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Dyes and Pigments 68 (2006) 197–204

DYES and PIGMENTS

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The effect of reactive dyes upon the uptake and anti bacterial action of poly(hexamethylene biguanide) on cotton. Part 2: Uptake of poly(hexamethylene biguanide) on cotton dyed with β-sulphatoethylsulphonyl reactive dyes

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Received 11 January 2005; accepted 28 January 2005

Abstract

Polyhexamethylene biguanide (PHMB) is a widely used bacteriocide. It is marketed as an aqueous solution of its hydrochloride from which it is readily adsorbed onto cotton, this process depending upon the ability of the cationic PHMB to form electrostatic links with the anionic carboxylate groups present on cotton. The introduction of chemically bound sulphonic acid groups into cotton, which takes place during the process of dyeing with reactive dyes, increases the capacity of cotton to take up PHMB. The saturation levels of PHMB on un-dyed cotton, and cotton dyed individually with a trichromat of warm dyeing dyes, has been measured. Additionally, the effective agent contents of the dyes and their percentage fixation on to the cotton were determined, thus allowing the concentration of sulphonic acid groups present on the cotton to be calculated. From this and knowledge of the saturation value of PHMB on dyed and un-dyed cotton the stoichiometry of the interaction between PHMB and sulphonic acid groups was deduced. For the disulphonated dye, C I Reactive Black 5, each sulphonic acid group appeared to be associated with uptake of an additional 1.12 equiv. of monomeric biguanide unit. For the monosulphonated dyes, C I Reactive Orange 16 and C I Reactive Orange 107, the corresponding values were 1.31.and 1.47, respectively.

Keywords: Polyhexamethylene biguanide (PHMB); Reactive dyes; Cotton

1. Introduction

The ability of un-dyed cellulosic fabrics to take up cationic species is well known and forms the basis of a quantitative method for the determination of the concentration of carboxylic acid groups present on such fabrics [1,2]. Unfortunately, the wet fastness of cellulosic fibres dyed with cationic dyes is generally poor and precludes such use commercially. This is attributed to the relatively easy disruption of the weak ion–ion linkage between cationic dye and carboxylic group in the cotton. In contrast, the dyeing of polyacrylonitrile with cationic dyes yields dyeings with better wet fastness properties [3]. This is attributable to the glass transition temperature, typically ca. 75 °C [4]. In similar manner, the adsorption of PHMB onto cotton is believed to depend upon the formation of weak ion–ion linkages, between cationic PHMB and carboxylate groups present on the cotton [5]. Weak electrostatic links of this type would be expected to dissociate readily and thereby liberate free PHMB, the likely bio-active species.

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doi:10.1016/j.dyepig.2005.01.017

The concentration of carboxylic acid groups present on a particular sample of cotton depends upon the source of the cotton and the chemical treatments, such as bleaching, to which it has been subjected; this will largely determine the capacity of cotton to take up a cationic species such as PHMB. The introduction of covalently bound reactive dyes, which invariably utilise sulphonic acid groups to confer solubility, might be expected to increase the capacity of dyed cotton to take up PHMB: additionally, release of free PHMB by dissociation might be less facile since sulphonic acids are much stronger than carboxylic [6,7]. As part of a study aimed at gaining a greater understanding of the effect of covalently bound dyes on the bacterial efficacy of PHMB adsorbed onto cotton, samples of cotton were dyed with "warm-dyeing" reactive dyes before treating with PHMB. The quantitative effect of such covalently bound dyes on the absorption of PHMB has been determined.

2. Experimental

2.1. Materials and apparatus

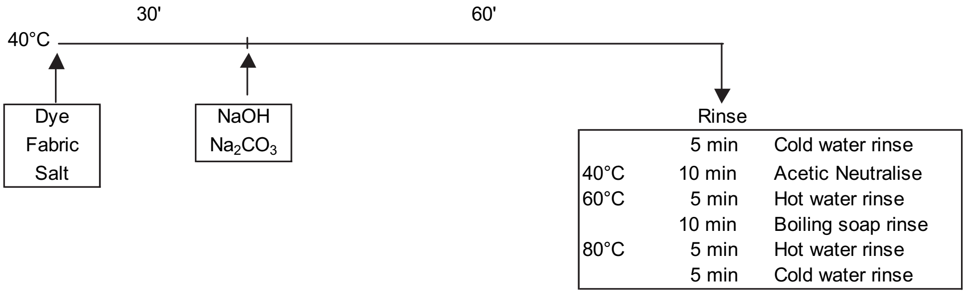
Three sulphatoethyl sulphone (SES) reactive dyes, namely, C I Reactive Black 5 (Everlight Industrial Chemical Corporation), C I Reactive Oranges 16 and 107 (DyStar) were applied separately to 50 g pieces of desized 100% knitted cotton fabric. All dyes were essentially homogeneous in terms of coloured species present, but each contained unidentified colourless formulating agents. PHMB hydrochloride was kindly supplied, as a 20% aqueous solution, by Avecia Ltd, Blackley, Manchester. All other chemicals were of laboratory reagent grade. Absorbance of dyes and PHMB were recorded using a Camspec M350 double beam ultraviolet–visible spectrophotometer. A Datacolor Spectroflash 600 spectrophotometer was used for the assessment of the optical strength of dyed fabrics.

2.2. Dyeing procedure

Knitted mercerised cotton pieces (50 g each) were dyed to five depths of shade, (1, 2, 4, 6 and 9% dye o.m.f.) using sodium chloride, sodium hydroxide and sodium carbonate, in a Roaches Ryrotec-S dyeing machine at a liquor-to-goods ratio of 10:1 using 1000 ml capacity stainless steel dyeing pots. Initially dye and salt were added to the machine set at 40 °C. After 30 min alkali (ash and caustic) were added (see Fig. 1 for quantities) and dyeing continued for a further 60 min at 40 °C. After completion of dyeing the fabric was given a cold rinse under running tap water (5 min.), washed with (a) 0.1% aqueous acetic acid (500 ml) at 40 °C for 10 min, (b) water (60 °C, 1000 ml, 10 min), (c) soap solution: Lanetor WLF 125 (1 g/l) (100 °C, 1000 ml, 10 min), (d) water (80 °C, 1000 ml, 10 min) and finally rinsed under cold running water for a further 5 min.

2.3. Assessment of optical strength of dyeings

A Datacolor Spectroflash 600 spectrophotometer was used to assess the build-up properties of dyes on fabric in terms of K/S values. These were obtained from the



	Depth of dye (%, o.m.f)				
	1	2	4	6	9
NaCl (g. / l)	50	50	50	80	80
NaOH (g. /l)	1	1	1	2	2
Na_2CO_3 (g. /l)	5	5	5	5	5
Acetic acid (ml. / l)	1	1	1	1	1
Soap (g. / l)	1	1	1	1	1

Fig. 1. Dyeing conditions for the application of sulphatoethane sulphonyl reactive dyes.

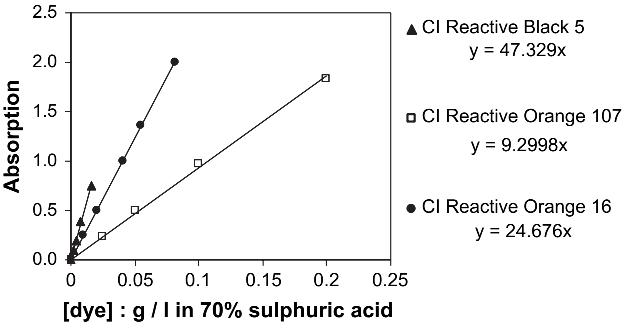


Fig. 2. Dye vs. absorbance of commercial dyes used in this study.

reflectance values at the wavelength of maximum absorption, λ_{max}, under D65 illuminant with 10 °C standard observer with UV component. Each sample was folded twice so as to provide a total of four thicknesses of fabric.

2.4. Determination of percentage dye fixation

This was determined as follows [8]. A known amount of solid dye was dissolved in 70% of sulphuric acid [8]. The absorbance was measured at the wavelength of maximum absorbance (λ_{max}) employing a Camspec M350 double beam ultraviolet–visible spectrophotometer, using 70% of sulphuric acid solution as reference solvent. The solution was diluted successively by a factor of 2, 4 and 8. In each case, the absorption was proportional to the concentration of dye, indicating adherence to Beer–Lambert's law (Fig. 2).

Subsequently, accurately weighed samples of dyed cotton (0.1 g) were dissolved, over 0.5–3 h, in 70% sulphuric acid (50 ml) at room temperature. From the absorbance of the resulting solution of degraded dyed cotton it was possible to determine the concentration of dye present on the dyed cotton sample and, knowing the concentration of dye applied, the percentage fixation of dye to fabric.

2.5. Determination of the effective agent content of dyes

Commercial reactive dyes always contain additional materials such as de-dusting agents, salt and water. The effective agent content of each dye was determined by titration against titanium (III) chloride [9–12] . Because titanium (III) chloride is readily oxidised by air it was standardised immediately prior to use, by titration against a standard dye [8]. In this case the standard dye was a sample of C I Reactive Red 5 (Fig. 3) of known effective agent strength.

Table 1
Weight (g) of PHMB applied to 5 g pieces of cotton fabric

Dye strength (% o.m.f)	Weight of PHMB applied (g)						
0, 1, 2	0	0.004	0.009	0.018	0.035	0.071	0.141
4	0	0.007	0.014	0.028	0.057	0.114	0.227
6	0	0.009	0.018	0.035	0.071	0.141	0.283
9	0	0.011	0.021	0.042	0.084	0.169	0.337

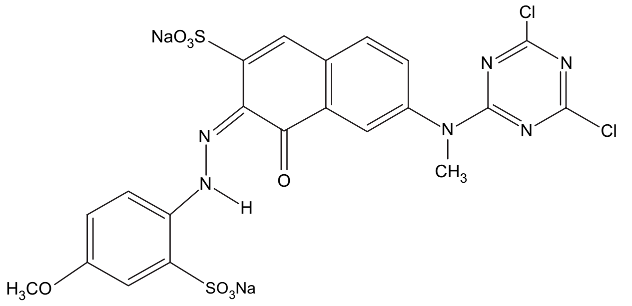


Fig. 3. Structure of C I Reactive Red 5.

Dye of unknown effective agent content (0.1 g) was then dissolved in distilled water (100 ml) and potassium sodium tartarate buffer (20 ml, 20% w/v) was added. The solution was boiled under argon and titrated against titanium (III) chloride solution (0.1 N) and the strength of each dye described by its Mole In, that is, the weight in grams of dye which contains 1 mol of dye.

2.6. Determination of uptake of PHMB by fabrics

In order to study the uptake of PHMB by cotton, a series of solutions of PHMB, of varying strengths, were prepared and adjusted to pH 7 with sodium bicarbonate. Seven 5 g pieces were cut from each un-dyed and dyed cotton sample (2 different samples of un-dyed fabric and 15 samples of dyed fabric – 3 dyes each dyed at 1, 2, 4, 6 and 9% dye o.m.f.). Each of these accurately weighed pieces was soaked in 6 different concentrations of PHMB solution (100 ml) in bottles. The bottles were sealed and placed on a roller mill for 24 h. Details of the PHMB solution strengths are shown in Table 1.

PHMB uptake was assessed optically by measuring the absorbance of each solution at 236 nm. The absorbance before ($Abs_{initial}$) and after (Abs_{final}) introduction of the cotton sample was measured and the percentage uptake, S, of PHMB onto cotton was calculated (Eq. (1)).

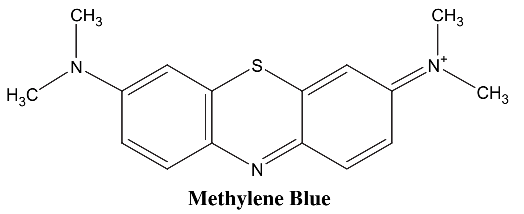


Fig. 4. Structure of Methylene Blue.

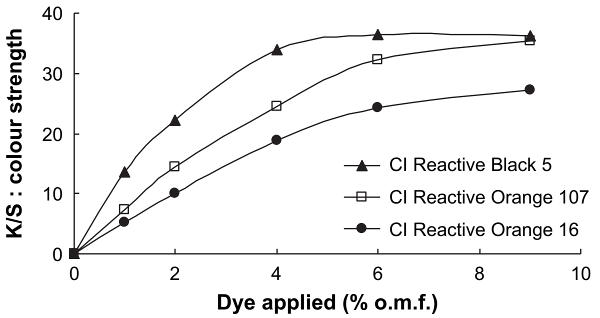


Fig. 5. Build-up properties of sulphatoethane sulphonyl reactive dyed cotton samples.

$$S = \frac{(\mathrm{Abs}_{\mathrm{initial}} - \mathrm{Abs}_{\mathrm{final}})}{\mathrm{Abs}_{\mathrm{initial}}} \times 100\% \qquad (1)$$

2.7. Carboxylic acid content of cotton

Two different samples of cotton fabric, designated Cotton A and Cotton B were used. Cotton A was dyed with C I Reactive Black 5 and Cotton B was dyed with C I Reactive Oranges 16 and 107. The concentration of anionic carboxylic acid groups present on cotton was determined by titration against a cationic dye, Methylene Blue (Fig. 4).

The quantitative estimation of the concentration of carboxylic acid groups present on each sample of undyed cotton fabric was conducted by titration of an accurately weighed sample of fabric against a cationic dye of known strength fabrics [1,2]. Thus, a known concentration of Methylene Blue (75 mg/l–1800 mg/l) in borax buffer, pH 8 (0.1 M of hydrochloric acid 120 ml/l, 0.025 M of sodium borate 400 ml/l and 480 ml of deionised water) was diluted successively and the absorbance values at the wavelength of maximum absorbance, $\lambda_{\max}$, 666 nm, recorded. A graph of absorbance vs. concentration, using a Camspec M350 double beam spectrophotometer, was a straight line, indicating adherence to Beer–Lambert's law. An accurately weighed piece of cotton fabric (1 g) was added to each solution of Methylene Blue (100 ml) and the resulting mixture, at liquor-to-goods ratio of 100:1, was placed on a roller mill for 24 h. The optical density of the solution of Methylene Blue was measured before and after addition of the cotton. The difference, after referral to the calibration graph, gave a measure of the amount of Methylene Blue adsorbed. Since each molecule of Methylene Blue is thought to form a single electrostatic bond with each unit of carboxylic acid on the fabric it was thus possible to calculate the concentration of carboxylic acid groups present on the fabric.

Table 2
Percentage fixation of dyes

Dye C I reactive	% Fixation (by % o.m.f.)				
	1%	2%	4%	6%	9%
Black 5	85.9	84.7	80.5	74.0	57.5
Orange 107	82.3	75.5	76.6	57.3	57.4
Orange 16	64.2	52.1	55.4	54.8	49.9

Table 3
Percentage effective agent contents and Mole-In values of dyes

Dyes C I Reactive	Black 5	Orange 107	Orange 16
Percent EA	78.1	58.0	58.3
Mole In	1270	980	1060

3. Results and discussion

3.1. Build-up and fixation of dyes

The build-up properties of dyes on textile substrates are usually assessed in terms of the visual strength of a particular dyeing. The visual colour yield of each of the fabrics was assessed spectrophotometrically and expressed as a *K*/*S* value. The Kubelka–Munk equation is used to describe this phenomenon (Eq. (2)).

$$K/S = \frac{(1-R)^2}{2R} \qquad (2)$$

K is the absorption coefficient, *S* is the scattering coefficient and *R* is the reflectance. The build-up properties of the three dyes, as assessed by *K*/*S* values at the wavelength of maximum reflectance are depicted in Fig. 5. In each case the dyes built up well as evidenced by *K*/*S* values (Fig. 5).

Additionally, the percentage fixation of each dye at each depth of shade was determined by dissolution of

Table 4
Dye fixation and concentration of sulphonic acid residues on dyed cotton pieces

Dye C I Reactive	% Applied[a]	[Fixed dye][b]	[SO_3Na][c]
Black 5	1	6.7	13.4
	2	14.1	28.3
	4	26.5	52.9
	6	33.4	66.8
	9	40.2	80.4
Orange 107	1	8.4	8.4
	2	15.4	15.4
	4	27.0	27.0
	6	38.3	38.3
	9	52.9	52.9
Orange 16	1	6.0	6.0
	2	12.0	12.0
	4	21.8	21.8
	6	29.6	29.6
	9	41.8	41.8

[a] Dye applied, g/100 g fabric.
[b] Dye fixed to fabric (mmol of dye/kg fabric).
[c] Concentration of fixed sulphonic acid groups (mequiv./kg fabric).

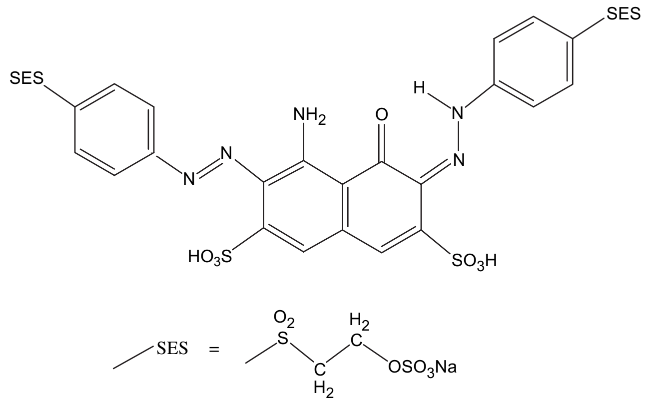


Fig. 6. Chemical structure of C I Reactive Black 5.

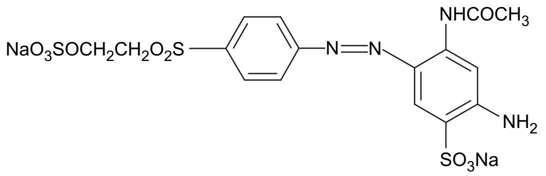


Fig. 7. Chemical structure of C I Reactive Orange 107.

dyed cotton in 70% sulphuric acid as already reported [8,12]. Fixation values are listed in Table 2.

As with all reactive dyes the percentage fixation reduces with increasing concentration of dye applied. This effect arises from the increasing net negative charge associated with the fibre as more anionic dye is fixed, this in turn resulting in increased electrostatic repulsion between dye and fibre. Additionally, as more dye fixes the concentration of sites available on the cotton, for further fixation, reduces.

3.2. Effective agent content of dyes

The reduction of an azo group can be accomplished cleanly and quantitatively with titanium (III) chloride [9–12]. Each such group formally requires 4 equiv. of titanium (III) chloride for complete reduction (Eq. (3)).

$$4\text{Ti}^{3+} \rightarrow \text{Ti}^{4+} + 4e^- \qquad (1)$$

$$\text{R}_1\text{-N=N-R}_2 + 4\,\text{H}^+ + 4e^- \rightarrow \text{R}_1\text{-NH}_2 + \text{R}_2\text{-NH}_2 \qquad (2)$$

$$\text{R}_1\text{-N=N-R}_2 + 4\text{Ti}^{3+} + 4\text{H}^+ \rightarrow 4\,\text{Ti}^{4+} + \text{R}_1\text{-NH}_2 + \text{R}_2\text{-NH}_2 \qquad (1)+(2)$$

$$(3)$$

By this method the effective agent content of each of the dyes was determined (Table 3). These were also conveniently expressed in terms of Mole In, which is the weight in grams of commercial dye containing 1 mol of pure dye.

With knowledge of the effective agent content and percentage fixation of each dye, it was possible to calculate the molar concentration of fixed dye per unit weight of cotton (Table 4). Additionally, knowing the chemical structures (Figs. 6–8) of each dye and, in particular, the degree of sulphonation the concentration of chemically bound sulphonic acid group per unit weight of cotton was also readily determined (Table 4).

3.3. Carboxylic acid content of cotton

Cationic PHMB groups attach to anionic carboxylic acid groups on un-dyed cotton via weak ion–ion linkages. The concentration of carboxylic acid groups present was assessed by titration against the cationic dye Methylene Blue. By this method Cotton A was found to possess ca. 42 mequiv. of COO^-/kg of cotton and Cotton B ca. 55 mequiv. of COO^-/kg of cotton.

3.4. Absorption of PHMB by dyed and un-dyed fabrics

PHMB is a polymeric biguanide of the type depicted in Fig. 9, where the average value of n is 11. Organic biguanides are extremely strong bases [13] and, at pH 7, are essentially fully protonated: this cationic species is believed to attach to the cotton via ion–ion linkages with the anionic carboxylate groups on the cotton (Fig. 10). The uptake of PHMB by the two samples of un-dyed cotton is shown in Fig. 11.

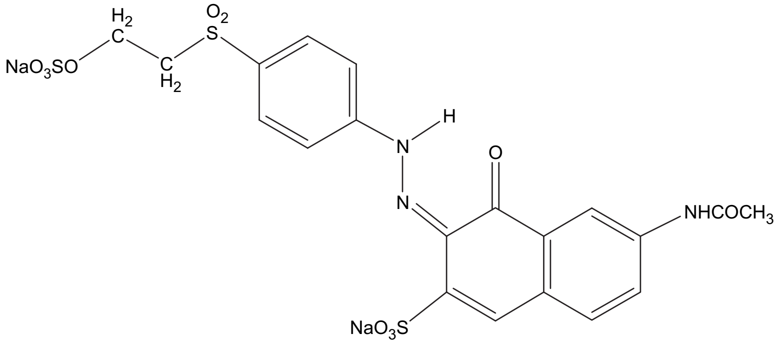


Fig. 8. Chemical structure of C I Reactive Orange 16.

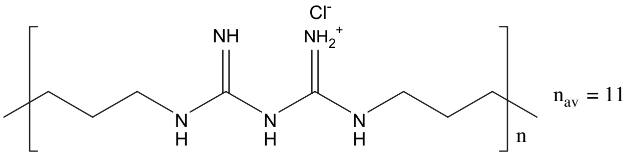


Fig. 9. Structure of PHMB.

It can be seen that, initially, as the concentration of applied PHMB increases so does the uptake of agent by both samples of cotton. By manual extrapolation it can be deduced that uptake of PHMB reaches “saturation” at ca. 8 g of PHMB/kg of fabric for Cotton A and ca. 12 g of PHMB/kg of fabric for Cotton B. At lower concentrations virtually all of the PHMB is taken up by the cotton.

In order to gain some further insight into the mode of attachment of PHMB to the un-dyed cotton, especially at heavier loadings of PHMB, and to ascertain whether a Langmuir or Freundlich type mechanism might be operative [14], a graph of 1/[$\text{PHMB}_{\text{fixed}}$] against 1/[$\text{PHMB}_{\text{solution}}$] was constructed (Fig. 12). This technique is routinely used as a tool in studies of the adsorption of dyes onto textiles [15] and other substrates [16–18]. At higher loadings of agent this approximated to a straight line indicating that the PHMB might be attached to the cotton by a Langmuir type absorption. Additionally, a graph of [$\text{PHMB}_{\text{fixed}}$]/[$\text{PHMB}_{\text{solution}}$] against [$\text{PHMB}_{\text{fixed}}$] (Fig. 13) for higher concentrations of PHMB yielded an approximate straight line, with the intercept on *x*-axis representing the saturation value of PHMB on the cotton.

The saturation value thus found (7.7 g/kg fabric) agreed well with that of manual extrapolation (8 g/kg fabric) and the latter method was thus used subsequently for such determinations.

The molecular weight of the repeating monomeric unit in PHMB is 184: thus 8 g PHMB equates to 8/184, or 0.043 equiv. of monomeric biguanide unit, which is very close to the concentration of carboxylic acid groups present on Cotton A. A similar broad situation obtains in the case of Cotton B. This might suggest that each carboxylic acid group is therefore associated with a single monomeric biguanide unit, perhaps via a salt linkage. However, it is difficult to envisage a situation where all of the carboxylate groups and all of the biguanidine units are spatially available for such salt bonding.

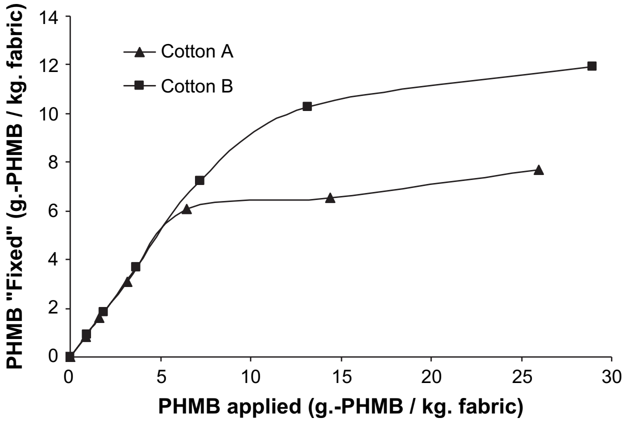


Fig. 11. Absorption of PHMB on undyed cotton A and B.

The dyed fabrics display a greater capacity for absorption of PHMB (Figs. 14–16). In addition, the absorptive capacity of the dyed fabric increases (for a given dye) with increasing concentration of fixed dye. Thus, for example, in the case of C I Reactive Black 5, the graphs can be extrapolated to provide approximate values for a “saturation” level of PHMB of ca. 11, 13, 17, 21 and 26 g of PHMB/kg of fabric dyed with 1,2, 4, 6 and 9%, respectively of dye o.m.f.

By plotting the values for the saturation concentration of PHMB against concentration of fixed dye it is possible to conclude that, for a given dye, the saturation concentration of PHMB is proportional to the concentration of dye which is fixed, and therefore proportional to the concentration of sulphonic acid groups attached

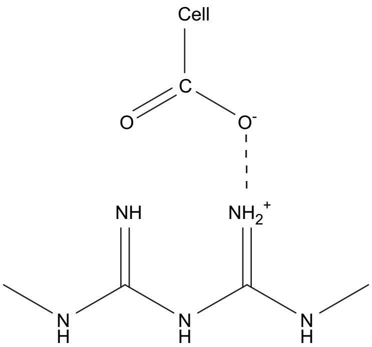


Fig. 10. Bonding of PHMB to cotton via salt linkage.

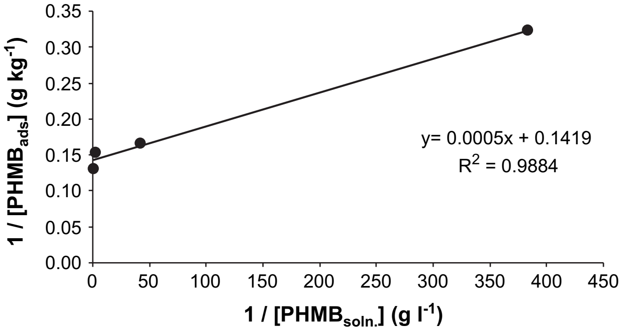


Fig. 12. Adsorption of PHMB on un-dyed Cotton A. 1/PHMB_{ads} vs. 1/$\text{PHMB}_{\text{soln}}$.

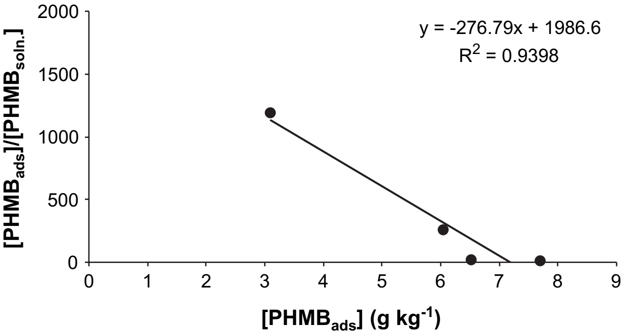


Fig. 13. Saturation value of PHMB on un-dyed Cotton A (Langmuir): $PHMB_{ads}/PHMB_{soln}$ vs. $PHMB_{ads}$.

to the fibre. C I Reactive Orange 16 and C I Reactive Orange 107 are both monosulphonated species whereas the C I Reactive Black 5 is disulphonated. Thus a graph of concentration of fixed sulphonic acid, $[SO_3^-]_{fixed}$, against PHMB uptake gives an approximate straight line relationship, Fig. 17, which yields information on the stoichiometry of the interaction between dye and PHMB.

From the slope of the line the number of biguanide units per sulphonic acid group can be determined: in the case of C I Reactive Black 5 each sulphonic acid group is associated with the uptake of an additional 1.12 equiv. of monomeric buiguanide unit. As each polybiguanidine comprises, on average, 11 monomeric units of biguanide, each sulphonic group is associated with the additional absorption of ca. 0.10 polymer unit (~1.12/11). For C I Reactive Orange 16 and C I Reactive Orange 107 the corresponding figures are 1.31 (~0.12) and 1.47 (~0.13). These figures suggest that the ability of sulphonic acid groups to cause absorption of PHMB varies with the nature of the dye to which they are attached: thus the single sulphonic acid group in C I Reactive Orange 107 appears to be more accessible than that in C I Reactive Orange 16 which in turn is effectively more accessible than those in C I Reactive Black 5.

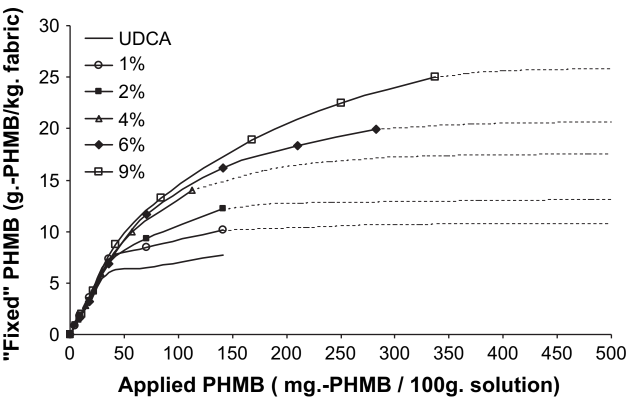


Fig. 14. Uptake of PHMB on un-dyed cotton and cotton dyed with C I Reactive Black 5 (solid lines – actual results; dotted lines extrapolated to saturation).

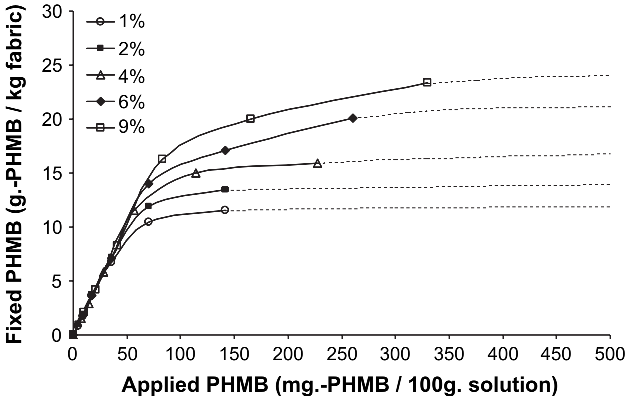


Fig. 15. Uptake of PHMB on un-dyed cotton and cotton dyed with C I Reactive Orange 107 (solid lines – actual results; dotted lines extrapolated to saturation).

4. Conclusions

The saturation uptake of PHMB by undyed cotton equates approximately to 1 equiv. of monomeric biguanide unit per carboxylic acid group present on cotton. This may well involve, predominantly though not exclusively, ion–ion linkages between anionic carboxylate residues on the cotton and cationic PHMB.

Cotton dyed with reactive dyes has a greater capacity to absorb PHMB than un-dyed cotton. The introduction of covalently bound sulphonic acid groups onto cotton, via a reactive dye, increases the capacity of the cotton to take up PHMB, probably via further ion–ion bond formation. The saturation capacity of PHMB

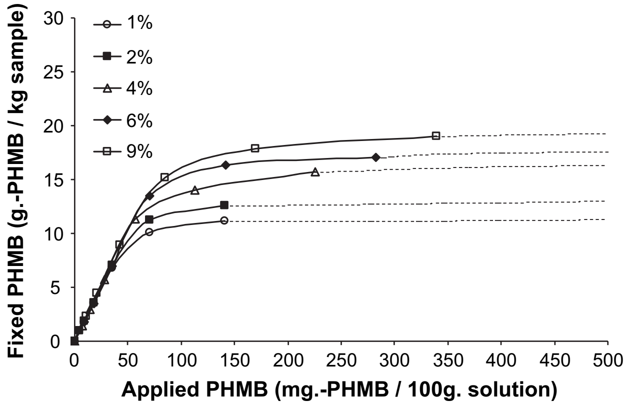


Fig. 16. Uptake of PHMB on un-dyed cotton and cotton dyed with C I Reactive Orange 16 (solid lines – actual results; dotted lines extrapolated to saturation).

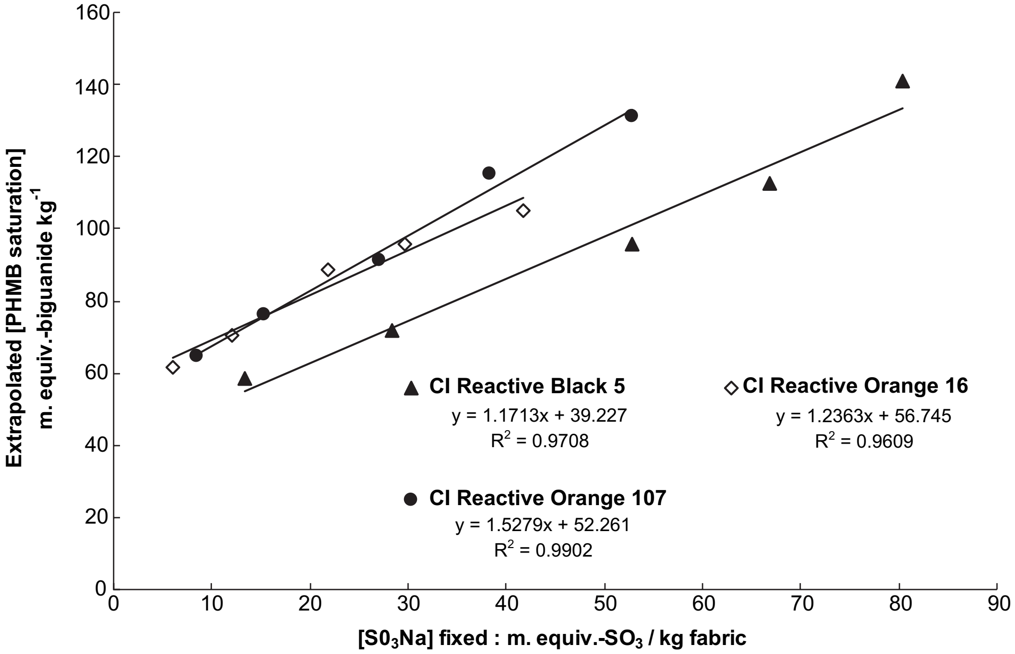


Fig. 17. Saturation concentration of PHMB (in mequiv./kg fabric) vs. "fixed" sulphonic acid concentration (in mequiv./kg fabric) for the three β-sulphatoethyl sulphonyl reactive dyes.

increases as the concentration of fixed dye, and therefore of fixed sulphonic acid, increases.

The ability to increase the absorptive capacity, of the cotton for PHMB, by incorporation of a reactive dye varies with the nature of the reactive dye. This may well depend upon the spatial accessibility of the sulphonic acid residues, present in the dye, to form ion–ion linkages with the cationic PHMB.

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