Decolorization Mechanism of Metal Complex Dyestuff I.

EDTA Treatment of Cloth Dyed with Premetalyzed Dye.

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ABSTRACT

The decolorization of silk cloth dyed with premetalized dye was studied by the dippiing treatment of the cloth into the solution containing ethylenediaminetetraacetic acid (EDTA) at pH 5-12.5 and at 75°C. The degree of decolorization increased with pH value and decreased with EDTA concentration except the very dilute EDTA concentration region. The metal ion bound between silk fiber and dye molecule was caught by EDTA anion rapidly, and the dye molecule was reduced gradually and eliminated from the silk fiber into the solution.

INTRODUCTION

In recent years, premetalyzed dye, metal mordant dye or after treatment by metal salts are widely introduced in dyeing process of dye factories because of high fastness of color. Moreover, many studies about these dyestuff[1-4] are going ahead.

But it is required to improve the dyeing process from a point of industrial pollusion of waste water[5,6,7].

On the other hand, it is possible to consider the metal complex dye as a model of biochemistry in point of view of interaction between macromolecular metal complex and low molecular ligand or between low molecular metal complex and macromolecular ligand. For example, fiber-metal-dye complex can be regarded as a model of metal transportation in a living body. There are scarecely any papers[8),9)] concerning with such points. And there are many papers about dyeing process, but, we can find few papers dealing with the decolorization of cloth dyed with metal complex dyes.

Thus, our interest has been paid on the mechanism of decolorization of metal complex dyes. In the present paper, a study on the decolorization of premetalized dye was made by the treatment of dyed cloth using low molecular chelate agent such as ethylenediaminetetraacetic acid (EDTA), for the purpose of the possibility of decolorization and of establishment of the mechanism of decolorization.

EXPERIMENTALS

Materials

1 Scoring: Crystalline sodium carbonate and marseilles soap were dissolved in bath ratio 1 : 40 ion-exchanged water, and pieces of colth of Kanebo Fujiginu 5 × 5 cm 0.160g (Surface reflectance 76.5) were dipped in this scoring bath. After 3 hours treatment under starring at 90°C, these cloths were taken out and were washed with the solution containing crystalline sodium carbonate 10g/l at 40～50°C, followed with hot water several times, and were dried at room temperature. The conditions of scoring bath were as following ;

$Na_2CO_3 \cdot 2H_2O$	5% owf
Marseilles soap	10% owf
ion-exchanged water	400% owf.

Surface reflactance and color difference of scored cloth were measured by Nihon Denshoku reflectance meter (CP6-1D3) and Nihon Denshoku color difference meter (ND-101DP). Table 1 shows the average value from at least five samples.

Table 1. Refrectance and color difference of the scored cloth and the cloth dyed with Irgalan Kahki GL.

REFLECTANCE (after scoring) (after dyeing)		COLOR DIFFERENCE (after scoring) (after dyeing)
	X	57.5 12.0
	Y	56.4 12.0
74.0	Z	66.3 6.6
1.0	L	76.0 34.5
	a	0.4 0.0
	b	2.0 13.5

2 Dyeing method : The dye, Irgalan Kahki GL, was used without purification. Dyeing conditions were as follows ;

dye concentration	5% owf
Na_2SO_4	10% owf
$(NH_4)_2SO_4$	3% owf
dyeing bath ratio	1 : 50 (ion-exchanged water)
dyeing temperature	80°C
dyeing period	20 minutes at 30°C followed 60 minutes at 80°C.

After dyeing, dyed materials were rinsed with ion-exchanged distilled water and color differences of dyed cloth were measured. Table 1 shows the results. Electronic spectra of dye solution before and after dyeing were measured on a Hitachi 228A spectrophotometer. All other reagents were analytical grade and used without further purifications.

Decolorization method

Decolorization method of dyed cloth was as follows ; a dyed cloth was dipped into the solution (50ml) containing ethylenediaminetetraacetate (Dotite 2Na) purified by recrystallization from methanol and sodium hydroxide (Wako special grade), and treated at 75 °C in water bath for 15 minutes, then dried in air. EDTA concentration change, pH change, temperature change and decolorization using hydrosulfite with EDTA were carried out. Electronic spectra of the solution after the decolorization were measured by spectrophotometer. One plot of these results was the average from at least four samples. All other chemicals were analytical reagent grade and used without further purifications.

RESULTS AND DISCUSSION

Irgalan Kahki GL has the remarkable absorptions, 445nm and 255nm, as shown in Figure 1. The cloth dyed with Irgalan Kahki GL is decolored dy the treatment with the solution containing ethylenediaminetetraacetic acid in the presence of an adequate amount of sodium hydroxide. Figure 1 also shows the spectrum of solution after the treatment. The treatment lightened the cloth of its color and the color fell into the decoloring solution. The slight shift of spectra is thought as a

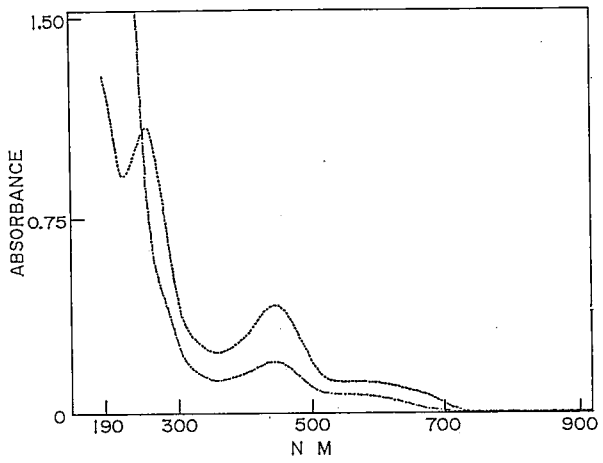

Figure 1. Electronic spectra of the dyeing solution of 5% owf Irgalan Kahki GL and the solution after the decolorization.

shift due to the change of electronic state of dye molecule caused from the interaction between metal and EDTA. We can observe the change of the decolorization reaction by detecing the remarkable absorption at 445nm.

First, the decolorization reaction was carried out under the condition that the cloth was dipped into the solution containing only large excess EDTA necessary to catch the metal ion of the premetalized dye. pH of this solution was 4.78. As the result, the dyed cloth was scarcely decharged and the spectrum of decoloring solution showed a little absorption at 445nm. Figure 2 is the spectrum of this solution.

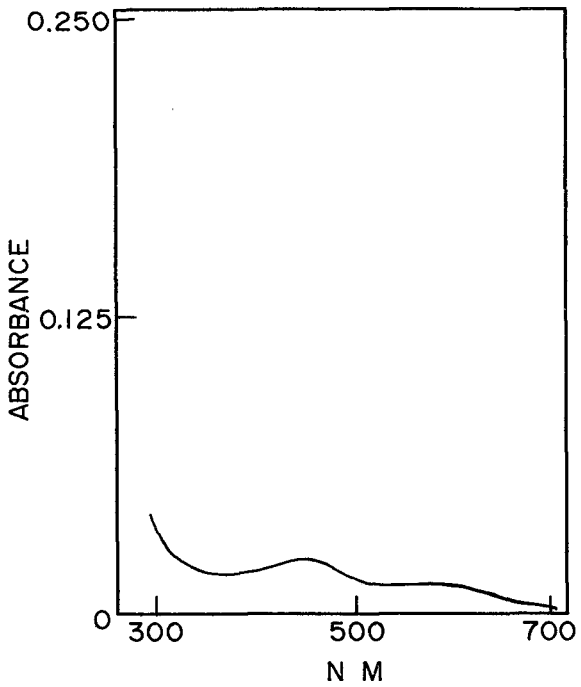

Figure 2. Electronic spectra of the solution after the decoloring treatment of 5.00×10^{-3}M EDTA at pH 4.78.

pKa of ethylendiaminetetracetic acid[10] are as follows ;

$pK_1=1.99$, $pK_2=2.67$, $pK_3=6.16$, $pK_4=10.23$ at 21.7°C and $\mu=0.1$.

Under this condition, it is reasonable to consider that EDTA does not act as a good reagent to capture the metal ion because of existing as EDTA-H_2. Generally EDTA-metal complexes are more stable at higher pH region. Therefore, the decolorization reactions were carried out at 75°C varying pH 6 to 12.5 with sodium hydroxide and keeping EDTA concentration constant. Figure 3 shows the several runs of electronic spectra of the reactions varying pH value. The relationship between the absorption at 445nm and the pH value are plotted in Figure 4.

The degree fo decolorization rises with pH value. Especially above pH 12 the line in Figure 4 goes up rapidly. But silk fiber is gradually dameged above pH 12.

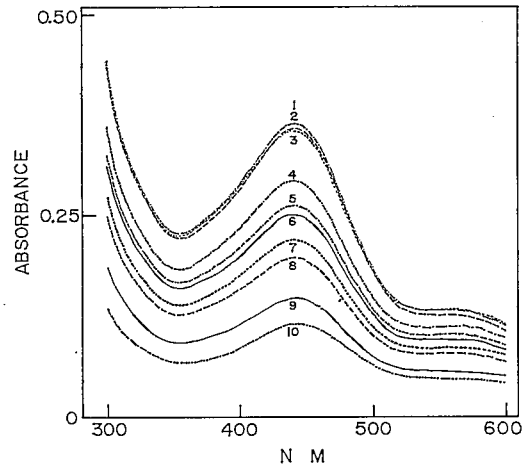

Figure 3. Electronic spectra of the solution after the decoloring treatment varying pH. 1:12.56, 2:12.53, 3:12.48, 4:12.44, 5:12.39, 6:12.28, 7:12.21, 8:12.04, 9:11.51, 10:9.64

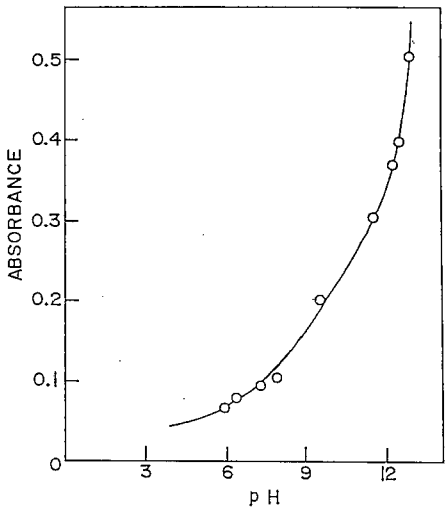

Figure 4. Relationship between the absorption at 445nm of the solution after the decolorization and pH values. [EDTA]=5.00×10^{-3}M, at 75°C

So the pH condition of decolorization is decided as pH 11.5 in following experiments. Next the decolorization reactions were carried out at pH 11.5 varying temperature and keeping the EDTA concentration constant. Figure 5 shows the electronic spectra of the reactions.

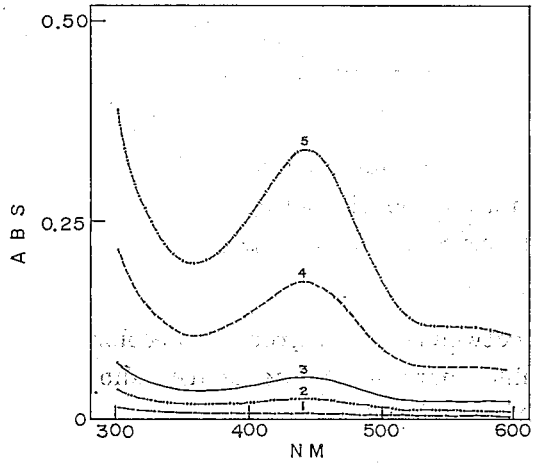

Figure 5. Electronic spectra of the solution after the decoloring treatment varying temperature.
1:room temp., 2:50°C, 3:65°C, 4:75°C, 5:85°C

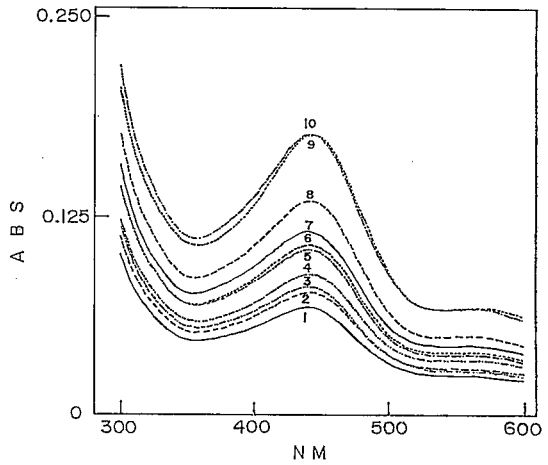

Figure 6. Electronic spectra of the solution after the decoloring treatment varying EDTA concentration at pH 11.5 and at 75°C.
1:6.00×10^{-2}M, 2:5.00×10^{-2}M, 3:4.00×10^{-2}M, 4:3.50×10^{-2}M, 5:3.00×10^{-2}M, 6:2.50×10^{-2}M, 7:2.00×10^{-2}M, 8:1.50×10^{-2}M, 9:5.00×10^{-3}M, 10:5.00×10^{-4}M

The values of temperature were at room temperature (about 25°C), 50°C, 65°C, 75°C and at 85°C. The degree of decolorization increased with temperature. At 85 °C the reproducibility of the data became uncertain though the intensity of absorption grew larger. Furthermore it is conceivable that the silk fiber is dameged above 85°C, but the damege of the cloth is not observed so far as looked at.

The decolorization reactions of the cloth dyed with premetalized dye were carried out at pH 11.5 and at 75°C varying EDTA concentration. Several spectra of this reaction were shown in Figure 6.

The range of EDTA concentration was from 5.00×10^{-4}mol to 6.00×10^{-2}mol. Figure 7 shows the relationship between the absorption at 445nm and EDTA concentration.

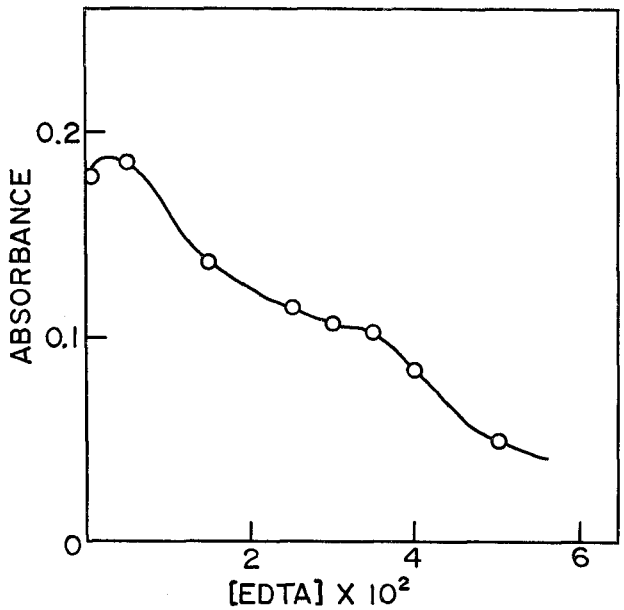

Figure 7. Relationship between the absorption at 445nm of the solution after the discoloring treatment and EDTA concentration at pH 11.5 and at 75°C.

As shown in this figure, the relationship between the degree of decolorization and EDTA concentration exhibits inconsiderable increase, subsequently shows decrease in proportion to the increase of EDTA concentration.

From these findings it is reasonable to consider that the metal ions bound between silk fiber and dye molecules are caught by EDTA anion rapidly, and the dye molecules are gradually reduced, at this time the elimination of the dye molecule is inhibited by the presence of excess EDTA anion.

Hydrosulfite as reducing agent is well used to discharge of color. Next the decolorization reactions were carried out using appreciable concentration of hydrosulfite and EDTA at pH 11.5 and at 75°C. The degree of decolorization was more increased

than the use of EDTA only, but the absorption at 445nm disappeared. The comparison of decolorization degree was achieved using reflectance meter.

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