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Reactive dyes containing a 4-*m*-carboxypyridinium-1,3,5-triazine-2-oxide reactive group: exhaust dyeing of cotton under alkaline and neutral fixation conditions

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Abstract

Two sulphonated reactive dyes, each carrying a 4-*m*-carboxypyridinium-1,3,5-triazine-2-oxide (triazinyl betaine) reactive group, were applied to cotton under both alkaline and neutral exhaust dyeing conditions and the dyeings compared to those of related chlorotriazinyl and β-sulphatoethylsulphonyl based products. The novel reactive dyes displayed good colour yields under alkaline fixation conditions, but unexpectedly performed very poorly under neutral dyeing conditions. The latter result runs counter to the dyeing performance of commercially available dyes of closely related structure (*Kayacelon React*; Nippon Kayaku). The exceptionally poor neutral dyeing behaviour is believed to be due to low substantivity at elevated temperature, a reactive group of low selectivity in acid medium at high temperature, and in part, to an acid labile dye–fibre bond.

Keywords: Triazinyl betaine; Nicotinic acid; Cotton; Exhaust dyeing; Neutral fixation

1. Introduction

The first 4-quaternary ammonium-1,3,5-triazine-2-oxide (**I**; Scheme 1) was reported by Tsujikawa [1], although triazinyl betaines of this type had been made some years earlier by Saure [2] and Menon [3] (Scheme 1), but the structures were wrongly assigned.

It has been shown recently [4,5] that 4-*m*-carboxypyridinium-*s*-triazinyl betaines (**II**; Scheme 2) can be prepared either by treatment of 6-chloro-1,3,5-triazin-2(1H)-ones (**III**) or, more conveniently, dichloro-*s*-triazines (DCT) (**IV**) with 3-carboxypyridine (nicotinic acid), and that such groups are reactive towards cellulosic fibres under alkaline fixation conditions.

Tertiary bases, e.g. 3-carboxypyridine, react with monochloro-*s*-triazinyl (MCT) dyes [6,7] to furnish products with quaternary ammonium leaving groups (**V**). Such cationic groups offer the important property of allowing fixation to cellulose to occur under both alkaline and neutral dyeing conditions. *Kayacelon React* dyes (Nippon Kayaku), have this general structure and are recommended for one-bath high temperature exhaust dyeing of polyester/cellulose blends under

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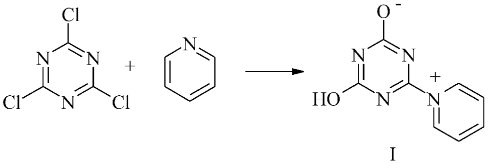
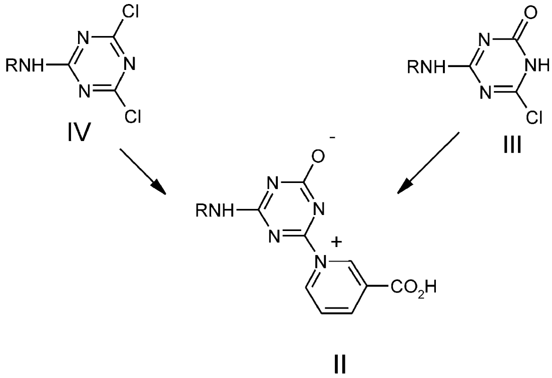


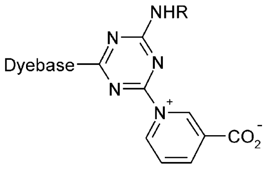
Scheme 1.



R = substituted aryl

Scheme 2.

essentially neutral conditions. Although structurally similar to the reactive group in *Kayacelon React* dyes, the triazinyl betaine group (**II**) is novel and no evaluation of this reactive system has been reported.



V

This paper describes the application of a red (**VI**) and a yellow (**VII**) reactive dye [5], carrying the novel triazinyl betaine reactive group, to cotton under both alkaline and "neutral" exhaust dyeing conditions. Their dyeing performances were compared with those of dyes derived from the same chromophores (**VIII** and **IX**), but carrying either an chloro-1,3,5-triazin-2(1H)-one (a), DCT (b), MCT (c,d) or β-sulphatoethylsulphonyl (e) reactive group.

2. Experimental

HPLC was performed with a Hewlett Packard 1100 series fitted with a quaternary pump.

The column was a 10 cm Purospher RP-18 (5 μm) packing and a LiChrocart 125-4 HPLC column cartridge; solvent A, acetonitrile; solvent B, water with 0.25% dicyclohexyl-ammonium phosphate; flow rate 2 ml/min; temperature 40 °C; injection volume 5 μl; samples were analysed using a diode array detector. The following gradient programme was used:

	min	% A	% B
	0	30	70
	5	50	50
	6	40	60
	7	30	70
Stop time	7		

Retention times (t_R) are in min.

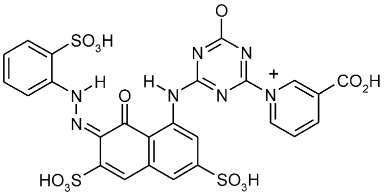
Mass spectra were recorded with a Micromass Instruments LCT orthogonal time-of-flight mass spectrometer fitted with a Z-spray electrospray ion source operating in negative mode at 3 kV needle potential. Nitrogen was used as a drying and sheath gas. Data were stored in the continuum mode on a Micromass Instruments MassLynx data station utilizing Version 3.5 software pack. Infusion was at a rate of 20 μl/min with a Harvard Instruments syringe pump utilized for sample introduction.

Procion Red MX-2B (**VIIIb**), *Procion* Red P-4BN (**VIIId**), *Procion* Yellow MX-3R (**IXb**) and *Procion* Yellow P-3R (**IXc**) were supplied by *DyStar*.

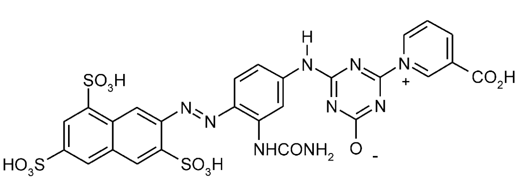
Syntheses of the red and yellow dyes containing a 3-carboxypyridinium-1,3,5-triazine-2-oxide reactive group (**VI** and **VII**) are described elsewhere [5].

*2.1. 6-Chloro-4-(2′-[o-sulphophenylhydrazo]-1′-oxo-3′,6′-disulpho-1′,2′-dihydronaphth-8′-yl)-amino-1,3,5-triazin-2(1H)-one (**VIII**; R = a)*

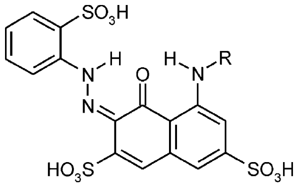
To 8-dichlorotriazinylamino-2-(*o*-sulphophenylhydrazo)-1-oxo-1,2-dihydronaphthalene-3,6-disulphonic acid (14 g; 52% strength; 0.01 mol;



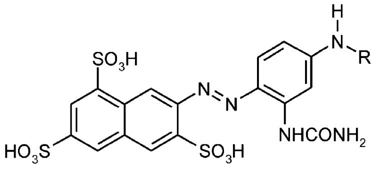
VI



VII

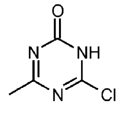


VIII

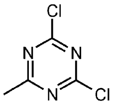


IX

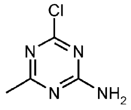
R



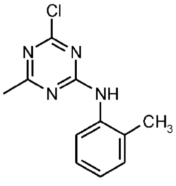
a



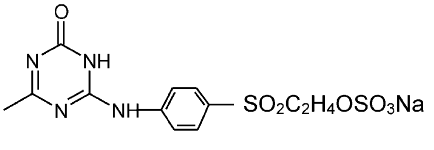
b



c



d



e

VIII; R = b) in water (100 ml) was added sodium carbonate (1 g) and the reaction stirred at 50 °C for 48 h. Salt (10 g, 10%w/v) was added and the reaction mixture left stirring for a further hour. The solid, which separated, was filtered off, washed with 20% brine, and dried in a desiccator to give the product (2.79 g). HPLC showed the product to be 100% organically pure with t_R 1.80, and mass spectrometry gave ions at m/z 631$(M-H)^-$ (40) and 613 $(M-H_2O)^-$ (35).

*2.2. 6-(*p*-β-Sulphatoethylsulphonyl)phenylamino-4-(2′-[o-sulphophenylhydrazo]-1′-oxo-3′,6′-disul-pho-1′,2′-dihydronaphth-8′-yl)amino-1,3,5-triazin-2(1H)-one (**VIII**; R = e)*

To the chloro-triazin-2(1H)-one (**VIII**; R = a; 3.48 g) in water (150 ml) was added *p*-amino-benzene-β-sulphatoethylsulphone (PABSES) (1.2 g) and the pH adjusted to 4–4.5. The reaction mixture was stirred at room temperature for 2 h while maintaining the pH with 2 M sodium carbonate. Sodium chloride (34.5 g) was added and the reaction mixture stirred for a further 2 h. The precipitate was isolated by filtration, washed with 20% brine and dried in an electric oven at 50 °C to give the product (5.15 g). HPLC showed the product to be 100% organically pure with t_R 2.32 and mass spectrometry gave ions at *m/z* 876 $(M-H)^-$ (35) and 796 $(M-H-SO_3)^-$ (48).

2.3. 4-{(3′-Ureido)-1″,3″,6″-trisulphonaphth-7″-yl-azo}phenylamino-6-chloro-1,3,5-triazin-2(1H)-one (**IX**; R = a)

To *N*-dichloro-*s*-triazinyl-3-ureido-4-(1′,3′,6′-trisulphonaphth-7′-yl-azo)aniline (10 g, 56% strength; IX; R = b) in water (150 ml) was added sodium carbonate (2.56 g) and the pH adjusted to 11. The reaction mixture was stirred for 2 days at pH at 11. Sodium chloride (22.5 g) was added and the reaction mixture stirred for 1 h. The precipitate so formed was isolated by filtration, washed with saturated brine and the solid oven dried at 50 °C to give the product (11.44 g). HPLC showed the product to be 100% organically pure with t_R 1.6 and mass spectrometry gave ions at *m/z* 673 $(M-H)^-$ (32), 655 $(M-H-H_2O)$ (18).

2.4. 4-{(3′-Ureido)-1″,3″,6″-trisulphonaphth-7″-yl-azo}phenylamino-6-(p-β-sulphato-ethylsulphonyl)phenylamino-1,3,5-triazin-2(1H)-one (**IX**; R = e)

To *N*-dichloro-*s*-triazinyl-3-ureido-4-(1′,3′,6′-trisulphonaphth-7′-ylazo)-aniline (7 g, 56% strength; **IX**; R = b) in water (150 ml) was added *p*-aminobenzene-β-sulphatoethyl sulphone (PABSES) (2.3 g) and the pH adjusted to 6. The reaction mixture was stirred at room temperature for 3 days while maintaining the pH at 4–4.5. Sodium chloride (16 g), potassium chloride (8 g) and methylated spirit (22 ml) was added to give an orange precipitate which was isolated by filtration. The solid was dried in an electric oven at 50 °C to give the product (5.3 g). HPLC showed the product to be 100% organically pure with t_R 2.29 and mass spectral analysis gave ions at *m/z* 919 $(M-H)^-$ (38), 902 $(M-H-NH_3)$ (24) and 804 $(M-H-NH_3–H_2SO_4)$ (100).

2.5. Determination of optimum alkaline dyeing conditions for the triazinyl betaines

Scoured, bleached, unmercerised, knitted cotton interlock was dyed, in turn, with the red dye (**VI**) and the yellow dye (**VII**). Samples of cotton fabric (5 g) were dyed at 1, 2, 4 and 8% omf in sealed stainless steel dye pots housed in a MATHIS LABOMAT BFA dyeing machine. Each dyeing process was carried out at liquor ratio 10:1 and dyeings were performed at 50, 60, 70, 80 and 90 °C. The electrolyte and alkali usage is summarised in Table 1 and the dyeing method shown in Fig. 1. At the end of the dyeing process, the dyed sample was removed, rinsed in warm running water at 50 °C, boiled for 20 min in water containing an anionic detergent (1 g/l) (*Symperionic PAE 25*; ICI), rinsed in cold water and air dried.

2.6. 'Neutral' dyeing conditions for the triazinyl betaine reactive dyes

The cotton fabric, dyeing equipment and dyeing strengths were as for alkaline dyeing.

Each dyeing process was carried at liquor ratio 10:1 and the dyeings were performed for 30 min at 98 °C and for 60 min at 130 °C, at pH 6.5 and 7.5. To obtain a pH of 6.5, 50 ml of 0.1 M KH_2PO_4 and 13.9 ml of 0.1 M NaOH were mixed together; to obtain a pH of 7.5, 50 ml of 0.1 M KH_2PO_4 and 40.9 ml of 0.1 M NaOH were used. For electrolyte usage, see Table 2.

The dyeing method is shown in Fig. 2. At the end of the dyeing process the dyed sample was removed, rinsed in warm running water (50 °C),

Table 1
Salt and alkali usage for triazinyl betaines (**VI**) and (**VII**)

Depth of shade (%)	Sodium chloride (g/l)	Sodium carbonate (g/l)
1	40	15
2	50	20
4	60	20
8	65	20

boiled for 20 min in water containing an anionic detergent (1 g/l), (*Symperionic PAE 25*; ICI), rinsed in cold water, and dried in the open air.

*2.7. Dyeing method for DCT dyes (**VIIIb** and **IXb**)*

The application profile is shown in Fig. 3 and the salt and alkali usage is shown in Table 3.

*2.8. Dyeing method for chloro-s-triazinyl-2(IH)-one dyes (**VIIIa** and **IXa**)*

The dyes were applied at 80 °C using the application profile shown in Fig. 1. The salt and alkali usage is shown in Table 4.

Table 2
Salt usage for the application of triazinyl betaine dyes to cotton under 'neutral' conditions

Depth of shade (%)	Sodium chloride (g/l)
1	40
2	50
4	60
8	65

*2.9. Dyeing method for C.I. Reactive Red 3:1 (**VIIId**) and C.I. Reactive Orange 12 (**IXc**)*

The dyes were applied at 80 °C as shown in Fig. 1 using the salt and alkali concentrations shown in Table 1.

*2.10. Dyeing method for β-sulphatoethylsulphonyl dyes (**VIIIe** and **IXe**)*

The application profile is shown in Fig. 1 ($T = 60$ °C) and the salt and alkali usage shown in Table 5.

2.11. Treatment of the triazinyl betaine dyed fabric under "neutral" conditions

Fabric (5 g) was inserted into a sealed stainless steel dye pot, housed in a MATHIS LABOMAT BFA dyeing machine, containing pH 7.5 buffer solution (see 'Neutral' dyeing conditions for triazinyl betaine reactive dyes), at liquor ratio 10:1. The temperature was adjusted to 98 °C and held for 30 min. The samples were air dried at room temperature and the K/S values are shown in Table 6.

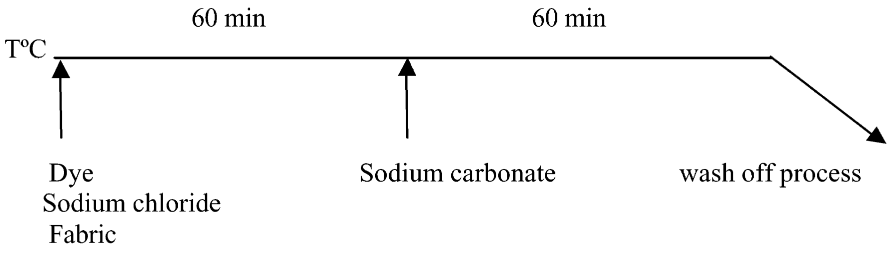


Fig. 1. Profile of the dyeing process used for the application of the synthesised *s*-triazinyl betaine reactive dyes.

Table 3
Salt and alkali usage for the application of DCT dyes (**VIIIb** and **IXb**) to cotton

Depth of shade (%)	Sodium chloride (g/l)	Sodium bicarbonate (g/l)	Sodium carbonate (g/l)
1	30	7.5	3.8
2	40	7.5	3.8
4	50	10	5
8	60	15	7.5

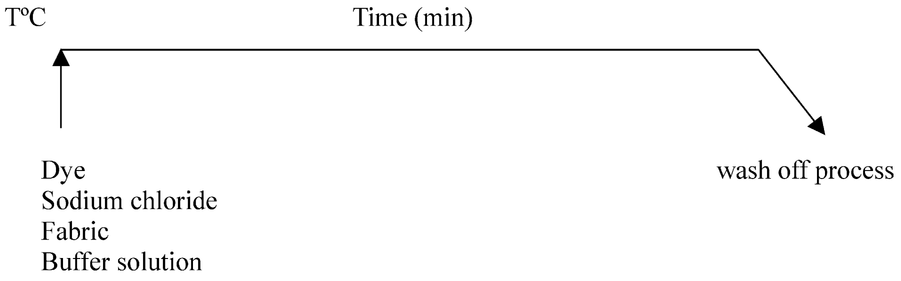


Fig. 2. Profile of the dyeing process used for the triazinyl betaine dyes under ‘neutral’ conditions.

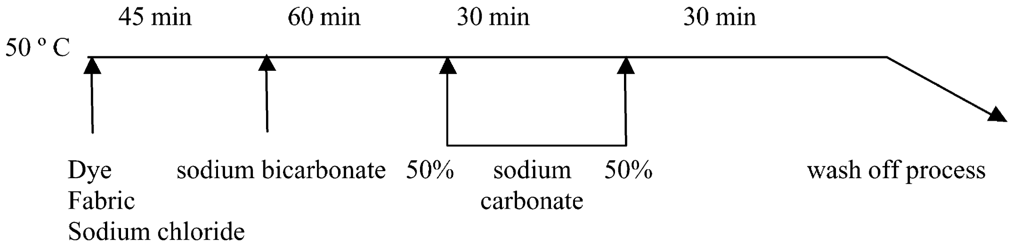


Fig. 3. Profile for the application of DCT dyes (**VIIIb** and **IXb**) to cotton.

Table 4
Salt and alkali usage for chloro-*s*-triazinyl-2(IH)-one dyes (**VIIIa** and **IXa**) to cotton

Depth of shade (%)	Sodium chloride (g/l)	Sodium carbonate (g/l)
1	40	15
2	50	15
4	60	20
8	65	20

Table 5
Salt and alkali for β-sulphatoethylsulphone dyes (**VIIIe** and **IXe**)

Depth of shade (%)	Sodium chloride (g/l)	Sodium carbonate (g/l)
1	30	4
2	40	6
4	50	8
8	60	10

2.12. Treatment of C.I. Reactive Red 221 and the triazinyl betaine dyes in water under “neutral” dyeing conditions

To separate dye pots, as above, were added 0.1 g of C.I. Reactive Red 221, red dye (**VI**) and the yellow dye (**VII**), and pH 7.5 buffer solution (50 ml). The temperature was increased to 98 °C and held for 30 min. HPLC showed C.I. Reactive Red 221 to be unchanged, red dye (**VI**; t_R 4.43) almost completely hydrolysed (t_R 4.80) and the yellow dye (**VII**; t_R 4.03) approximately 50% hydrolysed (t_R 4.25).

2.13. Visual colour yield of dyes on cotton

The K/S values of the dyed samples were measured on a Spectroflash 600 spectrophotometer (ex Datacolor) using the large aperture, with UV included and specular reflection excluded.

3. Results and discussion

Replacement of the reactive chlorine atom in MCT dyes by a quaternary nicotinic acid leaving group is a well-established reaction [6,7] and leads

Table 6
K/S values before and after the treatment of triazinyl betaines fabrics under "neutral" conditions

Applied depth (%)	*K/S* value of dyed red cotton fabric before the treatment	*K/S* value of dyed red cotton fabric after the treatment	*K/S* value of dyed yellow cotton fabric before the treatment	*K/S* value of dyed yellow cotton fabric after the treatment
0	0	0	0	0
1	2.9365	2.8723	4.2493	4.1825
2	7.1825	6.3528	8.392	7.9928
4	13.669	12.654	15.265	14.096
8	21.499	20.705	22.129	19.165

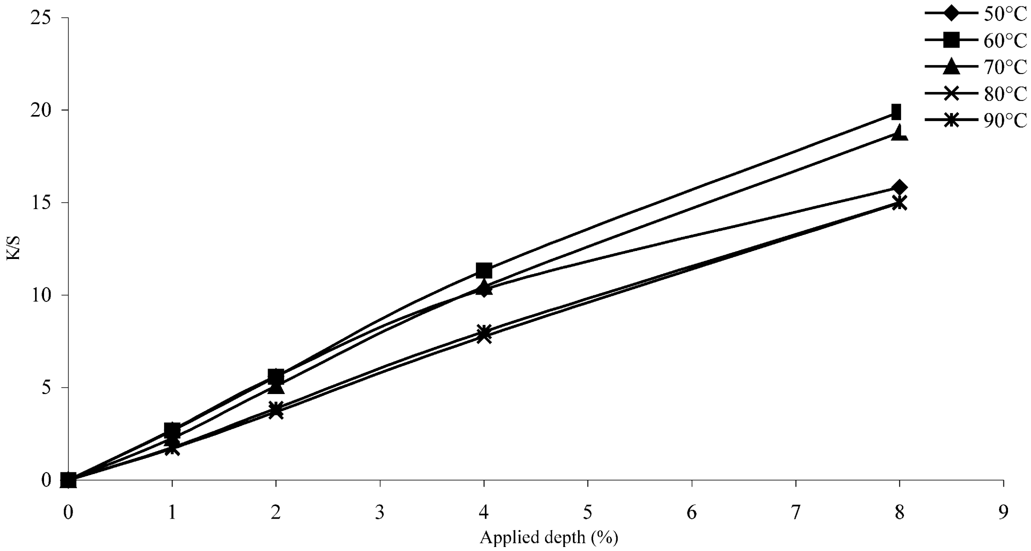


Fig. 4. Relationship between visual colour yield (*K/S*) and applied depth for red triazinyl betaine dye (**VI**) under alkaline conditions at various temperatures.

to dyes (**V**; R = substituted aryl) with enhanced reactivity.

However, triazinyl betaines are a novel class of reactive dye with unknown optimum dyeing temperatures. Accordingly, for alkaline fixation, the red (**VI**) and the yellow (**VII**) reactive dyes were dyed at temperatures of 50–90 °C with 10 °C intervals and the results shown in Figs. 4 and 5.

Using the electrolyte and alkali concentrations shown in Table 1, the optimum dyeing temperature was found to be 70 °C for the yellow dye (**VII**) and 60 °C for the more reactive [8] H-Acid based red dye (**VI**). However, since 60 °C gave only a marginally superior visual yield to 70 °C for dye (**VI**), an application temperature of 70 °C was used for both dyes when assessing their technical performance against analogous yellow and red reactive dyes containing a series of different reactive groups. The results are shown in Figs. 6 and 7.

Figs. 6 and 7 show that the red and yellow triazinyl betaine dyes, although not the best of the series under evaluation, performed well in alkaline medium. The poorest dyes, as expected, were the 6-chloro-1,3,5-triazin-2(1H)-ones (**VIIIa** and **IXa**), demonstrating the powerful deactivating effect of a O^- group (via the hydroxytriazine tautomer) on the remaining chlorine atom.

The triazinyl betaines were then applied under "neutral" dyeing conditions and the results are

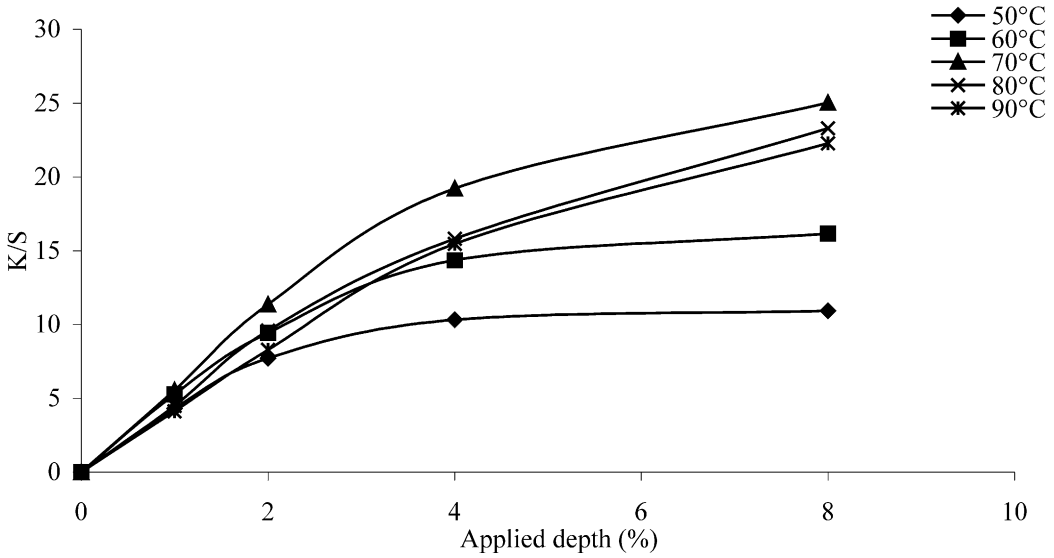


Fig. 5. Relationship between visual colour yield (*K*/*S*) and applied depth for yellow triazinyl betaine dye (**VII**) under alkaline conditions at various temperatures.

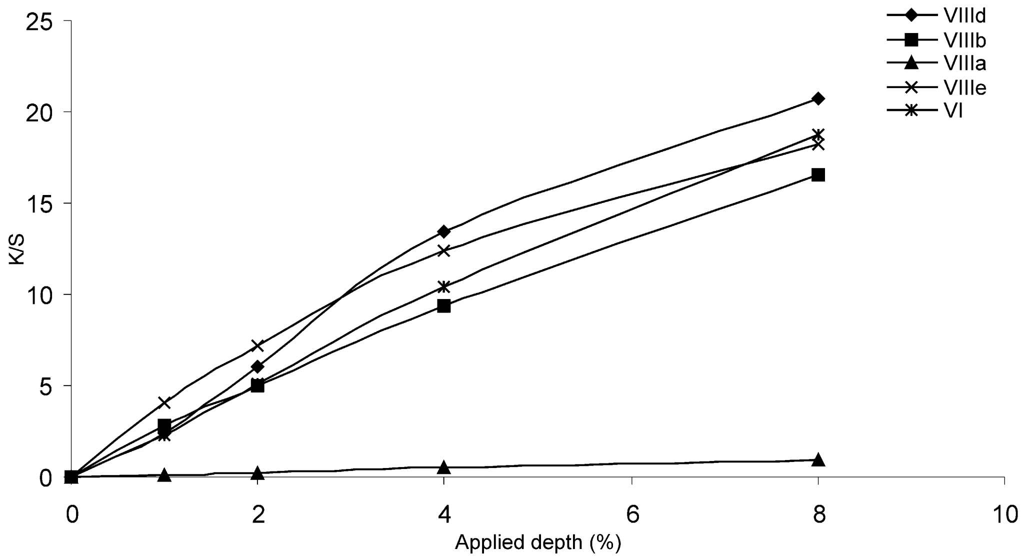


Fig. 6. Comparison of the visual colour yield (*K*/*S*) of the novel red triazinyl betaine dye (**VI**) with that from other related reactive dyes under alkaline fixation conditions.

shown in Figs. 8 and 9. The results clearly show both triazinyl betaine dyes to be very much inferior under neutral dyeing conditions. Accordingly, unlike conventional *m*-carboxypyridinium-*s*-triazinyl reactive dyes of type (**V**), triazinyl betaines (**VI** and **VII**) are not suitable for ‘neutral’ fixation.

One explanation for the poor neutral performance is the relative instability of the dye–fibre

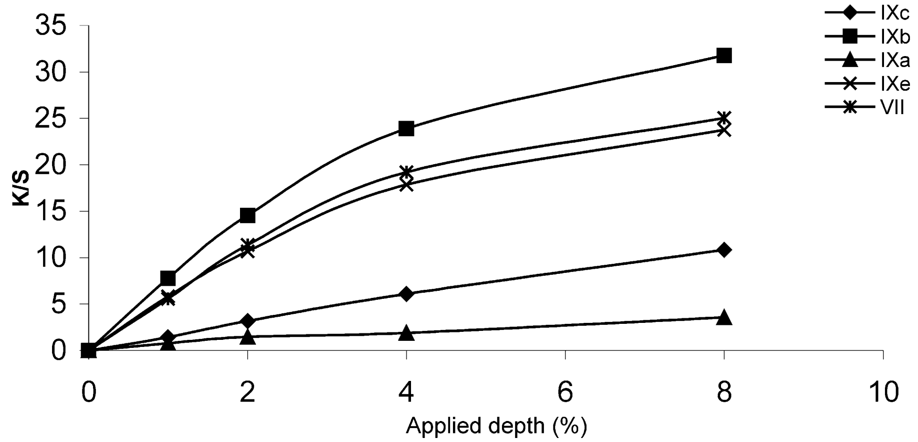


Fig. 7. Comparison of the visual colour yield (*K*/*S*) of the novel yellow *s*-triazinyl betaine dye (**VII**) with that from other related reactive dyes under alkaline fixation conditions.

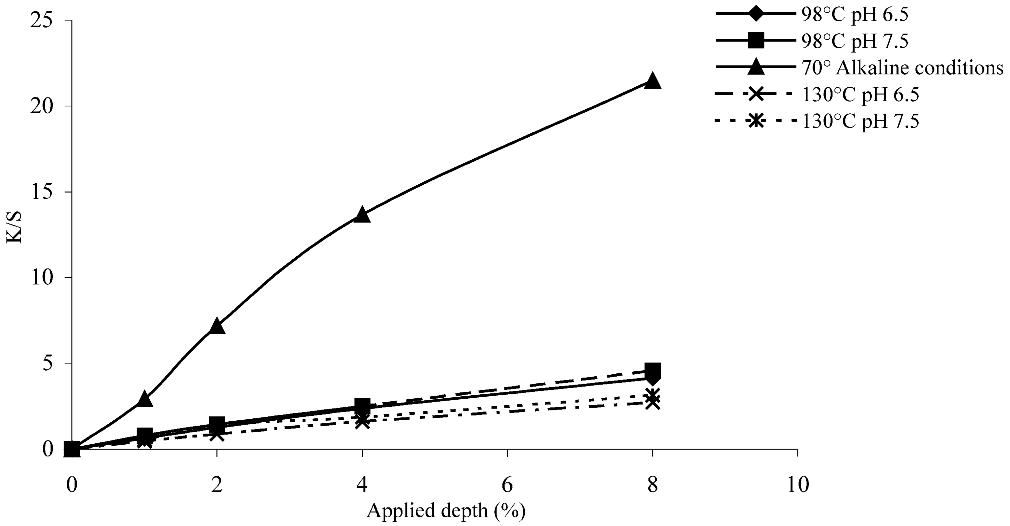
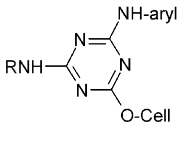


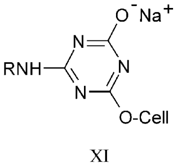
Fig. 8. Relationship between visual colour yield (*K*/*S*) and applied depth for the red triazinyl betaine dye (**VI**) under neutral and alkaline conditions.

bond generated on fixation of the triazinyl betaine dyes.

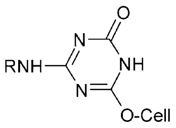
Structure (**X**) represents fixation of a traditional quaternary ammonium triazine (**X**), and structure (**XI**) is the product of triazinyl betaine (**II**) fixation under alkaline conditions. The triazinyl-O-Cell bonds in structures (**X**) and (**XI**) are stabilised by the electron donating NH-aryl and the O^- groups respectively. On the other hand, neutral fixation of triazinyl betaines results in the formation of product (**XII**). This is a triazin-2(1H)-one derivative,



X



XI



XII

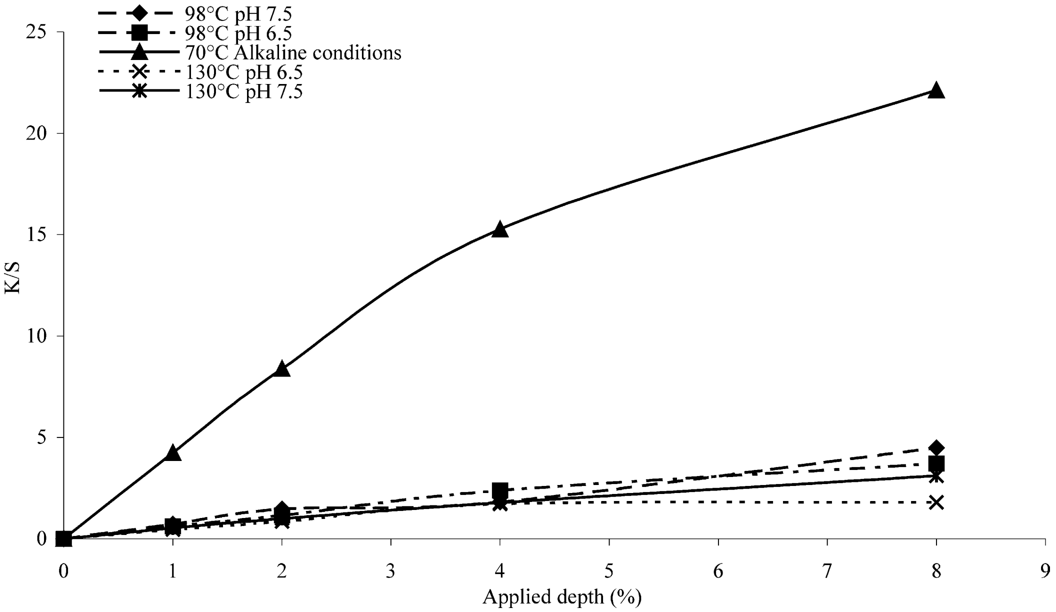
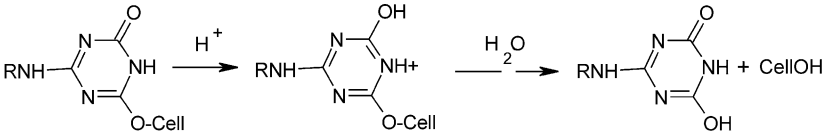


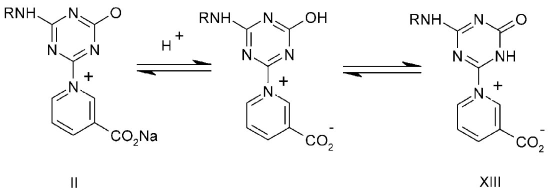
Fig. 9. Relationship between visual colour yield (*K*/*S*) and applied depth for the yellow triazinyl betaine dye (**VII**) under neutral and alkaline conditions.



Scheme 3.

which is known to hydrolyse under weakly acidic medium [4,9–12]. Indeed, structure (**XII**) gives rise to the phenomenon of “acid-bleed” in DCT dyes [13,14] (Scheme 3).

To determine if this was a contributing factor, fabric dyed with each triazinyl betaine dye under alkaline conditions, was subjected, in turn, to the “neutral” dyeing conditions. This resulted in a variable reduction in colour value of the fabric but in the worst case of only 13.4% (see Experimental). Accordingly, some other factors must also be contributing to the poor “neutral” dyeing performance. Subjecting both triazinyl betaine dyes, in turn, to the “neutral” dyeing conditions, but without the presence of fabric, resulted in virtually complete hydrolysis of the red dye (**VI**) and approximately 50% hydrolysis of the yellow dye (**VII**) (see Experimental). For comparison, a sample of C.I. Reactive Red 221 (general structure V; chromophore of type **VIII**) was also subjected to the same “neutral” dyeing conditions. In this case the reactive dye was returned unchanged. This demonstrates some hydrolytic instability of the triazinyl betaine dyes (**VI** and **VII**) to the “neutral” dyeing conditions. This difference in hydrolytic instability is probably due to the presence of the triazin-2(1H)-one tautomeric form (**XIII**) in the case of the triazinyl betaines (Scheme 4).



Scheme 4.

However, approximately 50% the yellow dye (**VII**) survived intact but little fixation to cellulose occurred. Increasing temperature results in a fall in substantivity [13], and poor substantivity of the triazinyl betaine dyes is also believed to be a contributing factor.

4. Conclusions

Two sulphonated reactive dyes, each carrying a 4-*m*-carboxypyridinium-1,3,5-triazine-2-oxide reactive group were applied to cotton under both alkaline and "neutral" exhaust dyeing conditions. Under alkaline fixation conditions, the dyes showed good colour yield with optimum exhaust dyeing in the range 60–70 °C. Under "neutral" dyeing conditions at elevated temperature ($\geqslant 98$ °C), the dyes exhibited poor colour yield in contrast to commercially available dyes of closely related structure (*Kayacelon React*). The poor "neutral" dyeing performance is attributed to a combination of low substantivity, poor selectivity of the reactive group under "neutral " high temperature dyeing conditions and an unstable dye–fibre bond.

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