

Absorption of Sulfonic Acids on Nylon in Ethylene Glycol

MAMORU NANGO, AKIRA KATAYAMA, and
NOBUHIKO KUROKI, *Department of Applied Chemistry, College of
Engineering, University of Osaka Prefecture, Sakai, Osaka, Japan*

Synopsis

The absorption isotherms of methanesulfonic acid, ethanedisulfonic acid, and R-acid on nylon fiber were determined in water and ethylene glycol at 80°C. The saturation values of the sulfonic acids on the nylon fiber were determined by extrapolation of a reciprocal plot of the absorption isotherms. In water, the saturation values of the three acids were near the amino group content of the fiber. In ethylene glycol, the saturation values of the dibasic acids, ethanedisulfonic acid and R-acid, were much larger than the stoichiometric quantity corresponding to the amino group content of the nylon fiber, approximately twice, though the saturation value of the monobasic acid, methanesulfonic acid, was near the amino group content. A dyeing model of nylon with polybasic dyes was proposed, in order to explain how a polybasic dye can physically saturate fixed sites.

INTRODUCTION

The following mechanism has been accepted currently as accounting for the uptake of acid dyes by nylon:



where Ny is the nylon chain separating the end amino and carboxyl groups and D⁻ is a dye anion. According to this mechanism, the dye anions taken up by nylon are attached to the positively charged amino groups.

So far as attention has been confined to the absorption of monobasic dyes, the physical model is clear, since it is possible to occupy each site with a dye anion. For polybasic dyes, however, it is difficult to visualize how a polybasic dye can physically saturate fixed sites. It has been well known that many polybasic dyes are absorbed stoichiometrically, that is, they occupy the equivalent number of sites in nylon.^{1,2,3} It is seen from the scale model of the polybasic dyes that the distance of sulfonic groups in the dyes is much smaller than that of amino groups in nylon estimated from a crude calculation.^{1,2,3} Therefore, it is evident that the polybasic dyes could not be combined directly to the equivalent number of sites; and yet it is inconceivable that the amino group in nylon should be disposed as to corresponding to the spatial arrangement of sulfonic groups in dye anions.

In previous papers^{3,4} we have introduced the $H_3O_4^+$ bridge hypothesis in order to explain how a polybasic dye can physically saturate fixed sites. That is, we have proposed a dyeing model of nylon with polybasic dyes in which a sulfonic group is linked to an amino group through a $H_3O_4^+$ bridge.

The present paper is concerned with the saturation values of methanesulfonic acid (monobasic) and of R-acid and ethanedisulfonic acid (dibasic) on nylon in ethylene glycol. Even in ethylene glycol, sulfonic acids are easily ionized,⁵ and the resulted ions will be strongly solvated by solvent molecules. However, there is no $H_3O_4^+$ in ethylene glycol. Therefore, it is very interesting to see whether dibasic sulfonic acids are absorbed stoichiometrically or not even in ethylene glycol.

EXPERIMENTAL

Materials

The nylon used in this work was 3 d, 64 m/m and had an amino group analysis of 54.9 meq/kg. The endgroup analyses were determined on several samples of the batch by dissolution in *m*-cresol/methanol and titration with 0.1*N* hydrochloric acid, using thymol blue as indicator. The nylon was dried 72 hr at 60°C over P_2O_5 in vacuo. Methanesulfonic acid was purified by vacuum distillation (bp 154° at 5 mm). Ethanedisulfonic acid sodium salt and R-acid sodium salt were purified by recrystallization from water and changed to the acid type by Amberlite IR-120 (A.G.).

Ethyleneglycol was distilled at atmospheric pressure, dried with anhydrous sodium sulfate, and redistilled under reduced pressure (bp 52° at 1 mm). Water content in ethylene glycol determined by the Karl-Fischer method was below 0.03%.

Method of Absorption

Absorption was carried out in which the fiber (0.55 g) was absorbed for 48 hr in water and 72 hr in ethylene glycol at 80°C, using a solution of 30 ml varying amounts of sulfonic acids in glass-stoppered tubes. The time allowed was adequate for the fiber to reach equilibrium at this temperature. Sulfonic acid-ethylene glycol solutions were prepared in a dry-box to protect them from moisture.

Measurement of Amounts of Absorption

At the end of the absorption period, the fiber was removed from the tube. The amount of acids absorbed on the fiber was determined by measurement of the acid concentration in the solutions before and after the absorption. The acid concentration was determined by titration with standard base to the phenolphthalein endpoint or optically by means of a spectrophotometer (Hitachi 124 Type).

RESULTS AND DISCUSSION

The absorption isotherms of the sulfonic acids used in this paper on the nylon fiber were determined in water and ethylene glycol at 80°C. The results are shown in Figures 1 and 2, where the acid absorbed (eq/g) is plotted as a function of the acid concentration (eq/l.) of the final solution. The saturation values of the sulfonic acids were determined by extrapolation of a reciprocal plot of the titration curves (the absorption isotherms). The results are shown in Table I.

TABLE I
Saturation Values of Sulfonic Acids on Nylon Fiber

Solvent	Saturation values, (meq/g) $\times 10^{-2}$		
	Methane-sulfonic acid	Ethane-disulfonic acid	R-acid
H ₂ O	4.2	4.4	5.6
(CH ₂ OH) ₂ 100%	5.3	11.1	12.5
99%		8.3	
90%		4.8	

^a Amino group analysis: 5.5×10^{-2} meq/g.

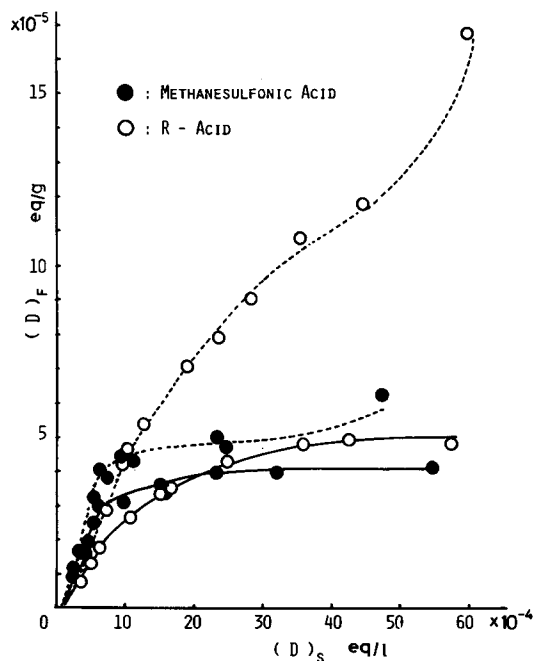


Fig. 1. Absorption isotherms of the sulfonic acids on nylon fiber in water (—) and ethylene glycol (-----) at 80°C.

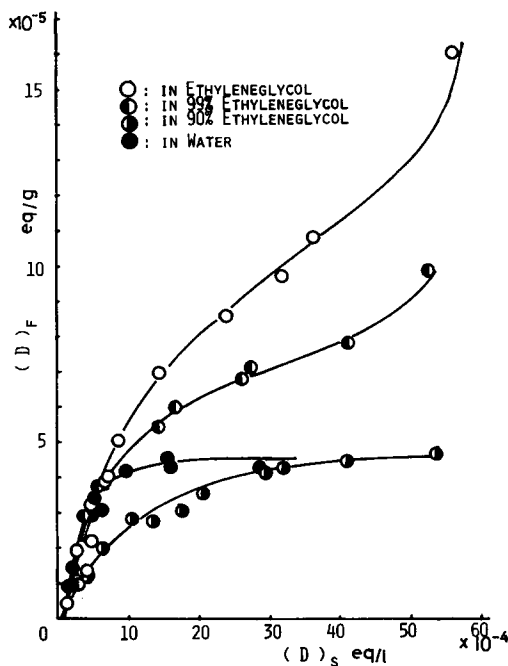


Fig. 2. Absorption isotherms of ethanesulfonic acid on nylon fiber at 80°C.

For methanesulfonic acid (monobasic), it is seen from Figure 1 and Table I that the saturation values in water and in ethylene glycol are near the amino group content of the fiber, though the latter is considerably larger than the former.

With a monobasic acid, there is no difficulty in supposing that the anions become closely associated with the positively charged amino groups in the fiber. Therefore, it is expected that the stoichiometric relation is observed in practice in both water and ethylene glycol. The results for methanesulfonic acid obtained in this paper are not far apart from this expectation.

For R-acid and ethanedisulfonic acid (dibasic), it can be seen from Figures 1 and 2 and Table I that their saturation values in water are near the stoichiometric quantity, though the saturation value of the latter is appreciably lower than the amino group content of the fiber. Here, it should be noted that in ethylene glycol the uptake of the two dibasic acids deviates much from the stoichiometric quantity. The saturation values of the two acids are much higher than the amino group content in the fiber, and approximately twice as large as the stoichiometric quantity.

From the scale model of R-acid and ethanedisulfonic acid, we can see that the distance between two sulfonic groups in the two acids are about 13 Å and 9 Å, respectively. On the other hand, a crude calculation^{1,2,3} gives a distance between neighboring amino groups in the fiber about 28 Å. This spacing of endamino groups in the fiber is much larger than the distance between two sulfonic groups in the two dibasic acids.

In water, a dibasic acid anion will be attached to two sites using a H_3O_4^+ bridge per each sulfonic group. According to the H_3O_4^+ bridge hypothesis,^{3,4} each $-\text{SO}_3^-$ group of a dibasic acid is attached to a H_3O_4^+ ion through a hydrogen bond or an electrostatic bond, and the H_3O_4^+ ion is linked to an amino group on nylon through a hydrogen bond. A crude calculation gave a value of about 9.7 Å for the length of a H_3O_4^+ bridge.³

In ethylene glycol, there is no H_3O_4^+ ion to form a bridge between $-\text{SO}_3^-$ and $-\text{NH}_2$ groups. Therefore, it is expected that a dibasic acid, in which the distance between two sulfonic groups is much smaller than the spacing of endamino groups in nylon, cannot occupy simultaneously two sites. The one $-\text{SO}_3^-$ group of the dibasic acid will be attached to an amino group, but the other will be located far apart from amino groups and not be attached to the sites. If a dibasic acid is absorbed in this way, the saturation values should exceed the equivalent amino group content by as much as 100%. The saturation values of R-acid and ethanedisulfonic acid in ethylene glycol obtained in this paper agree with this expectation.

Here, let us examine the effects of addition of water into ethylene glycol on the absorption isotherm and the saturation value of a dibasic acid. The absorption isotherms of ethanedisulfonic acid on nylon were determined in 99% and 90% (volume) ethylene glycol-water solutions at 80°C. From these absorption isotherms, the saturation values in the two solutions were determined by reciprocal plot. The results are shown in Figure 2 and Table I.

It can be seen from Figure 2 and Table I that an addition of 1% water to ethylene glycol lowers the saturation value of ethanedisulfonic acid on nylon to some extent, though the saturation value still clearly exceeds the equivalent amino group content. Such a reduction suggests that there are two ways in which ethanedisulfonic acid is absorbed on nylon from 99% ethylene glycol-water solutions. The one is that in which the dibasic acid is attached to the equivalent number of sites. The other is that in which the dibasic acid is attached to only one site.

An addition of water to ethylene glycol will enable protons to be in the form of H_3O_4^+ and ethanedisulfonic acid to be attached to two sites. However, in an ethylene glycol-water solution of very low water content, only small portion of protons will be in the form of H_3O_4^+ and the amount of H_3O_4^+ will not be enough to bind each ethanedisulfonic acid molecule absorbed on nylon to two sites. Some ethanedisulfonic acid molecules will be attached to two sites, but others to only one site. This is the case in 99% ethylene glycol-water solutions.

As can be seen from Figure 2 and Table I, the saturation value of ethanedisulfonic acid in 90% ethylene glycol-water solutions is near the equivalent amino group content of the fiber. This indicates that each ethanedisulfonic acid molecule absorbed on nylon is attached to two sites.

The work presented here confirms that the presence of water is necessary for the binding of dibasic acids to two sites of nylon. This would be an indirect evidence for the dyeing mechanism of nylon with polybasic acid

dyes in which a $-\text{SO}_3^-$ group is linked to an amino group through a H_9O_4^+ bridge.

In this paper, the results have been discussed without any consideration of a difference in the ionization character of the dibasic sulfonic acids between the solvents, water, and ethylene glycol.

When using organic solvents, it is likely that the acids will only be partially dissociated, and it may be that a high proportion of singly charged ions is present. If this is true, these ions should be preferentially absorbed.

In ethylene glycol, however, the ionization character of the acids may not differ greatly from that in water. The dissociation constants of methanesulfonic acid in water and ethylene glycol have been determined in our laboratory. They were based on the measurement of the proton chemical shifts and yielded values of 50.3 (mole/l.) in water and 26.3 (mole/l.) in ethylene glycol at 34°C .⁵ The difference between them was considerably small.

We have no data on the dissociation constants of the two acids in ethylene glycol. The results for methanesulfonic acid, however, suggest that there may be no great difference in the ionization character of sulfonic acids between water and ethylene glycol.

References

1. E. Atherton, D. A. Downey, and R. H. Peters, *Text. Res. J.*, **25**, 977 (1955).
2. K. Kanno and T. Iijima, *Kogyo Kagaku Zasshi*, **73**, 1169 (1970).
3. A. Katayama, H. Takasawa, and N. Kuroki, *Kolloid-Z. Z. Polym.*, **251**, 158 (1973).
4. M. Nango, A. Katayama, and N. Kuroki, *Kolloid-Z. Z. Polym.*, to be published.
5. M. Nango, A. Katayama, and N. Kuroki, *Sen-i Gakkaishi*, **29**, T-216 (1973).

Received November 8, 1973

Revised January 24, 1974