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The Influence of Histidine on the Color of Cu-Complex Azo Dyes on Cellulose

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ABSTRACT

On immersing cellophane films dyed with four reactive Cu-complex azo dyes in aqueous histidine, the copper atoms of the dyes were abstracted by the histidine and the absorption spectra of the dyes were changed with time depending upon the conditions of immersion. After the abstraction of the copper atoms, the absorption spectra varied also with the pH of the aqueous solutions in which the dyed film was re-immersed. From the spectral variations with pH, the values of pK_{a1} *and* pK_{a2} *(*K_{a1} *and* K_{a2}*: the first and second acid dissociation constants) of the hydroxyl or carboxyl group in the dyes were estimated. The smaller the values of* pK_{a1}*, the larger the rates of copper abstraction, when the dyes examined have a common ligand center. Copyright © 1996 Elsevier Science Ltd*

1 INTRODUCTION

It was reported in previous papers[1,2] that histidine undergoes additional adsorption caused by coordination to the copper atom of a Cu-complex azo dye on cellulose, beyond the ordinary adsorption on cellulose, on immersing the dyed film in aqueous histidine. On this coordination, copper atoms to which the oxo ligands of the dye are coordinated may be initially coordinated also by histidine, and the oxo ligands then substituted by histidine to generate

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o-hydroxyl groups.[2] In spite of the color variation observed with Blue-Cu, immersion in aqueous histidine gave no abstraction of copper, but regeneration of hydroxyl groups.[2] As a result, Blue-Cu on dyed films re-immersed in buffer solutions at different pH values showed acid dissociation behavior in the absorption spectra, indicating dissociation of the hydroxyl groups of the dye. The additional adsorption of histidine was also observed on cellophane dyed with Blue-Cu even after the completed color variation on immersion in aqueous histidine, although the adsorption depended upon the pH of the aqueous histidine in which the dyed films were immersed.

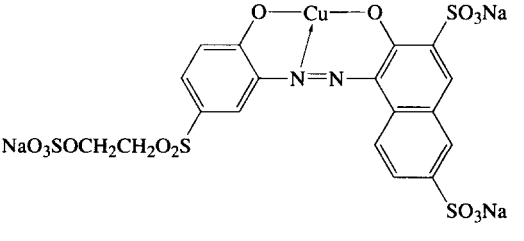
It has been considered, however, that on the immersion in aqueous histidine, histidine coordinates to the copper atom of Cu-complex azo dyes on the fiber to abstract the atom.[3] In the present study, therefore, we have examined how the absorption spectra of two vinylsulfonyl (VS) and two monochlorotriazinyl (MCT) reactive Cu-complex azo dyes on cellulose vary with time on immersing the dyed films in aqueous histidine and ethylenediaminetetraacetic acid (EDTA) at different pH values. The abstraction of copper atoms from various Cu-complex azo dyes on cellulose is investigated by spectral variations of the dyes. The spectral variations of the dyes with pH after the abstraction of copper atoms by histidine and EDTA are also examined in order to determine the values of pK_{a1} and pK_{a2} (K_{a1} and K_{a2}: the first and second acid dissociation constants). The results for the four dyes which are examined in the present study are compared with the results for Blue-Cu, reported in previous papers.[1,2]

2 EXPERIMENTAL

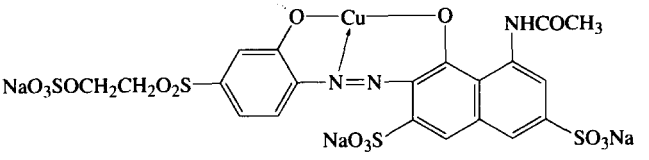
2.1 Dyes used

Three VS reactive dyes, CI Reactive Red 23, CI Reactive Violet 5, and a Cu-complex azo dye (Blue-Cu[1,2]), supplied by DyStar Japan Ltd, and two MCT dyes, a 1 : 1 Cu-complex disazo dye and a 2 : 1 Cu-complex disazo dye, supplied by Nippon Kayaku Co. Ltd, were used. They were used without further purification for dyeing. Their structures are shown below:

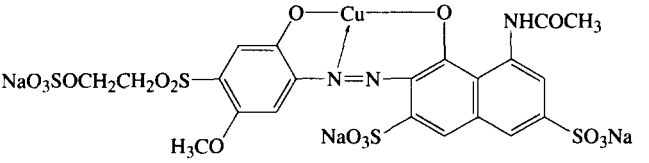
(1) CI Reactive Red 23; CI 16202



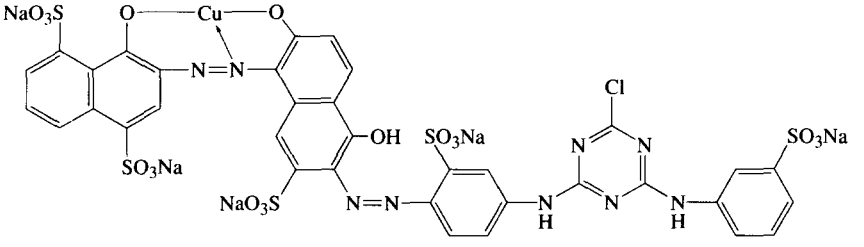
(2) CI Reactive Violet 5; CI 18097



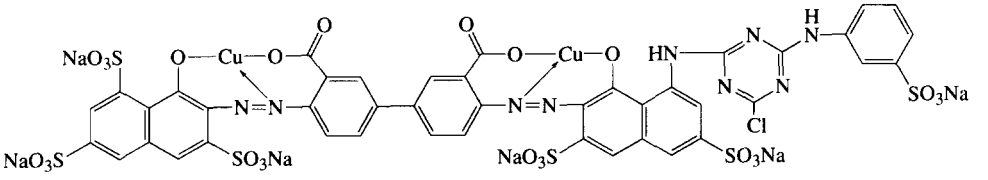
(3) A Cu-complex azo dye (Blue-Cu)



(4) A 1 : 1 Cu-complex disazo dye (Blue-1Cu)



(5) A 2 : 1 Cu-complex disazo dye (Blue-2Cu)



2.2 Dyeing of cellophane and immersion of the dyed films in aqueous histidine and EDTA

Cellophane sheets were dyed by the previously reported method.[4,5] The dyed film, treated by the given conditions for purification, was immersed in aqueous histidine and EDTA at various pH values.[1,2] The absorption spectra of the dyed cellophane were measured, usually in the wet state, using a Ubest 50 spectrophotometer (Jasco Corp.).

3 RESULTS AND DISCUSSION

3.1 Spectral variations of dyed film in aqueous chelating agent

3.1.1 o,o'-*Dihydroxyazo Cu-complex VS dyes*

The light absorption of CI Reactive Red 23 and CI Reactive Violet 5 on the dyed film immersed in aqueous histidine of 0·0050 mol dm^{-3} (+ NaCl 0·050 mol dm^{-3}) at pH 9 and 10 slowly increased with time of immersion on the long wavelength side of the main band and with a red shift of λ_{max} (Figs 1 and 2). Spectral variations occurred more rapidly with increase in the pH of the solution and in the concentration of histidine. Full variations of spectra were attained on immersing in aqueous histidine at pH 9 and 25°C for two days for CI Reactive Violet 5 and for 10 days for CI Reactive Red 23, while Blue-Cu took four days[2] (Table 1). After this, both CI Reactive Red 23 and CI Reactive Violet 5 gave absorption spectra differing with pH,

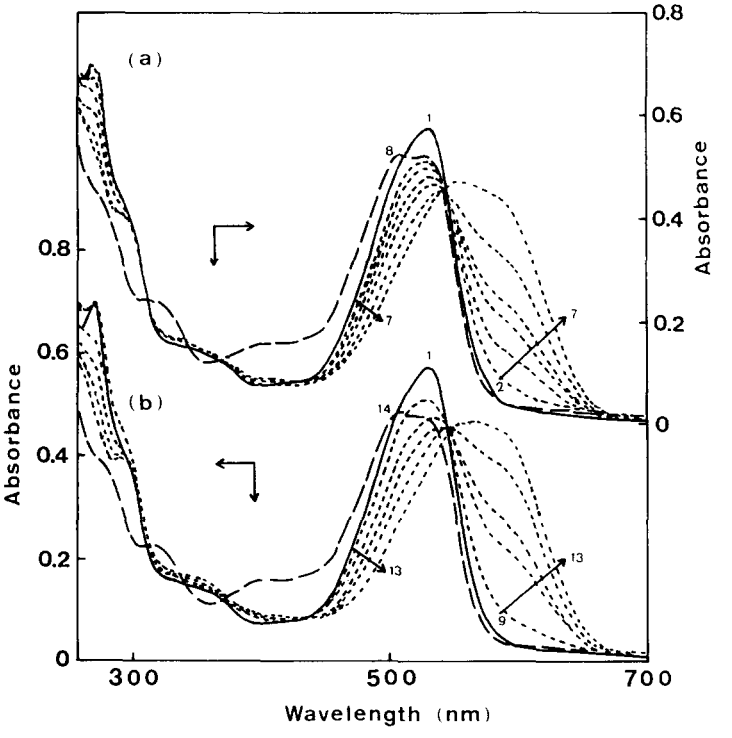


Fig. 1. (a) Absorption spectra of CI Reactive Red 23 (1) ($9{\cdot}49 \times 10^{-3}$ mol kg^{-1}) on dyed cellophane immersed in aqueous histidine of 0·0050 mol dm^{-3} (+ NaCl 0·050 mol dm^{-3}) at pH 9·03 for 40 min (2), 24 h (3), 48 h (4), 4 days (5), 6 days (6), and 10 days (7), and then dipped in water for 24–48 h (8), and (b) absorption spectra of the dyed film (1) immersed in the same solution at pH 10·02 for 40 min (9), 24 h (10), 48 h (11), 4 days (12), 6–10 days (13), and then dipped in water for 24–48 h (14).

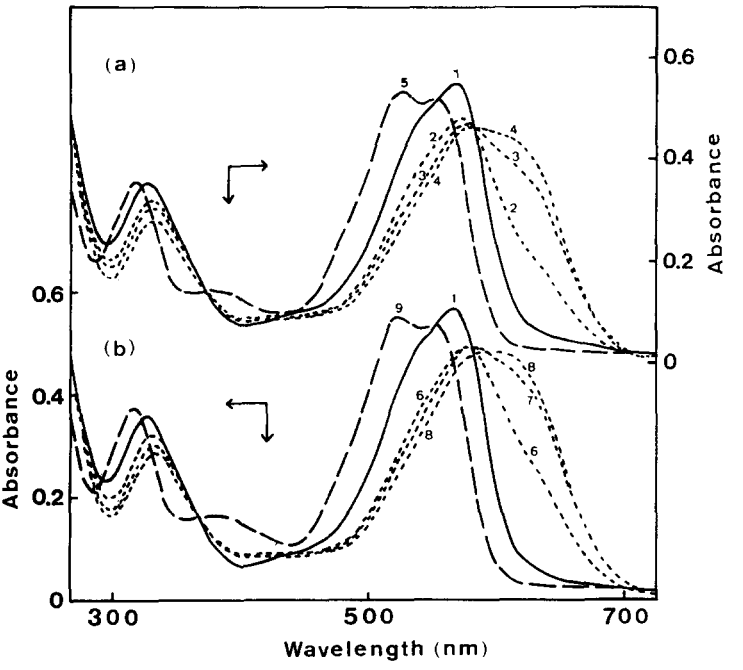


Fig. 2. (a) Absorption spectra of CI Reactive Violet 5 (1) ($8{\cdot}74 \times 10^{-3}$ mol kg^{-1}) on dyed cellophane immersed in aqueous histidine of 0·0050 mol dm^{-3} (+ NaCl 0·050 mol dm^{-3}) at pH 9·03 for 40 min (2), 24 h (3), 48 h (4), and then dipped in water for 48 h (5), and (b) absorption spectra of the dyed film (1) immersed in the same solution at pH 10·02 for 40 min (6), 24 h (7), 48 h (8), and then dipped in water for 48 h (9).

TABLE 1

Values of pK_{a1} and pK_{a2} for the Dissociation of Substituents, (i.e. Hydroxyl, Carboxyl etc.), of Dyes on Cellulose, and Time for Full Color Change of Dyed Films on Immersion in Aqueous Histidine

Dye	*Values[a] of pK_{a1} and pK_{a2}*	*Time for complete color change[b]*	*Figs to be referred to*
Red 23	7·0,11·8	10 days	1, 3, 7
Violet 5	7·2,11·5	2 days	2, 6
Blue-Cu	8·0,>14	4 days	4, 5 of Ref. (2)
Blue-2Cu	4·2,*c*.13·5	< 5 min	4, 7
Blue-1Cu	7·4,14·5–15	Undetermined[c]	5, 7

[a]Estimated from color variation with pH at 25°C after the copper abstraction.
[b]At pH 9·03 in aqueous histidine of 0·0050 mol dm^{-3} (+0·050 mol dm^{-3} NaCl) at 25°C.
[c]See Sec. 3.1.3.

implying a change in the dissociation of the hydroxyl groups on re-immersing the films in buffer solutions of different pH values (cf. 3.3).

In order to examine whether or not the copper atoms of the dyes on cellulose were abstracted by histidine and EDTA on immersing the dyed films in the aqueous solutions, the immersed films were re-immersed in solutions of sodium peroxodicarbonate and copper(II) sulfate, as was reported for Blue-Cu.[2] The variations in the absorption spectra after the re-immersion are

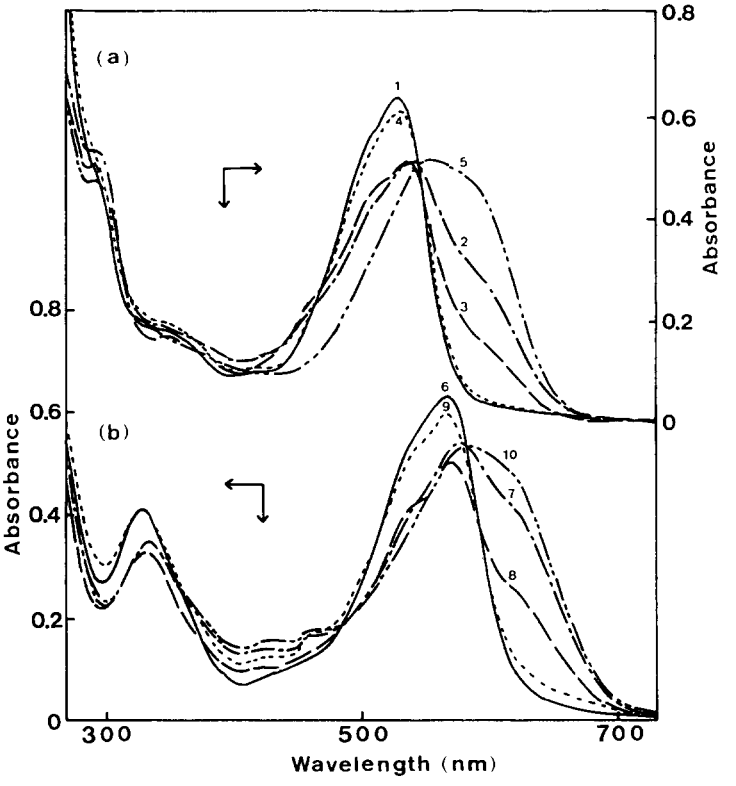


Fig. 3. (a) Absorption spectra of CI Reactive Red 23(1) ($1{\cdot}02 \times 10^{-2}$ mol kg^{-1}) on dyed cellophane immersed in aqueous histidine of 0·050 mol dm^{-3} (+ NaCl 0·050 mol dm^{-3}) at pH 11·01 for 48 h (2) and then dipped in aqueous sodium peroxodicarbonate (0·10%) for 30 min (3), or in copper(II) sulfate solution (0·10 mol dm^{-3}) for 30 min (4), and absorption spectra of the same dyed film immersed in aqueous EDTA (0·050 mol dm^{-3}) at pH 12·00 for 6 h (5) and then dipped in aqueous sodium peroxodicarbonate (0·10 %) for 30 min (3), or in copper(II) sulfate solution (0·10 mol dm^{-3}) for 30 min (4), and (b) absorption spectra of CI Reactive Violet 5 (6) ($1{\cdot}02 \times 10^{-2}$ mol kg^{-1}) on the dyed film immersed in aqueous histidine (0·050 mol dm^{-3} + NaCl 0·050 mol dm^{-3}) at pH 11·01 for 48 h (7) and then dipped in aqueous sodium peroxodicarbonate (0·10%) for 30 min (8), or in copper(II) sulfate solution (0·10 mol dm^{-3}) for 30 min (9), and absorption spectra of the same dyed film immersed in aqueous EDTA (0·050 mol dm^{-3}) at pH 12·00 for 6 h (10) and then dipped in aqueous sodium peroxodicarbonate (0·10 %) for 30 min (8), or in copper(II) sulfate solution (0·10 mol dm^{-3}) for 30 min (9). (The same spectra, spectra 3 and 4, and 8 and 9, were obtained in both cases.)

shown in Fig. 3(a) for CI Reactive Red 23 (spectra 2–4 in the case of histidine and spectra 3–5 in the case of EDTA) and in Fig. 3(b) for CI Reactive Violet 5 (spectra 7–9 for histidine and spectra 8–10 for EDTA). When cellulose films dyed with two VS dyes were immersed in aqueous EDTA of 0·050 mol dm^{-3} at pH 12·0, the abstraction of copper atoms from the dye was confirmed by the absorption spectra, implying that the treatment of the immersed films with aqueous copper(II) sulfate regenerated the original dyes, but that treatment with aqueous sodium peroxodicarbonate did not. The incomplete reversion to the original dyes by peroxodicarbonate spectra (2 (or 5) and 3 for CI Reactive Red 23 and spectra 7 (or 10) and 8 for CI Reactive Violet 5 in Fig. 3) could indicate the coexistence of the histidine or EDTA coordinated species of Cu-complex dyes as the first stage of copper abstraction, as in the case of Blue-Cu. On immersing the dyed films in aqueous histidine, the two VS days showed the same spectral variations as those observed in the case of EDTA, as shown in Fig. 3 (see figure caption), implying a similar abstraction of copper atoms by histidine and by EDTA, although the conditions of immersion were different.

When garments dyed with Cu-complex azo dyes are soaked with sweat, color variations caused by the coordination of histidine will occur, but whether or not, and how rapidly, if at all, the copper atoms in dyes on garments are abstracted in practice may be difficult to infer. It may depend upon the various conditions of wetting the garments with perspiration. Dyes showing color variation over a shorter time (cf. Table 1) may show a faster color change in practice, under comparable conditions of soaking with sweat.

Factors which determine the order of the rate of color variations for these VS dyes are discussed in Section 3.3.

3.1.2 o,o'-*Carboxyhydroxyazo Cu-complex MCT dye (Blue-2Cu)*

Spectral variations of Blue-2Cu on cellulose immersed in aqueous solutions of histidine (spectra 1 and 2) and EDTA (spectra 1, 4 and 5) are shown in Fig. 4(a) and (b). Completed color changes brought about by histidine were attained within 5 min on immersing in the same aqueous histidine as the other dyes, while that by EDTA required one day (see below). The spectral variations in the neutral region were small for Blue-2Cu, since the variations due to the dissociation of carboxyl or hydroxyl groups occur at pH 2–4 and above pH 12 (cf. 3.3.2). The abstraction of copper by histidine as well as EDTA was proved by the complete regeneration of the absorption spectra of the original dye by the treatment with aqueous copper(II) sulfate, as well as by the absence of spectral variations or the non-regeneration of the spectra by aqueous sodium peroxodicarbonate (spectra 2 and 3 of Fig. 4(a), and spectra 5 and 6 of Fig. 4(b)). The same absorption spectra were obtained, after immersing in aqueous histidine or EDTA, in the three cases: viz. (i) by immersing in

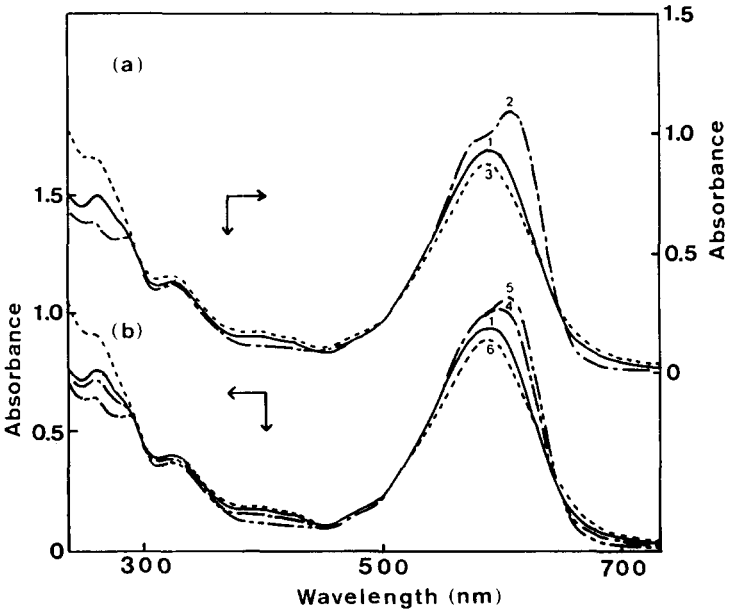


Fig. 4. (a) Absorption spectra of Blue-2Cu (1) ($8{\cdot}18 \times 10^{-3}$ mol kg^{-1}) on dyed cellophane immersed in aqueous histidine of 0·0050 mol dm^{-3} (+ NaCl 0.050 mol dm^{-3}) at pH 9·02 for 5 min–24 h (2); the specrum for the sample of spectrum 2 after washing in water for 2 h (2); and the spectra of the same sample on immersing in aqueous sodium peroxodicarbonate (0·10 %) for 60 min (2) and in $CuSO_4$ solution (0·010 mol dm^{-3}) for 30 min (3) at 25°C, and (b) absorption spectra of Blue-2Cu (1) ($8{\cdot}18 \times 10^{-3}$ mol kg^{-1}) on the dyed film immersed in EDTA (0·0050 mol dm^{-3} + NaCl 0·050 mol dm^{-3}) solution at pH 9·03 for 4 h (4), 1–3 days (5); the spectrum for the sample of spectrum 5 after washing in water for 2 h (5); and the spectra of the same sample on immersing in aqueous sodium peroxodicarbonate (0·10 %) for 60 min (5) and in the $CuSO_4$ solution (0·010 mol dm^{-3}) for 30 min (6) at 25°C.

aqueous histidine or EDTA at pH 9, (ii) by washing in water after the immersion, and (iii) by immersing in peroxodicarbonate solution, because the Cu-abstracted species of Blue-2Cu shows no spectral change within these conditions of immersion.

It is notable that the abstraction by EDTA is much slower than that by histidine, unlike the other dyes. The slow abstraction by EDTA may be attributable to the specific coordination of histidine to this type of Cu-complex, as well as to the special structure of this dye, as noted below.

Copper is hexavalent, taking an octahedral structure in copper(II)-histidine complexes.[6–12] On the other hand, polar positions and one position of the square planar configuration may be vacant in *o,o'*-dihydroxyazo Cu-complex dyes, which occupy three positions of a square planar configuration as a tridentate form.[13,14] During the progress of the abstraction on immersion of the dyed film, copper may exchange either of the *o*-oxo ligands of the dyes

for histidine, when copper atoms are coordinated by both the dye and histidine, which may donate hydrogen to the oxo ligands. At this stage, additional adsorption of histidine on the dyed film may be observed. In the case of Blue-Cu, no further ligand exchange for histidine proceeded,[2] but in the case of CI Reactive Red 23 and CI Reactive Violet 5, copper may also exchange the second *o*-oxo ligands for histidine, resulting in the abstraction of copper by histidine which acts as a tri- or bi-dentate ligand on coordination to the copper atom giving a 1 : 1 or 1 : 2 copper(II)-histidine complex in the immersing solution.[6–12]

Blue-2Cu is a 2 : 1 Cu-complex dye with two *o,o'*-carboxyhydroxyazo centers, a system which forms many stereoisomers in the case of 1 : 2 Cr- or Co-complex dyes.[13,14] *o,o'*-Carboxyhydroxyazo tridentate ligands can take one of four kinds of configuration, viz. one meridial configuration to give only one Drew–Pfitzner type stereoisomer, and three facial configurations to give five Pfeiffer–Schetty (sandwich-type) stereoisomers, although they take the configurations as in the case of 1 : 2-type metal complex, but with copper as the complexing metal. Since histidine ligands would occupy the neighboring two positions of the square planar configuration of the copper(II) atoms,[6–12] histidine may be able to coordinate to the Cu-atom in Blue-2Cu without substituting the oxo or carboxo ligand, except for the meridial configuration, and then abstract the copper atoms with ease. Moreover, since *o,o'*-carboxyhydroxyazo complexes have a lower stability than *o,o'*-dihydroxyazo complexes,[14–20] the copper atoms of Blue-2Cu may be abstracted more easily by histidine.

On the other hand, since copper(II) and ethylenediaminetetraacetic acid disodium salt formed a monoaquo pentadentate octahedral complex,[21,22] the coordination of EDTA to the copper atom of the dye, which was accompanied by abstraction of the copper atom, may require complete ligand exchange for Blue-2Cu on immersing in aqueous EDTA, and it is for this reason that the rate of abstraction by EDTA is slower than that by histidine, unlike the case with the other dyes.

3.1.3 o,o'-*Dihydroxyazo Cu-complex MCT dye (Blue-1Cu)*

Figure 5(a) shows the unusual spectral variations of cellophane films dyed with Blue-1Cu immersed in aqueous histidine of 0·050 mol dm^{-3}, unlike that with the other dyes. The immersion of the dyed films gave a slow decrease in the main absorption band of Blue-1Cu on cellulose and gradual increases in the absorption in the visible (λ_{max} = 530 nm) and UV (<230 nm) regions (the UV part of the spectra are not shown in the figure), implying that azo groups (the second ones from the triazinyl groups) may be partially decomposed, but the triazinyl groups bound with cellulose may remain intact. Increase of the absorption near 700 nm attained a maximum (Fig. 5(a), spectra 3–5), after which a decrease was observed (spectrum 6).

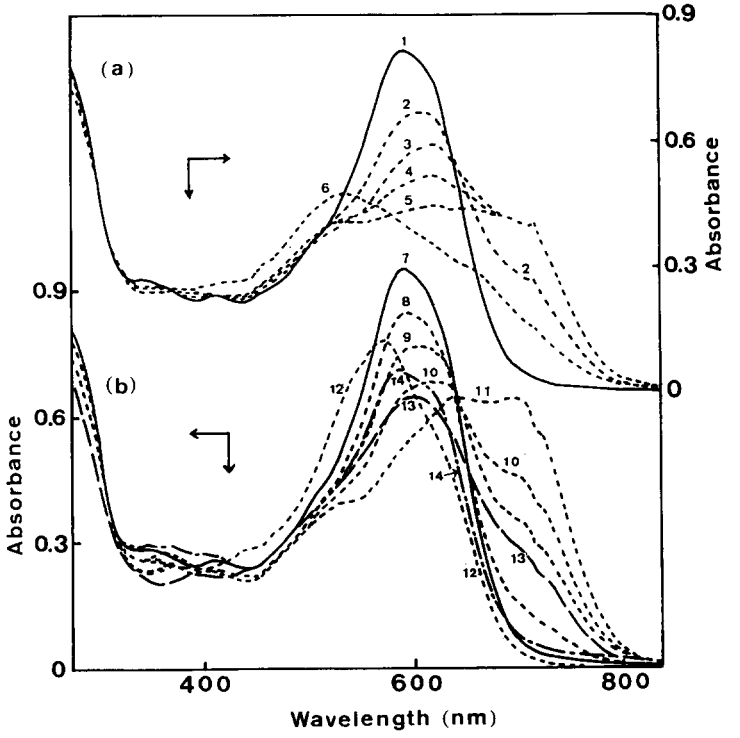


Fig. 5. (a) Absortion spectra of Blue-1Cu (1) ($1{\cdot}28 \times 10^{-2}$ mol kg^{-1}) on dyed cellophane immersed in aqueous histidine of 0·050 mol dm^{-3} (+ NaCl 0·050 mol dm^{-3}) at pH 10·01 for 30 min (2), 4 h (3), 24 h (4), 48 h (5), and 15 days (6), and (b) absorption spectra of Blue-1Cu (7) ($1{\cdot}42 \times 10^{-2}$ mol kg^{-1}) on the dyed film immersed in an EDTA (0·0050 mol dm^{-3} + NaCl 0·050 mol dm^{-3}) solution at pH 9·03 for 4 h (8), 24 h (9), 48 h (10), and 7 days (11); the spectrum for the sample of spectrum 11 after washing in water for 2 h (12); and the spectra of the sample of spectrum 12 on immersing in aqueous sodium peroxodicarbonate (0·10 %) for 60 min (13) and in $CuSO_4$ solution (0·010 mol dm^{-3}) for 30 min (14) at 25°C.

In addition to the above decreases, the abstraction of copper atoms of Blue-1Cu by histidine, as well as the coordination of histidine to the copper atom were observed, as shown by the increase in the absorption on the long wavelength side of λ_{max}, as in the case of CI Reactive Red 23 and CI Reactive Violet 5 (Fig. 5(a), spectra 2–5). Moreover, the abstraction of the copper atom, and the partial decomposition, were also confirmed by the following observations. Treatment of the dyed films, which had been previously immersed in aqueous histidine, in aqueous sodium peroxodicarbonate gave an incomplete reversion in the shape of the absorption spectra to the original dye (Fig. 5(b), spectrum 13), but treatment in aqueous copper(II) sulfate showed complete reversion in the spectrum shape (spectrum 14), although

the intensity of the main absorption band was considerably reduced. However, immersion of the dyed films in buffer solution at pH 10 gave little decrease in the main band. Histidine and EDTA seem to possess a low ability to reduce the azo groups furthest from the triazine ring in Blue-1Cu. The partial abstraction of copper atom on immersing in aqueous histidine was proved by comparing the spectral variations with those of the immersion in EDTA solution (spectra 5 and 11). It was also observed, as for the other dyes except for Blue-2Cu, that EDTA abstracted the copper atoms faster than histidine.

Since the copper atom abstraction was accompanied by simultaneous decomposition of the dye, the immersion of dyed films in an aqueous EDTA of lower concentration (0·005 mol dm^{-3}) reduced the decomposition. However, only incomplete abstraction was attained despite prolonged immersion, although the decrease in the main band became smaller than that observed with immersion in aqueous histidine of 0·05 mol dm^{-3}, as shown in Fig. 5(b). It was impossible, therefore, to estimate accurately the rate of abstraction from the change in absorbance, since some decomposition simultaneously occurred.

3.2 Re-immersion of dyed films in buffer solutions

After the attainment of the full color change in aqueous histidine, on re-immersion of the dyed film, in buffer solutions at different pH values, the absorption spectra also varied with pH, as shown in Fig. 6(a) for CI Reactive Violet 5 as an example. Before the immersion of the dyed cellophane in aqueous histidine or EDTA, no variation of absorption spectrum was observed by immersion in buffer solutions except for the case of Blue-1Cu.

3.2.1 Cu-complex VS dyes

When the absorbance at the λ_{max} of the dye is plotted against pH to give a 'spectrophotometric titration curve of neutralization reaction,' the value of pK_{a1} for CI Reactive Violet 5 can be estimated from Fig. 6(b). From the 'titration curve' for CI Reactive Violet 5 below pH 9, the pK_{a1}-value was estimated to be 7·2 and that of pK_{a2} in the alkaline region to be 11·5.

Similar plots for CI Reactive Red 23 are shown in Fig. 7; the values of pK_{a1} and pK_{a2} estimated from the figures are summarized in Table 1.

3.2.2 Cu-complex MCT dyes

The variations of absorbance for Blue-1Cu and Blue-2Cu on re-immersion of the dyed film in buffer solutions at different pH values are shown in Fig. 7. The value of pK_{a1} for Blue-2Cu was estimated to be 4·2, the smallest value of the dyes examined. This factor may be responsible for the instantaneous

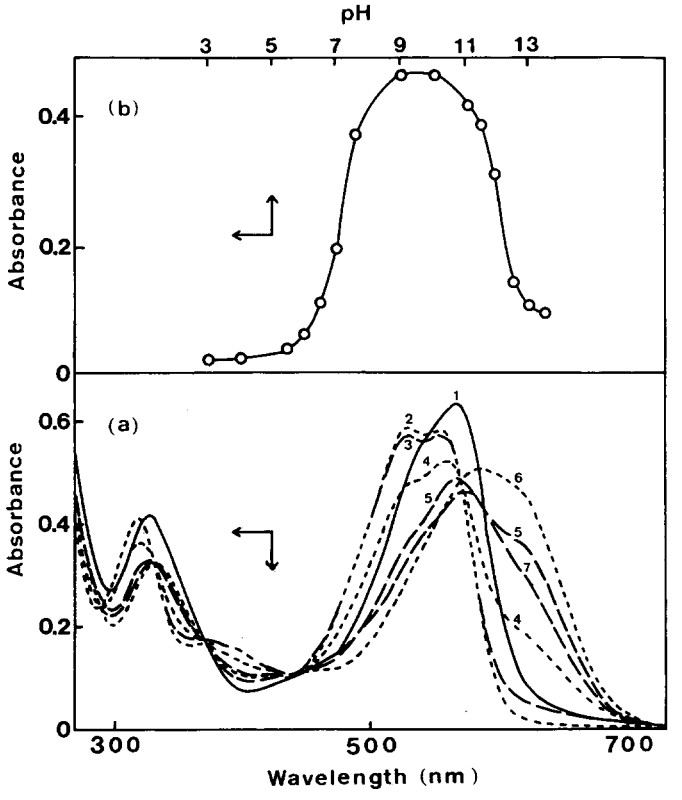


Fig. 6. (a) Absorption spectra of CI Reactive Violet 5 (1) ($1{\cdot}01 \times 10^{-2}$ mol kg^{-1}) on dyed cellophane, after being immersed in aqueous histidine of 0·050 mol dm^{-3} (+ NaCl 0·050 mol dm^{-3}) at pH 11·01 for 2 days and being washed in water for 2 h, then dipped in buffer solution at pH 3·01 (2), pH 6·01 (3), pH 7·00 (4), pH 7·60 (5), pH 10·01 (6), and pH 12·00 (7), and (b) plots of the absorbance at 615 nm (○) for CI Reactive Violet 5 on the cellophane immersed in various buffer solutions against pH.

abstraction of copper atoms for this dye. The value of pK_{a2} for Blue-2Cu was estimated from the starting point of the 'titration curve' to be *c*13·5. Since the structure of Blue-2Cu is not symmetric, this dye may have four dissociation constants. The dissociation at pH 4·2 may be attributed to that of the carboxyl groups, both of which have almost the same dissociation constant values. A similar state of affairs may be inferable for the dissociation behavior of Blue-2Cu near pH 13·5, which may be due to the two different hydroxyl groups.

In case of Blue-1Cu, little spectral variation of the original dyed film was observed on immersion in various buffer solutions below pH 13, but a large variation in the absorption spectra on cellophane was found at pH 14, as shown in Fig. 7. From the starting point of 'titration curve,' a very high

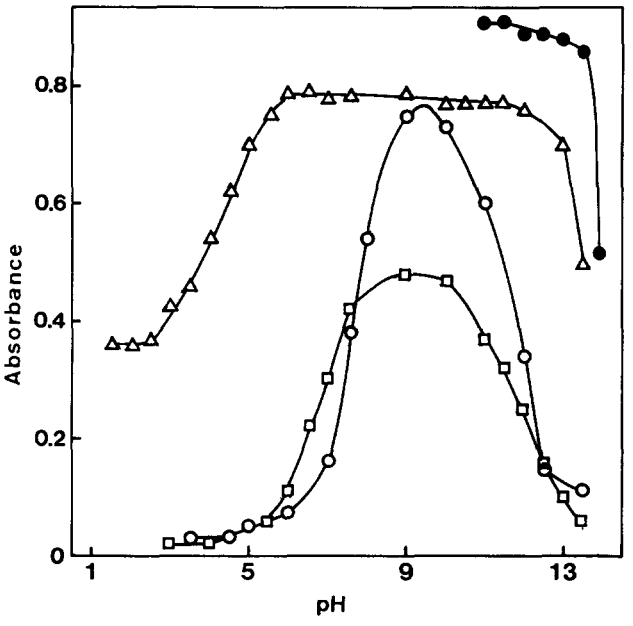


Fig. 7. Relationships between the absorbance at 588 nm (□) for CI Reactive Red 23 ($1{\cdot}02 \times 10^{-2}$ mol kg^{-1}), at 700 nm (○) for Blue-1Cu ($1{\cdot}43 \times 10^{-2}$ mol kg^{-1}), and at 630 nm (△) for Blue-2Cu ($7{\cdot}82 \times 10^{-3}$ mol kg^{-1}) on cellophane, after being immersed in aqueous histidine (0·050 mol dm^{-3}) at pH 11·01 for 2 days and then being washed in water for 2 h, and the pH in which the dyed film was immersed, and the same relationship at 592 nm (●) for original Blue-1Cu ($1{\cdot}43 \times 10^{-2}$ mol kg^{-1}) on cellophane as dyed (see text).

value of pK_a (*c*.15) was estimated. This may be attributed to the dissociation of free hydroxyl groups in the intermediate 2,5-bis(arylazo)-1-naphthol. The value may be too high to determine precisely, because of the stabilization of the hydroxyl group by hydrogen bond formation.

After the abstraction of the copper atom, Blue-1Cu has three kinds of hydroxyl groups. The acid dissociation constant of the hydroxyl groups nearest the triazine ring may be changed by the abstraction the copper atom. The value of pK_{a1} was estimated from the 'titration curve' to be 7·4, irrespective of the incomplete abstraction of the copper atom. This dissociation may be attributed to the hydroxyl group of the α-naphthol moiety furthest from the triazine ring. The 'titration curve' above pH 10 looks unsymmetrical, and superposition of the dissociation for the hydroxyl groups of the α- and β-naphthol residues may exist, but from the 'titration curve' and the end point, a value of 11·5 was estimated, as shown in Table 1.

It was not possible to estimate the value of pK_{a3} for the hydroxyl groups in the intermediate 2,5-bis-(arylazo)naphthol because of its high value, as in the case before the abstraction.

3.3 Stability of Cu-complex dyes and the rates of color variation

The values of pK_{a1} for many dyes, which may correspond to the dissociation of the hydroxyl groups for naphthols, except for Blue-2Cu, were estimated to be within a narrow, neutral or weakly alkaline, range. This is the reason why Cu-complex azo dyes on cellulose show large color variations, due to the dissociation of hydroxyl groups which are generated by the coordination of histidine on immersing in weakly alkaline aqueous histidine.

The order of the rates of coordination followed by the gradual abstraction of copper viz., Blue-2Cu > CI Reactive Violet 5 > Blue-Cu > CI Reactive Red 23, was estimated by the color variation of dyed films immersed in aqueous histidine under a defined condition as summarized in Table 1. On the other hand, it has been noted that the most acidic dye forms the least stable complex in a strictly comparable series of ligands.[17–22] By comparing the above order for the rates of color variations by histidine with the values of pK_{a1} estimated in this present study, this observation seems to hold, except for CI Reactive Red 23, since these three dyes consist of 2-(*o*-hydroxy- or *o*-carboxyphenylazo)-l-naphthols having a common center of an *o,o'*-dihydroxy- or *o,o'*-hydroxycarboxyphenylazo ligand. CI Reactive Red 23, with a ligand center of 1-(*o*-hydroxyphenylazo)-2-naphthol, has a greater stability than the three dyes with a 1-naphthol center.

The second values of pK_{a2}, on the other hand, seem to have no correlation with the stability of the metal complex dyes. The copper atoms of Blue-Cu, which has the highest pK_{a2} value, could not be abstracted by aqueous histidine. The second values may thus contribute partially to the stability of metal-complex dyes.

4 SUMMARY

On immersing cellulose film dyed with Cu-complex azo dyes in aqueous histidine, the rates of variation in the absorption spectra of the dyes change widely depending upon their chemical structure. On immersion, histidine coordinates to the copper atoms and abstracts them from the dyes. Thus, when cellulose garments dyed with Cu-complex azo dyes are sweated, the dyes on fabrics undergo irreversible structural changes, the extent of which depends upon the sweating and environmental conditions. Since there are no methods of preventing the coordination of histidine to copper atoms in the Cu-complex dyes on cellulose, it is therefore advantageous to wash the garments as frequently as possible after they have been exposed to perspiration.

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REFERENCES

1. Okada, Y., Kawanishi, T., Motomura, H. & Morita, Z., *Dyes and Pigments*, **24** (1994) 99.
2. Okada, Y., Kawanishi, T. & Morita, Z., *Dyes and Pigments*, **27** (1995) 271.
3. Bühler, M., *Melliand Textilber.*, **39** (1958) 285.
4. Okada, Y, Kato, T., Motomura, H. & Morita, Z., *Dyes and Pigments*, **12** (1990) 197.
5. Okada, Y., Satoh, E., Motomura, H. & Morita, Z., *Dyes and Pigments*,, **12** (1992) 1.
6. Sundberg, R. J. & Martin, R. B., *Chem. Rev.*, **74** (1974) 471.
7. Kruck, T. P. A. & Sarkar, B., *Can. J. Chem.*, **51** (1973) 3563.
8. Camerman, N., Fawcett, J. K., Kruck, T. P. A., Sarkar, B. & Camerman, A., *J. Am. Chem. Soc.*, **100** (1978) 2690.
9. Ono, T., Shimanouchi, H., Sasada, Y., Sakurai, T., Yamauchi, O. & Nakahara, A., *Bull. Chem. Soc. Jpn*, **52** (1979) 2229.
10. Yamauchi, O., Sakurai, T. & Nakahara, A., *J. Am. Chem. Soc.*, **101** (1979) 4164.
11. Cassella, L. & Gullotti, M., *J. Inorg. Biochem.*, **18** (1983) 19.
12. Sasada, Y., Takenaka, A. & Furuya, T., *Bull. Chem. Soc. Jpn*, **56** (1983) 1745.
13. Zollinger, H., in *Color Chemistry*, 2nd rev. edn, Sec. 7.11. VCH, Weinheim, 1991.
14. Gordon, P. F & Gregory, P., in *Organic Chemistry in Colour*, Sec. 3.4. Springer, Berlin, 1983.
15. Johnson, A., Mort, M. S., Peters, R.H. & Wada, M. J., *Tex*, **21** (1962) 453.
16. Snavely, F. A., Fernelius, W. C. & Douglas, B. E., *J. Soc. Dyers Colour.*, **73** (1957) 491.
17. Snavely, F. A., Fernelius, W. C. & Block, B. P., *J. Am. Chem. Soc.*, **79** (1957) 1028.
18. Snavely, F. A., Krecker, B. D. & Clark, C. G., *J. Am. Chem. Soc.*, **81** (1959) 2337.
19. Snavely, F. A. & Krecker, B. D., *J. Am. Chem. Soc.*, **81** (1959) 4199.
20. Snavely, F. A., Trahanovsky, W. S. & Suydam, F. H., *Inorg. Chem.*, **3** (1964) 123.
21. Smith, G. S. & Hoard, J. L., *J. Am. Chem., Soc.*, **81** (1959) 556.
22. Lee, B., *Inorg. Chem.*, **11** (1972) 1072.