ELSEVIER

Dyes and Pigments, Vol. 27, No. 4, pp. 271–285, 1995

0143-7208/95 $9.50 + 0.00

0143-7208(94)00057-3

Adsorption of Histidine on Cellulose and its Effect on Histidine Coordination to Copper-Complex Azo Dyes on Cellulose

Yasuyo Okada,* Takako Kawanishi

School of Domestic Science, Ohtsuma Women's University, Sanban-cho, Chiyoda-ku, Tokyo 102, Japan

&

Zenzo Morita

School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

(Received 8 August 1994; accepted 12 September 1994)

ABSTRACT

The adsorption of histidine on cellophane and on film dyed with a Cu-complex azo dye (Blue-Cu) and other dyes was measured from aqueous histidine at 25°C. In addition to the adsorption of histidine on cellophane, and on film dyed with CI Reactive Red 22, a copper phthalocyanine dye, or a formazan dye, additional adsorption was observed on the film dyed with Blue-Cu. On immersion of the dyed films in aqueous histidine, the complete variation of the absorption spectra of Blue-Cu on the film occurred over a long period of time. Histidine adsorbed by both of the films was readily desorbed by dipping them in water. When histidine coordinated to the Cu-complex dyes on cellulose, substitution of the histidine ligand for the oxo one occurred, giving spectral variations dependent on the pH of the aqueous solution in which the dyed film was immersed. The substituted dyes on cellulose reverted to the original dye on oxidation with aqueous sodium peroxodicarbonate. On immersing cellophane dyed with Blue-Cu in aqueous EDTA, the copper atom in the dye was abstracted. Unlike the case of histidine, the original absorption spectra were regenerated by treatment with aqueous $CuSO_4$ but not by treatment with aqueous peroxodicarbonate.

* To whom correspondence should be addressed.

1 INTRODUCTION

Histidine shows multiple dissociation behavior in aqueous solution depending upon the pH, i.e. five species of different dissociation, $HisH_2^{2+}$, $HisH^+$, His, His^- and His^{2-} (cf. Fig. 1 of Ref. 1). At least three species of these five species formed the 1 : 1 coordination complex with a Cu-complex azo dye, with different stability constants not only in the aqueous solution but also on cellulose immersed in aqueous histidine.[1] These species of histidine showed different adsorption on cellulose depending upon the pH. The coordination of histidine to the copper atom in the Cu-complex azo dye on cellulose was also influenced by the adsorption of histidine on cellulose. The spectral variation by histidine coordination to Cu-complex dyes occurred initially very rapidly in aqueous solution, but on cellulose the rates of spectral variation due to histidine coordination and the absorption spectra of coordinated dyes depended on the pH and the concentration of aqueous histidine in which the dyed film was immersed.[1]

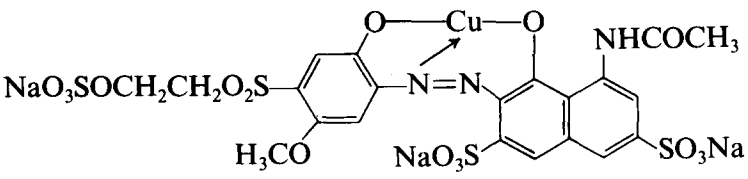
Many workers[2–15] have shown that histidine undergoes mainly histamine-like coordination of a six-membered ring to copper in the neutral region, and a glycine-like coordination of the five-membered ring in both acidic and alkaline regions. Thus, histamine-like, glycine-like, and a mixture of histamine-like and glycine-like Cu(II)-$(histidine)_2$ complexes are possible. In acidic solution, histidine contains the imidazolium cation, while in an alkaline solution the deprotonated imidazole nuclei is present. The 1 : 1-complexes between Cu(II) and histidine exist only in the acid region and the 1 : 2-complexes in weakly acid and alkaline regions.[3–13] Since there are three vacant sites of coordination in a Cu-complex *o,o'*-dihydroxyazo dye, various coordination modes may be possible for histidine.

In the present study, the adsorption of histidine on cellophane, and on the film dyed with a Cu-complex reactive dye and other dyes, is measured at various pHs. The adsorption and desorption of histidine are examined as a function of the time of immersion under various conditions. Variations of the absorption spectra with pH for Blue-Cu on cellulose after immersing the dyed film in aqueous histidine are examined. The spectral variation accompanied by the coordination of histidine to Cu-complex azo dyes on cellulose is shown to be due to substitution of the histidine ligand for the oxo ligand in the dye molecule.

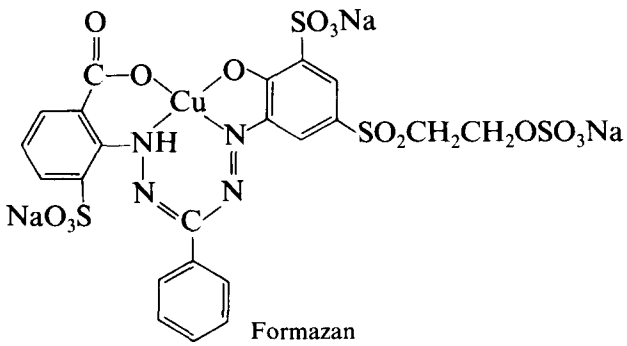
2 EXPERIMENTAL

2.1 Materials

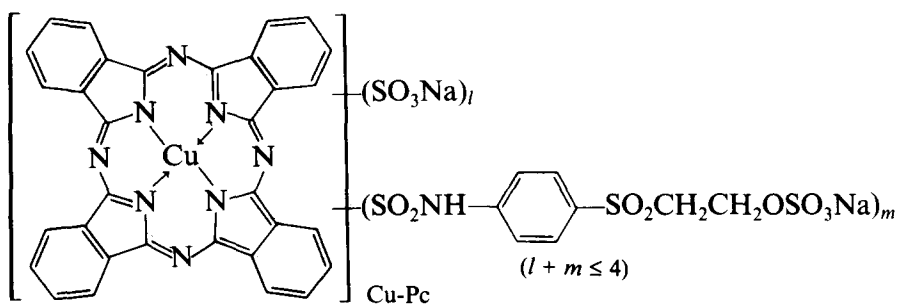
A Cu-complex vinylsulfonyl azo dye (Blue-Cu), a Cu-complex formazan dye (Formazan), supplied by Hoechst Mitsubishi Kasei Co. Ltd, a copper



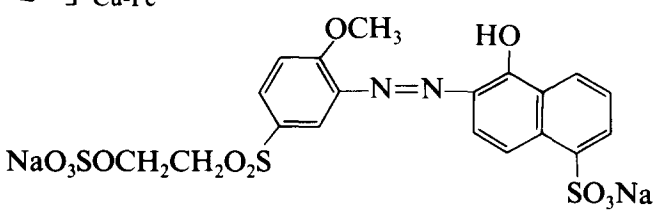
Blue-Cu



Formazan



Cu-Pc



CI Reactive Red 22

phthalocyanine (Cu-Pc), and CI Reactive Red 22, supplied by Sumitomo Chemical Co. Ltd, were used for dyeing without further purification. Their chemical structures are shown above.

2.2 Determination of adsorption

The adsorption of histidine on cellophane was determined by the same method as previously reported.[1] Cellophane films were immersed in aqueous histidine (0·020 and 0·050 mol dm^{-3} + NaCl (0·050 mol dm^{-3})) after the

films were dipped in water for more than 30 min. Dyeing of cellophane sheets and measurements of absorption spectra were made by the methods described earlier.[16] The adsorption of histidine on dyed film was estimated by the differences of the absorbance at 212 nm (the wavelength of the maximum absorption for histidine) between the dyed films unimmersed and immersed in aqueous histidine at various pHs for a defined time. L-Histidine (reagent grade, Kyowa Hakko Co. Ltd) was used as received.

3 RESULTS AND DISCUSSION

3.1 Adsorption of histidine on undyed cellulose and the desorption

The adsorption on cellulose for the three species, $^{+}H_3NCH(CH_2Im^{+})COO^{-}$ ($HisH^{+}$), $^{+}H_3NCH(CH_2Im)COO^{-}$(His), and $H_2NCH(CH_2Im)COO^{-}$(His^{-}), where Im denotes the 4-imidazole moiety of histidine, was measured at pH 4·0, 7·6, and 11·0 at 25°C. The results are shown in Fig. 1. Almost all the adsorption of the three species on cellophane occurred within several minutes, i.e. a quite large initial adsorption. On immersing cellophane in aqueous histidine of concentration 0·020 mol dm^{-3}, histidine attained the equilibrium adsorption in about 6 h, while it took a longer time at lower concentration and a shorter time at higher temperature.

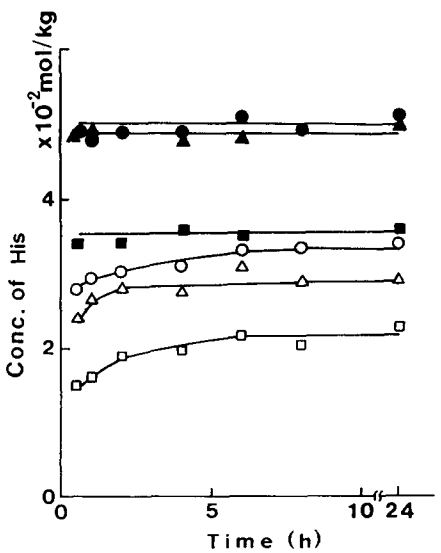


Fig. 1. Rates of histidine adsorption on cellophane (open symbols) and on film dyed with Blue-Cu ($1·19 \times 10^{-2}$ mol kg^{-1}) (closed symbols) from aqueous histidine (0·020 mol dm^{-3} + NaCl (0·050 mol dm^{-3})) at pH 4·00 (○, ●), 7·56 (△, ▲), and 11·00 (□, ■) at 25°C.

When cellophane on which histidine has been adsorbed at various pHs to attain equilibrium was dipped into either solutions or water the histidine on the cellulose was readily desorbed into the aqueous phase; the time for this washing off of the histidine was not dependent upon the amount of adsorption. Drying of the histidine-adsorbed cellophane had no effect on the rates of desorption.

3.2 Adsorption on cellophane dyed with Blue-Cu

3.2.1 Additional adsorption of histidine

The absorption spectra of histidine on dyed cellophane at wavelengths above 200 nm (which were obtained from the differences of absorbance between the immersed and unimmersed films in aqueous histidine) were similar to those on the undyed film, even when the absorbance of Blue-Cu (0·01–0·02 mol kg^{-1}) on cellophane ranged from 0·7 to 1·5 at the wavelength used. The adsorption of histidine on the dyed film from aqueous histidine of concentrations 0·020 and 0·050 mol dm^{-3} at various pHs is shown in Fig. 2. Comparison of the adsorption on dyed film with that on undyed film suggests that Blue-Cu on cellulose may cause additional adsorption of histidine, but no additional adsorption of histidine on cellophane dyed with CI Reactive Red 22, Formazan and Cu-Pc occurred. Only Cu-complex azo dyes on cellulose, which might provide histidine with the additional sites for adsorption due to coordination, gave additional adsorption of histidine by cellulose, beyond the ordinary adsorption on the undyed film.

The adsorption studies from aqueous histidine at the two concentrations showed that the adsorption on cellulose increased linearly with increase in the concentration of the aqueous histidine. At pH <8, additional adsorption on dyed cellulose increased with increase in the concentration of the dye on cellulose. At pH ≥ 8, however, no increase in additional adsorption was observed with increase in the concentration of Blue-Cu on cellulose, although the adsorption on the dyed films was larger than that on the undyed ones. Since Blue-Cu, to which histidine is once coordinated, may become more anionic at alkaline pH (cf. 3·3), histidine may be partially excluded from the dyed cellophane.

The differences between the total adsorption on the dyed and undyed cellophane show that the net additional adsorption is proportional to the adsorption on the undyed cellulose over all the pH range examined (cf. Fig. 2). The adsorption of histidine on the dyed cellophane in the pH region between 5 and 8 was larger than that in the acidic or alkaline pH regions, implying that the histidine adsorbed by the cellulose contributes to the coordination of the Cu-complex dye on cellulose;

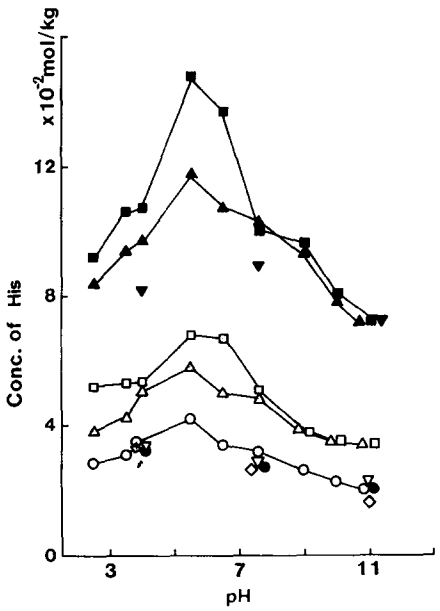


Fig. 2. Equilibrium adsorption of histidine on cellophane and on film dyed with reactive dyes from aqueous histidine (0·020 mol dm^{-3} + NaCl (0·050 mol dm^{-3})) at various pHs at 25°C for 2 days.

	—	Blue-Cu		CI Reactive Red 22	Formazan	Cu-Pc
Conc. of dyes on cellophane ($\times 10^{-2}$ mol kg^{-1})	0	1·12	2·38	2·26	(0·491)[a]	2·02
Conc. of histidine						
0·020 mol dm^{-3}	▽	△	□	○	◇	●
0·050 mol dm^{-3}	▼	▲	■	—	—	—

[a] The optical density measured at λ_{max} (=628 nm) on a sheet of dry cellophane.

this is the reason why the adsorption of histidine seems to promote coordination.[1]

In order to determine precisely the adsorption on cellulose, the excess adsorption, contained in the imbibed solution and which was measured in addition to the intrinsic amount of adsorption, must be subtracted from the total absorption, although the excess is usually negligible if the adsorption is large. The affinity of histidine for cellulose is very low; it may be estimated to be of the order of one as partition coefficient, although the coefficients in the neutral region are larger than those in the acid and alkaline regions. Thus, since the accurate amount of the net adsorption is difficult to estimate, the adsorption of histidine measured in this present study should be considered only as relative values.

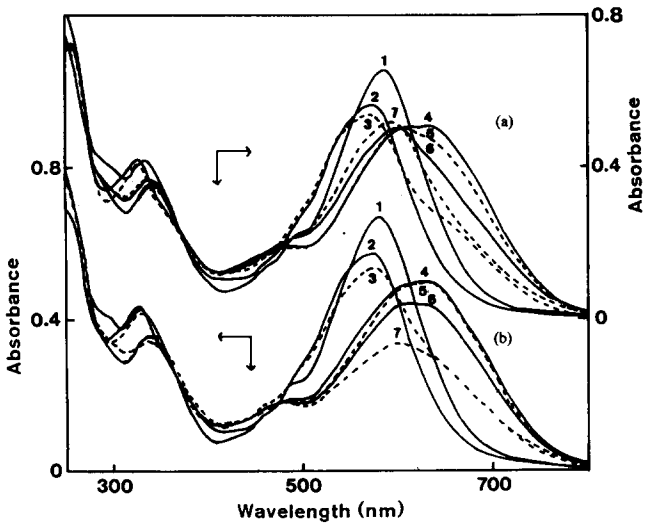


Fig. 3. (a) Absorption spectra of Blue-Cu (1) ($1{\cdot}17 \times 10^{-2}$ mol kg^{-1}) on cellophane immersed in aqueous histidine (0·050 mol dm^{-3}) at pH 5·52 (2), pH 7·60 (3), pH 9·00 (4), pH 10·01 (5), pH 10·54 (6) and pH 11·05 (7) at 25°C for 24 h. (b) Absorption spectra of Blue-Cu (1) ($1{\cdot}17 \times 10^{-2}$ mol kg^{-1}) on cellophane immersed in aqueous histidine (0·050 mol dm^{-3}) at pH 5·52 (2), pH 7·60 (3), pH 9·00 (4), pH 10·01 (5), pH 10·50 (6) for 8 days, and at pH 11·00 (7) for 4 days at 25°C.

It may be impossible to estimate precisely to what extent the dye molecules on cellulose contribute to the addition adsorption of histidine. However, the net additional adsorption, the amounts of which corresponded approximately to the concentration of dye on cellulose, suggest that the coordination of histidine to the copper atom in Blue-Cu occurred in an equimolar ratio, as in the case of solution studies,[1] where a 1 : 1 complex was formed between histidine and Blue-Cu.

3.2.2 Rates of the additional adsorption and desorption

The adsorption of histidine on the dyed films was also estimated at different times from aqueous histidine at pH 4·0, 7·6 and 11·0 (Fig. 1). Histidine showed a large initial adsorption, attaining equilibrium adsorption within 30–50 min. Although there were some differences in the amount of total adsorption for the three species of histidine, higher rates of adsorption on the dyed films were observed than in the case of undyed cellophane.

With the adsorption of histidine on the dyed film, the absorption spectra of Blue-Cu on cellulose changed, but the rates of spectral variation did not correspond to those of the adsorption on the dyed film.[1] The absorption spectra on immersion in aqueous histidine at pH between 5 and 11 are shown in Fig. 3, although the extent of attainment of the final spectra

was different. The spectra after immersion for 24 h (Fig. 3(a)) are the intermediate ones, and those for 4 and 8 days (Fig. 3(b)) almost the final ones. The spectral variations due to both the effects of pH and histidine-coordination on the modified dyes can be observed in the figures, as mentioned below (cf. 3.3.1 and 3.3.4).

Except for the initial period, the coordination of histidine to the original Blue-Cu on cellulose proceeded very slowly compared to the adsorption of histidine. The rates of spectral variation due to the coordination of histidine to Blue-Cu became slower with time of immersion to attain the final spectrum.

When the dyed films with adsorbed histidine were dipped into water at room temperature, most of the histidine on the cellulose was desorbed within a few minutes, although the absorption spectra of Blue-Cu did not revert to the original spectra.

3.3 Blue-Cu after the desorption of histidine adsorbed by the dyed film

3.3.1 Variation of absorption spectra with pH

On immersing the dyed film in various buffer solutions after complete desorption of histidine, pH variations of the absorption spectra of Blue-Cu (Fig. 4) were also observed, as in the case of the immersion of dyed film in aqueous histidine at various pHs. When the absorbance at 540 nm of these spectra was plotted against pH, it was apparent that a type of dissociation phenomenon may exist (Fig. 5). This may imply that the

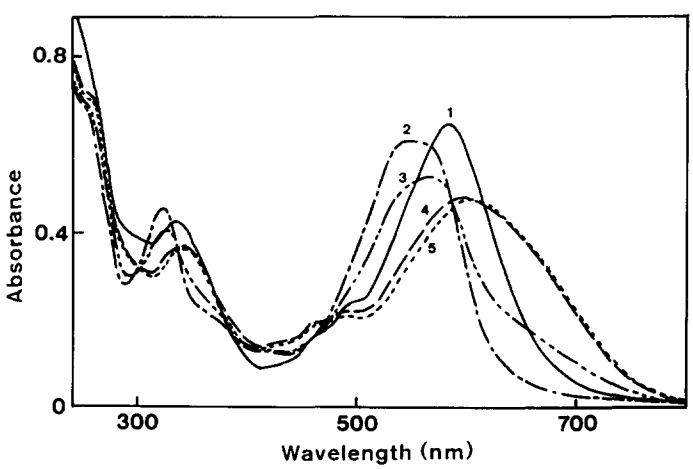


Fig. 4. Absorption spectra of Blue-Cu (1) ($1{\cdot}13 \times 10^{-2}$ mol kg^{-1}) on cellophane after being immersed in aqueous histidine ($0{\cdot}050$ mol dm^{-3} + NaCl ($0{\cdot}050$ mol dm^{-3})) at pH 11·01 for 2 days and then washed in water for 2 h, in buffer solutions at pH 4·01, 5·52 and 6·52 (2), at pH 7·60 (3), at pH 9·01 (4), at pH 10·00 and 11·01 (5) at 25°C.

spectral variations with pH are attributed to the dissociation of *o*-hydroxyl groups, formed by the substitution of histidine for the oxo groups (cf. 3.3.3).

3.3.2 Reformation of original dye by oxidation

In order to confirm the generation of *o*-hydroxyl groups and no abstraction of the copper atom by histidine, the dyed films, after coordination and then removal of histidine, were immersed in aqueous sodium peroxodicarbonate (0·1%) solution for several hours at room temperature. This treatment of the dyed film reproduced the original absorption spectrum of Blue-Cu, which showed no variation with pH when the film was immersed in buffer solutions of different pHs. This suggests the generation of *o*-hydroxyl groups, and no abstraction of the copper atom by histidine, over the pH range examined. The spectral variations by histidine coordination to Cu-complex azo dyes on cellulose is reversible in a broad sense, if no azo groups are broken (cf. 3.4).

3.3.3 Scheme of histidine coordination to Blue-Cu

The various phenomena which were observed by immersing the dyed films in aqueous histidine at different pHs are summarized as follows:

(1) Histidine coordinates to the copper atom in Blue-Cu on cellulose, when additional adsorption of histidine and spectral variations of Blue-Cu occur, depending on the pH of the histidine solution.
(2) The rates of adsorption of histidine on dyed cellophane are larger than those of the spectral variation.
(3) Although histidine adsorbed on the dyed films is completely desorbed

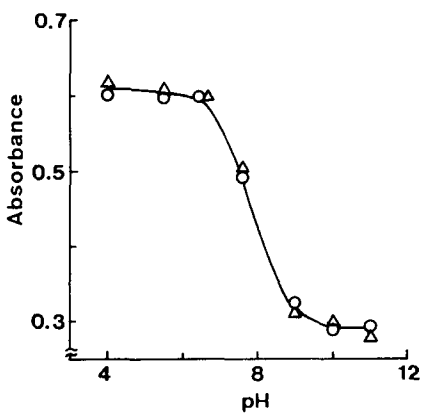


Fig. 5. Relationship between the absorbance at 540 nm for Blue-Cu on cellulose, after being immersed in aqueous histidine (0·050 mol dm^{-3}) at pH 11·01 for 2 days (○) (cf. Fig. 4) and in EDTA solution (0·050 mol dm^{-3}) at pH 12·00 for 6 h (△) and then washed in water for 2 h, and the pH in which the dyed film was re-immersed.

by the immersion in water, the absorption spectra of Blue-Cu on cellulose does not revert to the original, i.e. there is an irreversible spectral variation.

(4) Once histidine coordinated, Blue-Cu on cellulose, after the histidine is completely desorbed, shows the following reversible spectral variations:
   (a) pH-dependent ones in buffer solutions in which the dyed films are immersed;
   (b) concentration-dependent ones in aqueous histidine at a given pH in which the dyed films are immersed (cf. 3.3.4).

(5) Blue-Cu on cellulose reproduces the original absorption spectra by treating the dyed films, after the coordination and the desorption of histidine, in sodium peroxodicarbonate solution.

These observations may be explained as follows: the coordination of histidine to Blue-Cu on cellulose may be caused by substitution of the histidine ligand for the oxo ligand (eqn (1), cf. eqn (8)).

$$\underset{(\mathbf{1})}{\text{Blue-Cu}} + \text{His} \longrightarrow \underset{(\mathbf{2})}{\text{Blue-Cu-OH-His}} \rightleftharpoons \underset{(\mathbf{2'})}{\text{Blue-Cu-O}^{-}\text{-His}} + \text{H}^{+} \quad (1)$$

Once such substitution occurs, generating modified Blue-Cu **3** or **3'** having free hydroxyl groups, they may be in equilibrium with histidine, as shown by eqns (2) and (3) at a given pH.

$$\underset{(\mathbf{2})}{\text{Blue-Cu-OH-His}} \rightleftharpoons \underset{(\mathbf{3})}{\text{Blue-Cu-OH}} + \text{His} \quad (2)$$

$$\underset{(\mathbf{2'})}{\text{Blue-Cu-O}^{-}\text{-His}} \rightleftharpoons \underset{(\mathbf{3'})}{\text{Blue-Cu-O}^{-}} + \text{His} \quad (3)$$

The concentration of the original Blue-Cu **1** is, initially, rapidly decreased and the rates of substitution then gradually decrease. Complete substitution then proceeds over a longer time, since the concentration of **1** decreases with the time of immersion. On immersing the dyed films in aqueous histidine, **1** on cellulose may be changed into **2**, **2'**, **3** or **3'**; they can be in equilibria as described by eqns (2), (3) and (4), depending on the pH and the concentration of aqueous histidine:

$$\underset{(\mathbf{3})}{\text{Blue-Cu-OH}} \rightleftharpoons \underset{(\mathbf{3'})}{\text{Blue-Cu-O}^{-}} + \text{H}^{+} \quad (4)$$

$$K_a = \log ([\text{Blue-Cu-O}^{-}][\text{H}^{+}]/[\text{Blue-Cu-OH}]) \quad (5)$$

Figure 5 shows that the value of K_a ($=-\log K_a$, defined by eqn (5)) is 8·1, where the concentrations of **3** and **3'** are equal. The values of pK_a for the

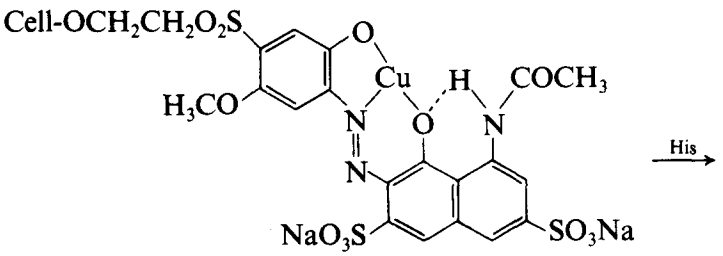
hydroxyl groups of 7-arylazo-H acid derivatives have been reported to be 10·5–12·9,[17] and those for *o,o'*-dihydroxyazonaphthalenes 7·4–8·4 and 11·6–11·9, respectively.[18] These results suggest that the value of 8·1 corresponds to dissociation of the *o*-hydroxyl groups of the phenylazo moiety, thus supporting the reaction scheme proposed above.

The regeneration of the original dye by oxidation with sodium peroxodicarbonate is shown by eqns (6) or (7).

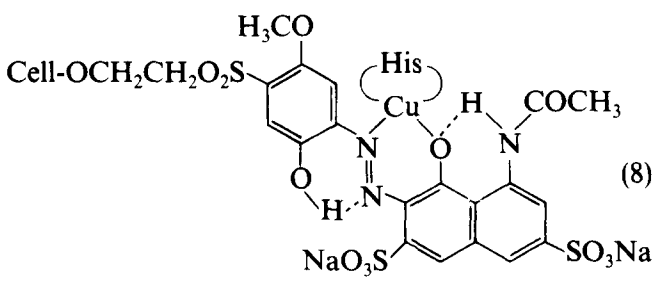
$$\underset{\textbf{(3)}}{\text{Blue-Cu-OH}} + Na_2C_2O_6 \longrightarrow \underset{\textbf{(1)}}{\text{Blue-Cu}} \qquad (6)$$

$$\underset{\textbf{(3')}}{\text{Blue-Cu-O}^-} + H^+ + Na_2C_2O_6 \longrightarrow \underset{\textbf{(1)}}{\text{Blue-Cu}} \qquad (7)$$

Since azo dyes may occupy three positions in the copper equatorial plane,[19,20] either *o*-oxo ligand of the dye must be substituted by the histidine ligand to satisfy the experimental observations of the present study. Since original Blue-Cu acts as a tridentate ligand, and the six-membered ring is more stable than the five-membered ring, the coordination of histidine (His) may occur as shown in eqn (8).[21] This reaction corresponds to eqn (1) and is the reverse of eqn (6). After substitution by histidine, Blue-Cu acts as a bidentate ligand, while histidine coordinates histamine-like (as tridentate) or glycine-like (as bidentate), depending on the pH of the



(1)



(8)

(2)

aqueous phase to occupy the neighboring two positions of the copper equatorial plane; details of the coordination for histidine are not shown in eqn (8).

3.3.4 Variation of absorption spectra by histidine coordination

Species **3** may coexist with the dissociated species **3'**, depending on the pH of the immersing solution. In order to show the coordination of histidine to both of the species **3** and **3'**, cellophane dyed with Blue-Cu, after complete desorption of the histidine which was adsorbed by immersing the dyed film in aqueous histidine (0·050 mol dm^{-3} + NaCl (0·050 mol dm^{-3})) at room temperature for a week, was immersed again in aqueous histidine of different concentrations at pH 4·0 (Fig. 6). Only species **3** and $HisH^+$ predominantly exist at pH 4·0. There are no simple components in the mixture solutions at other pHs. At all the pHs examined, the absorption spectra of Blue-Cu on cellophane immersed in aqueous histidine showed that the larger coordination occurred with increase in the concentration of histidine, as in the case of the coordination in aqueous solution.[1] Since no accurate amounts of adsorption of histidine were determined (cf. 3.2.1), the stability constants of the histidine coordination or of the equilibrium constants for eqns (2) and (3) on cellulose could not be obtained.

As shown by Fig. 6, histidine may coordinate reversibly to **3**, implying the equilibria described by eqn (2) at this pH. Thus, spectrum 2 of Fig. 3(b) coincided approximately with spectrum 5 of Fig. 6, a spectrum of a mixture of species **1**, **2** and **3**.

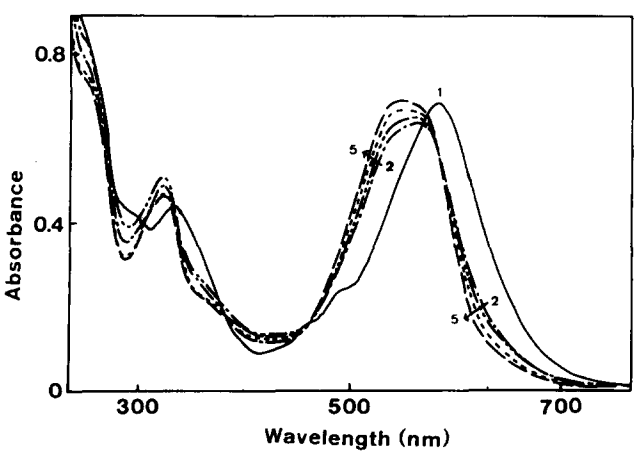


Fig. 6. Absorption spectra of Blue-Cu (1) ($1{\cdot}13 \times 10^{-2}$ mol kg^{-1}) on cellophane after being immersed in aqueous histidine (0·050 mol dm^{-3}) at pH 4·00 for a week and then washed in water for 2 h, in aqueous histidine of 0·002 (2), 0·01 (3), 0·02 (4) and 0·05 (5) mol dm^{-3} at pH 4·00 at 25°C for 2 days.

The most typical phenomenon on immersion of cotton dyeings with Cu-complex azo dyes in aqueous histidine was the higher rate of color variations in the weakly alkaline region than in the acidic region[1] (cf. Figs 5–8 in Ref. 1). As substitution of Blue-Cu on cellulose progresses, the most marked spectral variations due to the dissociation of free hydroxyl groups are observed around pH 8, and the largest due to the histidine coordination around pH 5·5 where histidine shows the largest adsorption. It is for this reason that the largest color variations of Cu-complex dyes on cellulose were observed in the weakly alkaline region.

3.4 Abstraction of copper by ethylene diamine tetraacetic acid (EDTA)

On immersing the dyed cellophane in aqueous histidine, no abstraction of the copper atom by histidine was observed, although substitution of histidine for the oxo ligand, or the coordination of histidine to Blue-Cu, occurred.

In order to confirm this, the coordination to, and the abstraction of, the copper atom of Blue-Cu on cellophane was examined by immersing the dyed cellophane in EDTA solution (0·05 mol dm^{-3}) at pH 12·0. The

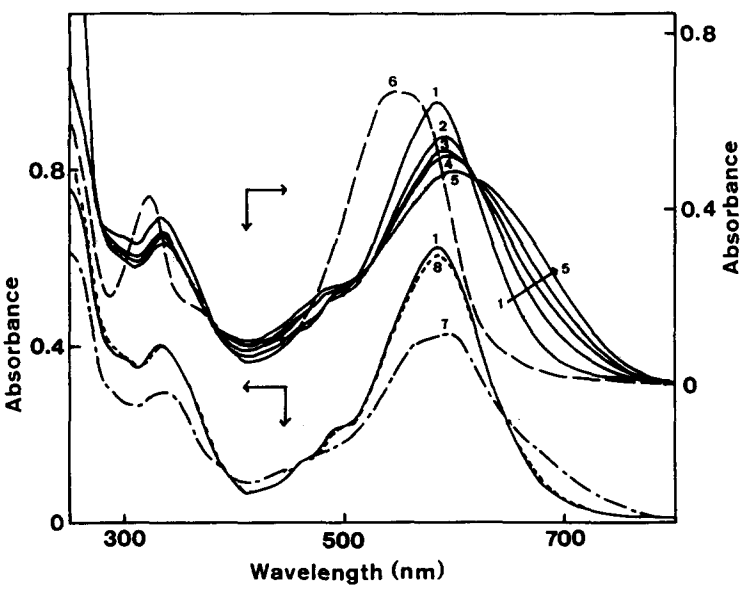


Fig. 7. Absorption spectra of Blue-Cu (1) ($1{\cdot}18 \times 10^{-2}$ mol kg^{-1}) on cellophane immersed in aqueous EDTA (0·050 mol dm^{-3}) at pH 12·0 for 15 min (2), 30 min (3), 1 h (4), 4 and 24 h (5) at 25°C; the spectrum for the sample of spectrum 5 after washing in water for 2 h (6); and the spectra of the sample of spectrum 5 on immersing in aqueous sodium peroxodicarbonate (0·1%) for 60 min (7) and in $CuSO_4$ solution (0·10 mol dm^{-3}) for 30 min (8) at 25°C.

absorption spectra of Blue-Cu varied with time on immersing in the EDTA solution, attaining the final spectrum after 4 h (spectra 1–5 in Fig. 7), no further change being apparent on continued immersion. The rates of the abstraction of the copper atom were lower in the neutral region than those in the acidic and alkaline regions. After washing the immersed film, Blue-Cu on cellophane showed similar spectral pH variation to those with histidine (cf. 3.3.1). No spectral variation of the dyed films was observed by the addition of EDTA or histidine into the re-immersing buffer solutions, an indirect proof of the abstraction of the copper atom. When the absorbance at 540 nm for Blue-Cu was plotted against pH, the same plots as in the case of histidine were obtained, as shown in Fig. 5. The pK_a value for Blue-Cu on cellulose, from which the copper atom was abstracted, was estimated to be 8·1, the same value as for **3**.

No regeneration of the original spectra for Blue-Cu was observed by treating the immersed film in aqueous sodium peroxodicarbonate (spectrum 7 in Fig. 7), but when the immersed film was dipped in $CuSO_4$ solution (0·10 mol dm^{-3}) the absorption spectra of Blue-Cu reverted to the original (spectrum 8 in Fig. 7). This implies the abstraction of the copper atom from Blue-Cu on cellulose by EDTA, unlike the case of histidine.

4 SUMMARY

The adsorption of histidine on dyed and undyed cellophane from aqueous solution was examined at 25°C over a wide range of pH. Histidine which was adsorbed by the dyed and undyed films was readily desorbed into water. After immersing the dyed film in aqueous histidine, the absorption spectra of the Cu-complex dye on cellophane varied with the pH of the aqueous solution in which the dyed film was re-immersed, irrespective of whether the histidine on the cellulose was washed off or not.

When histidine coordinated to the copper atom of Cu-complex dyes on cellulose, on immersion in aqueous histidine an exchange or the substitution of the oxo ligands for histidine ligands occurred. The substituted dyes were oxidized by aqueous sodium peroxodicarbonate to give the original dyes. Although similar spectral variations to those in the case of histidine were observed on immersing the dyed films in aqueous EDTA, treatment with aqueous sodium peroxodicarbonate gave no original dyes, but treatment with aqueous $CuSO_4$ solution regenerated the original dyes. Histidine was shown not to abstract the copper atom from Cu-complex azo dyes on cellulose, but chelating agents such as EDTA did abstract the copper atom on immersing the dyed film in aqueous solutions.

When cotton dyeings with Cu-complex azo dyes are wet with perspira-

tion the histidine in the perspiration may have similar influences on the dyes on textiles to those described in this study, although the degree of influence may depend on the conditions under which the textiles are soaked with perspiration.

ACKNOWLEDGEMENTS

The authors thank Hoechst Mitsubishi Kasei Corp. and Sumitomo Chemical Co. Ltd for their cooperation in the preparation of this paper.

REFERENCES

1. Okada, Y., Kawanishi, T., Motomura, H. & Morita, Z., *Dyes and Pigments*, **24** (1994) 99.
2. Sundberg, R. J. & Martin, R. B., *Chem. Rev.*, **74** (1974) 471.
3. Kruck, T. P. A. & Sarkar, B., *Can. J. Chem.*, **51** (1973) 3549.
4. Kruck, T. P. A. & Sarkar, B., *Can. J. Chem.*, **51** (1973) 3563.
5. Pettit, L. D. & Swash, J. L. M., *J. Chem. Soc., Dalton Trans.*, (1976) 588.
6. Yamauchi, O., Sakurai, T. & Nakahara, A., *J. Am. Chem. Soc.*, **101** (1979) 4164.
7. Casella, L. & Gullotti, M., *J. Inorg. Biochem.*, **18** (1983) 19.
8. Nair, M. S., Santappa, M. & Natarajan, P., *J. Chem. Soc., Dalton Trans.*, (1980) 1312.
9. Basosi, R., Valensin, G., Gaggelli, E., Froncisz, W., Pasenkiewicz-Gierula, M., Antholine, W. E. & Hyde, J. S., *Inorg. Chem.*, **25** (1986) 3006.
10. Pasenkiewicz-Gierula, M., Froncisz, W., Antholine, W. E. & Hyde, J. S., *Inorg. Chem.*, **26** (1987) 801.
11. Brown, C. E., Antholine, W. E. & Froncisz, W., *J. Chem. Soc., Dalton Trans.*, (1980) 590.
12. Aiba, H., Yokoyama, A. & Tanaka, H., *Bull. Chem. Soc. Jpn*, **47** (1974) 1003.
13. Itabashi, M. & Itoh, K., *Bull. Chem. Soc. Jpn*, **53** (1980) 3131.
14. Camerman, N., Fawcett, J. K., Kruck, T. P. A., Sarkar, B. & Camerman, A., *J. Am. Chem. Soc.*, **100** (1978) 2690.
15. Henry, B., Boubel, J.-C. & Delpuech, J.-J., *Inorg. Chem.*, **25** (1986) 623.
16. Okada, Y., Kato, T., Motomura, H. & Morita, Z., *Dyes and Pigments*, **12** (1990) 197.
17. Bredereck, K. & Schumacher, C., *Dyes and Pigments*, **21** (1993) 23.
18. Diehl, H. & Ellingboe, J., *Analyt. Chem.*, **32** (1960), 1120.
19. Ooi, S., Carter, D. & Fernando, Q., *J. Chem. Soc. Chem. Commun.*, (1967) 1301.
20. Gyepes, E., Kuchar, E. & Jurikova, A., *Acta Fac. Rer. Nat. Univ. Comen. Chimia*, **29** (1981) 69.
21. Gordon, P. F. & Gregory, P., In *Organic Chemistry in Colour*. Springer, Berlin, 1987, pp. 116.