Note

(Received February 29, 1988)

ADSORPTION OF CATIONIC DYE BY POLY(VINYL ALCOHOL) FIBER TREATED WITH SULFURIC ACID

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Abstract

When acid groups were introduced in poly(vinyl alcohol) (PVA) fibers by treating with 20~30% sulfuric acid at 74°C for 90 minutes, they were dyeable with cationic dyes. The acid groups of PVA introduced by this treatment were stable in neutral or alkaline condition, but the most of them were unstable in acidic one. From these results, it was assumed that the most of acid groups in PVA treated with sulfuric acid were sulfuric ester types and adsorbed cationic dyes.

1. Introduction

It is generally known that vinylon fiber is dyed with various cationic dyes to medium or deep shade \(^1\). Two mechanisms of dyeing are proposed, which are the adsorption of the dye cations by the carboxylate anion in vinylon fiber and the dispersion of the dyes into it.

On the other hand, we have reported the following facts.

In acetalization of PVA fiber using sulfuric acid as catalyst the combined sulfuric acid may play greater role as the adsorption site of dyes than that of carboxyl groups \(^2\). For example, in formalization or benzalization of PVA fiber using 20~30% sulfuric acid as catalyst, the fiber is improving in its dyeability for cationic dyes remarkably \(^3,4\).

The acid groups in PVA fiber, e.g. carboxyl group \(^5\), sulfuric ester group \(^6,7\) and sulfonic acid group \(^8\), may be introduced by the treatment described above.

The mechanism of adsorption of cationic dyes had already been discussed briefly \(^9\). In the present paper, the dyeing mechanism was clarified in detail, particularly the relationship between the content of acidic groups in the treated fiber and the amount of the cationic dyes adsorbed by it was discussed.

2. Experimental

2.1 Dye and reagents

C. I. Basic Red 18 (Aizen Cathilon Red GTLH, Hodogaya Kagaku Co. Ltd.) was used for the measurement of the amount of dye in the fibers. The dye was purified by means of the column chromatography on alumina using methanol as a solvent. Alumina, methanol and sodium hydroxide of guaranteed grade reagents were used for purification of the dye and analyses of the reaction product. Sodium sulfate, sodium carbonate and sulfuric acid of extra pure grade reagents were used for the treatment of the fibers.

2.2 PVA Fiber

A tow of PVA fiber (1.0 denier) supplied by Kuraray Co. Ltd. was used in this experiment. It was made by means of wet spinning process in an alkaline bath. The heat treatment of fiber was carried out under a certain tension after drying. The fiber was washed with nonionic surfactant solution before the reaction with sulfuric acid.

2.3 Treatment of PVA fiber with sulfuric acid

The fiber was treated with the aqueous solution containing sulfuric acid 20~30% and sodium sulfate 10% (by weight), at 74°C for 90 minutes in a liquor ratio of 25:1, then the fiber was washed with running water and neutralized with sodium carbonate. After the above procedure, the fiber was thoroughly washed with distilled water and
air-dried at room temperature.

2.4 Measurement of the dye uptake

The amount of dye in the fiber was determined by measuring the concentration of dye in the bath before and after the dyeing employing a Hitachi Model 100-50 spectrophotometer.

2.5 Adjustment of the pH values of the dye solution

In order to control pH of the dyebaths, the pH values between 3.2 and 3.4 were adjusted with acetic acid, between 3.8 and 6.0 were with acetic acid and sodium acetate, pH 7.0 were with tris-(hydroxymethyl)amino methane, mareic acid and sodium hydroxyde and between 9.0 and 10.0 were adjusted with guricne and sodium hydroxyde.

2.6 Measurement of the sulfur content

Measurement was carried out by Schoniger combustion flask method10). The mixture of Methyl Red and Methylene Blue was used as an indicator.

2.7 Measurement of the acid groups

The treated fiber was immersed in a 3% solution of hydrochloric acid for 3 hours at 30°C. After the above procedure, the acidic fiber was washed with distilled water and air-dried at room temperature and then dried in vacuo at 60°C to the constant weight.

An accurately weighted quantity of the fiber was immersed in a 0.02 N sodium hydroxide solution for 3 hours at 74°C and the amount of acid groups was titrated with sodium hydroxyde. The indicator used was the same as in the case of sulfur measurement.

3. Results and discussion

3.1 Adsorption isotherm of the dye on the treated fiber

Showing the adsorption isotherm in Fig. 1, it is clear that the amount of adsorbed dye increases with increasing the dye concentration in the bath and then reaches a limiting value when the dye concentration exceeds over a certain value. It seems that the dyeing is proceeded by the adsorption of cationic dye on some sites.

Scatchard plot obtained from Fig. 1 is shown in Fig. 2. The curved line pass through the experimental points indicates the existence of the different kinds of adsorption site of dyes in the treated fiber.

![Fig. 1 Adsorption isotherm of C. I. Basic Red 18 on the fiber.](image1)

The fiber was treated in the solution containing sulfuric acid 30% and sodium sulfate 10% (by weight) at 74°C for 90 minutes in a liquor ratio of 25:1. The dyeing was carried out at 97°C for 90 minutes in a liquor ratio of 150:1 and pH values of the dye solution were 5.6~6.0.

![Fig. 2 Scatchard plot of the result which is shown in Fig. 1.](image2)

3.2 Relation between pH values of dye solution and the amount of dye uptake

It is assumed that acid groups such as carboxyl group, sulfuric ester group and sulfonic acid group are introduced in PVA fiber which has been treated with sulfuric acid. As shown in Fig. 3, the amount of dye uptake on PVA fiber increases very slightly with increasing pH of the dyebath up to pH 5, then increases gradually above pH 5. This relationship seems to be similar to one which was obtained by the dyeing of the acrylonitril fiber containing...
small quantity of weak acid groups and large quantity of strong acid groups with cationic dye. Accordingly, the results obtained in this experiment seems to suggest the existence of strong acid groups which may play greater role as adsorption site of dye than carboxyl group.

3.3 Infrared absorption spectra of PVA treated with sulfuric acid

I.R. spectra of treated and untreated PVA are the same in their characteristic absorption band at 1720 cm\(^{-1}\) due to carboxyl group, at 1150 ~ 1260 cm\(^{-1}\) or 1010 ~ 1080 cm\(^{-1}\) due to sulfonic acid and sulfonic acid ion, 1150 ~ 1260 cm\(^{-1}\) and 1350 ~ 1440 cm\(^{-1}\) due to sulfuric ester.

3.4 The interrelationships of the amount of the dye uptake, the sulfur content and the acid groups content

As shown in Fig. 4, the dye uptake, the sulfur content and the acid groups content increase with increasing sulfuric acid content in the solution.

Linear relationships between the sulfur content and the dye uptake, and between the sulfur content and the acid groups content are observed as shown in Fig. 5. From the results mentioned above, most of the dye molecules seem to be adsorbed by the acid groups containing sulfur atom.

3.5 Hydrolysis of the treated fiber and the relationship between the dye uptake and sulfur content

In order to distinguish whether the adsorption site of dyes containing sulfur is sulfonic acid group or sulfuric ester group, the later tends to be hydrolyzed in acidic solution, the hydrolysis of the treated fiber with hydrochloric acid was experimented.
The change in the amount of the dye uptake and the sulfur content with time of hydrolysis are shown in Fig. 6. The figure shows that both the sulfur content and the amount of the dye uptake are greatly decreased with time. The figure also shows that the molar ratio of the residual sulfate atom to the dye uptake is almost 1. These findings indicate that main part of the acid groups which act as the adsorption site of dyes may be sulfuric ester group, and the residuals are sulfonic acid group and carboxyl group, but the later is negligibles.

3.6 Stability of the treated fiber in hot water and alkaline solution

When the treated fiber is immersed in 2% solution of sodium hydroxide at 74°C for 18 hours, the amount of the dye uptake slightly decreased. In the case of immersion in the distilled water at 97°C for 15 hours, 3~4% of the dye uptake decreased. The results are shown in Fig. 7. The stability of the treated fiber in alkaline or neutral solution is similar to that of the powdered sulfuric ester of PVA reported in previous paper[12).

4. Conclusion

When PVA fiber is treated with 20~30% sulfuric acid at 74°C for 90 minutes the absorption sites of dyes to which cationic dyes combine may be formed. The stability of the dyeing sites in alkaline or hot neutral solution is very similar to that of sulfuric ester of PVA. The main part of the adsorption site of dye seems to be sulfuric ester group, while most of the residual ones seem to be sulfonic acid group.

Acknowledgement

The authors are grateful to Kuraray Co. Ltd. for supplying the PVA fibers and also to Hodogaya Kagaku Co. Ltd. for supplying the dye.

This communication was partly presented at the Annual Meeting of the Society of Fiber Science and Technology, Japan (14 May, 1986, Tokyo).

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硫酸処理ポリビニアルコール繊維に対するカチオン染料の吸着

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ポリビニアルコール（PVA）繊維を、20〜30％の硫酸で、74℃において90分間処理すると、カチオン染料がイオン結合により吸着する酸性基が導入される。この処理によって導入された染着座席は、中性またはアルカリ性溶液中では安定しているが、それらの大部分は酸性溶液中では不安定である。以上の結果から、硫酸処理によりPVA繊維に硫酸エステル基が導入され、それがカチオン染料の主な染着座席となることが推定された。