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Studies of the ζ-Potential of Natural and Synthetic Fibers in Dye Solutions. XVII. ζ-Potential and Surface Dyeability of Drawn Nylon 6 Fiber in an Acid Dye Solution

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In order to ascertain the relation between the change in the fine structure and the dyeability of the nylon 6 fiber with its drawing, the ζ-potential, the surface dye adsorption, and the total dye adsorption of the drawn nylon 6 fiber in an acidic solution (pH 3.0) of acid dye—Orange II and Orange I were determined. The crystallinity and the birefringence of the fiber increase as the draw ratio increases. The isoelectric points of the fibers with the draw ratios of 1 (undrawn), 3, and 4 are pH 5.2, pH 5.4, and pH 5.4 respectively. The increase in the dye concentration changed the sign of the ζ-potential of these fibers in a dye solution from positive to negative and increased the absolute values of the ζ-potential. Moreover, it was suggested that these fibers combine with dye by electrostatic bonds. The surface dye adsorption as calculated from the difference between the surface charge density, $\Delta\sigma$, of the system with dye and that without dye increased in any case as the dye concentration increased. These values became smaller in the order of draw ratios: 1 (undrawn), 3, and 4. The total dye adsorption as well as the surface dye adsorption increased with the increase in the dye concentration and decreased with the drawing. Moreover, the surface areas covered by adsorbed dye molecules, which were calculated from the slope of the graph between the surface dye adsorption and the total dye adsorption, were 4.4, 2.9, and 1.8×10^6cm^2/g fiber in the order of draw ratios: 1 (undrawn), 3, and 4. Also, the effect of the molecular structure of the dye on the ζ-potential, the surface dye adsorption, and the total dye adsorption was discussed.

In manufacturing synthetic fibers such as polyamide nylon fibers, heat—setting and drawing are the usual processing practices. It is known that these treatments cause changes in the fibrous structure, especially in the fine structure.

Hitherto, some articles on the relation between the changes in the fine structure and the dyeability of the nylon 6 fiber caused by the heat—setting treatment have been published,[1] but few reports on the changes due to the drawing treatment are to be found.

In our laboratory the ζ-potential of several kinds of fibers in a dye solution has been measured in relation to the dyeability of the fiber surface.[2] However, the dyeability of the fiber surface caused by the changes in the fine structure of fibers has not been considered. In this report the dyeability of the drawn nylon 6 fiber surface in an acid dye solution is studied in relation to the ζ-potential, the surface dye adsorption, and the total dye adsorption in order to ascertain the influence of the changes of the fine structure upon the dyeability on the fiber surface.

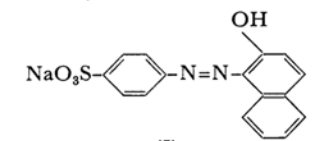
Experimental

Fiber. Nylon 6 filaments (manufactured by the Toyo Rayon Co., Ltd.) were extracted with ethanol for about 24 hr at room temperature and then dried in air. Three kinds of fiber were used. Some of the filaments were drawn as follows, while the rest were undrawn specimens.

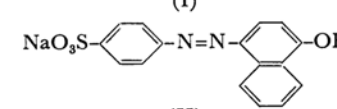
TABLE 1. NYLON 6 FIBER USED

Draw ratio of fiber	Denier
1 (undrawn)	unknown
3	unknown
4	200
(All are composed of 30 filaments)	

Dye. The acid dyes Orange II (I) and Orange I (II), which had been purified by recrystallization from an aqueous solution, were used.



(I)



(II)

ζ-Potential. The ζ-potential was measured by the

1) *E.g.*, A. Koshimo and T. Kakishita, *Chem. High Polymers Japan*, **19**, 506 (1962).
2) *E.g.*, T. Suzawa, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **64**, 573 (1961).

method of the streaming potential and was calculated by means of the Helmholtz-Smoluchowski equation (1)[3]:

$$\zeta = \frac{H}{P} \cdot \frac{4\pi\eta\kappa}{D} \qquad (1)$$

The dye solution was kept at pH 3.0 with hydrochloric acid at 25°C. Sodium chloride was added to the solution in order to prevent any influence of the ionic strength on the ζ-potential; its concentration was 10^{-4}mol/*l*.

Surface Charge Density and Surface Dye Adsorption. From the value of the ζ-potential obtained, the surface charge density of nylon 6 fiber in an acid dye solution was calculated by means of Eq. (2),[4] which was derived from Boltzmann's distribution law and from Gouy's theory:

$$\sigma = \pm(\boldsymbol{k}TD/2\pi)^{\frac{1}{2}}\left[\sum_j n_j \cdot \{\exp(-e_j\zeta/\boldsymbol{k}T)-1\}\right]^{\frac{1}{2}} \qquad (2)$$

$\boldsymbol{k}$: Boltzmann constant, T: absolute temperature, D: dielectric constant, n_j: number of j-cations or anions per unit of volume in the bulk solution. $e_j = Z_j\boldsymbol{e}$. $\boldsymbol{e}$: electronic charge, Z_j: valency of the j-cation or anion.

The surface dye adsorption was calculated from the difference between the surface charge density, $\Delta\sigma$, of the system with dye and that without dye; this difference is proportional to the number of dye molecules per unit of area of the fiber surface.

Total Dye Adsorption. The dye adsorbed by the fibers which had been used to measure the ζ-potential was extracted from the fibers with a 25% aqueous pyridine solution; its amount was determined by spectrophotometry.

Crystallinity. The crystallinity was determined by the density-gradient tube method. A toluene—carbon tetrachloride system was used as the density solution.

Intrinsic Viscosity. Intrinsic viscosity [η] of fiber was measured with the usual method using an Ostwald viscometer at 30°C in concentrated sulfuric acid.

Birefringence. The birefringence, which is supposed to be proportional to the degree of orientation, was measured with a polarization microscope. The monochromatic light of a sodium lamp was used as the light source, and a Berek compensator was used.

Determination of End Groups. The end amino group was determined by conductometric titration in the solvent mixture of phenol, ethanol, and water. The end carboxyl group was determined by neutralization titration. The fiber was dissolved in benzyl alcohol at 175°C and titrated with a KOH-ethanol solution.

Results and Discussion

End Groups, Crystallinity, Birefringence, and Intrinsic Viscosity of Nylon 6 Fiber. The values determined are shown in Table 2.

All of the fibers contained the same quantity of amino and carboxyl group within the limits of experimental error. Moreover, the intrinsic viscosities of all the fibers were almost equal. These results suggest that the degree of polymerization of these fibers does not change with the drawing. The crystallinity and the birefringence increase as the draw ratio increases. These results show the change in the fine structure of the fiber with the drawing.

The Isoelectric Point of Fiber. The ζ-potential of the fiber in solutions of hydrochloric acid or sodium hydroxide in various concentrations was measured in order to ascertain the influence

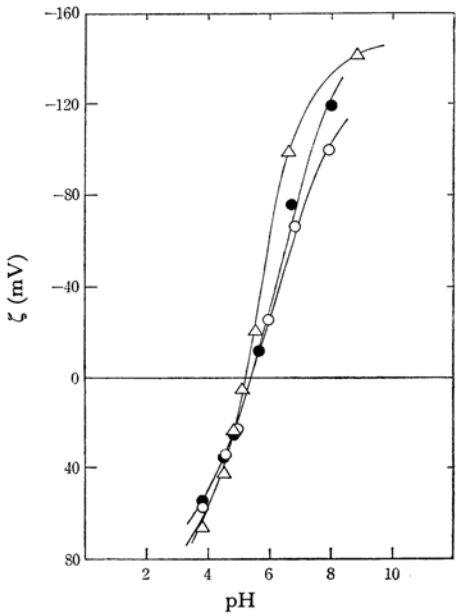


Fig.1. Influence of pH on ζ-potential of drawn nylon 6 fibers at 25°C.
Draw ratios: (△) 1.0; (○) 3.0; (●) 4.0.

Table 2. End groups, crystallinity, birefringence and intrinsic viscosity of the nylon 6 fiber used

Draw ratio	End amino group (mol/g fiber) ×10⁵	End carboxylic group (mol/g fiber) ×10⁵	Crystallinity %	Birefringence ×10³	[η]
1 (undrawn)	4.88	6.44	31.1	13.4	0.902
3	4.93	6.63	37.3	49.8	0.902
4	5.09	6.46	39.5	51.4	0.915

3) Helmholtz, *Wied. Ann.*, **7**, 337 (1897).

4) T. Suzawa, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **63**, 148 (1960).

of the pH on ζ. The results are shown in Fig. 1.

The ζ-potential of any fiber is positive in an acidic solution and negative in an alkaline one. From these results it was found that the isoelectric point of the undrawn fiber is pH 5.2, while those of fibers of the draw ratios of 3 and 4 are both pH 5.4.

ζ-Potential with Dye Concentration. The ζ-potential of the fiber *vs.* dye concentration is shown in Fig. 2 and Fig. 3. The ζ-potential was measured every hour on the hour; the values recorded in Fig. 2 and Fig. 3 are the equilibrium values, which were approximated after four hours of immersion.

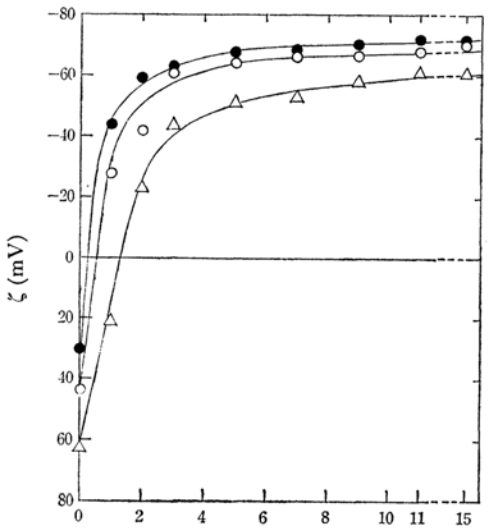


Fig. 2. ζ-potential of the fibers with Orange II concentration. Draw ratios: (△) 1.0; (○) 3.0; (●) 4.0.

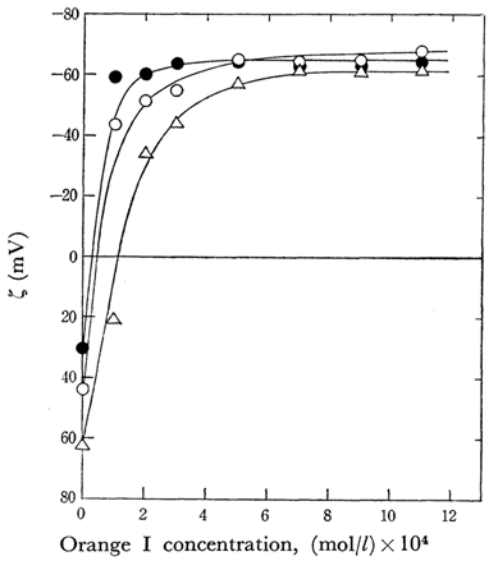


Fig. 3. ζ-potential of the fibers with Orange I concentration. Draw ratios: (△) 1.0; (○) 3.0; (●) 4.0.

As is shown by the curve with Orange II in Fig. 2, the ζ-potential of any fiber is positive in a solution without dye; this behavior caused by the NH_3^+ end group of the fiber. Moreover, the values in the system without dye decrease as the draw ratio increases. This may be attributed to the change in the fibrous structure with the draw ratio; this change causes the decrease of NH_3^+, accompanied by the decrease in the amorphous region.

Upon the addition of dye to this system, the ζ-potential changes from positive to negative as a result of the electrostatic bond between the NH_3^+ of the fiber and the SO_3^- of the dye. The ζ *vs.* dye concentration curves change rapidly in the range of concentrations smaller than 3×10^{-4} mol/*l*, and then the ζ-potentials (negative) approximate the saturated value.

The curves with Orange I in Fig. 3 resemble those with Orange II, but the approximation occurs at a more diluted dye solution.

Surface Dye Adsorption with Dye Concentration. The surface dye adsorption values increase with the dye concentration, as Fig. 4 and Fig. 5 show. In the range of dye concentrations of more than $2-3\times10^{-4}$ mol/*l*, the undrawn fiber has the largest value of the surface dye adsorption, and the value decreases with the drawing. This may be due to the increase in the crystalline region and the decrease in the effective dyeing sites—the end amino groups of the fiber, the increase and the decrease both being caused by the drawing.

The change in the surface dye adsorption of Orange II with the drawing, which is less than that of Orange I, may be due to the difference in the molecular structure of the dye—especially as regards the position of the OH group.

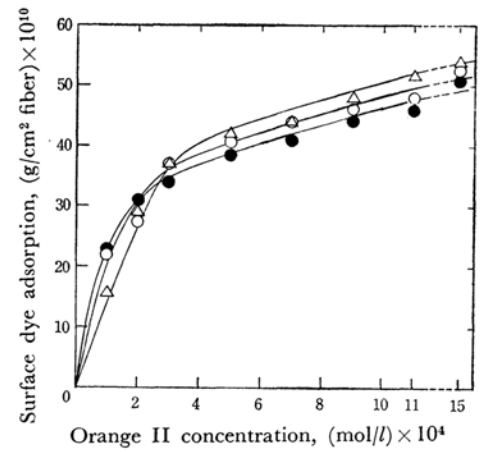


Fig. 4. Surface dye adsorption with Orange II concentration. Draw ratios: (△) 1.0; (○) 3.0; (●) 4.0.

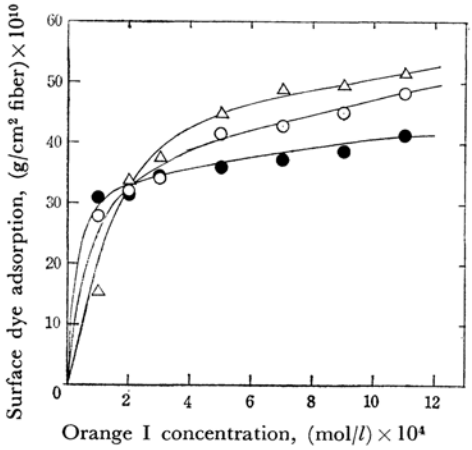


Fig. 5. Surface dye adsorption with Orange I concentration. Draw ratios: (△) 1.0; (○) 3.0; (●) 4.0.

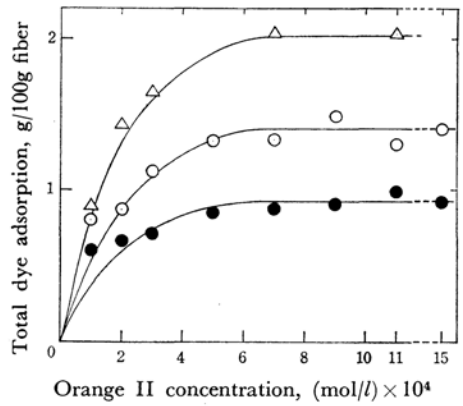


Fig. 6. Total dye adsorption with Orange II concentration. Draw ratios: (△) 1.0; (○) 3.0; (●) 4.0.

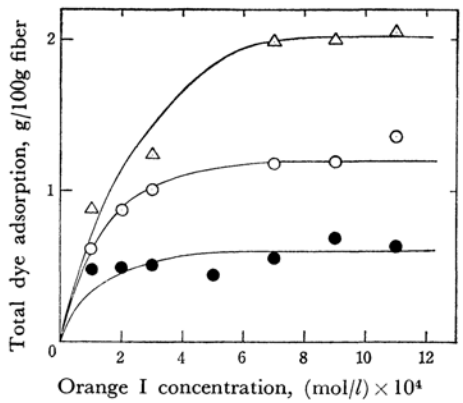


Fig. 7. Total dye adsorption with Orange I concentration. Draw ratios: (△) 1.0; (○) 3.0; (●) 4.0.

Total Dye Adsorption with Dye Concentration. The total dye adsorption values increase with the dye concentration, as is shown in Fig. 6 and Fig. 7. Moreover, the plateau regions are attained at higher dye concentrations. The total dye adsorption and the surface dye adsorption decrease with the drawing. This means that the undrawn fibers with small crystallinities and low degrees of orientation adsorb more dye than the drawn fibers with larger crystallinities and higher degrees of orientation.

When the total dye adsorptions of Orange II are compared with those of Orange I, the adsorbability of these two dyes by the undrawn fibers is found to be nearly the same, while in the case of drawn fibers a definite difference is observed, more Orange II being adsorbed than Orange I. This is probably because of the difference in the molecular structure of the two dyes, Orange II and Orange I; namely, Orange II, which has an OH group in the position ortho to the azo group, may be a little more adsorbed than Orange I. However, the undrawn fibers may have a large amorphous region; therefore, the difference in the molecular structure of dyes may not be reflected in the adsorbability.

Surface Area Covered by Adsorbed Dye Molecules on Fiber. The surface dye adsorption *vs.* the total dye adsorption curves were found to be linear, as Fig. 8 shows. These slopes are considered to be the reciprocal of the surface area covered by adsorbed dye molecules on the fiber. These surface areas, as calculated from Fig. 8, are shown in Table 3.

These values decreasd as the draw ratio increases.

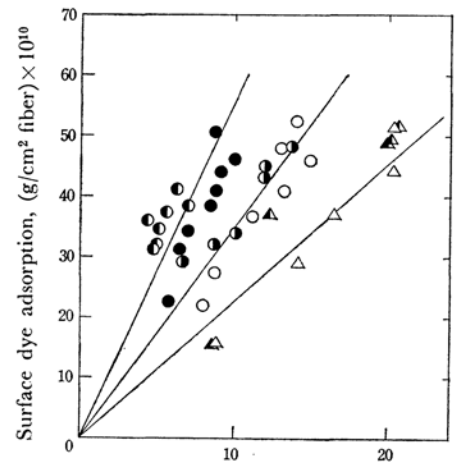


Fig. 8. Relation between surface dye adsorption and total dye adsorption.

Draw ratios of fibers	Dye
1.0	Orange II (△) Orange I (▲)
3.0	Orange II (○) Orange I (◑)
4.0	Orange II (●) Orange I (◐)

Table 3. Surface area covered by dye molecules on fiber

Draw ratio	Surface area (cm^2/g fiber)
1 (undrawn)	4.4×10^6
3	2.9×10^6
4	1.8×10^6

The surface area of the fibers with the draw ratio of 3 is 2/3 that of the undrawn fibers, while that of the fibers with the draw ratio of 4 is 2/5 that of the undrawn fibers. As has previously been mentioned, these results may be caused by the decrease in the amorphous region as the draw ratio increases.

The authors wish to thank Toyo Rayon Co., Ltd., for providing the fiber and the measurement of its birefringence.