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Oxidative and Reductive Fading of Monochlorotriazinyl Reactive Dyes on Cellulose under Wet Conditions

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ABSTRACT

The photofading of three monochlorotriazinyl (MCT) reactive dyes was examined in the absence or presence of oxygen and substrate under wet conditions. These dyes on cellulose showed no fading on exposure in deaerated water and oxidative fading in aerated water, whereas they underwent reductive fading in the presence of DL*-mandelate in a nitrogen atmosphere. C.I. Reactive Blue 2 and a phthalocyanine dye showed a multi-step photoreduction. Their reduction intermediates were oxidized to re-form the original dyes as in the case of thermal reduction. The azo group nearer the triazine ring of a copper-complex disazo dye was readily photoreducible, and the other was oxidizable. The relationship for a phthalocyanine dye among the rates of fading in aerated water, the degree of association, and the concentration of dye on cellulose was examined. The fading behavior of C.I. Reactive Blue 19 was compared with that of Blue 2 under various conditions.*

1 INTRODUCTION

In a previous paper,[1] it was observed that some monochlorotriazinyl (MCT) reactive dyes underwent reductive fading on exposure in deaerated water even in the absence of a substrate. They show reductive or oxidative fading

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on exposure in aerated water and oxidative fading on exposure in aerated Rose Bengal solution. When they are dyed in admixture, they act as a sensitizer for the partner dyes, which undergo oxidative fading as in the case of vinylsulfonyl (VS) dyes.[3,4] In the presence of oxygen and a substrate, simultaneous oxidative and reductive photofading for VS dyes occurs depending upon the conditions.[5,6]

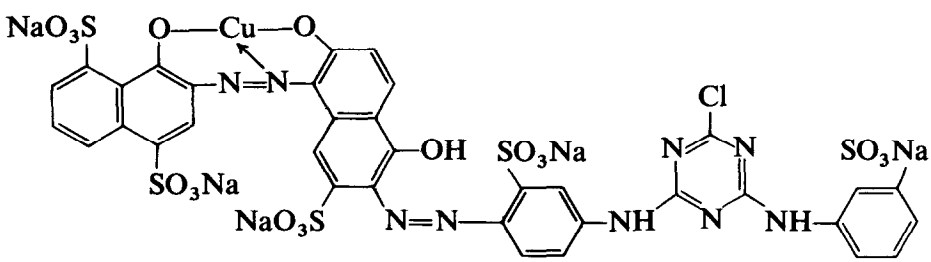
In the present paper, the fading behavior of three MCT dyes on cellulose, showing no fading on exposure in deaerated water, in contrast to other MCT dyes[1] is examined. It is shown that they have a similar fading behavior to that of many VS dyes.[5]

2 EXPERIMENTAL

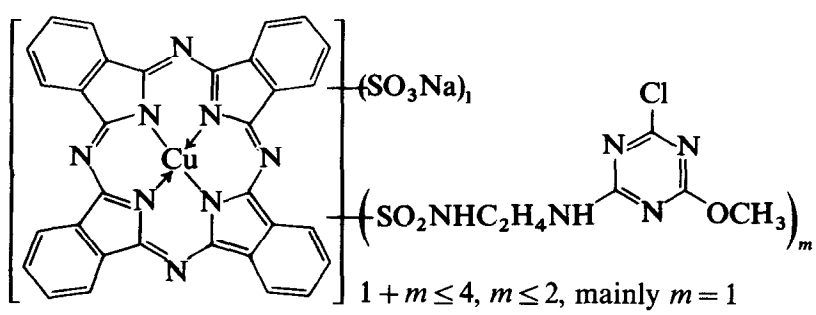
2.1 Dyes used

The three MCT dyes used were the same as those used in previous studies.[2] The chemical structure of the dyes, supplied by Nippon Kayaku Co. Ltd, Tokyo, Japan, and their abbreviations are as follows:

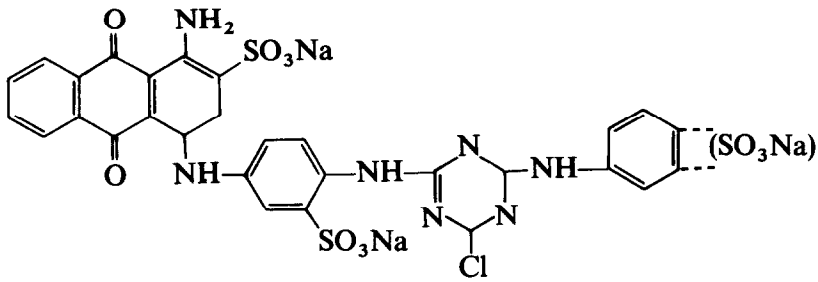
(1) a 1:1 Cu-complex disazo dye (Blue–Cu)



(2) a copper phthalocyanine dye (Cu–Pc)



(3) C.I. Reactive Blue 2; C.I. 61211 (Blue 2)



C.I. Reactive Blue 19, C.I. 61200, was supplied by Sumitomo Chemical Co. Ltd, Osaka. These dyes were used for dyeing cellophane without further purification.

2.2 Dyeing and exposure

Cellophane films were dyed by the same method as before.[1] The method of exposure and the apparatus were also the same as before.[1] A sheet of dyed film was set in a glass cell filled with an aqueous solution and was exposed in a fadeometer. Aqueous sodium DL-mandelate solutions were freshly prepared before every exposure experiment by neutralizing the acid solutions with aqueous sodium hydroxide, and the concentrations were adjusted by dilution.[5,6] The other chemicals used were of reagent grade.

3 RESULTS AND DISCUSSION

3.1 Thermal and photochemical reduction of MCT dyes on cellulose

3.1.1 Blue–Cu

In order to obtain the thermal-reduction product of Blue–Cu, a sheet of dyed cellophane was immersed in aqueous sodium dithionite (0·1 mol dm^{-3}) solution at 70°C for 30 min, the dyes on cellulose being readily reduced and showing changes in color (Spectrum 2 in Fig. 1).

On exposure of Blue–Cu on cellulose in anaerobic aqueous sodium DL-mandelate (0·05 mol dm^{-3}) solution, the photoreduction product was obtained, the absorption spectrum of which was the same as that for the thermal product (Spectra 3–6 in Fig. 1).

The shape of the absorption spectra of the photoreduction products for Blue–Cu on exposure in an aqueous DL-mandelate solution did not vary significantly with time of exposure, which implied that little monoazo

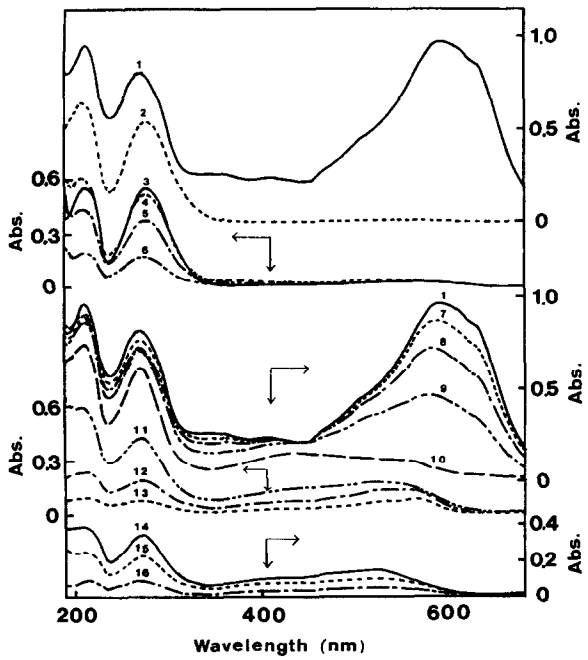


Fig. 1. Absorption spectra for Blue–Cu ($1{\cdot}41 \times 10^{-2}$ mol kg^{-1}) on cellophane before (1) and after (2) immersion in aqueous sodium dithionite (0·1 mol dm^{-3}, 70°C, 30 min) solution; those for the photoreduction products of Blue–Cu ($1{\cdot}48 \times 10^{-2}$ mol kg^{-1}) on cellophane after exposure in anaerobic aqueous sodium DL-mandelate (0·05 mol dm^{-3}) for 6 h (3), 3 h (4), 1·5 h (5), and 1 h (6) after subtracting the spectrum of Blue–Cu of the corresponding concentration; those for Blue–Cu ($1{\cdot}41 \times 10^{-2}$ mol kg^{-1}) after exposure in aerobic Rose Bengal ($1{\cdot}0 \times 10^{-5}$ mol dm^{-3}) solution for 10 min (7), 20 min (8), 40 min (9), and 8 h (10); those for the oxidation products of Blue–Cu after exposure for 40 min (11), 20 min (12), and 10 min (13) after subtracting the spectrum of Blue–Cu of corresponding concentration; those for the oxidation products of Blue–Cu after exposure in aerated water for 20 h (14), 10 h (15), and 2 h (16) after subtracting the spectrum of Blue–Cu of corresponding concentration.

intermediate showing absorption in the visible regions was formed from the reduction of the azo groups further away from the triazine ring (Fig. 1). It was also shown that the same absorption spectrum for the reduction product was obtained by treating the sample exposed for different times with dithionite solution. Thus, the azo group nearer the triazine ring for Blue–Cu is easily photoreduced and the other one hardly at all.

3.1.2 Cu–Pc

The immersion of Cu-Pc on cellulose in the dithionite solution yielded a reversible reduction intermediate (Spectrum 2 in Fig. 2), which quickly reverted to the original dye on air oxidation (Spectra 2 and 3). The intermediate on cellulose was further reduced by repeating the treatment

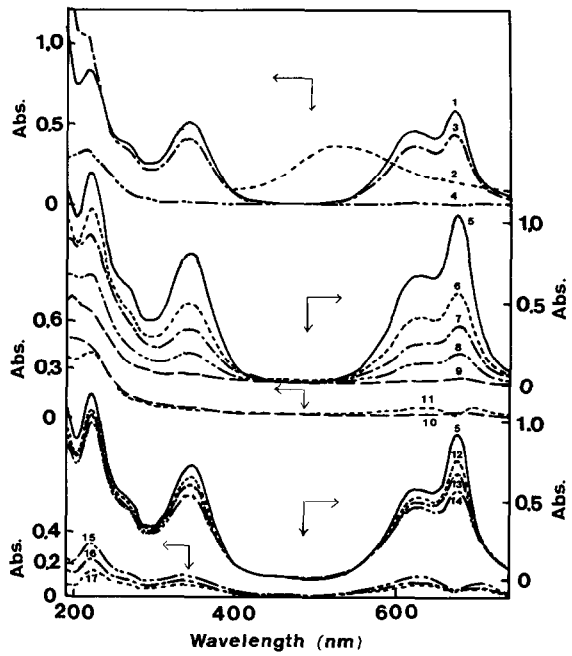


Fig. 2. Absorption spectrum for Cu–Pc ($2{\cdot}26 \times 10^{-3}$ mol kg^{-1}) on water-swollen cellulose (1); visible spectrum for Cu–Pc (2) immediately after thermal reduction with aqueous sodium dithionite (0·1 mol dm^{-1}, 70°C, 20 min) (the spectrum of reduced Cu–Pc on cellophane was measured by immersion in the dithionite solution; this sample was reversible to spectrum (3) on water-swollen cellulose by air oxidation); spectrum of the thermal product(4) for Cu–Pc after repeating the treatment with dithionite solution more than ten times; those for Cu–Pc ($2{\cdot}94 \times 10^{-3}$ mol kg^{-1}) on cellophane before (5) and after exposure in anaerobic aqueous DL-mandelate (0·50 mol dm^{-3}) for 2 h(6), 5 h(7), 10 h(8), and 20 h(9) (Spectra 6–9 were measured after air oxidation); and those for the photoreduction products after exposure for 20 h(10) and 2 h(11) after subtracting the spectrum of Cu–Pc of corresponding concentration; spectra for Cu–Pc ($2{\cdot}46 \times 10^{-3}$ mol kg^{-1}) on cellophane before (5) and after exposure in aerobic Rose Bengal ($1{\cdot}0 \times 10^{-5}$ mol dm^{-3}) solution for 5 h(12), 10 h(13), and 20 h(14); those for the oxidation products of Cu–Pc after exposure for 20 h(15), 10 h(16), and 5 h(17) after subtracting the spectrum of Cu–Pc of corresponding concentration (Spectra 4–17 were measured on dry cellulose).

more than six times with dithionite solution to give the end-product (Spectrum 4 in Fig. 2).

As in the case of a VS phthalocyanine dye,[7,9] on exposure in a DL-mandelate (0·5 mol dm^{-3}) solution, Cu–Pc on cellulose formed the photoreduction intermediate, which was reversibly oxidized to yield the original dye by air oxidation. The absorption spectrum of the intermediate seems to be similar to that of the thermal product. The absorption spectra of Cu–Pc and the photoreduction products on cellulose after the exposure followed by air oxidation are shown in Fig. 2 (Spectra 5–9).

The intermediate of Cu–Pc was further reduced by prolonged exposure in DL-mandelate solution to give the end-product (Spectra 10 and 11 in Fig. 2), a multi-step photoreduction. Since the reductive fading of a VS phthalocyanine dye yields an amino compound bound with cellulose via decomposition of sulfonamide groups,[7] the same decomposition as that of the VS dye may occur.

Although a decrease in absorption of Cu–Pc in the visible and UV regions occurred on exposure for at least 2 h, an increase in the absorption of the photoproducts at the wavelengths below 380 nm was observed on exposure for less than 2 h. The increase in the photodecomposed products for Cu–Pc during the exposure did not coincide with the decrease in absorbance at λ_{max}, a non-stoichiometric photodecomposition that remains to be investigated (Fig. 2).

3.1.3 Blue 2

The immersion of a sheet of dyed cellophane in the dithionite solution caused the thermal reduction of Blue 2 on cellulose. As in the case of Cu–Pc, Blue 2 on cellulose yielded a reduction intermediate (leuco compound; Spectrum 2 in Fig. 3), part of which reverted to the original form when dipped in an aqueous sodium percarbonate (5 g dm^{-3}) at 30°C or in aerated water (Spectra 2 and 3 in Fig. 3). The immersion of the exposed sample in aerated water required a longer time for it to revert to the original form. In addition to the reversible oxidation to the original form, the leuco compounds on cellulose were partially split off from the cellulose by oxidation, as shown by the decrease in the UV and the main visible-absorption band. This is the reason why the leuco compound is incompletely reversible. The leuco compound, on the other hand, was further reduced by repeating the treatment with dithionite to give the thermal-reduction end-product (Spectrum 4 in Fig. 3).

On exposure of Blue 2 on cellulose in an anaerobic aqueous DL-mandelate (0·5 mol dm^{-3}) solution, Blue 2 underwent the same two-step photoreduction as that in the thermal one, although a high concentration of substrate was used to obtain the photoreduction products (Spectra 5–8 in Fig. 3). Thus the photoreduction intermediate (leuco compound) that partially reverted to the original form by dipping in percarbonate solution was formed (Spectra 6 and 9 in Fig. 3). The absorption spectrum of the photoreduction intermediate was the same as that of the thermal leuco compound. Continuation of the exposure resulted in a photoreduction end-product, the spectrum of which was similar to that from thermal-reduction.

Since the absorption spectra of the thermal and photochemical end-products for Blue 2 (Spectra 4 and 8 in Fig. 3) are very similar to those for Blue–Cu (Spectrum 2 in Fig. 1), the imino bridge groups between the

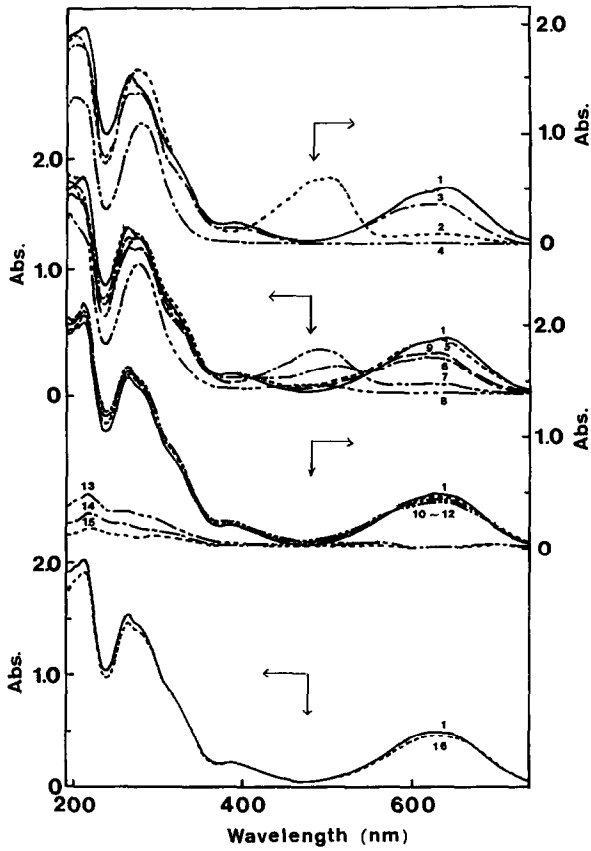


Fig. 3. Absorption spectra for Blue 2 ($1{\cdot}48 \times 10^{-2}$ mol kg^{-1}) on cellophane before (1) and after immersion in aqueous sodium dithionite (0·1 mol dm^{-3}, 70°C, 30 min) solution (2) (this sample was partially reversible to spectrum (3), when dipped in aqueous sodium percarbonate (5 g dm^{-3}) at 30°C), and after repeating twelve times (4) immersion in dithionite solution; those for Blue 2 ($1{\cdot}44 \times 10^{-2}$ mol kg^{-1}) on cellophane after exposure in anaerobic aqueous sodium DL-mandelate (0·50 mol dm^{-3}) for 2 h(5), 5 h(6) (this sample was partially reversible to spectrum (9) when dipped in aqueous sodium percarbonate solution (5 g dm^{-3}) at 30°C), 10 h(7), and 20 h(8); those of Blue 2 ($1{\cdot}36 \times 10^{-2}$ mol kg^{-1}) on cellophane before (1) and after exposure in aerobic Rose Bengal ($1{\cdot}0 \times 10^{-5}$ mol dm^{-3}) solution for 10 h(10), 20 h(11), and 40 h(12); those for the oxidation products of Blue 2 after exposure for 40 h(13), 20 h(14), and 10 h(15) after subtracting the spectrum of Blue 2 of corresponding concentration; those of Blue 2 ($1{\cdot}36 \times 10^{-2}$ mol kg^{-1}) on cellophane before (1) and after exposure in aerated water for 40 h(16). (All the spectra were measured on dry cellulose.)

anthraquinonyl and phenyl nuclei may be split off by thermal and photochemical reduction. The imino group of the leuco compound may be easily cleaved by oxidation.

Although Wegerle[10] reported the reduction of amino groups of anthraquinone dyes on poly(ethylene terephthalate), the present study may

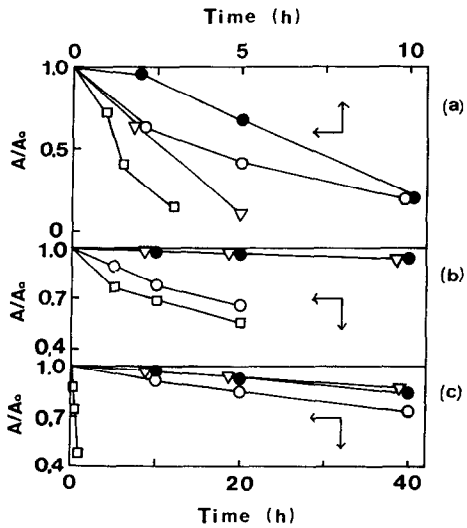


Fig. 4. Fading behavior for monochlorotriazinyl dyes on cellulose on exposure (a) in anaerobic aqueous sodium DL-mandelate (Blue–Cu in 0·05 mol dm^{-3} + 0·5 mol NaCl dm^{-3}, and Blue 2, Cu–Pc, and Blue 19 in 0·50 mol dm^{-3}), (b) in aerated water, and (c) in aerated Rose Bengal ($1·0 \times 10^{-5}$ mol dm^{-3} + 0·5 mol Na_2SO_4 dm^{-3}) solution. Dyes (initial concentration on cellulose $\times 10^{-2}$ mol kg^{-1}): Blue–Cu, □ ((a) 1·48); (b) 1·90; (c) 1·41); Blue 2, ● ((a) 1·44; (b) 1·36; (c) 1·36); Cu–Pc, ○ ((a) 0·294; (b) 0·235; (c) 0·246); Blue 19, ▽ ((a) 2·23; (b) 2·06; (c) 2·11).

indicate the reversible reduction of the quinone group for Blue 2 on exposure in the presence of substrate and by thermal reduction. The reduction of the amino group for Blue 2 on exposure may be viewed with suspicion because the first step of the reduction is reversible.

In a previous paper,[7] the reductive fading of C.I. Reactive Blue 19 on cellulose was explained according to the observations of Wegerle.[10] Blue 19, however, was confirmed as having a similar reversibility to that of Blue 2. The bond stability of the imino bridge groups between anthraquinonyl and phenyl nuclei of the leuco compound for Blue 19 was considerably lower than that for Blue 2. The fading behavior of aminoanthraquinone dyes thus remains to be fully elucidated.

3.2 Fading in an anaerobic DL-mandelate solution

The fading behavior of the three dyes on cellulose on exposure in anaerobic aqueous DL-mandelate (0·05 and 0·5 mol dm^{-3}) solutions is shown in Fig. 4. The order of the rates of fading on exposure, together with those of the other MCT dyes examined previously,[1] was as follows:

$$\text{Blue–2Cu} \doteqdot \text{Red 7} > \text{Blue–Cu} > \text{Brown} > \text{Red 4} > \text{Yellow R} > \text{Cu–Pc} > \text{Orange} > \text{Yellow} > \text{Blue 2} \quad (1)$$

Since the azo groups nearer the triazine ring are very easily photoreduced, Blue–Cu belongs to the dye type having low light-fastness to reductive fading. In spite of the higher concentration of DL-mandelate, Blue 2 and Cu–Pc showed slower reductive fading than Blue–Cu in the substrate solution. Blue 2 and Cu–Pc have high fastness to reductive fading.

In order to compare the rates of fading for C.I. Reactive Blue 19 with those for Blue 2, the fading behavior for Blue 19 on exposure under the same conditions is also shown in Fig. 4. The rates of reductive fading for Blue 19 were considerably higher than those for Blue 2, while the rates of oxidative fading were similar to each other.

3.3 Exposure in deaerated water

In contrast to other MCT dyes,[1] Blue 2, Blue–Cu, and Cu–Pc on cellulose underwent no fading on exposure in deaerated water as in the case of many VS dyes.[3] Because of the absence of fading of these dyes on cellulose in deaerated water, oxidative fading in the presence of oxygen (cf. Section 3.4.2), and photosensitized fading (cf. Section 3.4.1), it is concluded that the fading of these dyes occurs via a singlet-oxygen mechanism in the absence of substrate.

3.4 Exposure of MCT dyes on cellulose under aerobic conditions

3.4.1 Fading in aerated Rose Bengal solution

Blue–Cu, Blue 2, and Cu–Pc on cellulose were exposed in aerated Rose Bengal (RB) solution to obtain the photo-oxidation products by the photosensitization of RB. Cu–Pc and Blue 2 had too high a light-fastness for the complete oxidation products to be obtained; their absorption spectra may be drawn by subtracting the spectrum of the original dye of corresponding concentration from the spectra of the dyed film after exposure.

The photo-oxidation of azo dyes in the azo group may result in benzoquinone or naphthoquinone derivatives being bound to cellulose via the triazine ring.[11–13] On exposure in RB solution, Blue–Cu was photodecomposed to yield products showing an absorption spectrum in the UV region below 310 nm and a broad spectrum of very weak absorption in the visible region (Spectra 7–13 in Fig. 1). The broad visible band may be attributed to the formation of a monoazo compound from Blue–Cu, whose azo group further from the triazine ring was oxidized. In order to examine the photo-oxidation of the azo groups nearer the triazine ring, the dyed films exposed in RB solution for different times were thermally reduced with aqueous sodium dithionite (0·1 mol dm^{-3}, 70°C, 30 min). They gave a

spectrum very similar to that of the reduction product, the amount of which was not decreased with time of exposure. This fact implies that no photo-oxidation of the azo groups nearer the triazine ring occurs for Blue–Cu even on exposure in RB solution. The azo groups in Blue–Cu further from the triazine ring are photo-oxidized to give a monoazo intermediate, which may then be photoreduced on subsequent exposure. The fading behavior of Blue–Cu under aerobic conditions and in anaerobic substrate solution is explained by the considerable ease of photo-oxidation for the azo groups further from the triazine ring and of photoreduction of the azo groups nearer the triazine ring.

The absorption spectra of the photo-oxidation products for Cu–Pc and Blue 2 are shown in Figs 2 (Spectra 12–17) and 3 (Spectra 10–15). A decrease in the absorbance at λ_{max} for the two dyes on cellulose on exposure was confirmed to be proportional to the increase in absorbance of the photo-oxidation products.

Together with the other MCT dyes examined previously,[1] the rates of fading for MCT dyes on cellulose in RB solution were in the following order:

$$\text{Blue–Cu} > \text{Red 7} \gg \text{Blue–2Cu} > \text{Red 4} > \text{Yellow} > \text{Brown} > \text{Cu–Pc} \doteqdot \text{Yellow R} > \text{Orange} > \text{Blue 2} \quad (2)$$

Blue–Cu has very low stability to oxidative fading because the azo groups further from the triazine ring are highly oxidizable. The rate constants of reaction with singlet oxygen for MCT dyes have been estimated elsewhere.[2]

3.4.2 Fading in aerated water

The absorption spectra of the photodecomposition products for Blue–Cu on cellulose on exposure in aerated water were similar to those on exposure in aerated RB solution (Spectra 14–16 in Fig. 1), although the rates of fading in the former were lower than those in the latter. Thus fading of Blue–Cu in aerated water is due to the photo-oxidation of azo groups further from the triazine ring as the first step, followed by photoreduction of the azo groups nearer the triazine ring.

The absorption spectra for Cu–Pc and Blue 2 on cellulose after exposure showed that they also undergo oxidative fading in aerated water. The appearance of visible absorption in the photo-oxidation products for Cu–Pc on cellulose on exposure is inevitable owing to changes in the y/x ratio (Spectra 15–17 in Fig. 2), although they must have no absorption in this region (see below).

Shah and Srinivasan[14] and the present authors[3] have reported that Cu–Pc exists as a mixture of monomer and dimer in cellulose. The state of aggregation for Cu–Pc can be described by the y/x ratio (the ratio of the optical density at 630 nm for Cu–Pc to that at 675 nm). As shown in Fig. 5,

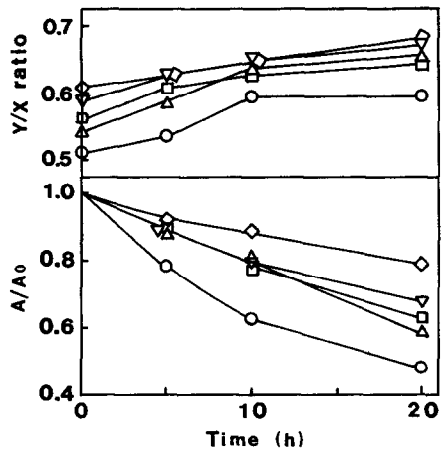


Fig. 5. Concentration-dependence of fading for Cu–Pc on cellophane at various concentrations under wet conditions and variation of the y/x ratio during fading. Concentrations of Cu–Pc on cellulose were (○) $5{\cdot}95 \times 10^{-4}$, (△) $1{\cdot}07 \times 10^{-3}$, (□) $1{\cdot}78 \times 10^{-3}$, (▽) $2{\cdot}35 \times 10^{-3}$, and (◇) $3{\cdot}65 \times 10^{-3}$ mol dm^{-1}.

the y/x values of dyed film increased with the concentration of Cu–Pc and further increased with the time of exposure. The higher the degree of aggregation, the higher was the light-fastness of Cu–Pc. However, it can be concluded from a series of these studies[1–4] that the chemical structure of the dye is the main factor that determines their light-fastness, the state of aggregation being a minor factor.

The absorption spectrum of Blue 2 on cellulose on exposure in aerated water is shown in Fig. 3 (Spectrum 16). It was similar to the spectra for oxidative fading in RB solution (Spectra 10–12). However, no photo-decomposition product remained on the cellulose, which implied that the alternative fading mechanism, where very slow fission of Blue 2 from cellulose occurs, may hold. This remains to be elucidated.

Together with the other MCT dyes examined previously,[1] the order of the rates of fading on exposure was as follows:

$$\text{Red 7} > \text{Blue–Cu} > (\text{Blue–2Cu}) > \text{Cu–Pc} > \text{Red 4} > \text{Yellow} > (\text{Brown}) > (\text{Orange}) > (\text{Yellow R}) > \text{Blue 2} \quad (3)$$

Although the dyes in parentheses undergo reductive fading in aerated water,[1] the rates of fading do not depend upon whether they show reductive or oxidative fading.

4 SUMMARY

The MCT dyes used in the present study underwent oxidative fading on exposure in aerated water and no fading in deaerated water. In the presence

of substrate, they showed multi-step photoreduction. On exposure in DL-mandelate solution, a copper phthalocyanine dye (Cu–Pc) and amino-anthraquinone dyes (Blue 2 and 19) formed reversible intermediates that partially reverted to the original form on thermal oxidation. The intermediates were further reduced on prolonged exposure, when phthalocyanine and anthraquinone nuclei were split off.

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