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Oxime Generation of Silk Fibers by Hydroxylammonium chloride Treatment

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ABSTRACT

This study was aimed to explain the essence of Hydroxylammonium hydrochloride(H.A.) effect on degummed silk fiber for increasing the colour acceptor sites due to oxime generating reaction. H.A. in aqueous solution causes to increase the amount of $[H^+]$ and reduce pH values as the concentration of H.A. increases. The rate of $[H^+]$ adsorption of silk fiber in acidic solution differs on the basis of solution pH and shows a specific uptake in each pH, the lower the pH of solution, the higher the amount of $[H^+]$ adsorption. The pH of solution after treating of silk fiber in H.A. and HCl, showed more remaining $[H^+]$ in H.A. solution due to $[H^+]$ releasing under the procedure of oxime production. Also it was revealed that in higher concentration of H.A. the reaction for oxime fixation on silk fiber carried out stronger and as a result the bigger gap with acid uptake curve appeared. FT-IR analysis of silk fiber treated with H.A. revealed the creating of intermolecular H-bond at the 2,981-2,930 cm^{-1}, which was not appeared for non-treated silk fibers and shows H-bond between N-OH group in one chain and C=O group in another chain of silk protein. Colourimetry of dyed silk fiber after H.A. treatment showed that the silk fiber treated with the high concentration of H.A. compare to low concentration, absorbed more dyeing molecules and so showed less percentage of whiteness.

Key words : Silk fiber, Oxime Generation, Dyeing Site, Hydroxylammonium chloride, Whiteness

INTRODUCTION

Silk fiber consists of various amino acids in its chemical structure. To improve the silk fiber quality, the basic amino acids of silk protein are sometimes used as active groups in finishing methods as well as being dyeing site for acid dyes. Nowadays more emphasis is imposed on the aspect of economic and environment balance in dyeing procedures. In this regard low temperature dyeing method and reducing the amount of dye substances in remained solution are employed to proceed economic benefit and to protect the environment hazard respectively. It is well known that the higher the rate of linkage between silk fiber and dye molecules, the lower the concentration of dyeing materials in the surplus sewage. The linkage of acid dyes and silk fiber mainly happen at amino group of silk protein which unfortunately in silk fiber the equivalent number of basic groups by analysis (per Kg) is about 1/6 of that on wool fiber (Peters, 1975). Using light colors for dyeing certainly would bring no problem meanwhile for dark colors it is not so easy to obtain full success using only optimum method of dyeing. To over come this difficulty in acid dyes, increasing of dyeing sites on silk fiber seems to be a remedy. On the other words, in case of increasing the number of such groups which can change to "+" charged groups in acidic condition, it would be easy to adsorb more acid dyes molecules that carry "+" charge in aqueous solution. One idea in this regard is to fix oxime group on silk fiber which is susceptible to change to a charged group and as a result a dyeing site in the vicinity of hydrogene ion. There are too many carbonyl groups in the chemical composition of silk fiber which readily change to oxime group with hydroxyl ammonium chloride treatment. It is expected that the number of sites for acid dyes increases, but in view of detailed informations about silk fiber and theoretical basis of this phenomena, the accomplished studies seem to be insufficient up to now. This report however aims to reveal more realities about the behaviour of oxime group due to silk fiber acid dyeing through the experimental arguments.

MATERIALS AND METHODS

Materials

1. Silk fibers

The commercial raw silk fibers were degummed by the following method. The raw silk fibers were treated with 15%(o.w.f.) marseilles soap and 10%(o.w.f.) sodium carbonate aqueous solution for 2 hours at 95 °C(L.R.=50:1). The fibers were washed with boiling water, rinsed with cold water several times, and finally dried at room temperature. The degumming ratio was 25.2%.

2. Reagents

Hydroxylamine hydrochloride, GR

Acetic acid, GR.

Hydrochloric acid, GR

Dye : C.I. Acid Red 114 (Erionyl Red RS)

Method

1. Adjustment of pH values by the various hydroxylamine hydrochloride (H.A). concentrations.

Different concentrations of H.A. were used in distilled water for making solutions at the levels of 1, 0.7, 0.5, 0.3, 0.1, 0.07, 0.05, 0.03, 0.01, 0.009, 0.007, 0.005, 0.003, 0.001, 0.0009, 0.0007, 0.0005, 0.0003, 0.0001 mol/L. Then after, the pH value of each solution was recorded.

2. Changes of pH value in solutions depending on the H.A. treatment.

Initial pH of distilled water (D.W) was adjusted to 4 by using acetic acid and then, different concentrations of H.A. were added at the level of 0.0, 0.005, 0.01, 0.03, 0.05 gr H.A./200cc and the pH obtained were recorded. Then with each sample(200cc), 1 gr. of commercial degummed silk fiber was treated at 70°C for 200 minutes. And the pH values of solutions were also determined.

3. $[H^+]$ uptake of silk fibers in various pH values.

The commercial degummed silk fiber was neutralized by treating at pH 7 solution for 2 hours at boiling condition and over night at room temperature in advance. After drying at 70°C, 7 samples were weighted at room temperature mean while for 1 sample providing high temp.(about 105~110°C) for 4 hours. Rate of weight loss was determined and the corrected weights of samples based on dry weight were calculated as: 0.1766, 0.5298, 0.883, 2.649, 4.415, 6.181, and 8.83 grams. The pH of original solution was adjusted at 3.45 using HCl. With the same amount of solution(200cc) for each sample, the treatment carried out at about 55°C over night and room temperature for 2 days. The pH values obtained at equilibrate condition of reaction between silk fiber and solutions were recorded.

4. FT-IR spectra of silk fibers treated with H.A.

2 samples of neutralized silk fiber were treated with H.A. solution at the concentration of 1×10^{-2} and 1×10^{-3} mol/L and then, dried in dry oven. These samples were used for FT-IR (Galaxy 7020A) analysis.

5. Dyeability of silk fibers treated with H.A.

The silk fiber was treated in H.A. solutions (L.R.= 1:40) at 1×10^{-4}, 5×10^{-4}, 1×10^{-3}, 5×10^{-3}, 1×10^{-2}, 5×10^{-2} and 1×10^{-1} mol/L. The treating temperature was maintained at 50°C for 30 minutes. The samples of silk fibers after rinsing with D.W. and drying were subjected for dyeing. The dyeing procedure carried out at 70°C for 1 hour at adjusted pH 5 by acetic acid, 1×10^{-4} mol/L concentration of C. I. Acid Red 114 dye was used. After dyeing the whiteness was measured by Colorimeter (CR 200).

RESULTS AND DISCUSSION

Hydroxylamine hydrochloride, a salt($NH_2OH\cdot HCl$) in aqueous solution causes the increasing of hydrogen ion concentration and decreasing of pH value in the procedure of Reation 1.

Reaction 1: $[NH_2OH\cdot HCl] \rightleftarrows {}^+NH_3OH+Cl^- \rightleftarrows NH_2OH+H^++Cl^-$

The amount of [H+] production and the rate of reaction at various concentrations of H.A. are different. The pH values obtained using different amount of H.A. are shown in Table I.

Using the above data, a linear relation obtained as below :

$$\log[H^+]=0.4872\ \log[H.A.]-3.072\ (r=0.998) \quad \text{eq. (1)}$$

Fig. 1 shows the relation between -log[H.A.] and pH.

Table I. *The pH values of various concentrations of H.A. solution*

H.A. concentration (mol/L)	-log[H.A.]	pH
1	0.000	3.02
7×10^{-1}	0.155	3.12
5×10^{-1}	0.301	3.21
3×10^{-1}	0.523	3.33
1×10^{-1}	1.000	3.59
7×10^{-2}	1.155	3.65
5×10^{-2}	1.301	3.71
3×10^{-2}	1.523	3.83
1×10^{-2}	2.000	4.03
9×10^{-3}	2.046	4.11
7×10^{-3}	2.155	4.15
5×10^{-3}	2.301	4.20
3×10^{-3}	2.523	4.29
1×10^{-3}	3.000	4.48
9×10^{-4}	3.046	4.58
7×10^{-4}	3.155	4.66
5×10^{-4}	3.301	4.70
3×10^{-4}	3.523	4.81
1×10^{-4}	4.000	4.92

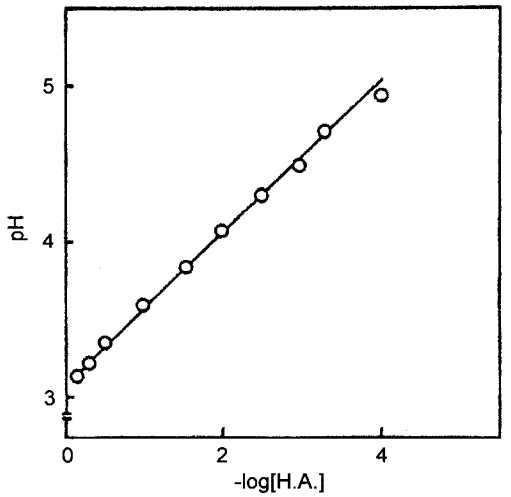


Fig. 1. *The pH values depends on hydroxylammonium chloride concentration.*

It is evident that the higher the H.A. concentration, the higher the $[H^+]$ will be produced in solution. It shows that H.A. in solution acts like acid although H.A. is a salt. An initial solution with adjusted pH 4 by using acetic acid was suffered to different concentrations of H.A.. After recording the pH changes in solution, 1 gram of silk fiber was treated in each solution (L.R.= 1:200) at 70°C for 200 minutes and the pH changes were checked again. The results obtained are shown in Table 2.

Fig.2 shows the relation between -log[H.A.] and pH value before treatment in a liner statement, but different slope of line with eq.(1) and is shown by eq.(2).

$$\log[H^+]=0.0546[\log H.A.]-3.784 \quad (r=0.9425) \quad \text{eq. (2)}$$

The different slope mostly should be due to the initial adjustment of pH. Therefore, using the same applied concentration in eq.(1), the value of $[H^+]$ concentration was calculated. On the other hand the initial pH of 3.997 will provide 1.007×10^{-4} mol/L of $[H^+]$ in solution which should be added to the above obtained concentrations of hydrogen ion. By this method it can be obtained the corrected pH. The relation exists between corrected pH values and the real concentration of H.A. is shown in eq.3 and Fig.2 (closed circle)

$$\log[H^+]=0.116\ \log[H.A.]-3.532 \quad (r=0.9918) \quad \text{eq. (3)}$$

Discussion about the results obtained after silk fiber treatment in H.A. solutions needs the knowledge about the amount of $[H^+]$ uptake by silk fiber in different pH. In this regard, more details would be explained after experiment, the acid uptake of silk fiber in different pH. It has already been known that the amount of acid adsorption of silk fiber would differ in pH changes in solutions. To obtain more detail information, one experiment was done as follows : First, silk fibers were treated with various concentrations of HCl solutions until equilibrium state, and then measured the final pH of solutions. It could be considered that the amount of decrease of pH between initial and final solution was adsorbed on silk fiber.

Fig.3 showed the fixed amount of acid adsorption by silk fiber unit at different pH conditions (open circle). Needless to add that the lower the pH of solution, the higher the quantity of hydrogen ion adsorption by silk fiber and at isoelectric point of silk fiber (about pH=4)

Table 2. *The pH changes of H.A. solutions according to the treatment of silk fibers*

No.	Amount of H.A. g/200cc	Concentration of H.A mol/L	-log[H.A]	Initial adjustment of pH	pH before treatment	pH after treatment
1	0.000	–	–	4	3.997	5.442
2	0.005	3.598×10^{-4}	3.444	4	3.965	5.211
3	0.010	7.195×10^{-4}	3.143	4	3.961	5.084
4	0.030	2.159×10^{-3}	2.666	4	3.936	4.849
5	0.050	3.598×10^{-3}	2.444	4	3.908	4.656

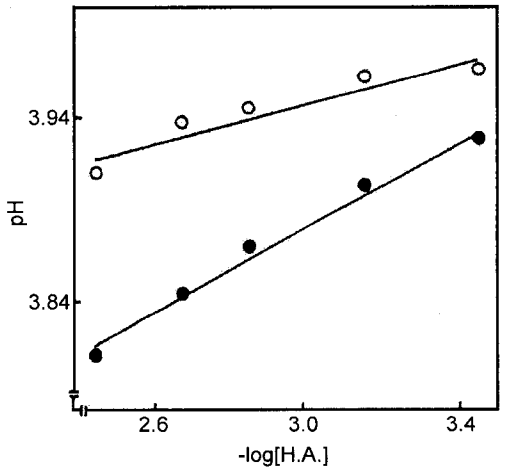


Fig. 2 *The pH values in the solution adjusted pH 4 by acetic acid and added various hydroxylammonium chliride concentrations.*
○—○; real pH
●—●; obtained by eq. (1).

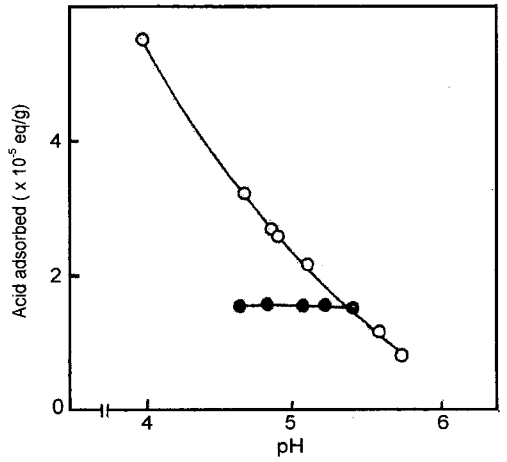


Fig. 3 *The acid uptake of silk fiber in different pH solutions.*
○—○; only HCl solutions
●—●; HCl and hydroxylammonium chloride solutions

the slope of curve appears more sharp. With due regard to above mentioned information, the results of silk fiber treatment in H.A. solution at different concentrations are summarized in Table 3.

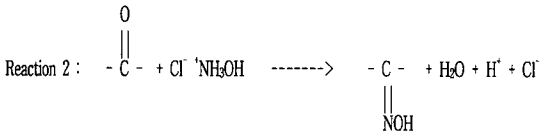
Table 3. *The amounts of acid uptake by silk fibers treated with H.A. solutions*

No.	pH of solution before treatment	pH of solution after treatment	Acid uptake by silk
1	3.997	5.442	1.94160×10^{-5}
2	3.965	5.211	2.04486×10^{-5}
3	3.961	5.084	2.02307×10^{-5}
4	3.936	4.849	2.03440×10^{-5}
5	3.908	4.656	2.03024×10^{-5}

Considering the acid uptake determined in Fig. 3, the above data show some what different tendency. However, sample No. 1(pH after treatment : 5.442) without using of H.A. can be supposed as same state of figure 3, the amount of acid uptake reading out from graph at pH=5.442 is about 1.46×10^{-5} which compare to real amount of adsorption, this quantity is about 1.33 times less. So this index can be used to modify the others figures :

No.	Acid uptake by silk fibers/1.33
1	1.460×10^{-5}
2	1.537×10^{-5}
3	1.521×10^{-5}
4	1.530×10^{-5}
5	1.526×10^{-5}

Using the calculated amounts of acid adsorption and pH values after treatment, the tendency is shown in Fig. 3 (close circle). Compare of two curves appears some gaps which grow due to the increase of H.A. concentration. On the other hand, the invariable amount of acid uptake by silk fibers at different pH has been already shown in Fig. 3 (open circle). It is known that the reaction between carboxyl group and hydroxylamine follows as Reaction by forming oxime (Allinger *et al.*, 1974a) :



It was considered that the reaction to make oxime between silk fiber and H.A. was possible, because silk fibers have many carboxyl groups. Thus under the process of oxime generation, H.A. releases hydrogen ion in solution and the obtained pH after treatment is lower than that of without H.A. The amount of differences between read out pH in H.A. and HCl solution based on the concentration of H.A. is shown in Fig. 4 (open circle).

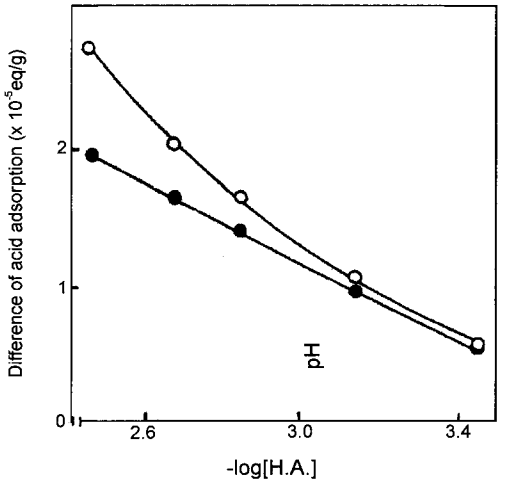


Fig. 4. *The differences of acid adsorption by hydroxylammonium chloride treatment.*
○—○ ; differences between only HCl and hydroxylammonium chloride solutions
●—● ; differences between only HCl solutions and calculated by eq. (2).

It is valuable to mention that the amount of $[H^+]$ in solution completely depends on the concentration of H.A. and on the other words it is determined by the amount of oxime generated on silk fibers. To prove this concept, the amount of $[H^+]$ produced by different concentrations of H.A. in Exp. 2 were calculated in eq. 2, considering the initial pH of solution. This relation can be shown as closed circle in Fig.4. The gaps observed between two lines show the specific amount of $[H^+]$ which released to solution under oxime generating process. The higher the concentration of H.A., the higher the effect of oxime reaction.

In order to know more details about the chemical structure of H.A. effect on silk fiber, FT-IR analysis was applied. The silk fibers treated in different concen- tration of H.A. at the level of 1×10^{-2} and 1×10^{-3} mol/L and one sample of none treated silk fiber were used for FT-IR spectrophotometry, in the range of 4,000-400 cm^{-1}.

Fig. 5 shows the comparision of nontreated(A) and treated silk fiber in 1×10^{-3} (B) and 1×10^{-2} (C) mol of H.A. per liter. All samples show a strong peak at about 3,400 cm^{-1}, which indicate the large amount of simple

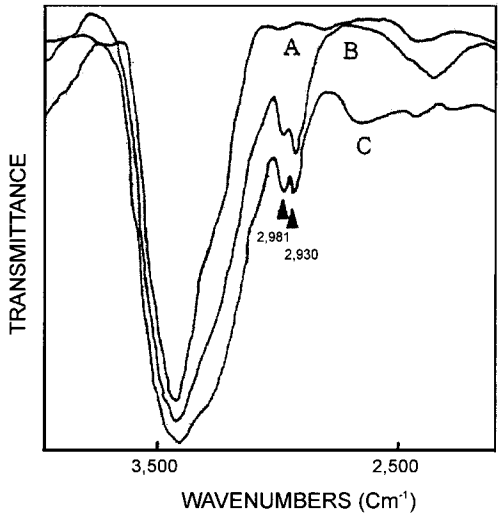


Fig. 5. *The FT-IR spectra of silk fibers treated hydroylammonium chloride.*
A ; Nontreated silk fiber
B ; 1×10^{-3} mol/l hydroxylammonium chloride treated silk fiber
C ; 1×10^{-2} mpl/l hydroxylammonium chloride treated silk fober.

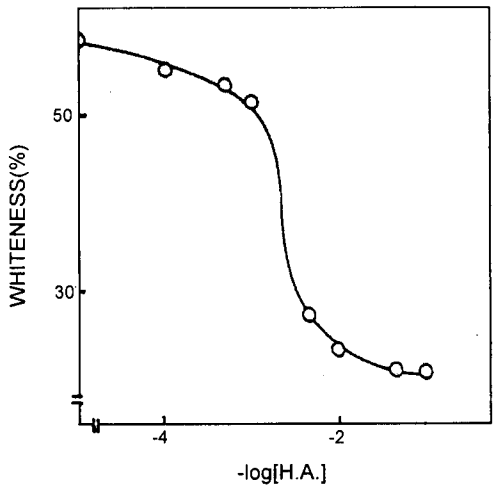


Fig. 6. *Thewhiteness of silk fibers treated with hydroxylammonium chloride and dyed.*

hydrogen bond. However, the peak at 2,981-2,930 cm^{-1} only appears for treated silk fiber which indicates the presence of intermolecular H-bond(Willard *et al.*, 1981). In case of oxime production in silk fiber, it is possible to generate this type of H-bond between oxime group in one chain and C=O group in another chain of silk protein. Intermolecular H-bond also exist in crystalline protein of silk fibroin naturally, but will not appear in FT-IR spectra, as the amount of this is not considerable. Surveying of C=N bond in molecular structure is very complicate. The concerned peak of this bond would appear at about 1700-1640 cm^{-1} which overlap with the amide bonds exist in silk fiber and appear at about 1635 cm^{-1} of wave number.

The main purpose of H.A. treatment is to increase the dye acceptor sites on silk fiber due to generating of oxime group on fiber. Several samples of treated silk fiber in different concentrations of H.A. were subjected for dyeing and then after checked by colourimeter device.

Reaction 3 :

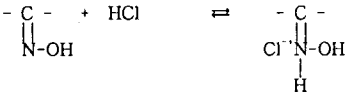


Fig. 6 shows the relation between percentage of whiteness in dyed silk fibers and treatment concentration of H.A.. It is evident that the higher the H.A. concentration, the lower the whiteness % and higher dyeing ability of silk fiber. For more explanation, it should be mentioned that oxime is an amphoteric group. According to the dyeing condition (acid or base), this group can act as a weak base or acid. So in acid dyeing method (with HCl), oxime is capable to absorb [H^+] and change to a charged group which attracts [Cl^-]. As a result, this ammonium form can be the site for acid dye (Allinger *et al.*, 1974b). This reaction is summarized as below:

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