

Reactive Dyeing of Cellulosic Fibers: Use of Cationic Surfactants and Their Interaction with Reactive Dyes

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ABSTRACT: Cotton fabrics were dyed with three reactive dyes, C.I Reactive Blue 263, C.I Reactive Red 269, and C.I Reactive Yellow 208, after pretreatment of the fabrics with three alkyl trimethyl-ammonium bromides (tmabs) having 12, 14, and 16 carbon atoms in the alkyl chain. The pretreated samples were dyed with standard dyeing methods using conventional, reduced amounts of electrolyte, and no electrolyte. Pretreatment with the three cationics (tmabs) resulted in an increase in dye exhaustion with all dyes used, whereas total dye fixation was lower for both red and blue dye and equal

for the yellow, when compared to the reference untreated samples dyed according to the same standard dyeing method. The interaction between dodecyl trimethyl-ammonium bromide and the three dyes was studied and the stoichiometry of the various dye/dodecyl trimethyl-ammonium bromide (12-tmab) complexes formed has been deduced. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1209–1215, 2008

Key words: cationics; reactive dyes; cellulosic fibers; electrolyte reduce

INTRODUCTION

The use of reactive dyes to dye cellulosic fibers is well established in the industry and is associated with high wash fastness properties of the dyed material.

However, many environmental problems arise from the use of these dyes, which could be focused mainly on: (a) the high amount of unfixed-hydrolyzed dye and (b) the high amount of electrolyte used during dyeing.

It is well known that the reactive dyes are covalently bonded with cellulose, with a simultaneous reaction of dye hydrolysis. The removal of the hydrolyzed dye requires expensive washing-off procedures, or extraction with organic solvents, or vacuum extraction, as was suggested by Broadbent.¹ According to Noah et al. dyeing process with reactive dyes takes place in aqueous alkaline media, where the cellulosic fiber develops a negative charge, because its dielectric constant is lower than that of water.² This is why a great amount of electrolyte is necessary to decrease the negative surface potential of the fiber. However, the overall fiber potential remains negative and thus involves a further repulsive effect.^{2,3} Additionally, the electrolyte reduces

the solubility of the dye and thus moves the partition of the dye over to the fiber from the aqueous phase. The most popular electrolytes used for the reactive dyeing of cotton are sodium chloride and sodium sulfate in high amounts, sometimes reaching even 100 g/L on heavy depths of shade.

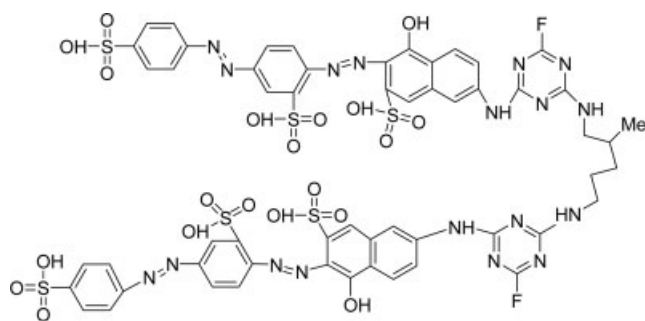
Several solutions to overcome the two aforementioned problems have been proposed, for example, the use of polyamide-epichlorohydrin resins,^{4–6} the production of cationic cotton,^{7,8} or the use of cationic fixing agents. These compounds can form complexes with the anionic group in the dyes, thereby producing larger dye-surfactant molecules less soluble in water. This concept has been expanded to produce polyfunctional fixing agents for reactive dyes, in which cationic groups ionically bond with sulfonic acid groups on the dye, and the reactive group in the dye crosslinks with the cellulosic fiber by polycondensation.⁹

Gatewood¹⁰ tried to reuse the unfixed hydrolyzed reactive dyes as direct ones, with the use of conventional cationic fixatives, which are commonly used for direct dyes as a means of improving the wet fastness.¹¹ However, investigations into reducing the amount of electrolyte used for the reactive dyeing of cotton are still of great interest and importance.^{12,13}

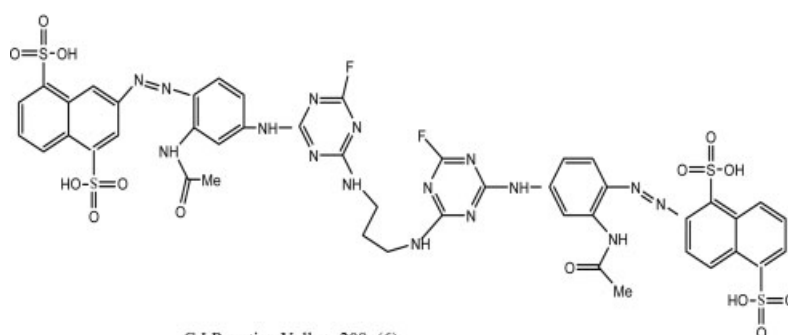
Recently, Cai et al. proposed a new method for improving the dyeability of cotton with reactive dyes under neutral to slightly acidic conditions in the absence of salt, after modification of cotton with a cationic acrylic copolymer, commercially named Polymer PL.¹⁴ However, the treated fabrics were inferior in softness compared to the untreated ones.

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C.I Reactive Red 269 (5)

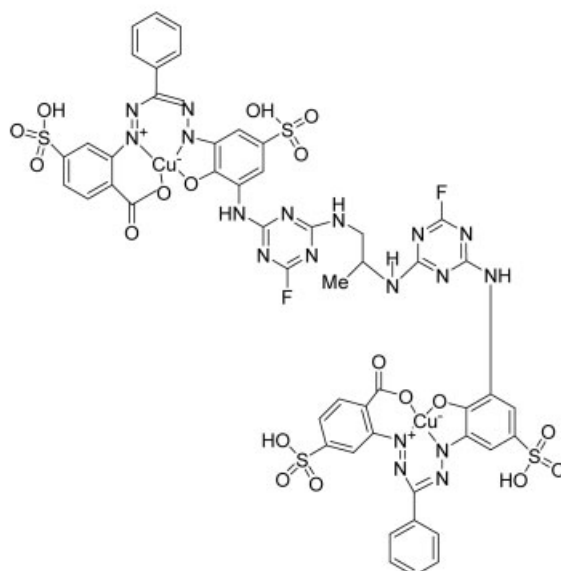
 λ_{\max} : 518.00nm

C.I Reactive Yellow 208 (6)

 λ_{\max} : 401.20 nm
 $C_nH_{2n+1}N^+(CH_3)_3Br^-$: 1-3, where 1: n=12

2: n=14

3: n=16



C.I Reactive Blue 263 (4)

 λ_{\max} : 591.60 nm**Scheme 1** Cationic tmabs and dyes used.

Rucker studied the reduction of electrolyte requirements in dyeing cotton with reactive dyes,¹⁵ using cationic surfactants with a range of chain lengths.

In this work, cotton fabrics were pretreated with three conventional cationic surfactants (with 12, 14, and 16 carbon atoms to the hydrophobic alkyl chain) in quantities below the corresponding critical micelle concentrations (CMC). The treated samples were then dyed with three reactive dyes, C.I Reactive Blue 263 (4), C.I Reactive Red 269 (5), C.I Reactive Yellow 208 (6), (Scheme 1) with a reduced amount of electrolyte, which would have been normally used in a typical dyeing process. These dyes have numerous sulfonic acid substituent groups, providing a net negative charge under aqueous conditions. The cationic *t*-mabs were used as an effort to reduce the negative potential of the cotton fiber, and thus making the fiber more accessible to the anionic dyes. An untreated sample was also dyed for comparison (reference sample). The aim was to reduce the amount of the electrolyte used, without decreasing the total dye fixation (T%).

The interaction between the three dyes used and the dodecyl trimethyl-ammonium bromide was also studied spectrophotometrically to explain some of the results found.

EXPERIMENTAL

Materials

Nonbleached cotton fabric was used in this work. Before dyeing, the fabrics were washed with a standard soap solution 2 g/L without optical brightening agent, BS EN 20105 : 1993, in a liquor ratio 1 : 30. The reactive dyes and the cationic tmabs used are given in Scheme 1. All dyes and the tmabs were of commercial grades and were applied without further purification.

Methods

Pretreatment of cotton fabrics with the tmabs

The cotton samples were treated with the tmabs 1–3, at 60°C for 60 min using a liquor ratio 1 : 30 in a Vistacolor, Lowboy, Zeltex dyeing machine, rinsed conventionally with 30 mL distilled water, squeezed, and dried.

Concentrations used, CMC^{16–18} and molecular weights of the tmabs 1–3 are given in Table I.

Dyeing of the cotton samples

Dyeings were carried out in a laboratory dyeing machine Zeltex, Vistacolor using a liquor ratio 1 : 30, at 2% depth of dyeing (o.m.f.). The dyeing was com-

TABLE I
Concentrations, Critical Micelle Concentrations (CMCs) and Molecular Weights of the Cationics Used

Cationic	Concentration (M)	CMC (M)	MW
1	7.62×10^{-3}	1.6×10^{-2}	308.35
2	1.01×10^{-3}	2.1×10^{-3}	336.41
3	4.11×10^{-4}	9.2×10^{-4}	346.46

menced at 60°C and temperature was raised to 85°C within 20 min. At this temperature of 85°C, various quantities of NaCl (0, 6.6, and 10 g/L for the tmabs pretreated samples and 20 g/L for the reference sample, 0, 1/3, 1/2, and industrial level quantity respectively, given by CIBA for this dye type) were added to the dyeing bath and dyeing was continued for another 60 min at 85°C. At this point, 12 g/L Na₂CO₃ was added and dyeing was continued for another 30 min. After completion of the dyeing, the dyed samples were removed, rinsed, squeezed, and dried at 50°C.

After dyeing, the samples were boiled repeatedly in a standard soap solution 2 g/L without optical brightener, BS EN20105 : 1993, for 15 min until no color was coming out in the washing-off solution, to eliminate the hydrolyzed unfixed dye and then were rinsed, squeezed, and dried at 50°C.

Measurement of the dye exhaustion

This was made spectrophotometrically by measuring the absorbance of the dyebaths at the λ_{\max} of the corresponding dyes with a Shimadzu UV 2101PC spectrophotometer. The percentage dyebath exhaustion (E%) was calculated using eq. (1)

$$E\% = \frac{A_o - A}{A_o} \times 100 \quad (1)$$

where A_o , A are the dyebath absorbances before and after dyeing, respectively.

Measurement of dye fixation

The color strength of the unwashed and washed dyed samples was measured using a reflectance spectrophotometer, Macbeth 3000 Color Eye type C.

The K/S values were calculated using the Kubelka–Munk eq. (2)

$$K/S = \alpha \times c = \frac{(1 - R)^2}{2R} \quad (2)$$

where K , absorbance coefficient; S , scattering coefficient; α , constant; C , dye concentration on the dyed sample; R , % reflectance.

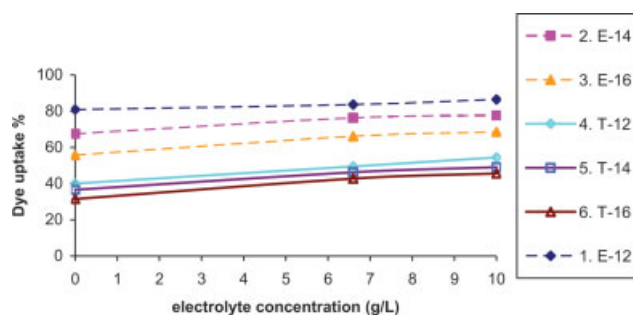


Figure 1 C.I. Reactive Blue 263 uptake versus electrolyte concentration for cotton samples pretreated with the three alkyl trimethyl ammonium bromides. E = exhaustion, T = total fixation, $E-n/T-n$ = exhaustion/fixation for the samples pretreated with the $C_nH_{2n+1}\cdot N^+(CH_3)_3Br^-$, where $n = 12, 14, 16$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The total dye fixation T % can be calculated using eq. (3)

$$T\% = \frac{K/S}{(K/S)_o} \times E\% \quad (3)$$

where $(K/S)_o$, (K/S) the color strengths of the dyed sample before and after the elimination of the unfixed dye and $(E\%)$ the dye exhaustion.

Measurement of the cationic exhaustion

This was made by titration of the pretreatment bath before and after the pretreatment using a standard sodium dodecyl sulfate solution 0.002M and two indicators: disulfine blue (anionic) and dimidium bromide (cationic).

Dye–dodecyl trimethyl-ammonium bromide (12 tmab) interaction

This was made spectrophotometrically with a Shimadzu UV 2101PC spectrophotometer by measuring the absorbencies of the dye–12 tmab mixtures in various molar ratios.

Quantitative determination of the tmabs in the dye baths

Titration of the cationic tmabs was made with a standard solution 0.002M anionic sodium dodecyl sulfate in the presence of two indicators: disulfine blue (anionic) and dimidium bromide (cationic).¹⁹

Surface tension measurement of the dye baths

These were contacted using a Sigma 70 KSV tensiometer using the Wilhelmy plate method.

RESULTS AND DISCUSSION

Figures 1–3 show the effect of electrolyte concentration (at 0, 6.6, and 10 g/L) on the extent of dye exhaustion in the dyeing of cotton samples pretreated with the tmabs 1–3, using the three reactive dyes.

The % dye exhaustion and fixation of the same dyes for the untreated cotton samples (reference samples) in the presence of 20 g/L electrolyte are given in Table II.

Apart from the reaction between dye and fiber reactive groups, exhaustion of the anionic dye is also attributed due to the attraction between the cationic groups of the compounds 1, 2, and 3 adsorbed on the fiber and the dye anions.²⁰ Thus the increase of the % dye exhaustion in most cases of pretreated samples could be explained in terms of surface charge modifications of the cotton fibers due to the presence of the cationic tmabs 1–3. The increased dye uptake is directly proportional to the exhaustion of the cationic tmabs that is higher for the smaller alkyl chain tmab. The smaller chain tmabs are adsorbed on the fiber and are easier to diffuse in the fiber at a higher rate than the bigger chain tmab which, after their initial exhaustion, are more difficult to diffuse inside the fiber. Thus the bigger chain tmabs remained on the surface and somehow blocked the diffusion of the dye molecules that were adsorbed during the dyeing. This results in lower dye exhaustion and thus the % exhaustion values for the pretreated samples follow the order $\% E_{12} > \% E_{14} > \% E_{16}$. (E_n : exhaustion obtained in the presence of cationic tmabs with n carbon atoms in the alkyl chain.)

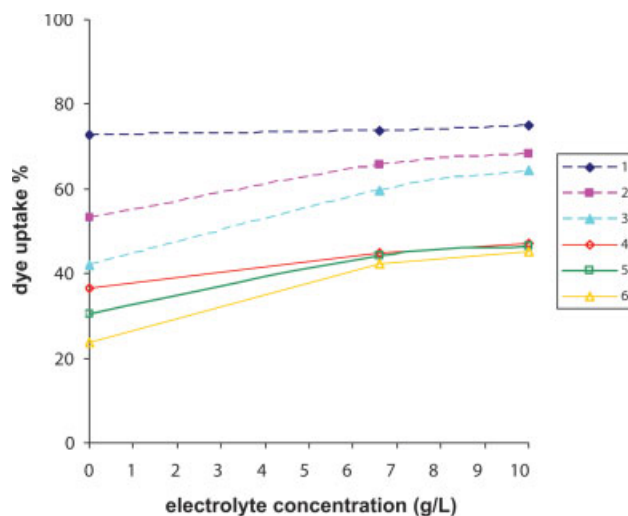


Figure 2 C.I. Reactive Red 269 uptake versus electrolyte concentration for cotton samples pretreated with the three alkyl trimethyl ammonium bromides. For key see Figure 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

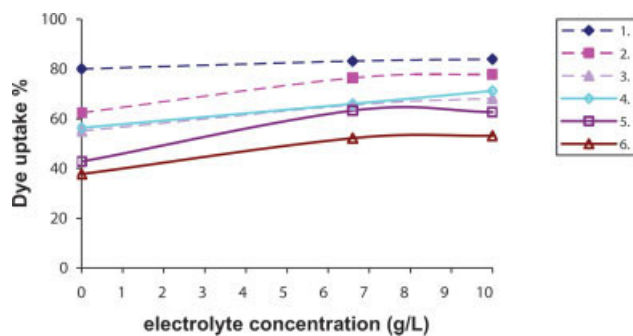


Figure 3 C.I. Reactive Yellow 208 uptake versus electrolyte concentration for cotton samples pretreated with the three alkyl trimethyl ammonium bromides. For key see Figure 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

During the dyeing, the cationic tmabs were desorbed from the fiber. Significant decreases of the surface tension values of the dye bath were observed during the course of dyeing (55.2 mN/m for the reference sample, 30.5–37.2 mN/m for the samples pretreated with the three cationics at given concentrations) show that a small fraction of the initially applied cationic tmab is still remaining adsorbed on the fiber after dyeing. Again the cationic with the shortest alkyl chain (dodecyl) is desorbed more easily leaving free positions for the dye molecule.

After soaping, the hydrolyzed unfixed dye is eliminated. The % fixation values are considerably lower than the % exhaustion values in all cases. Although the dye–cationic complex enhances exhaustion, it does not do the same for the dye fixation since complex formation may be blocking the dye diffusion, inhibiting the approach of the dye molecules to the fiber and thus inhibiting fixation.

This inhibition of the dye fixation is directly dependent on the dye structure. The presence of six sulfonic acid groups adjacent to the reactive groups for C.I. Reactive Red 269, and the presence of four sulfonic acid groups and a Cu ion adjacent to the reactive groups for the metal complex C.I. Reactive Blue 263, results in a bulky dye–tmab complex lowering dye solubility and hindering not only the adsorption–diffusion of the dye inside the fiber but also, due to stereochemic hindrance, the formation of the dye–fiber bond. Thus, the big dye–tmab complex stays mainly adhered to the surface of the fiber being easily desorbed during dyeing. This explains

TABLE II
Exhaustion and Fixation of the Dyes Used in the Presence of 20 g/L Electrolyte

Dye	<i>E</i> (%)	<i>T</i> (%)
4	72.0	58.0
5	73.0	55.7
6	70.2	65.6

TABLE III
Colorimetric Data of the Dyes C.I. Reactive Blue 263, C.I. Reactive Red 269, and C.I. Reactive Yellow 208

Dye	λ_{\max} (nm)	<i>A</i> ^a	<i>K/S</i>
Rea Blue 263	591.6	0.458	9.5870
Rea Red 269	518.0	0.818	14.1223
Rea Yellow 208	401.2	0.857	14.8720

^a $C = 3 \times 10^{-2}$ g/L.

the lower fixation values when compared to the reference sample.

However, this is not the case for the more planar C.I. Reactive Yellow 208, with four sulfonic acid groups far away from the fluorotriazine reactive groups. In this case, it seems that there is no steric hindrance and the dye can be adsorbed, diffused, and react easier with the cotton reactive groups. Fixation values equal or comparable to those of the reference sample, even after a substantial reduction in the quantity of salt used (Fig. 3, Table II) could thus be explained.

Moreover, from the study on the interaction between the same dyes and tmabs in several molar ratios, it was observed that addition of tmabs in the

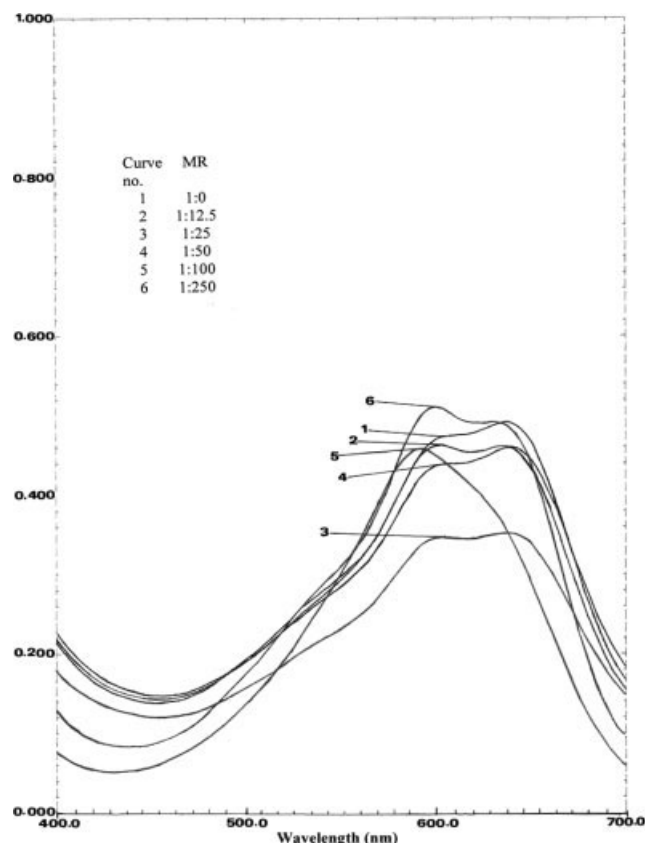


Figure 4 Absorption spectra of C.I. Reactive Blue 263 in the presence of various molar proportions of dodecyl trimethyl-ammonium bromide.

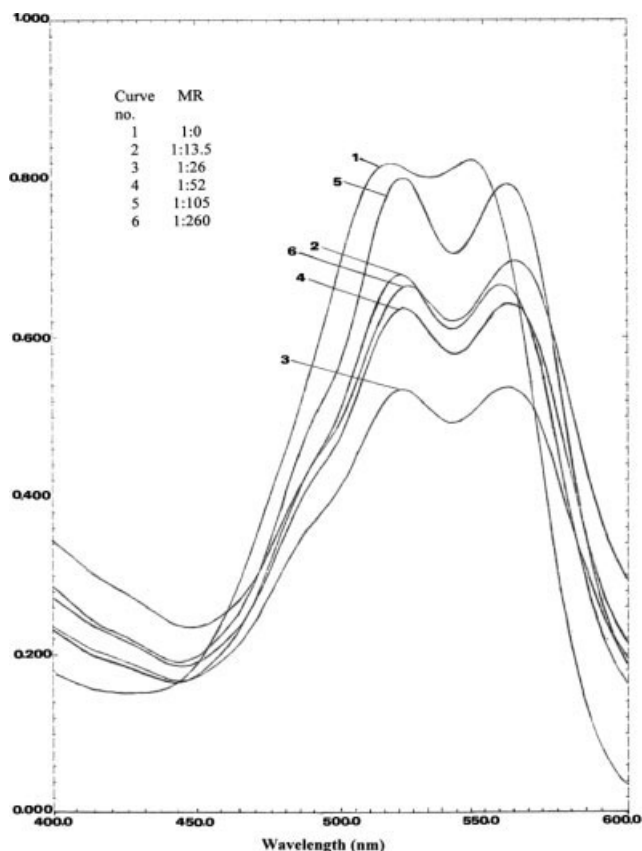


Figure 5 Absorption spectra of CI Reactive Red 269 in the presence of various molar proportions of dodecyl trimethyl-ammonium bromide.

blue and red dye solutions resulted in the formation of dye aggregates. This also confirms that the formation of dye aggregates especially on the fiber surface not only results in lower exhaustion (especially with the higher alkyl tmabs) but also in lower fixation values due to the lower reactivity of the bulky tmab-dye complex.

Dye-cationic interaction—Spectrophotometric analysis

The colorimetric data in solution of the three reactive dyes used are given in Table III.

The absorption curves are very similar to the curves derived from the Kubelka-Munk analysis. The K/S values of the samples dyed with the same concentration for all dyes have a direct correlation to the A values obtained.²¹

To determine whether an interaction between the dyes and the tmabs takes place, absorption spectra of the dye solutions with various amounts (molar ratios dye/tmab) of dodecyl-trimethyl-ammonium bromide present were examined (Figs. 4–6).

The changes in absorption and λ_{\max} do indicate the existence of such interactions. The presence of

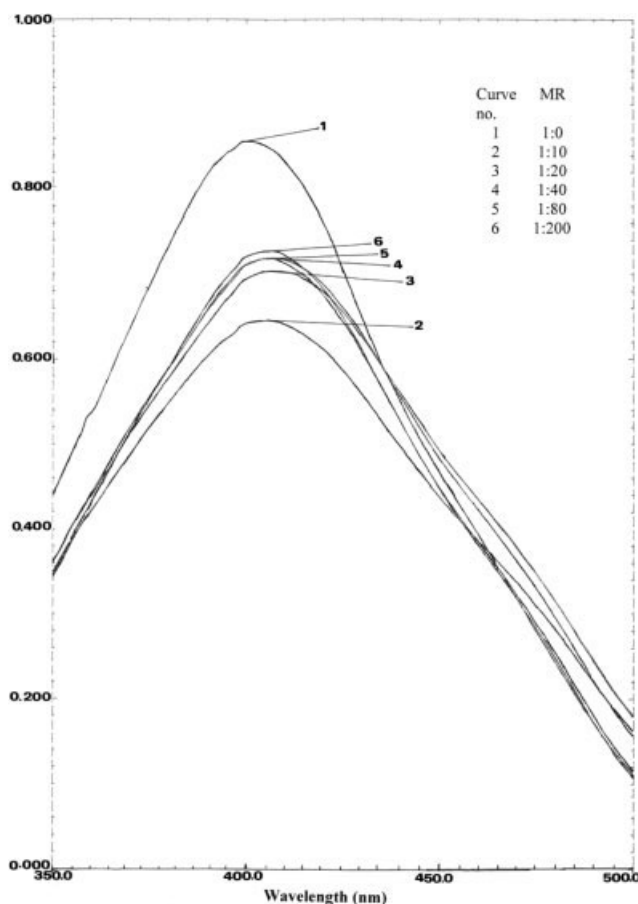


Figure 6 Absorption spectra of C.I. Reactive Yellow 208 in the presence of various molar proportions of dodecyl trimethyl-ammonium bromide.

isosbestic points in the dye-tmabs absorption curves shows the existence of equilibrium states. Such equilibrium states were also detected by previous workers investigating other dyeing systems.^{22,23}

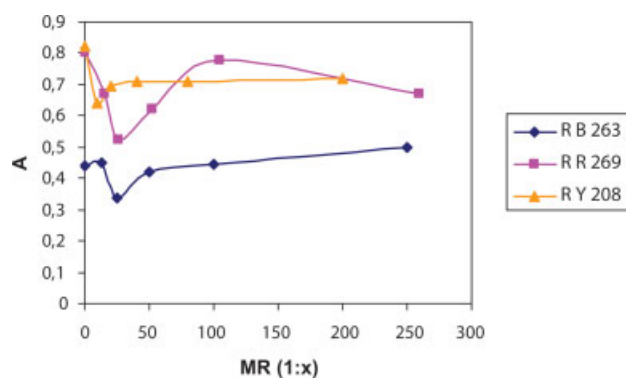
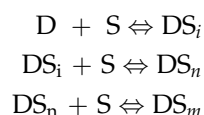


Figure 7 Absorption of C.I. Reactive Blue 263, C.I. Reactive Red 269, and C.I. Reactive Yellow 208 in the presence of dodecyl trimethyl-ammonium bromide as a function of the molar ratio dye:tmab. RB = Reactive Blue; RR = Reactive Red; RY = Reactive Yellow. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Amount of 12-tmab in the Complexes Formed

Type of complex	Moles of 12-tmab per mole of dye		
	Rea Blue 263	Rea Red 269	Rea Yellow 208
<i>i</i>	≤25	≤26	≤10
<i>n</i>	50	52	20
<i>m</i>	100	105	40

These equilibrium states can be represented as follows:



where D is the dye, S is the auxiliary product (tmab) and the indices *i*, *n*, *m* represent an insoluble complex, a normal one and a micellar one, respectively.²²

Figure 7 shows the absorption of the dye solutions against the dye/12-tmab molar ratios.^{22,23} The values *i*, *n*, and *m* depend on the structure of the dye and are given in Table IV.

The molar ratios of the three dyes/12-tmab adsorbed on the fabric during the dyeing are 1/4.3, 1/5.0, and 1/3.5 for the blue, red, and yellow dye respectively.

The existence of insoluble aggregates in the dye liquor for the case of blue and red dye can be explained in terms of the more than double, *i*, *n*, *m* values for the blue and red dyes compared to those of the yellow dye (Table IV).

CONCLUSION

The main purpose of this work was to reduce the electrolyte used in the dyeing of cotton with reactive dyes, without significant decrease of dye exhaustion and fixation, by pretreatment of the cotton fabric with cationic agents (tmabs).

This was only achieved with the yellow dye, whereas for the red and blue a decrease in dye fixation was observed in the presence of tmabs. This indicates that both the size of the tmab and the dye structure play a critical role in dye fixation.

Dye exhaustion increases in all cases after pretreatment of the fabric with the cationic tmabs, whereas pretreatment with dodecyl-trimethyl-ammonium bromide (the cationic with the shortest alkyl chain) results in the highest increase in dye exhaustion and the highest values of dye fixation followed by the tetradecyl- and hexadecyl-trimethyl-ammonium bromide.

Study on the interaction of the three dyes with the dodecyl-trimethyl-ammonium bromide in various molar ratios, dye/tmab, indicates that the dyes, C.I Reactive Blue 263 and C.I Reactive Red 269 form insoluble complexes with 12-tmab in much smaller molar ratios than C.I Reactive Yellow 208.

References

1. Broadbent, A. D. *Can Assoc Text Col Chem* 1986, 18, 19.
2. Noah, A. O.; Marthius, C. M.; Brainah, J. A. *J Appl Polym Sci* 1988, 32, 5841.
3. Gonzales-Caballero, F. *J Colloid Interface Sci* 1988, 123, 537.
4. Lewis, D. M.; Lei, X. P. *J Soc Dyers Col* 1991, 107, 102.
5. Burkinshaw, S. M.; Lei, X. P.; Lewis, D. M. *J Soc Dyers Col* 1989, 105, 391.
6. Wu, T. S.; Chen, K. M. *J Soc Dyers Col* 1993, 109, 153.
7. Goynes, W. R.; Benerito, R. *J Appl Polym Sci* 1988, 36, 1255.
8. Evans, G. E.; Shore, J.; Stead, C. V. *J Soc Dyers Col* 1984, 28, 38.
9. Robinson, T.; Egger, W. B. *Text Chem Col* 1983, 15, 13.
10. Gatewood, B. M. *Text Chem Col* 1996, 28, 38.
11. Burkinshaw, S. M.; Collins, G. W. *J Soc Dyers Col* 1998, 114, 12.
12. Yang, Y.; Li, S. *Text Res J* 1994, 64, 433.
13. Guo, L. N.; Petit-Ramel, M.; Gauthier, R.; Chabert, B.; Jacquet, A. *J Soc Dyers Col* 1993, 109, 213.
14. Cai, Y.; Pailthorpe, M. T.; David, S. K. *Text Res J* 1999, 69, 440.
15. Rucker, J. W. *Book of Papers, International Conference and Exhibition-American Association of Textile Chemists and Colorists, Atlanta, GA, 1997*, p 329.
16. Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley: New York, 1978.
17. Stache, H. *Tensidaschenbuch*, 2nd ed.; Carl Hansen Verlag: München, 1981.
18. Chwala, A.; Anger, V.; *Handbuch der Textilhilfsmittel*, 2nd ed.; Verlag Chemie: Weinheim, 1977.
19. Rosen, M.; Goldsmith, H.; *Systematic Analysis of Surface Active Agents*; Wiley Interscience: New York, 1972.
20. Youssef, Y. A. *J Soc Dyers Col* 2000, 116, 297.
21. Sinclair, R. S. In *Colour Physics and Industry*, 2nd ed.; McDonald, R., Ed.; Society of Dyers and Colourists, Bradford, 1997, p 38.
22. Cegarra, J.; Valldeperas, J.; Navarro, J. A.; Navarro, A. *J Soc Dyers Col* 1983, 99, 291.
23. Tsatsaroni, E. G.; Eleftheriadis, I. C.; Kehagioglou, A. H. *J Soc Dyers Col* 1990, 106, 245.