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Coordination of Histidine to the Copper Atom of a Metal-Complex Reactive Azo Dye on Cellulose

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ABSTRACT

The absorption of histidine on cellulose at various pHs was measured at 25°C. Histidine had some affinity to cellulose and showed pH dependence of adsorption. The addition of histidine to an aqueous solution of a Cu-complex reactive azo dye gave a 1 : 1 complex formation, the stability constants of which were estimated to be 63–115 mol^{-1} dm^3, depending on pH, at 25°C. On immersing the dyed cellophane in aqueous histidine, a red shift of the main band occurred at pH 9 and 10, while a blue shift of the main band was observed at pH <8. The coordination of histidine to Cu-complex dyes on cellulose seemed to be promoted by the adsorption of histidine on cellulose. The absorption spectra of the dyed film immersed in aqueous histidine of pH > 7 varied with time during drying, whilst those immersed in the solution of pH <6 showed little variation.

1 INTRODUCTION

It has been considered that the testing methods for colour fastness to perspiration of ISO, European and North American countries and Japan

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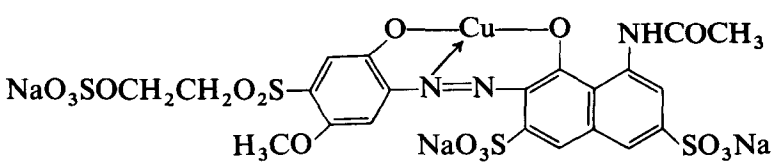
examine the ease with which histidine coordinates to or abstracts the copper of metal-complex dyes on fabrics.[1-4] Complexes between transition metals and α-amino acids have been extensively studied to elucidate the functions of metals in metalloproteins.[5-7] Histidine is bi- or tridentate, forming various types of copper complexes depending on the pH of the solutions.[7] Copper (II) ions prefer a square-planar or an extremely distorted octahedral geometry to bind a maximum of two histidine ligands or some mixed ligands, when Cu(II) ions are added to a solution of a mixture of α-amino acids containing histidine. Since the stability constant of the $Cu(His)^2$ complex is of an order of magnitude greater than that of other amino acids,[7-11] histidine shows special behaviour in the complexation of Cu(II). The mixed-ligand Cu-complexes of histidine and other amino acid have also been investigated.[12-16] The coordination of histidine to copper was reported to result in the appearance of a characteristic absorption band.[17]

In previous papers,[18,19] we have reported that the copper atom of vinylsulphonyl Cu-complex azo dyes might be abstracted by chelating agents. In this present study, how the absorption spectra of reactive metal-complex dyes on cellulose vary with time on immersing the dyed film in aqueous histidine of different pHs is examined. In order to clarify the reason why the spectral variations of blue-Cu on cellulose immersed in aqueous histidine are greater than those in an aqueous solution of the same concentration, the adsorption of histidine on cellulose has been examined under various conditions. It is shown that, after immersion of the dyed film in aqueous histidine, the absorption spectra of the dye are changed depending on the pH of the buffer solutions in which the film is re-immersed.

2 EXPERIMENTAL

2.1 Dyes used

A copper-complex azo dye (blue-Cu), supplied by Hoechst Mitsubishi Kasei Co. Ltd, Tokyo, was used for dyeing without further purification; its structure is shown:



Blue-Cu

2.2 Hydrolysis and purification

Blue-Cu was hydrolysed in aqueous sodium hydroxide (0·2 M) solution for 2 h at 80°C. Completion of hydrolysis was checked by paper chromatography,[20] by which the absence of the vinylsulphonyl for and the presence of red impurities could be established. The hydrolysates were separated by recrystallization from water; the red impurities were found to be reduced considerably in amount. The purity of the sample was checked with respect to a sample purified by the dimethylformamide method.[21] The purified samples was used for complex formation in aqueous solution (cf. Section 3.1). The pH of aqueous histidine was adjusted by adding hydrochloric acid (1·0 mol dm^{-3}) or sodium hydroxide (1·0 mol dm^{-3}) solution.

2.3 Adsorption of histidine on cellulose

The adsorption of histidine on cellophane was determined by measuring the absorbance of the adsorbed film at wavelength 214 nm after drying. The swollen film with adsorbed histidine was immediately pressed between filter papers and dried within multiple sheets of papers. L-Histidine free base (Kyowa Hakko Co. Ltd) was used as received.

2.4 Dyeing and spectral measurements

Cellophane sheets were dyed by the previously described method.[22] The dyed film treated under the given conditions for purification was immersed in aqueous histidine at various pHs and at room temperature. Other chemicals of reagent grade were used as received. The absorption spectra of the histidine-coordinated dyes on cellophane were measured as dipped in aqueous histidine or in buffer solution in a cell in the visible and near-UV region. Those of the wet film were also measured in the UV region by use of the wet undyed film as reference. All spectral measurements in this study were carried out using a Ubest-50 UV/Vis spectrophotometer (Jasco Ltd).

3 RESULTS AND DISCUSSION

3.1 Complex formation between blue-Cu and histidine in aqueous solutions

The values of pK_a for histidine are 1·96, 6·12, 9·17 and 14·4 at 25°C.[7,23] The fractions of various species in the pH range between 1 and 14 can be

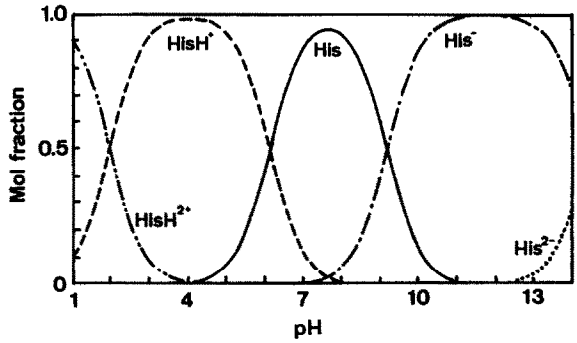


Fig. 1. Distribution diagram of five species of histidine at various pHs.

calculated as shown in Fig. 1.[24] Two or three types of ionized species for histidine ligands may exist at each pH within the range of the present experimental conditions. The largest fraction (0·984) of $HisH^+$ exists at pH 4·0, that (0·943) of His at pH 7·5, and that (0·995) of His^- at pH 11·7. The complex formation between blue-Cu and histidine was examined at pH 4·00, 7·58 and 11·00. The spectral variations of blue-Cu in aqueous solution at pH 4·00 by adding histidine of concentration higher than that of the dye are shown in Fig. 2. A red shift of the main band was observed with the addition of histidine at pH 11, and a blue shift at pH 7·6 and 4·0, although the spectral variations of blue-Cu at pH 7·6 and 11 are not shown. Since the plots of the reciprocal of the histidine concentrations, C_H (mol dm^{-3}), against the reciprocal of (one minus the absorbance ratios, A/A_0, of dye solutions with and without histidine addition) gave a straight line (as shown in Fig. 3), it was confirmed that 1:1 complex formation between histidine and blue-Cu occurred.[25] From the intercept of this line, the values of the stability constant for the formation of the 1:1 complex were estimated to be 62·7 mol^{-1} dm^3 for $HisH^+$ at pH 4·0,

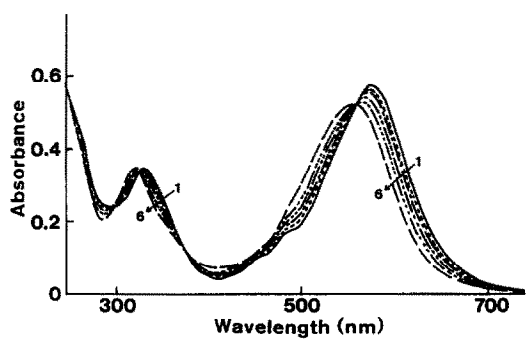


Fig. 2. Absorption spectra of an aqueous solution of a mixture of blue-Cu (2·24 × 10^{-4} mol dm^{-3}) and histidine (spectra: 1, 0; 2, 0·002; 3 0·005; 4 0·010; 5, 0·020; 6, 0·050 mol dm^{-3}) at pH 4·00.

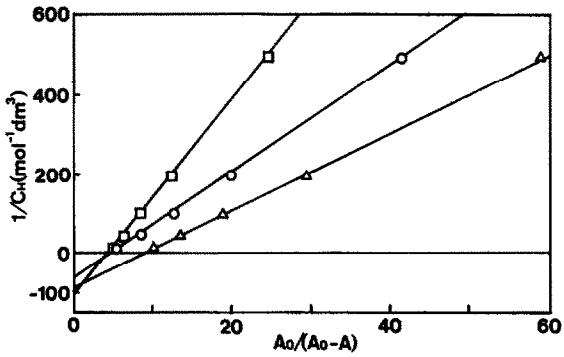


Fig. 3. The plots of the reciprocal concentration of histidine versus the reciprocal of (1 minus the absorbance ratios) from the variations in the absorbance at λ_{max} of blue-Cu in the aqueous solution by the addition of histidine at pH 4·00 (○), 7·58 (□), and 11·00 (Δ).

115 mol^{-1} dm^3 for His at pH 7·6, and 84·0 mol^{-1} dm^3 for His$^-$ at pH 11·0. Thus histidine of different dissociation forms a 1:1 coordination complex having differing stability. Since the circular dichroism spectra of the aqueous solutions of a mixture of dye and histidine are also changed by pH (unpublished work by Y. Okada, H. Motomura & Z. Morita), the coordination of histidine to the copper atom of the dye is established.[17,26] Berthon *et al.*[12] showed also that Cu(II) forms three kinds of ternary complexes with histidine, where the molar ratio of Cu: histidine: α-amino acids is 1:1:1.

3.2 Adsorption of histidine on cellulose

Since histidine shows differing dissociation behaviour and cellulose contains carboxyl groups, histidine may show a complicated pH dependence with respect to adsorption on cellulose. Figure 4 shows the adsorption of histidine on cellulose from aqueous histidine in the pH range between 2·5 and 11·0. In order to avoid the exclusion of histidine, sodium chloride was added to the solution. Since the pK_a of the carboxyl groups in cellulose has been estimated to be 3·8,[27] an increase in adsorption from pH 2·5 to pH 5 may be attributed to the dissociation of the carboxyl groups and a change in the dissociation of histidine cations from $HisH_2^{2+}$. A decrease in the adsorption from pH 5 to pH 9 may be due to the change from a HisH+ cation to His, an amphoteric ion which may have low affinity for cellulose. Although histidine cations and anions may show adsorption depending on the ionic strength as well as the pH, an analysis of the contributions of various species of histidine to the adsorption on cellulose may not be easy.

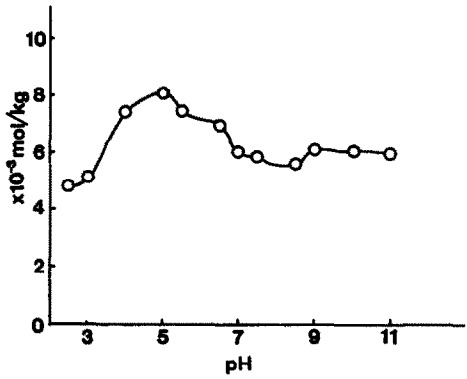


Fig. 4. Adsorption of histidine on cellophane from aqueous solutions (0·005 mol dm^{-3} + NaCl 0·05 mol dm^{-3}) at various pHs at 25°C for 5 days.

3.3 Immersion of dyes film in aqueous histidine at pH 9 and 10

On immersing a sheet of cellophane dyed with the Cu-complex azo dye in aqueous histidine of different pH5, the absorption spectra of the dye on cellulose developed slowly with time, depending upon the concentration and the pH of the histidine solution.

When the dyed film was immersed in aqueous histidine (0·005 mol dm^{-3} + NaCl 0·05 mol dm^{-3}, pH 9 and 10), the absorption for blue-Cu increased on the long wavelength side of the main absorption band, with a red shift of λ_{max} (Figs 5 and 6, spectra 1–5). The absence of sodium chloride delayed the rate of spectral variation. When the dyed film was immersed in 0·002 mol dm^{-3} aqueous histidine, the coordination of histidine occurred slowly to a lower degree. The variation of absorption spectra became faster and larger with increase in the concentration of histidine (at conc. < 0·05 mol dm^{-3}) and in the pH of the histidine solution (at pH ≤ 10).

The red shift of the main band for blue-Cu on cellulose at alkaline pH may correspond to the coordination of the His^- species as in the case of aqueous solution (cf. Section 3.1). The absorption on the short wavelength side of the main band after the coordination of histidine at pH 9 was larger than that at pH 10, and the absorption on the long wavelength side was slightly smaller (cf. Figs 5 and 6, spectra 5), implying that the His^--coordination dyes at pH 10 are more prevalent than those at pH 9. These facts correspond well to the larger fraction of the His^- species at pH 10 than at pH 9.

The main bands of the absorption spectra for blue-Cu coordination by histidine at pH 9 and 10 seem to be a superposition of two absorption bands for uncoordinated and His^--coordination species. The coordination of

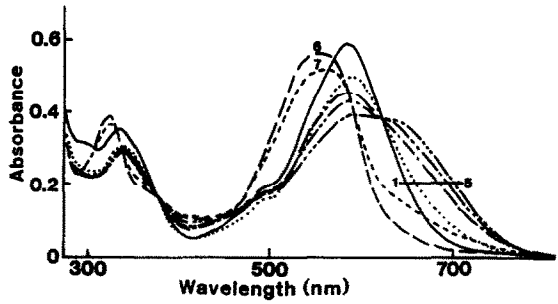


Fig. 5. Absorption spectra of blue-Cu(1) ($1{\cdot}06 \times 10^{-2}$ mol kg^{-1}) on the dyed film immersed in an aqueous histidine ($0{\cdot}005$ mol dm^{-3} + NaCl $0{\cdot}05$ mol dm^{-3}) solution at pH $9{\cdot}00$ for 1 h(2), 24 h(3), 48 h(4) and 96 h(5), and then dipped in buffer solution (pH $4{\cdot}0$) for 48 h(6) and in buffer solution (pH $6{\cdot}9$) for 48 h(7).

His species, however, could not be confirmed, although the coexistence of three species, i.e. uncoordinated, His and His^--coordinated dyes, on cellulose is expected from the dissociation behaviour of histidine in the aqueous solution (cf. Fig. 1). Thus, the absorption spectra of histidine-coordinated dyes on cellulose at various pHs seem to correspond incompletely with the pH variation in the fractions of different species in aqueous solution. But, compared with the spectral variation in aqueous solution, the histidine coordination to dye on cellulose seems to show a larger apparent stability constant of complex formation than that in aqueous solution. This may be attributed to the high affinity of histidine to cellulose.

Blue-Cu forms a Cu-complex with a very high stability, in which the dye acts as a tridentate ligand, which takes three positions having a square planar configuration. When blue-Cu on cellulose is immersed in aqueous histidine, the histidine may take two or three positions, which

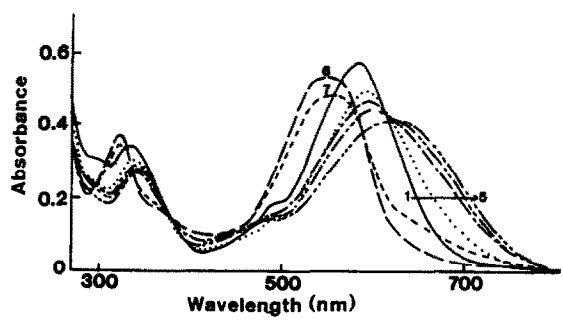


Fig. 6. Absorption spectra of blue-Cu(1) ($1{\cdot}06 \times 10^{-2}$ mol kg^{-1}) on the dyed film immersed in an aqueous histidine ($0{\cdot}005$ mol dm^{-3} + NaCl $0{\cdot}05$ mol dm^{-3}) solution at pH $10{\cdot}02$ for 1 h(2), 24 h(3), 48 h(4) and 96 h (5), and then dipped in buffer solution (pH $4{\cdot}0$) for 48 h(6) and in buffer solution (pH $6{\cdot}9$) for 48 h(7).

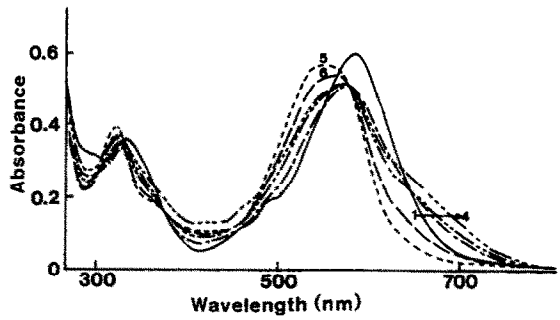


Fig. 7. Absorption spectra of blue-Cu(1) ($1{\cdot}22 \times 10^{-2}$ mol kg^{-1}) on the dyed film immersed in an aqueous histidine ($0{\cdot}02$ mol dm^{-3} + NaCl $0{\cdot}05$ mol dm^{-3}) solution at pH 7·58 for 1 h(2), 24 h(3) and 72 h(4), and then dipped in buffer solution (pH 4·0) for 48 h(5) and in buffer solution (pH 9·0) for 48 h(6).

form another planar configuration which is perpendicular to the plane of dye. But, since the three donor atoms cannot all occupy a planar site simultaneously on steric grounds,[28] histidine may act only as a bidentate. The mode of coordination of histidine has been found to be glycine- or histamine-like, although it depends upon pH.[7,29,30] Histidine ligands may involve rings with five, six and seven members. A five membered (glycine-like) ring involves only the carboxyl and the amino groups, a six membered ring (histamine-like) the amino and the active nitrogen in the imidazole group, and a seven membered ring the carboxyl groups and imidazole nitrogen. However, these structural assignments are open to discussion.

3.4 Immersion in aqueous histidine at pH <8

When the dyed film was immersed in $0{\cdot}02$ mol dm^{-3} aqueous histidine at pH 4·0 and 7·58, a blue shift of the absorption spectra occurred, as in the case of the aqueous solution (spectra 1–4 of Figs 7 and 8). Since the coordination was too slow to attain equilibrium at a concentration of $0{\cdot}005$ mol dm^{-3}, a higher concentration of histidine was used. In spite of the high adsorption of histidine on cellulose, the attainment of coordination equilibrium was slowest at pH 4, compared with the other cases. The absorption spectra at pH 7·58 had a shoulder at wavelengths >630 nm, implying the coexistence of His^--coordinated species in a small amount. Thus, uncoordinated, His^-- and His^--coordinated species may exist at pH 7·58, and uncoordinated, His^-- and $HisH^+$-coordinated species at pH 4. Whether the absorption spectra of blue-Cu to which $HisH^+$ and His was coordinated coincided with each other or not, could not be determined in the present study.

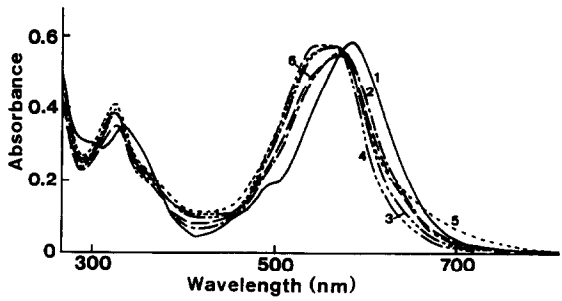


Fig. 8. Absorption spectra of blue-Cu(1) ($1{\cdot}20 \times 10^{-2}$ mol kg^{-1}) on the dyed film immersed in an aqueous histidine ($0{\cdot}02$ mol dm^{-3} + NaCl $0{\cdot}05$ mol dm^{-3}) solution at pH 4·02 for 24 h(2), 72 h(3) and 192 h(4), and then dipped in buffer solution (pH 6·9) for 48 h(5) and in buffer solution (pH 9·0) for 48 h(6).

3.5 Re-immersion of the coordinated film in buffer solution

On re-immersing the dyed films in buffer solutions of pH 6·9 and pH 4·0 after the coordination equilibrium was attained in aqueous histidine at pH 9·0 and 10·0, the absorption spectra for blue-Cu on cellulose varied with time, showing a distinct blue shift of λ_{max} (Figs 5 and 6, spectra 6 and 7). The absorption spectra after re-immersion at pH 7 had a shoulder at wavelengths > 630 nm, as in the case of immersion in aqueous histidine at pH 7·6 (cf. Fig. 7, spectrum 4; Figs 5 and 6, spectra 6), implying the coexistence of His^--coordinated species. Since the fraction of His^- species may be negligible in aqueous solution at pH 7·6, the coordination on cellulose shows an incomplete correspondence with that in aqueous solutions (cf. Section 3.3).

On re-immersing the dyed film in a buffer solution at pH 7 after coordination at pH 4, a shoulder on the long wavelength side was observed, without a red shift of the main band (Fig. 8, spectrum 5). This spectrum (5) was very similar to spectrum 2.

The absorption spectra of dyed cellophane previously immersed in aqueous histidine of pH <8 showed a red shift of λ_{max} on re-immersion in a buffer solution of pH 9, and a small shoulder on the long wavelength side of the main band, which might correspond with the His^--coordinated species, (Fig. 8, spectrum 6). The reason why no significant shoulder appeared could not be clarified.

The fact that the absorption spectra of dyed film previously immersed in aqueous histidine were varied by dipping the film in another buffer solution of different pH, to give the spectra obtained on immersing in aqueous histidine of the latter pH, may show that histidine coordinated to dyes on cellulose changes the state of coordination before being stripped. The stripping of histidine and/or the abstraction of copper by

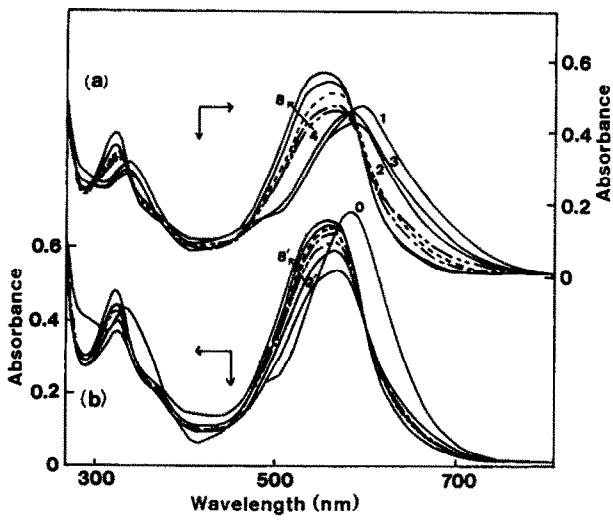


Fig. 9. (a) Absorption spectra of blue-Cu ($1{\cdot}08 \times 10^{-2}$ mol kg^{-1}) on cellulose on re-immersing the dyed film, which attained co-ordination equilibrium in aqueous histidine of pH 10·00 (0·02 mol dm^{-3} + NaCl 0·05 mol dm^{-3}), whose spectrum is (1), in buffer solutions of pH 11·00(2); 10·49(3); 10·02(4); 8·99(5); 6·90(6); 6·01, 5·01 and 4·51(8); 4·01 and 3·01(7); for 48 h; (b) the spectrum of the original dye (0) on dry film and the spectra (2'–8') of the same film after drying.

histidine from the histidine-coordinated samples may be very slow, if it is possible at all.

In order to elucidate the spectral variations on re-immersion at different pH 5, the dyed film was re-immersed in buffer solutions at various pHs after the coordination equilibrium at pH 10 (Fig. 9(a)). The absorption spectrum (Fig. 9(a), spectrum 1) of blue-Cu after the coordination equilibrium in aqueous histidine (0·02 mol dm^{-3} + NaCl 0·05 mol dm^{-3}) at pH 10, where a small blue shift and a decrease in the main absorption band from the original spectrum were observed, were different from that (Fig. 6, spectrum 5) in aqueous histidine (0·005 mol dm^{-3} + NaCl 0·05 mol dm^{-3}). This phenomenon also shows the disparity between the coordination behaviour of histidine to Cu-complex dyes on cellulose and the dissociation behaviour in aqueous solution (cf. Section 3.3). The absorption spectra at pH 10·5 and 11 (Fig. 9(a)) clearly show the existence of His^--coordinated species, but those at pH 7, 9 and 10 show only a shoulder on the long wavelength side of λ_{max}, although the order of spectra was different with that of pH. The spectra at pH <6 practically coincided with each other, although those at pH 3 and 4 were slightly different from the others. This may imply that, in addition to the change in the coordination mode of histidine depending upon the pH of the re-immersing

solution, histidine coordinated to Co-complex dyes was partially stripped during the re-immersion in buffer solution.

Histidine which was adsorbed on cellulose during the immersion of dyed film in aqueous histidine was considerably desorbed during the re-immersion in buffer solution at various pHs for 2 days. This was confirmed by the disappearance of the absorption of histidine around 210 nm by the re-immersion.

3.6 Spectral variation on drying

After attainment of the coordination equilibrium of histidine at various pHs, the absorption spectra of the film varied during drying, as shown in Fig. 9(b). With an increase in the pH of the immersing buffer solution before drying, the peak height of the main band for blue-Cu on dry cellophane decreased, and the absorption on the long wavelength side of the main band increased slightly. The dyed films after drying appeared bluer and paler with increase in pH. No variation in the absorption spectrum seemed to occur at pH ≤ 6 during drying. This may imply that the pH in dry cellulose is weakly acid.

The partial reversion of the order of pH in the absorption spectra (Fig. 9(b)) may show that partial stripping of histidine occurred during the re-immersion, depending on the pH of the solution (cf. Section 3.3 and 3.5).

Since immersion of copper-complex azo dyes on cellulose in aqueous histidine results in the coordination of histidine, accompanied by spectral variation depending on the pH of solution and the spectral change during drying, the testing method of colour fastness to perspiration should take these phenomena into consideration. In the case of reactive cotton dyeings, the coordination equilibrium may be attained without bleeding. Then, testing methods more severe than the present ones can be applied to reactive dyeings. Since the adsorption of histidine is high in the neutral region and is considerably changed with change in pH, and since the coordination of histidine is highly dependent upon pH, a testing method to assess the colour-fastness to perspiration for reactive cellulose dyeings is thus not easy to establish. However, since there may be no easy method to strip histidine which is coordinated to the copper atom of a dye on cellulose, deterioration of light fastness for such dyes may be inevitable.

4 SUMMARY

When histidine was added to an aqueous solution of blue-Cu, a 1:1 histidine-coordinated complex was formed, the stability constants of which, were

estimated to be 62·7 mol^{-1} dm^3 at pH 4·0, 115 mol^{-1} dm^3 at pH 7·6, and 84·0 mol^{-1} dm^3 at pH 11·0 at 25°C.

Histidine had some affinity for cellulose, but the amounts adsorbed were dependent on pH. Maximum adsorption was observed around pH 5. The pH-dependence of adsorption may be explained by the dissociation of the carboxyl groups of cellulose and relative amounts of the various species of histidine.

On immersing the dyed cellophane in aqueous alkaline histidine, a red shift of the main band was observed, while a blue shift of the main band occurred by dipping the immersed film in acid buffer. On re-immersing the dyed film in buffer solutions of different pH after the coordination equilibrium in aqueous histidine, the absorption spectra of histidine-coordinated blue-Cu were changed depending upon the pH of the re-immersing buffer solutions.

The absorption spectra of the dye on cellulose immersed in aqueous alkaline histidine varied depending on the method of drying, but the spectra immersed in the acidic solution showed a small or no variation. This may imply that the pH in cellulose is weakly acid.

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