 425.
3. A Uygur and M Hall, *J.S.D.C.*, 112 (1996) 167.
4. D Agarwal, K Sen and M L Gulrajani, *J.S.D.C.*, 112 (1996) 10, 321 and 113 (1997) 174.
5. K Imada, M Sasakura and T Yoshida, *Textile chemist and colorist*, 22 (1990) 18.
6. T Omura, K Yokogawa, Y Kayane and Y Tezuka, *Dyes and Pigments*, 29 (1995) 1.