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The synthesis and application of a new reactive dye based on disulfide-bis-ethylsulfone

D.M. Lewis *, A.H. Renfrew, A.A. Siddique

Department of Colour Chemistry, University of Leeds, Leeds LS2 9JT, UK

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Dedicated to Dr Arnie Peters on his retirement as Editor of *Dyes and Pigments*. The authors note their appreciation of his kindly approach and attention to detail during his long service in this capacity

Abstract

A new reactive dye containing a bis-ethylsulfone-disulfide has been synthesised. This dye is able to eliminate to two small vinylsulfone dye molecules under alkaline conditions. When applied to cotton fabrics the bis-ethylsulfone-disulfide dye shows higher primary exhaustion than a corresponding model sulfatoethylsulfone dye and can be covalently bonded to the substrate by raising the pH to 11.5. Any hydrolysed dye produced is approximately half the size of the starting dye molecule and thus soaping-off properties are the same as the normal sulfatoethylsulfone dye. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive bis-ethylsulfone-disulfide dyes; Exhaustion/fixation behaviour; Cotton dyeing

1. Introduction

In 1954 Rattee and Stephen showed that dyes containing a dichlorotriazinyl (DCT) reactive group could react with cellulosic fibre in the presence of alkali to form covalent bonds, resulting in a fixation yield of approximately 60% [1,2]. This discovery led to the introduction of the Procion MX range of reactive dyes by ICI in 1956. In 1957 Hoechst (now DyStar) introduced Remazol dyes for cotton, which contain a vinylsulfone reactive group capable of forming covalent bonds with cellulosic fibres under alkaline conditions [3]. Most of the Remazol dyes initially do not contain free vinylsulfone reactive groups but instead contain non-reactive β-sulfatoethylsulfone (SES) groups, which ß-eliminate during the dyeing process to form the vinylsulfone reactive group, which reacts with nucleophiles (water, alcohols, amines and cellulose) by a nucleophilic addition reaction [4–6].

The major drawback of reactive dyes from the environmental viewpoint stems from their susceptibility to hydrolysis during their application, which gives rise to problems with colour in the effluent from dye-houses. During the application of reactive dyes, alkaline conditions are generally employed in order to generate sufficient nucleophilic cellulosate anions. Furthermore, under these conditions some dye hydrolysis is unavoidable [7]. A further concern, particularly in exhaustion dyeing is the use of high concentration of electrolyte (50–100 g dm^{-3}). The electrolyte used in the application of

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* Corresponding author. Tel.: +44-113-2332930; fax: +44-113-2332947.

E-mail address: ccddml@leeds.ac.uk (D.M. Lewis).

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conventional reactive dyes on 100% cellulosic materials is normally sodium chloride but when dyeing cellulose/polyester blends in one bath processes it is necessary to use sodium sulfate, to avoid attack by sodium chloride solution on the stainless steel dyeing vessel. High concentrations of either sodium chloride or sodium sulfate are undesirable in aqueous effluent but sulfate discharge may be even more suspect, since it attacks concrete pipes [8] and also increases the undesirable accumulation of sulfate ions in water courses. Using a high concentration of electrolyte not only produces environmental problems but also contributes to the time consuming, energy intensive and expensive washing-off procedure [9]. During soaping-off dilution of electrolyte concentration reduces the substantivity of unfixed dye; the latter must be effectively removed from the dyed cotton otherwise poor wet-fastness properties will be apparent. The countermeasures for these problems include selection of dyes that give high exhaustion and fixation, optimisation of dyeing conditions and synthesising highly substantive dyes requiring a lower salt concentration than normally used in reactive dye application. The drawback of using highly substantive dyes is that the unfixed dye requires prolonged soaping, especially in deep shades; using lower substantivity dyes, such as monosulfatoethylsulfone dyes, leads to lower dyebath exhaustion values and, especially in deep shades, a 'colour in effluent' problem, but soaping-off is facilitated.

The first full range of homo-bifunctional reactive, bis-monochlorotriazine Procion HE dyes, was launched by ICI in the late 1960s and these offered improved fixation efficiency. In 1979, the first range of hetero-bifunctional reactive dyes (Sumifix Supra) was marketed by Sumitomo [10]; these dyes contain two reactive groups on the same triazine ring — the sulfatoethylsulfoneanilino-triazine and the monochloro-triazine (MCT/SES) — and show good robustness towards changes in exhaust dyeing parameters such as temperature, electrolyte concentration, alkali concentration and liquor ratio. The Procion H-EXL range of bis-MCT dyes for cellulosic fibres was developed in the 1980s by ICI (now BASF); these were designed to have almost identical substantivity, exhaustion and fixation (SEF) profile, good migration and good build-up, easy wash-off and favourable dyeing characteristics. Ciba developed Cibacron LS dyes, which are bis-monofluoro-s-triazine (MFT) dyes for exhaustion dyeing. They have very high substantivity towards cotton and other cellulosic fibres reducing the amount of electrolyte required in the dyebath.

This work describes a method to temporarily increase the substantivity of reactive dyes for cellulosic fibres by preparing a dye with a disulfide-bis-ethylsulfone (DSBES) cross-link. Such a system can β-eliminate during the alkaline fixation stage of dyeing to form two small vinylsulfone reactive dye molecules. Thus these dyes should fit the objective of achieving good dyebath exhaustion and yet the system would allow ready soaping-off of unfixed dye. Lewis and Smith [11] previously prepared a disulfide-bis-ethylsulfone dye from a model sulfatoethylsulfone dye and studied its wool dyeing properties, but no work was done on cellulosic fibres.

2. Experimental

2.1. Materials

1-Aminobenzene-4-β-sulfatoethylsulfone was supplied by a leading dye manufacturer. 1-naphthol-3,6-disulfonic acid, thioglycollic acid and other chemicals were supplied by Aldrich Chemical Company Limited (UK). The cotton fabric was a plain weave bleached cloth (130 g m^{-2}), supplied by Whalleys of Bradford (UK).

2.1.1. Preparation of 1-aminobenzene-4-S-thiosulfatoethylsulfone (Bunte salt)

1-Aminobenzene-4-β-sulfatoethylsulfone (20.7 g; 0.07 moles; 95% pure) was dissolved in water (200 ml) (pH 6.5) and a solution of sodium thiosulfate (22.12 g; 0.14 moles) in water (100 ml) was added to the clear solution. The reaction mixture was refluxed for 4 h; the solution was then cooled to 40°C and any precipitate present was filtered off. The resulting Bunte salt was precipitated out by adding sodium chloride (15% w/v). The precipitate formed was filtered, washed with a saturated sodium chloride solution and dried at room temperature under vacuum. The yield was 19.7 g (88.2%).

2.1.2. *Preparation of disulfide-bis-ethylsulfone diamine intermediate*

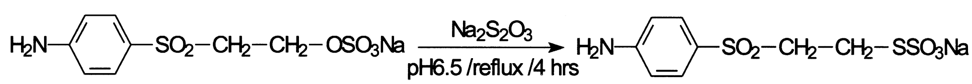
1-Aminobenzene-4-*S*-thiosulfatoethylsulfone (Bunte salt) (10 g; 0.03 moles) was dissolved in water (250 ml) at pH 7. To this a solution of thioglycollic acid (2.8 g; 0.03 moles) adjusted to pH 7 with dilute sodium hydroxide, was added in small portions over 20 min. at room temperature and the reaction continued for a further 2 h. During the course of the reaction a white precipitate came out of solution; after 2 h the reaction was complete as confirmed by precipitation and FTIR analysis (loss of the Bunte salt absorbance peak at 1028 cm^{-1}). The white precipitate was filtered, washed with distilled water and dried in an oven at 40°C for 1 h. The yield was 10.3 g (79.3%).

2.1.3. *Preparation of disulfide-bis-ethylsulfone (DSBES) dye*

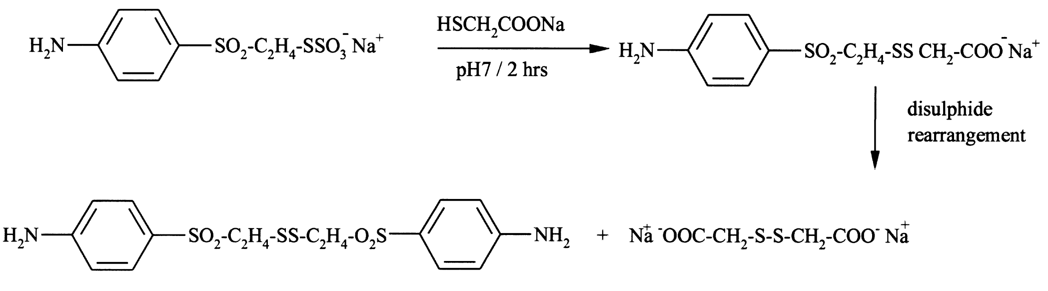
The disulfide intermediate (5.2 g; 0.012 moles) previously prepared was dissolved in concentrated sulfuric acid (98%; 10 ml) and poured over ice (100 g). A solution of sodium nitrite (2.0 g; 0.029 moles) in water (25 ml) was added in a drop-wise manner to the resulting white suspension, maintaining the temperature below 5°C. The excess nitrous acid was removed by adding a small amount of sulphamic acid. The tetrazotised disulfide-bis-ethylsulfone salt solution was added in small portions to a neutral solution of 1-naphthol-3,6-disulfonic acid (8.36 g; 0.024 moles) dissolved in water (100 ml) at a temperature below 4°C and the pH adjusted to 5–6 by adding 2 M sodium hydroxide solution. The resulting orange dye was stirred under the above conditions for a further 2 h. The orange dye was salted out by adding sodium chloride (15% w/v), then filtered, washed with a saturated sodium chloride solution and dried at room temperature under vacuum. The yield was 10.42 g (76%).

2.1.4. *Synthesis of 1-aminobenzene-4-β-sulfatoethylsulfone (SES) dye*

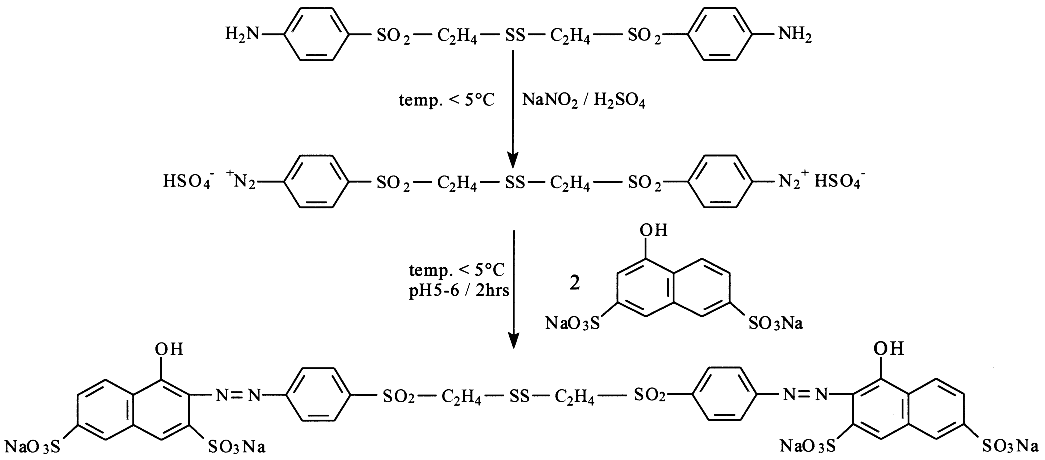
1-aminobenzene-4-β-sulfatoethylsulfone (PABSES; 95%) (10 g; 0.034 moles) was suspended in water (100 ml) at 20°C. The pH of the suspension was raised to 5.5 by adding 2 M sodium carbonate solution and the resulting solution was filtered. To this solution hydrochloric acid (36%; 8.6 ml; 0.085 moles) and ice (50 g) were added. When the temperature of the above solution was below 4°C a solution of sodium nitrite (2.65 g; 0.037 moles) dissolved in water (20 ml) was introduced in small portions over 30 min. After the addition of sodium nitrite the reaction was stirred under the above conditions for 30 min. The excess nitrous acid was destroyed by adding sulfamic acid. The diazotised PABSES was added slowly to a neutral



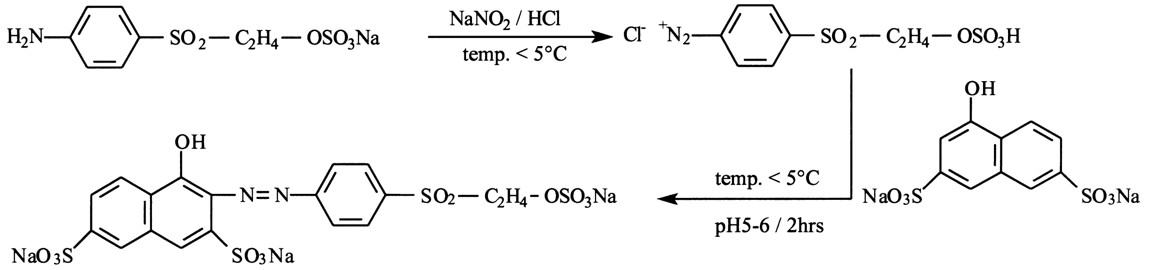
Scheme 1. The synthesis of 1-aminobenzene-4-*S*-thiosulfatoethylsulfone (Bunte salt).



Scheme 2. The synthesis of disulfide-bis-ethylsulfone diamine intermediate.



Scheme 3. The synthesis of disulfide-bis-ethylsulfone (DSBES) dye.



Scheme 4. The synthesis of 1-aminobenzene-4-β-sulfatoethylsulfone (SES) dye.

solution of 1-naphthol-3,6-disulfonic acid (11.84 g; 0.034 moles) dissolved in water (100 ml), the pH was maintained at 5–6 and the temperature was maintained below 5°C. The resulting orange dye solution was stirred under the above conditions for 2 h. On the completion of the coupling reaction the dye was precipitated using sodium chloride (15% w/v), filtered, washed with a saturated solution of sodium chloride and dried at room temperature under vacuum. The yield was 19.7 g (87.2%).

2.2. Measurements of dye exhaustion and fixation

2.2.1. Exhaustion (E)

The uptake of the dye by the cotton was measured by sampling the dye-bath before and after the dyeing process. The absorbance of the diluted dye solution was measured at the wavelength of maximum absorption (λ_{max}) of the dye using a UV–Visible spectrophotometer (Phillips Pye Unicam PU8600). Percentage dye-bath exhaustion (%E) was calculated using the following equation:

$$\%E = \frac{1 - A_1}{A_0} \times 100$$

where A_0, A_1 are the absorbance values of the dye-bath before and after the dyeing respectively.

2.2.2. Fixation (F)

Measurement of the extent of fixation of the reactive dye absorbed on cotton was carried out by stripping any unfixed dye from the dyed material using 25% (w/w) pyridine in water solution (100°C, LR 10:1). The stripping treatment (2 min per strip) was carried out repeatedly using fresh aqueous pyridine solution until no further dye was removed. The colour yield (K/S) values of the stripped, dyed samples were than measured at λ_{max} using a Macbeth colour eye measurement system. Assuming K/S was proportional to dye concentration on the fibre the extent of fixation of the dye could be calculated using the equation shown below:

$$\%F = \frac{K_2/S_2}{K_1/S_1} \times 100$$

where K_1/S_1 and K_2/S_2 represent the colour yield of the dyeing before and after stripping respectively.

An alternative use of the term 'fixation' is sometimes used, which refers to the overall amount of original dye that is covalently bonded. This overall fixation efficiency (T) is related to F (the fraction of exhausted dye fixed) by the following equation:

$$\%T = \frac{\%E \times \%F}{100}$$

2.3. CE analysis

The capillary zone electrophoresis (CZE) technique was employed to follow the preparation of intermediates and dyes. Additionally the micellar electrokinetic capillary electrophoresis (MEKCE) technique was used to analyse derivatives of the model dyes formed in the β-elimination studies. The CE analysis of samples was carried out with the Dionex Capillary electrophoresis system CSE 1, incorporating a 60 cm silica capillary with a 50 μm internal diameter. The samples were prepared as a 0.01% w/w solution in distilled deionised water; the background electrolytes were potassium dihydrogen phosphate buffer (10 mM) at pH 9 for the CZE technique and 10 mM disodium hydrogen phosphate (Na_2HPO_4) plus 40 mM sodium dodecyl sulfate (SDS) (pH 9) for the MEKCE technique. The separated compounds were detected using a UV/Vis detector set at the wavelength of maximum absorption (λ_{max}) of the analyte samples. Gravity injection was fixed at 50 mm for 15 s, and the current was controlled at 30 μA.

2.4. Infrared (IR) analysis

FTIR–ATR spectroscopy was used to follow the preparation of the disulfide intermediate. The solution trough contained a zinc selenide crystal, which is resistant to water and thus allowed easy analysis of aqueous Bunte salt solutions. Transmission IR spectra were also produced of solid samples of intermediates and dyes, by mixing 5 mg of the relevant intermediate or dye with 1 g of KBr, and pressing the mixture into a disc under 10 tons pressure. The instrument employed for all analyses was a Perkin Elmer 1725 spectrometer linked to the Perkin Elmer IR Data manager programme on an Epson computer.

2.5. Procedure for studying β-elimination reactions of the disulfide-bis-ethylsulfone (DSBES) dye

The DSBES dye was dissolved in distilled water and the pH was raised to 10,11 and 12. The temperature was raised to 60 and 80°C, and the solution stirred for 1 h under these conditions. On cooling, a sample of each activated DSBES dye solution was taken and analysed using CE.

2.6. Dyeing procedure

All dyeings were carried out using 2% o.m.f. pure dye. The dyeing of DSBES dye was carried out in distilled water using fabric (5 g) at a liquor ratio of 20:1 with anhydrous sodium sulfate (20, 30, 40, and 50 g/l) using the Rotadyer (John Jefferys) laboratory dyeing machine. Primary exhaustion was carried out at 60°C, pH 7 for 20 min, then the pH of the dye-bath was adjusted to various values (10.5, 11, 11.5, 12 and 12.5) and the dyeing continued at 60°C for a further 60 min. In the case of SES dye, the recommended normal dyeing procedure was employed as a control for the experiments: i.e.

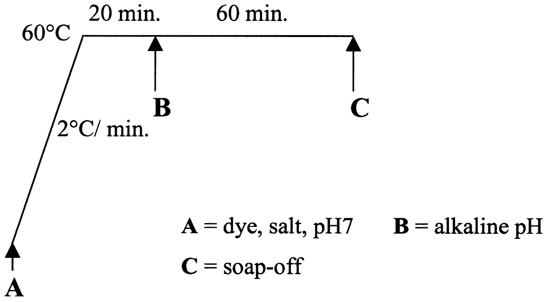


Fig. 1. Dyeing profile for DSBES and SES dyes.

dyeing in the presence of salt (50 g dm^{-3}), 60°C for 20 min, and fixing at pH 11.5 [soda ash (20 g dm^{-3})].

2.7. Rinsing and soaping-off

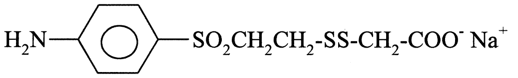
At the end of the dyeing process, the samples were removed from the dye pots, rinsed in cold water for 10 min and then rinsed in warm water for 10 min. The samples were soaped-off using Sandozin NIE (5 g dm^{-3}) and soda ash (2 g dm^{-3}) at 98°C for 30 min. The absorbance values of the liquor after each wash-off cycle were measured as well as the reflectance values of the dried sample.

3. Results and discussion

3.1. Analysis of intermediates and dyes prepared

From capillary zone electrophoresis (CZE) analysis, it is quite apparent that the synthesised 1-aminobenzene-4-*S*-thiosulfatoethylsulfone (Bunte salt) was reasonably pure, giving one major peak at a retention time of 5.24 min. The hydrolysed sample of PABSES when analysed by CZE gave a peak with a retention time of 2.85 min and the peak for the PABSES appeared at a retention time of 5.84 min. Microanalysis (Table 1) indicated that the Bunte salt was obtained in good purity with one molecule of water of crystallisation.

The ATR–FTIR spectra (water spectrum subtracted) shown in Fig. 2 represents the Bunte salt in aqueous solution before the addition of thioglycollic acid (spectrum A) and the solution after the disulfide-bis-ethylsulfone diamine intermediate synthesis (spectrum B). By comparing the spectra it can be seen that (2 h after addition of thioglycollate) the peaks at 1028 cm^{-1} and 1205 cm^{-1} corresponding to (-SSO_3^-) had completely disappeared, confirming that at this stage of the reaction, mainly mixed disulfide,



had been formed (aqueous solution solubility achieved through the carboxylate anion). This outcome is supported by the previous observation of Milligan and Swan that Bunte salts react almost instantaneously with thiols to give the mixed disulfide [12]. Further support that the mixed disulfide is present in the aqueous solution comes from Spectrum B, which shows carboxylate absorbances at ca. 1380 cm^{-1} and ca. 1580 cm^{-1}. Studies of wool cystine chemistry have led to a good understanding of the stability of mixed or unsymmetrical disulfides; Asquith and Puri [13] demonstrated that the mixed disulfide reaction product of cystine and thioglycollate was reasonably stable under acidic conditions but rapidly rearranged to the corresponding symmetrical disulfide at pH values $\geqslant 7.0$.

The FTIR transmission spectrum for the solid disulfide-bis-ethylsulfone diamine intermediate also shows no peak at (1028 cm^{-1}) corresponding to the –SSO_3^- group and gave no indication for the presence of –COOH or –COONa groups; results obtained from elemental analysis (Table 1) confirmed the product to be the disulfide-bis-ethylsulfone-diamine intermediate.

It is quite apparent from CZE analysis (Fig. 3) that both dyes are reasonably pure in terms of coloured material, giving one major peak. However, in the case of the sulfatoethylsulfone (SES) dye, 92%, of the total colour corresponds to SES dye,

Table 1
Elemental analysis results for the Bunte salt (a) and disulfide-bis-ethylsulfone diamine (b) intermediates

Species	% Required				% Found			
	C	H	N	S	C	H	N	S
(a) $C_8H_{10}NO_5S_3H_2O(Na)$	28.49	3.56	4.15	28.49	28.47	3.55	4.13	28.48
(b) $C_{16}H_{20}N_2O_4S_4$	44.20	4.66	6.48	29.64	43.9	4.65	6.48	29.65

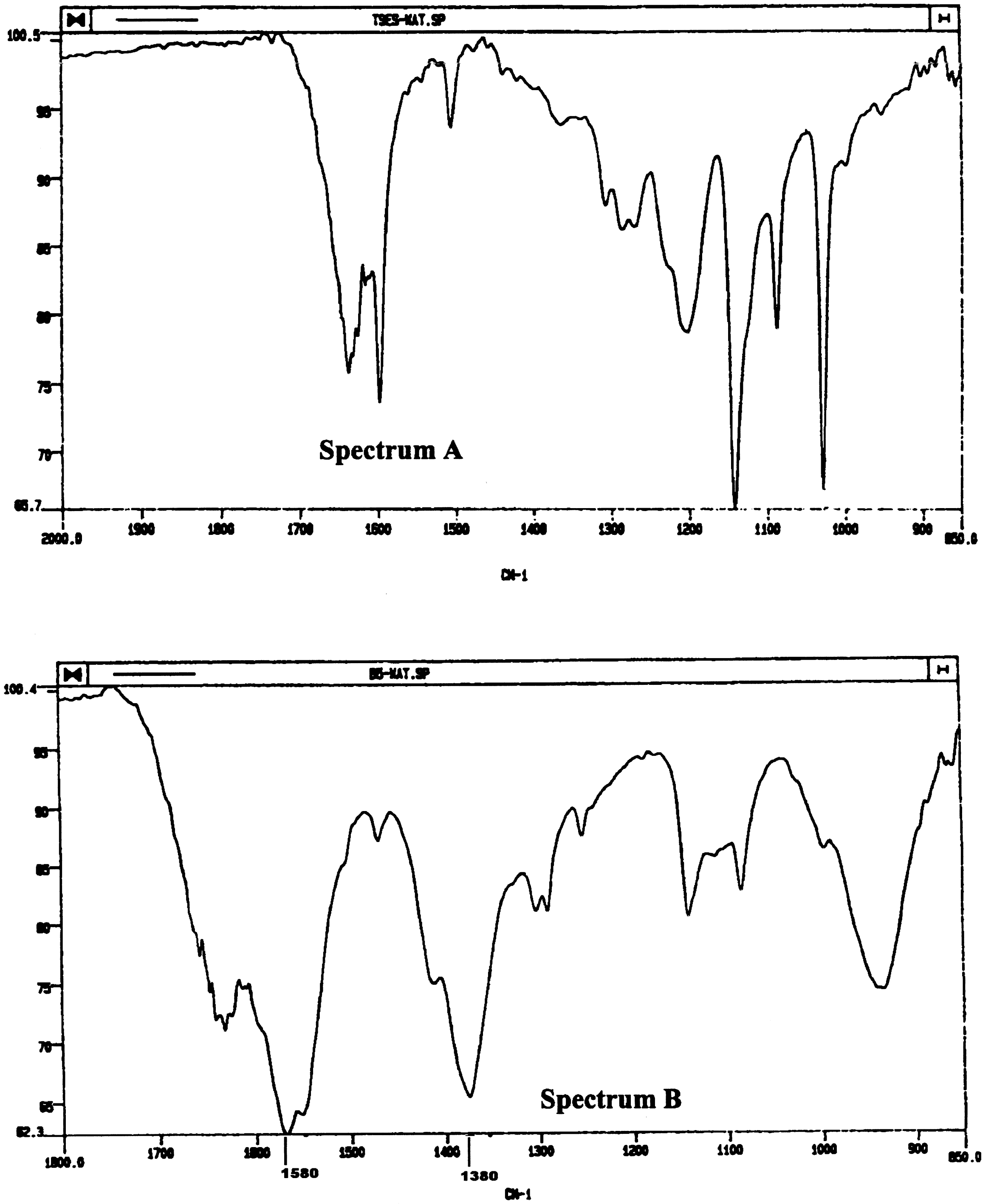


Fig. 2. FTIR spectrum of the Bunte salt sample in water (spectrum A) and reaction mixture 2 h after the addition of sodium thioglycollate to the Bunte salt solution (spectrum B).

8% corresponds to VS dye and 2% corresponds to HES dye.

3.2. Results of β-elimination study

The following species are likely to be present in dyebaths following β-elimination of the DSBES dye:

Ⓓ—SO_2-CH=CH_2 ; Ⓓ—SO_2-CH_2CH_2-OH

vinylsulfone dye hydroxyethylsulfone dye

Ⓓ—SO_2-CH_2CH_2-S-CH_2CH_2-SO_2 Ⓓ

thioether dye

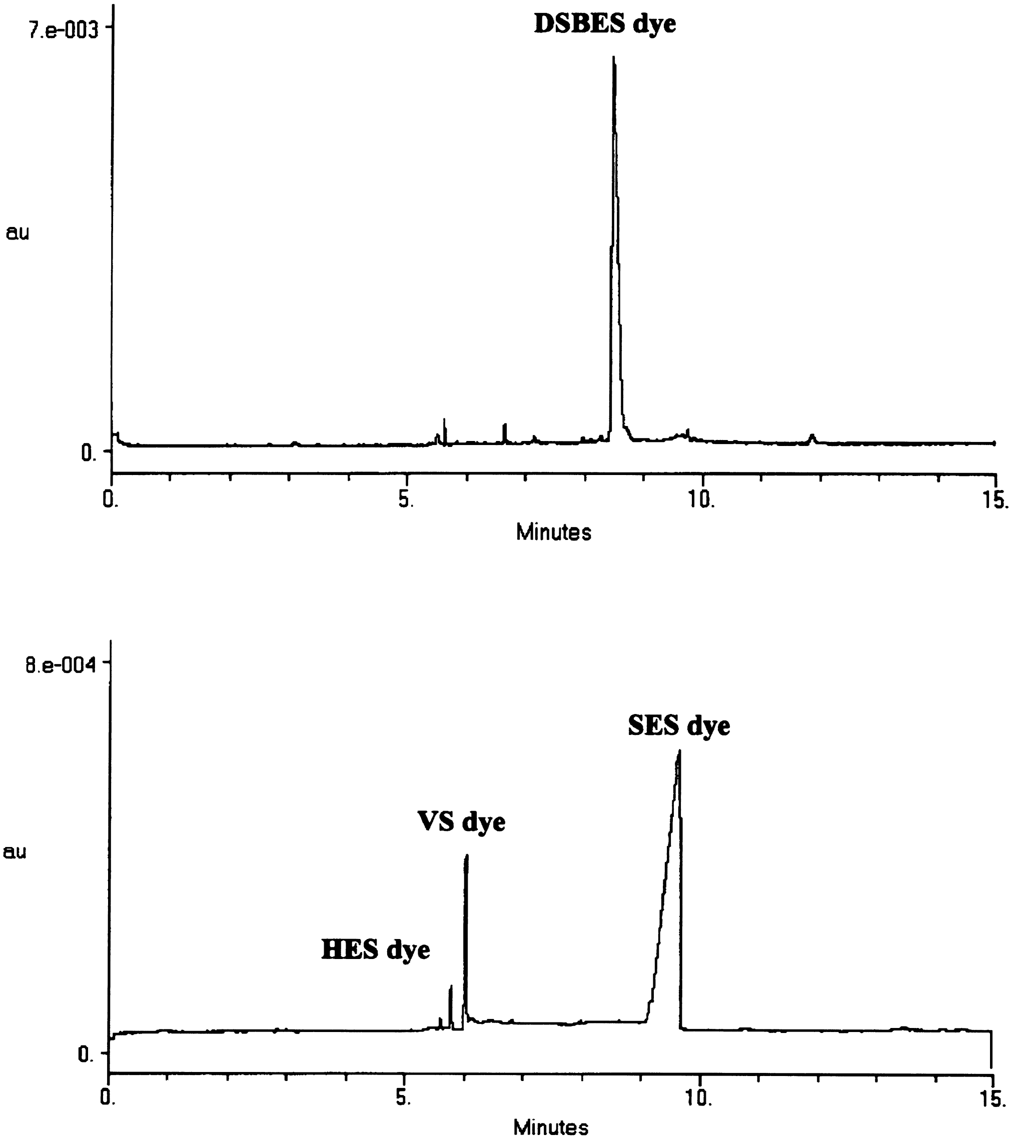


Fig. 3. Electropherograms of disulfide-bis-ethylsulfone (DSBES) dye and sulfatoethylsulfone (SES) dye.

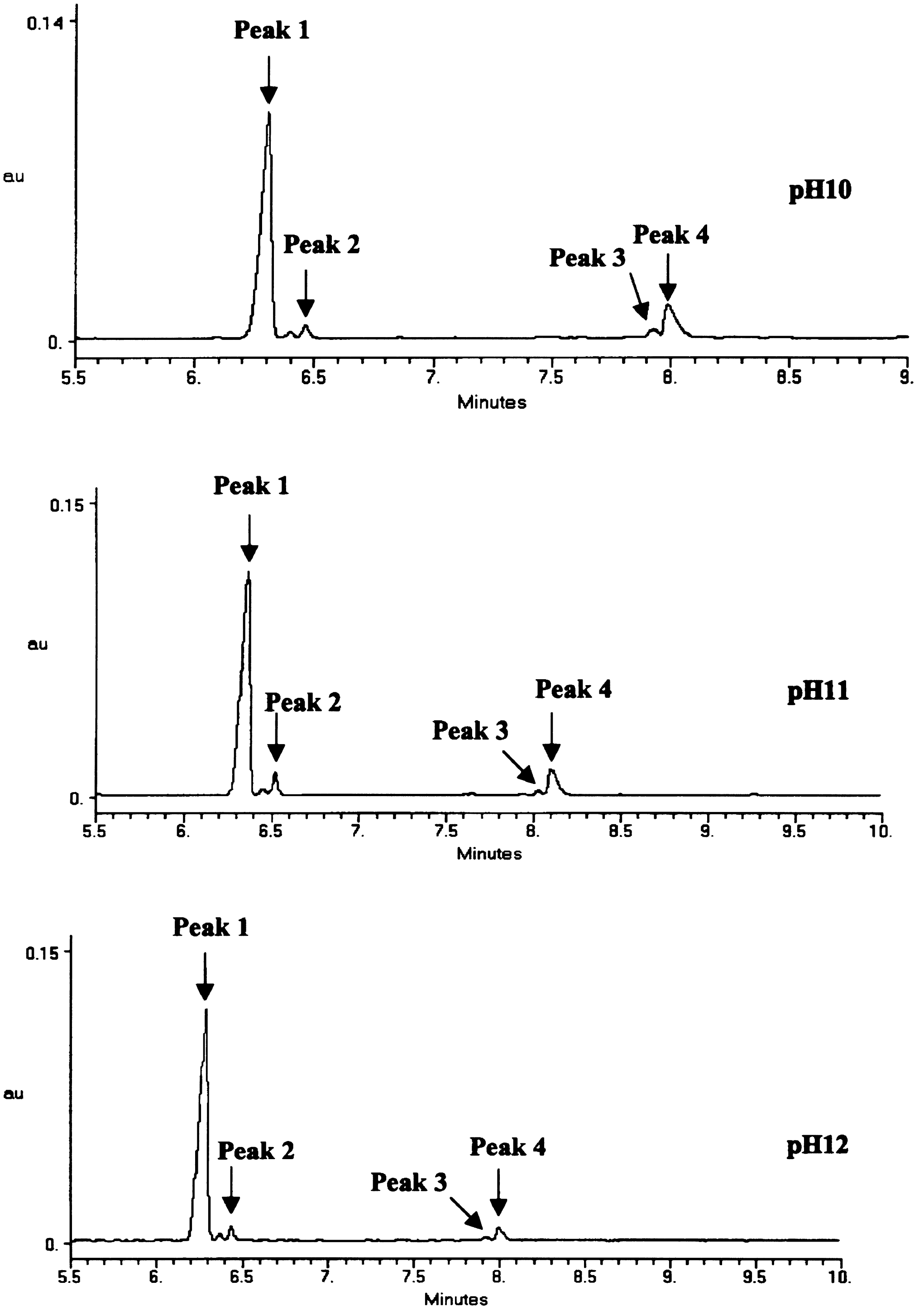


Fig. 4. Micellar CE analysis of DSBES dye treated at pH (10, 11 and 12) and 60°C.

where D represents the sulfonated chromophore. The above vinylsulfone, hydroxyethyl sulfone and thioether dyes were synthesised using the methods described by Lewis and Smith [14] and used as models in the MEKCE studies of the various DSBES dye reactions under β-elimination conditions.

The MEKCE electropherograms presented in Fig. 4 are from solutions treated at 60°C for 1 h at pH 10, 11 and 12. The electropherograms of the hydrolysed DSBES dye show four peaks when analysed under the above conditions. It can be seen from Fig. 4 and Table 2 that the peak corresponding to DSBES dye was present even at pH12, albeit in very small amounts. As expected, the amount of DSBES dye decreased in terms of % coloured material as the pH of the activating solution increased from 10 to 12. The pH 10, 60°C activated DSBES dye solution, was spiked with each standard and analysed by MEKCE to determine which peak corresponded to which standard. Cross-checking of the reacted DSBES dye samples with the spiked standards confirmed that the four peaks present were due to hydroxyethylsulfone dye (peak 1), vinylsulfone dye (peak 2), disulfide-bis-ethylsulfone dye (peak 3) and thioether dye (peak 4). Table 2 summarises the species present in the activated DSBES dye solutions in terms of % coloured material. The remaining minor peaks (which corresponded to about 2% in total) could not be assigned to any of the standard dyes prepared.

Fig. 5 and Table 2 summarise the MEKCE analysis results obtained for DSBES dye solution treated at 80°C for 60 min at pH 10, 11 and 12. The pH 10 activated DSBES dye solution gave four peaks. The electrophoregram of the pH 11, 80°C activated DSBES dye solution shows one major peak, which was due to hydroxyethylsulfone dye, along with small peaks corresponding to vinylsulfone dye, DSBES dye and thioether dye. The activation of DSBES dye solution at 80°C, pH 12 for 60 min shows just one major peak corresponding to the hydroxyethylsulfone dye. The amount and type of species present after the activation of DSBES dye under various pH and different temperatures conditions are summarised in Table 2.

Table 3 shows the% peak area of the four major peaks before and after the activated DSBES dye solution was spiked with the standards. Fig. 6(a) represents DSBES dye solution activated at pH 10, 60°C, spiked with the standard hydroxyethylsulfone dye. The electropherogram obtained shows an increase in the intensity of peak 1, which corresponds to hydroxyethylsulfone dye. Fig. 6(b) shows the MEKCE analysis of the sample from the DSBES dye solution activated at pH 10, 60°C, spiked with the standard vinylsulfone dye; peak 2 attributed to vinylsulfone dye has increased in intensity. Fig. 6(c) shows the MEKCE analysis of the sample from the DSBES dye solution activated at pH 10, 60°C, spiked with the standard DSBES dye; it can be seen that the intensity of peak 3 has increased. Fig. 6(d) shows the MEKCE analysis of the sample from the DSBES dye solution activated at pH 10, 60°C, spiked with the standard thioether dye; the increased intensity of peak 4 confirms it is thioether dye.

The products found using MEKCE analysis confirmed that the disulfide in the DSBES dye underwent similar reactions as those reported for cystine disulfide hydrolysis [15].

A potential reaction mechanism for the alkaline activation of DSBES dye is summarised in Scheme

Table 2
Coloured species (%) present after activation of DSBES dye at various pH values and different temperatures

Peaks	Dye present	% Total colour present at 60°C			% Total colour present at 80°C		
		pH 10	pH 11	pH 12	pH 10	pH 11	pH 12
1	Hydrolysed dye	68.4	85.7	95.4	80.1	95.3	97.8
2	Vinylsulfone dye	6.5	4.1	1.5	6.2	0.9	–
3	Disulfide dye	5.7	1.3	0.8	3.5	0.7	–
4	Thioether dye	18.2	6.7	2.0	9.6	1.9	–

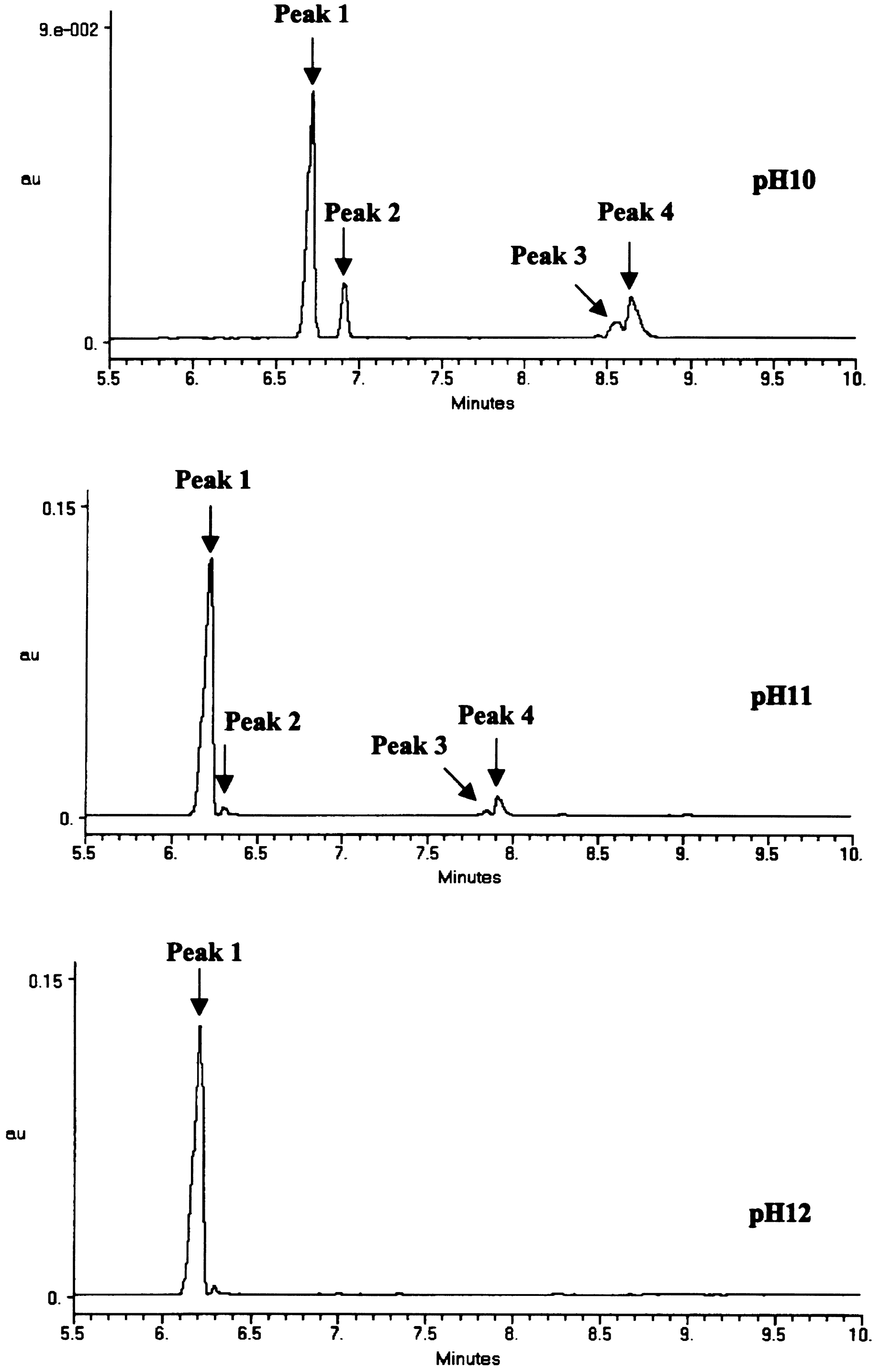


Fig. 5. Micellar CE analysis of DSBES dye treated at pH (10, 11 and 12) and 80°C.

Table 3
Peak area (%) before and after the activated solution (pH10/ 60°C) was spiked with the standards

Peaks	% Peak area before spiking	% Peak area after spiking
1	68.4	76.7
2	6.5	82.3
3	5.7	41.2
4	18.2	31.8

5, which shows the vinylsulfone (**1**) and perthioethylsulfone (**2**) dyes as probable intermediates produced during β-elimination of the DSBES dye. Under certain conditions (pH10), the perthioethylsulfone dye formed can produce some thioethylsulfone dye (**3**) (route1). By way of analogy it has been demonstrated that perthiocysteine decomposes to cysteine and sulphur or sulphide anion, which supports this proposal [16]. The thioethylsulphone dye would react with the vinylsulfone dye (**1**) to produce some thioether dye (**4**), which clearly cannot form a covalent bond with the fibre. The presence of unreactive thioether dye was confirmed, when (pH 10) activated DSBES dye solution was analysed by MEKCE. However, as the alkaline conditions became increasingly severe (pH 12), the amount of product corresponding to thioether dye reduced and eventually disappeared; this could be explained in terms of reaction Scheme 5, route (**2**). The perthioethylsulfone formed from β-elimination of DSBES under severe alkaline conditions rapidly breaks down to produce vinylsulfone, which in turn forms hydroxyethylsulfone dye (**5**). In Scheme 5, it is not intended that route (**2**) cannot be followed at pH10; but it is significant that pH 12 activation gives only route (**2**) products.

4. Application of DSBES dye

4.1. Effect of salt concentration

In the case of the standard SES dye applied under typical commercially used conditions (50 g dm^{-3} salt and fixation at pH 11.5), the exhaustion and fixation results are as follows:

Primary exhaustion (S) = **35%**
Secondary exhaustion (E) = **75%**
Fixation (F) = **72%**
Overall fixation efficiency (T) = **54%**

It can be seen from Fig. 7 that the DSBES dye shows much higher primary exhaustion (%S) values than the SES dye even when applied under 'low-salt' concentrations. This feature of the DSBES dye can be attributed to it being approximately twice the molecular size of the SES dye; therefore it is expected to have much higher primary exhaustion (%S) values. After the addition of alkali, the DSBES dye β-eliminates to produce two smaller reactive vinylsulfone dye molecules, which have reduced substantivity for the fibre. The small dye molecules have the ability to desorb from the fibre back to the dye-bath. The desorption of the dye is not solely due to the reduction in substantivity of the VS dye, since electrostatic repulsion by fixed sulfonated dye [17] as well as by cellulosate anion can also prevent further movement of the sulfonated dye into the fibre from the dye-bath. High concentrations of electrolyte are needed to suppress the negative potential of fixed sulfonated reactive dye and cellulosate anion as well as increasing the substantivity of the small VS dye. It can be seen from Fig. 7 that secondary exhaustion (%E) values increased as the concentration of salt increased from 20 g dm^{-3} to 50 g dm^{-3}. The higher primary and secondary exhaustion values obtained for the DSBES dye when applied using 50 g dm^{-3} salt compared with values for the SES dye, means that at the fixation stage the probability of dye–fibre covalent reaction would increase, resulting in the DSBES dye giving higher fixation (%F and %T) values.

4.2. Effect of dye-bath pH values

It can be seen from Fig. 8 that maximum exhaustion (%E) and fixation (%F and %T) values for DSBES dye are produced when dyeing at pH 11.5. Before fixation commences, an equilibrium exists between dye in the dye-bath and dye diffused in the fibre. Once covalent fixation takes place the equilibrium is altered as the dye in the fibre is covalently bonded to the nucleophilic sites in the fibre. The effect of this change in the equilibrium is overcome by diffusion of more dye from the external dyebath into the fibre, hence exhaustion increases during the alkaline fixation process. If the pH of the dye-bath was not high enough to produce β-elimination of the disulfide bond, then the amount of the reactive vinylsulfone (VS) dye form generated would be reduced and therefore

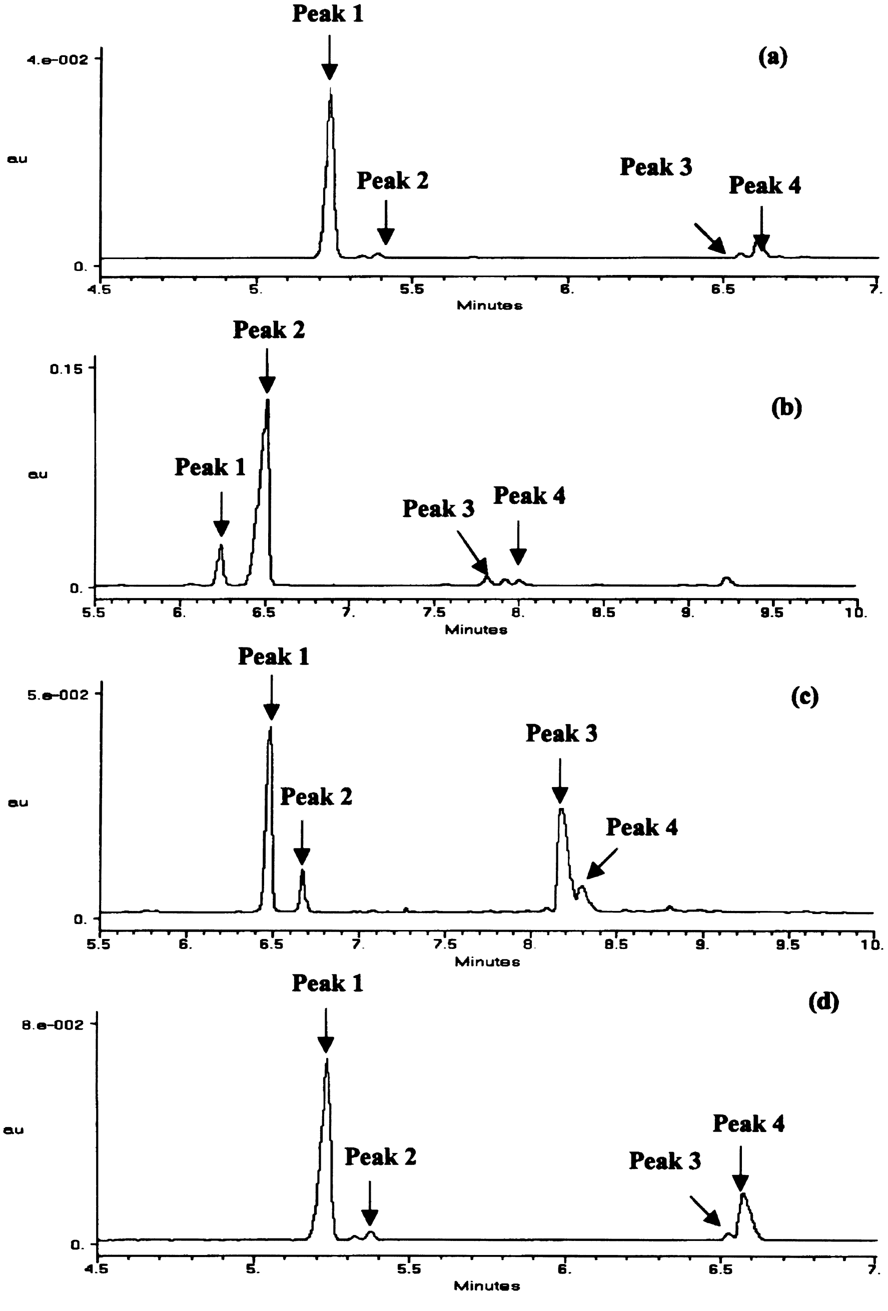
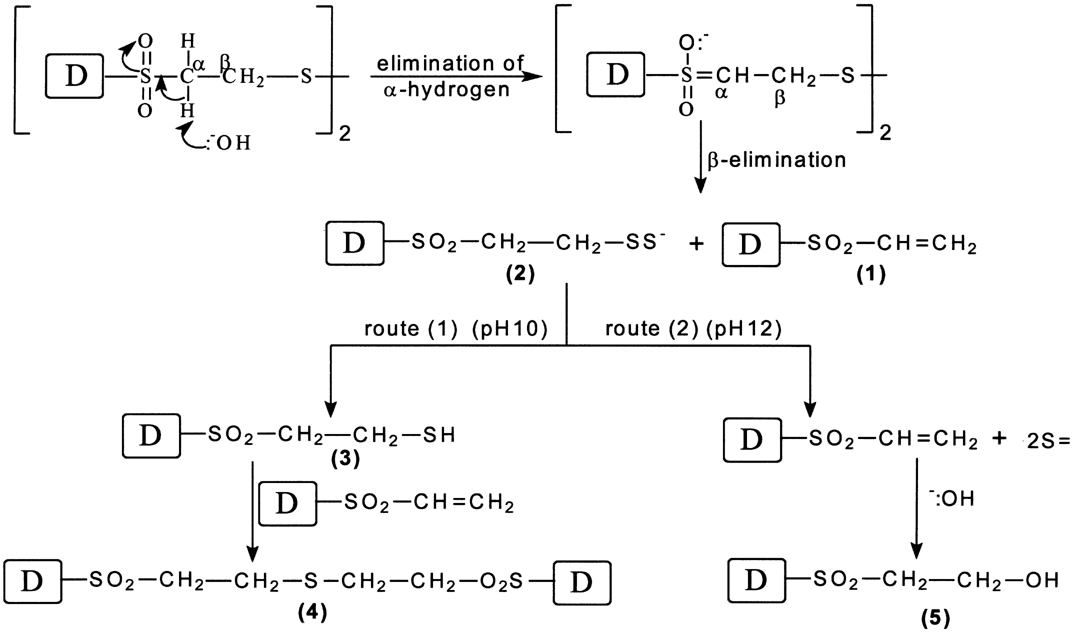


Fig. 6. DSBES dye solution activated at pH 10, 60°C and spiked with standard hydrolysed dye (a), vinylsulfone dye (b), disulfide-bis-ethylsulfone dye (c) and thioether dye (d).



Scheme 5. Possible elimination mechanisms for the disulfide-bis-ethylsulfone (DSBES) dye under various alkaline conditions.

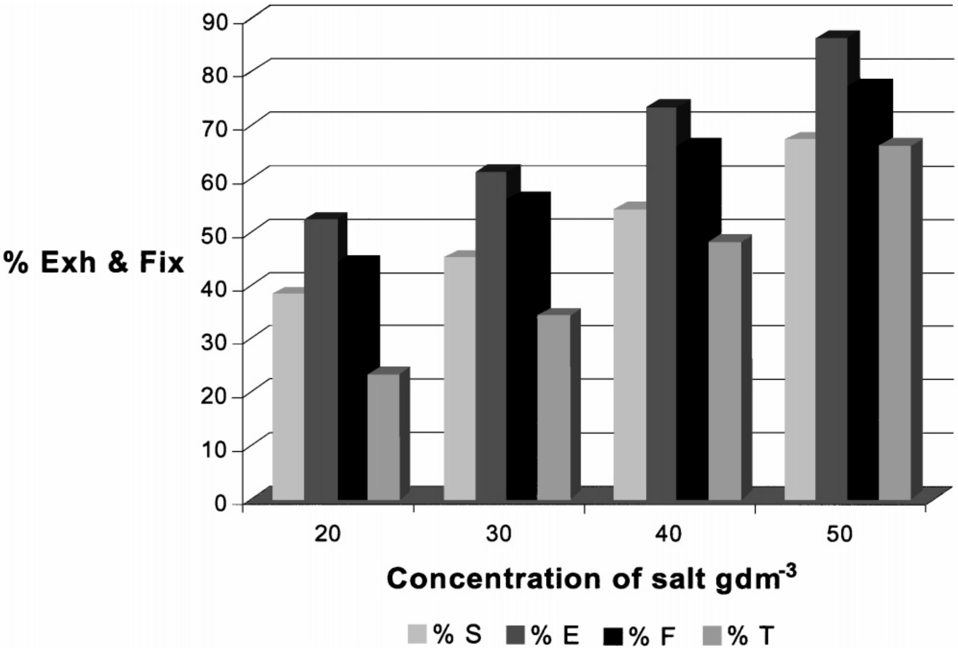


Fig. 7. % Exhaustion and fixation of DBSES dye versus different dye-bath salt concentrations.

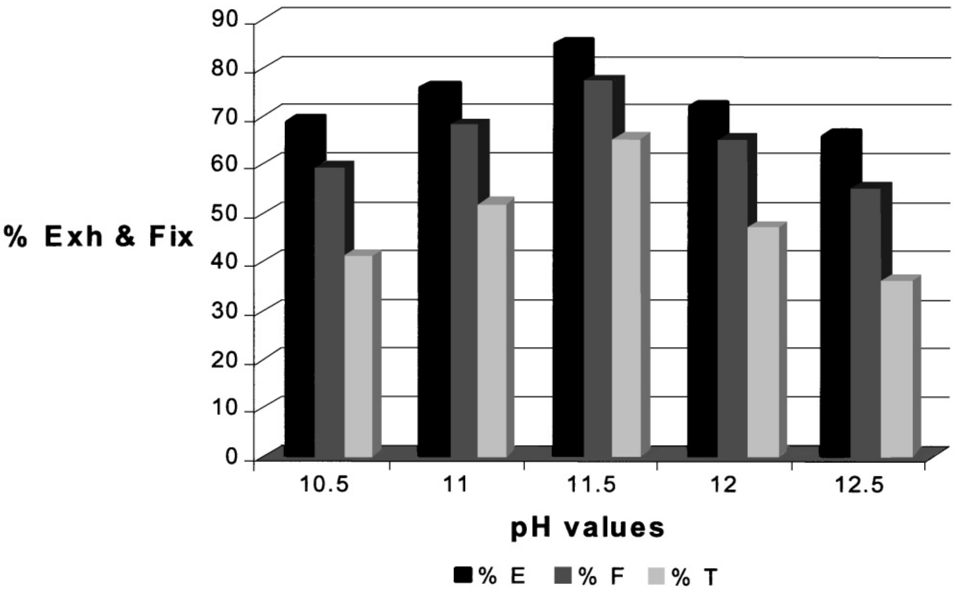


Fig. 8. % Exhaustion and fixation of DBSES dye versus different dye-bath pH values.

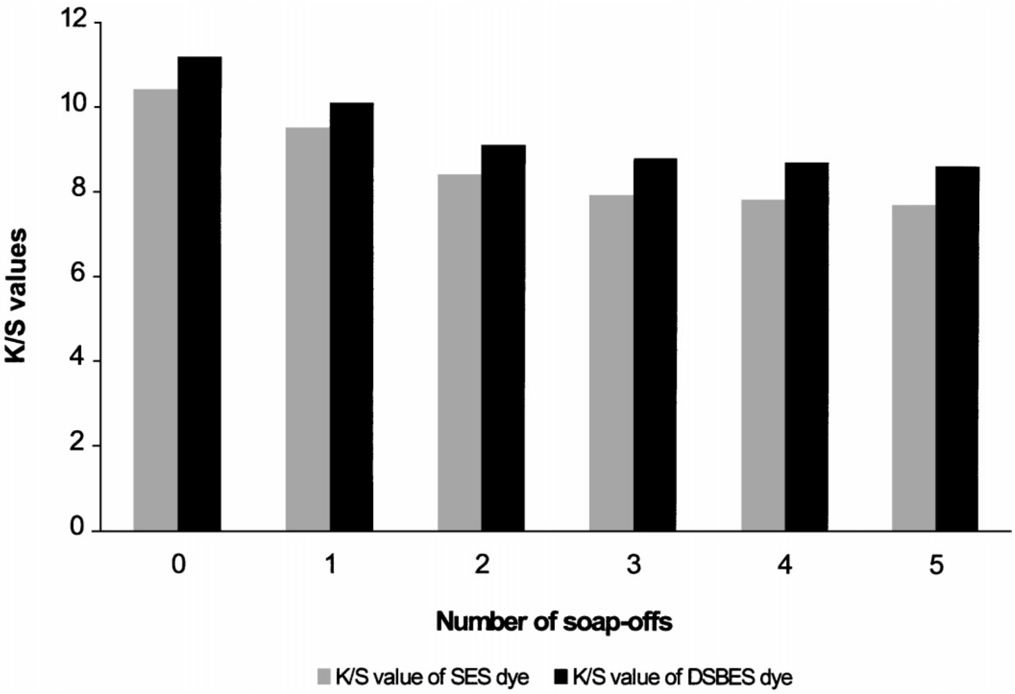


Fig. 9. K/S values versus number of soap-offs.

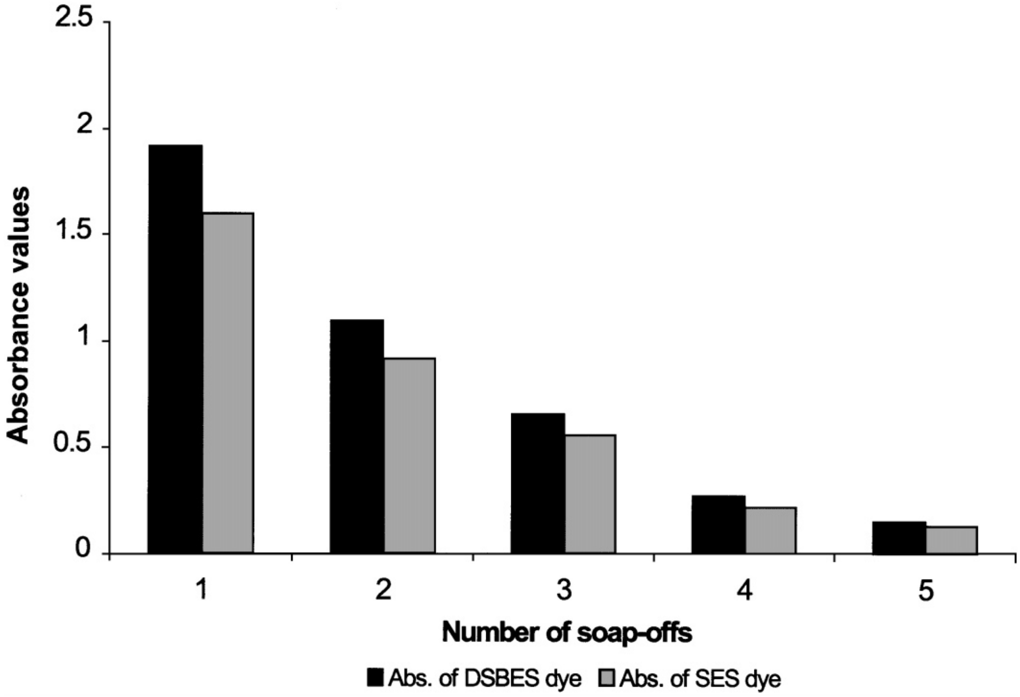


Fig. 10. Absorbance values versus number of soap-offs.

the exhaustion and fixation values would also decrease. On the other hand, if the pH of the dyebath was too high then the VS formed as a result of disulfide β-elimination would be too rapidly hydrolysed, resulting again in lower exhaustion and fixation values.

4.3. Soap-off study

It can be seen from Figs. 9 and 10 that *K*/*S* values and absorbance values decreased as the number of soap-off cycles increased. It is also apparent that most of the unfixed hydrolysed dye was washed-off after the third soap-off cycle, since the consecutive values of *K*/*S* and absorbance obtained after the third soap-off showed very small change. For both SES and DSBES dye the unfixed hydrolysed dye obtained after the β-elimination of both dyes is the same, hence the observed identical soap-off rate was expected.

5. Conclusions

A model dye based on a disulfide-bis-ethylsulfone (DSBES) intermediate was synthesised by diazotising and coupling the tetrazotised disulfide-bis-ethylsulfone-arylamino intermediate with a naphthol coupling component. The β-elimination characteristics of the disulfide bond were investigated under various pH values and different temperature conditions. The manner in which β-elimination occurs and the nature of the products resulting from β-elimination of disulfide-bis-ethylsulfone dye was determined using capillary electrophoresis.

The model disulfide dye was applied to cotton from baths set with different salt concentrations and at various pH values; the analogous SES dye was applied under standard conditions. The disulfide dye, due to its higher molecular mass, showed higher substantivity compared to the SES dye. Optimum exhaustion and fixation values were obtained when the disulfide dye was applied at pH

11.5, in the presence of salt (50 g dm^{-3}), at a temperature of 60°C for 60 min. At pH 11.5, most of the disulfide dye β-eliminated to produce vinylsulfone (VS) dye, which was indirectly confirmed from CE analysis.

The wash-off rate for the disulfide dye was identical to that of the SES dye. β-Elimination of the disulfide dye results in smaller VS dye molecules, bringing about a reduction in substantivity towards the fibre.

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