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Studies of the Nylon Monolayer. III. The Interaction between the Nylon Monolayer and Acid Dye

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The interaction of the monolayers of the Nylons 6 and 8 with the acid dye Orange II was studied by measuring the surface pressure of the nylon monolayers with and without Orange II in the substrate water. No change in the surface tension with the time was observed for the aqueous solution of Orange II in the concentration and pH ranges studied. The interaction between the nylon monolayers (film B) and Orange II was examined by observing the change in the *F-A* curve of the nylon monolayer due to the addition of Orange II to the substrate and the spreading of the solution. The presence of dye in a spreading solution has little effect, while the pH's of the both the spreading solution and the substrate exhibit a marked effect on *F-A* curves. The observed interaction is compared with the behavior of practical dyeing in bulk of the solution.

The interaction between monolayer and dye has been studied by several investigators[1-5] as a simple model of actual dyeing phenomena. It is evident that pressure-area (*F-A*) measurement does not offer reliable information about the interaction between dye and monolayer unless the measurement is conducted for a monolayer of exactly-defined conditions, conditions which produce a sufficiently reproducible *F-A* curve characteristic of the monolayer. The published reports are not satisfactory[6,7] from this point of view. In our previous paper,[8] the conditions of the formation of a reproducible monolayer characteristic of the Nylons 6 and 8 were reported. The present paper will describe our study of the interaction between the monolayers of the Nylons 6 and 8 prepared under such conditions and Orange II, which is commonly used for dyeing nylon.

Experimental

Materials. For the preparation of Orange II, 3.5 g of sulfanilic acid were reacted with 1.2 m*l* of hydrochloric acid and 1.4 g of sodium nitrate. The diazo compound thus obtained was slowly added to a dilute aqueous sodium hydroxide solution containing 3 g of *β*-naphthol. After coupling had been completed, the product was precipitated by adding 8 g of sodium chloride to the solution. The Orange II thus obtained was purified by repeated recrystallization from ethyl alcohol, followed by a Soxhlet extraction with ethyl ether to remove the residual impurities. The product was finally dried *in vacuo*. The Nylons 6 and 8 were purified by dissolving them in an aqueous solution of formic acid and in one of methyl alcohol respectively, and by then precipitating them by adding water to these solutions. The precipitates were extracted with ethyl ether and dried *in vacuo*.

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[1] C. H. Giles and E. L. Neustädter, *J. Chem. Soc.*, **1952**, 918, 1864, 3806.

[2] C. H. Giles, E. L. Neustädter and M. M. Allingham, *Discuss. Faraday Soc.*, **16**, 92 (1954).

[3] C. H. Giles and A. Cameron, *J. Chem. Soc.*, **1957**, 3140.

[4] C. H. Giles, A. Cameron and MacEwan, *ibid.*, **1957**, 4304; **1958**, 1224.

[5] C. H. Giles and MacEwan, *ibid.*, **1959**, 1791.

[6] M. Hayashi, T. Tachibana and A. Yabe, *Kogyo Kagaku Zasshi*, **63**, 1545 (1960).

[7] M. Hayashi, T. Tachibana and A. Yabe, *ibid.*, **64**, 170 (1961).

[8] T. Seimiya, This Bulletin, **43**, 301 (1970).

Water was obtained by refluxing an aqueous solution of acidic potassium permanganate and by subsequent distilling, first with the addition of excess alkali, and then without the addition.

Methods. The surface tension and surface pressure were measured by means of a Wilhelmy torsion balance. The pH of the substrate water for the nylon monolayer was controlled with hydrochloric acid to about unity (called acid) or without any special control (pH$\simeq$6; called "neutral"). The change in the pH between before and after the *F*-*A* measurements was less than 0.1. The spreading solution was prepared by dissolving the Nylon 6 in methyl alcohol saturated with calcium chloride (CM), and the Nylon 8 in methyl alcohol (MA) or an aqueous solution of formic acid (FA). The concentrations of the spreading solutions were 0.3 mg/m*l*. The details of the experimental procedures were the same as those presented in a former report.[8]

Results and Discussion

Surface Tension of an Aqueous Orange II Solution. It has been reported that the surface tension of an aqueous Orange II solution gradually decreases with the time as a result of the adsorption of Orange II at the air-water interface.[6] It is of interest whether or not the Orange II is really surface-active and how long it takes the surface tension of its aqueous solution to attain its equilibrium. For this purpose, we measured the change in the surface tension of an aqueous Orange II solution with the change in the concentration with the time. No change with the time was observed for any concentration or pH of the solutions studied. The surface tension *vs.* the concentration of the aqueous Orange II solution is shown in Fig. 1. It is confirmed that the surface tension of water is not affected by the addition of Orange II up to a concentration of 1×10^{-3} mol/*l*, while beyond that point it gradually decreases. The adsorption of Orange II is, therefore, considered to be zero for solutions with concentrations of less than 1×10^{-3} mol/*l*. Figure 2 shows the pH dependence of the surface tension of an aqueous solution of 2.57×10^{-4} mol/*l* Orange II. A considerable decrease in the surface tension can be seen in the strongly acid region. It may be noted in this connection that an appreciable decrease in surface tension extending over a period of 20 hr has been reported for an aqueous Orange II solution.[6] In the present experiment, however, the change in the surface tension with time was not observed during a period of 180 min for the ranges of the concentration of

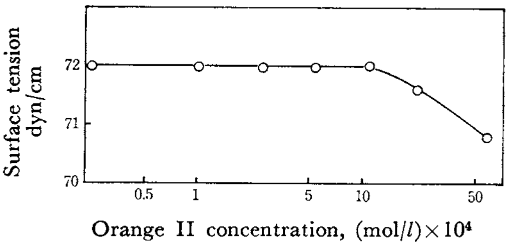

Fig. 1. Surface tension *vs.* concentration of aqueous Orange II solution.
Solution: neutral

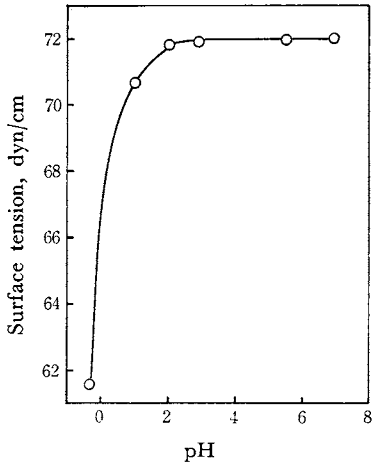

Fig. 2. Surface tension *vs.* pH of aqueous Orange II solution.
Dye concentration: 2.57×10^{-4} mol/*l*

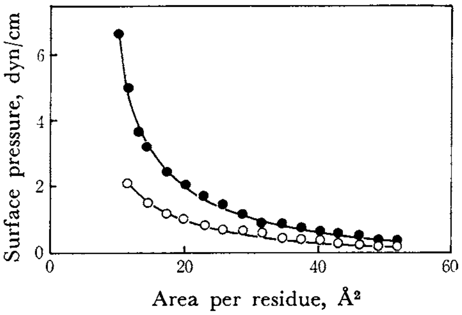

Fig. 3a. *F*-*A* curves of Nylon 6 dissolved in CM spread on 5.73×10^{-4} mol/*l* aqueous Orange II solution (●) and on blank substrate (○).
pH: 6.4, film A

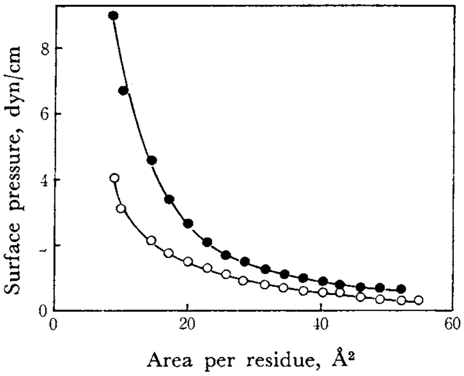

Fig. 3b. *F*-*A* curves of Nylon 6 dissolved in CM spread on 5.73×10^{-4} mol/*l* aqueous Orange II solution (●) and on blank substrate (○).
pH: 1.6, film A

Orange II and the pH of the substrate studied. Here, it may be suggested that the trace of an impurity present in distilled water sharply influences the results obtained.

***F-A* Curves of Nylons 6 and 8 on an Aqueous Orange II Solution.** The *F-A* curves for the Nylon 6 spread from CM on 5.73×10^{-4} mol/*l* Orange II solutions of pH 6.4 and 1.6 are shown in Fig. 3. Here, and in all of the following experiments, the surface pressure is expressed as the difference between the surface tension of water or an aqueous Orange II solution with and without a monolayer. The *F-A* curves measured on an aqueous Orange II solution for both neutral and acid substrates show those of a more expanded type than the blank *F-A* curve on the substrate containing no dye. This behavior is in good agreement with results reported in the literature.⁶⁾

The *F-A* curves of the Nylon 8 spread from neutral MA on both neutral and acid substrates containing Orange II are shown in Fig. 4. Here, the two types of monolayers, A (expanded type) and B (condensed type), were distinguished, as is shown in Fig. 5, by the gradual change in surface pressure beyond a certain compression, much as in former reports.⁸,⁹⁾ This decrease in the surface pressure of the nylon monolayer spread on the Orange II substrate appearing at a high compression is opposite to what has been previously reported.⁶⁾ The monolayers of both A and B film on the acid substrate undergo expansion as a result of the presence of Orange II; the expansion is especially remarkable for the film B (Fig. 4b). In the case of the neutral substrate, the A film rather condenses on the Orange II substrate, while the B film is not affected by the presence of the dye (Fig. 4a). The surface pressure was further measured for the nylon monolayer prepared by adding Orange II to both the substrate and the spreading solution. The *F-A* curves obtained are shown in Fig. 6 for a neutral spreading solution and in Fig. 7 for an acidic one.

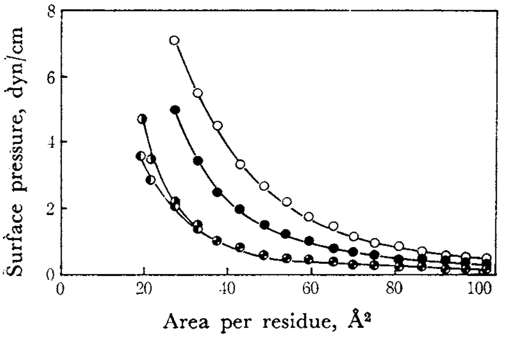

Fig. 4a. *F-A* curves of Nylon 8 dissolved in MA.
Substrate pH: 6.3
2.60×10^{-4} mol/*l* Orange II
●: Film A ◐: Film B
Blank substrate
○: Film A ◑: Film B

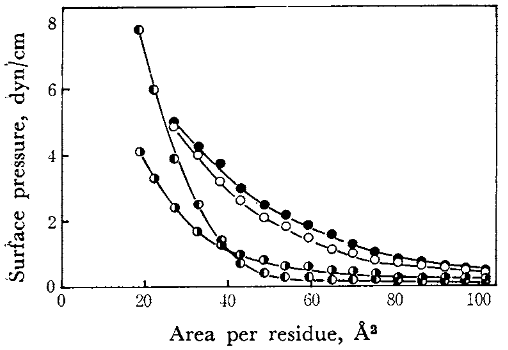

Fig. 4b. *F-A* curves of Nylon 8 dissolved in MA.
Substrate pH: 1.2
2.60×10^{-4} mol/*l* Orange II
●: Film A ◐: Film B
Blank substrate
○: Film A ◑: Film B

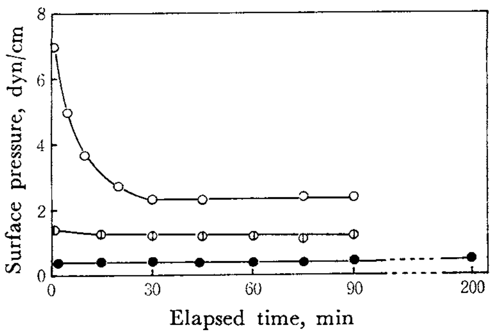

Fig. 5. Surface aging of Nylon 8 film on aqueous Orange II solution.
Dye concentration: 2.60×10^{-4} mol/*l*
Substrate pH: 6.3
○: 26.9 Å/residue
⦶: 53.9 Å/residue
●: 102.5 Å/residue

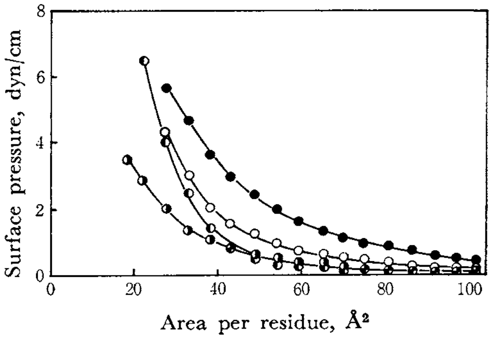

Fig. 6. *F-A* curves of Nylon 8 dissolved in MA with dye spread on 2.61×10^{-4} mol/*l* aqueous Orange II solution.
Substrate pH 1.8
●: Film A ◐: Film B
Substrate pH 6.5
○: Film A ◑: Film B

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9) T. Seimiya, This Bulletin, **43**, 306 (1970).

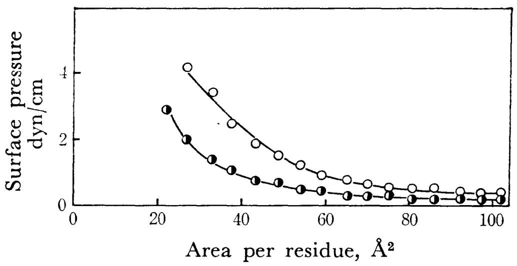

Fig. 7. *F-A* curves of Nylon 8 dissolved in MA with dye spread on 2.62×10^{-4} mol/*l* aqueous Orange II solution.
Spreading solution: acid
Substrate pH: 1.1
○: Film A ◑: Film B

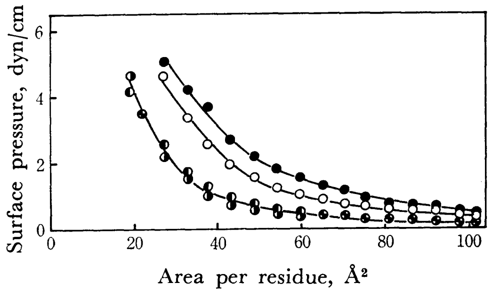

Fig. 8. *F-A* curves of Nylon 8 dissolved in MA with dye.
Spreading solution: acid
On distilled water,
○: Film A ◑: Film B
On 0.1 N HCl,
●: Film A ◐: Film B

We further plotted *F-A* curves for the monolayer spread from the mixed solution of Nylon 8 and Orange II in MA on distilled water and on a 0.1 N hydrochloric acid solution (Fig. 8), and those for monolayers spread from the solution of Nylon 8 dissolved in FA (with and without the dye) on the

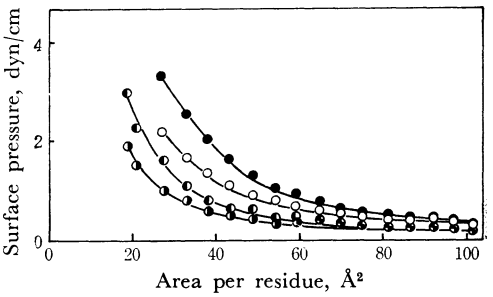

Fig. 9a. *F-A* curves of Nylon 8 dissolved in FA.
Spreading solution: acid
Substrate pH: 1.2
On 2.59×10^{-4} mol/*l* Orange II
●: Film A ◐: Film B
On blank substrate
○: Film A ◑: Film B

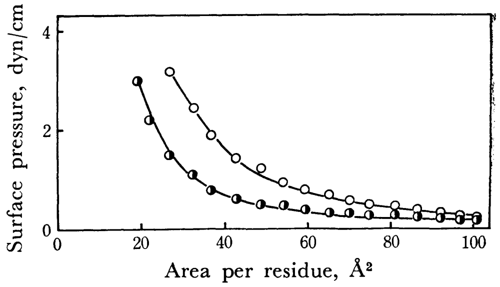

Fig. 9b. *F-A* curves of Nylon 8 dissolved in FA with dye spread on 2.59×10^{-4} mol/*l* aqueous Orange II solution.
Spreading solution: acid
Substrate pH 1.7
○: Film A ◑: Film B

TABLE 1. MUTUAL INTERACTION BETWEEN NYLON 8 MONOLAYER AND ORANGE II

System No.	Spreading solution		Substrate		Mutual interaction		Fig. cited
	Solute	Acidity	Solute	Acidity	film A	film B	
	MA as spreading solvent						
1	Nylon	Neutral	Dye	Neutral	0	0	4a
2	Nylon	Neutral	None	Neutral	—	—	4a
3	Nylon	Neutral	Dye	Acid	0	+	4b
4	Nylon	Neutral	None	Acid	—	—	4b
5	Nylon+Dye	Neutral	Dye	Neutral	0	0	6
6	Nylon+Dye	Neutral	Dye	Acid	0	+	6
7	Nylon+Dye	Acid	Dye	Acid	0	0	7
8	Nylon+Dye	Acid	None	Neutral	0	0	8
9	Nylon+Dye	Acid	None	Acid	0	0	8
	FA as spreading solvent						
10	Nylon	Acid	Dye	Acid	+	+	9a
11	Nylon	Acid	None	Acid	—	—	9a
12	Nylon+Dye	Acid	Dye	Acid	+	+	9b

+: distinct } interaction between Nylon 8 and dye
0: imperceptible }
—: control system

same substrate (Figs. 9a and 9b).

The results mentioned above are summarized in Table 1. In this table we can see differences in the behavior of monolayers, particularly the interactions between the dye and the Nylon 8 in the states of monolayers spread under different conditions. Several remarks can be made:

(1) The A-type film spread on the substrate without Orange II is sensitive to the pH, while the B-type film is not (Nos. 2 and 4).

(2) The difference is hardly observable between the *F-A* curves of monolayers spread from the solutions containing and not containing the dye, if the rest of the conditions are the same (Nos. 1 and 5, 3 and 6, 7 and 10).

(3) The change in pH markedly influences the *F-A* curves. The surface pressure of B-type films compared at a high compression of $A=20$ Å^2/residue showed the largest film pressure for the neutral spreading solution on the acid substrate (Nos. 3 and 6), but in other cases the film pressure was fairly low (Nos. 1, 2, 4, 5, 7, 8, and 9). If the interaction between dye and nylon is expressed as an increase at a certain pressure of the area of the nylon monolayer due to the introduction of a dye in the substrate water, the B-type film spread from a neutral solvent on an acid substrate containing dye shows the largest interaction in the case of MA (Nos. 3 and 6). However, under the same conditions the interaction is rather ambiguous for the A-type film (Nos. 3 and 6). This is because of the unstable nature of the A film, as has been stated in the former report. Thus, because of its reproducible nature, the B film proved to be useful for the study of interactions of this kind.

(4) However, when FA was used as a spreading solvent, the interaction between dye and nylon has been confirmed for the monolayer spread from an acidic solution on an acidic substrate, judging from the expansion of the monolayer (Nos. 10 and 12).

(5) As will be shown in a later section, the Nylon 8 becomes insoluble in MA when treated with hydrochloric acid, but the solubility in FA is not affected by such treatment. These facts are considered to be closely related to the reactivity of the dye with the nylon spread from FA even under acidic conditions. While the H$^+$ ion in the substrate helps the expansion of the Nylon 8 and dyeing with Orange II, the above effect of the H$^+$ ion on the solubility of nylon in a spreading solvent proved to play an important role. Thus, the results of the present study confirm the view that, for the monolayer dyeing, the state of the monolayer and the dye should be taken into account; the overall conditions for optimum deying correspond to the systems Nos. 3 and 6 for MA, and Nos. 10 and 12 for FA.

(6) It should be noted that, as has been mentioned above, the interaction between monolayer and dye inferred in the present paper is marked in the smaller-area region (Nos. 3 and 6). However, a reverse case of monolayer interactions has also been reported, a case in which the increase in surface area is marked at a smaller surface pressure and vanishes at a larger surface pressure of the monolayer.[10] Such a difference in behavior might be closely related to the nature of the interaction in the monolayer, the interaction presumably being stronger in the present experiment, where it appears at a high compression.

(7) In the case of bulk dyeing, that is, the usual dyeing of nylon fibers in a dyeing solution, the spreadability of molecules has no significance, and the diffusion of dye into the nylon fiber is the rate-determining step for dyeing, so a relatively long time (more than a day) is required for dyeing. On the other hand, in the case of monolayer dyeing the process of dyeing is sensitive to the spreading conditions, but the rate itself is very fast. Thus, the monolayer dyeing can offer some useful knowledge for the study of the mechanism of dyeing, apart from the rate problem.

(8) As has already been stated, we made an experiment in which the spreading solution contained both Orange II and the Nylon 8, but the results were not appreciably different from the monolayer spread from the solvent containing the Nylon 8 alone, as may be seen by comparing, for instance, Experiments Nos. 1 and 5, 3 and 6, or 10 and 12.

Further Experiments Concerning the Interaction between the Nylon and Dye in the Bulk of the Solution. *(1) Bulk Dyeing.* The amount of Orange II taken up in the dyeing process was measured by colorimetry for 100 mg of the Nylon 8 in a 2.61×10^{-4} mol/*l* solution of Orange II. The amounts of equilibrium dyeing measured after about 24 hr were 3.28×10^{-5} mol/g Nylon 8 for the neutral solution, and 4.70×10^{-4} mol/g for the acid solution of pH unity. The amount of the end amino group of the Nylon 8, as determined by potentiometric titration,[11] was 3.50×10^{-5} equivalent/g nylon; this value was in agreement with the amount of Orange II dyed from the neutral solution, while the amount dyed from the acid solution was far more than the amount expected from the amino content. This is essentially in agreement with the general trend of the dyeing mechanism of nylons with acid dyes.[12]

(2) Paper Chromatography. A drop of aqueous Orange II was placed as a spot on filter paper (Toyo Roshi, No. 50) previously soaked with a 1% nylon-methanol solution. After the paper had been dried, the spot was eluted with water of 6 and 1 pHs. The distance of the spot eluted was then

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10) T. Sasaki, R. Matuura and N. Fujimoto, This Bulletin, **24**, 203 (1951).

11) J. E. Waltz and G. B. Taylor, *Anal. Chem.*, **19**, 448 (1947).

12) T. Vickerstaff, "The Physical Chemistry of Dyeing," Oliver and Boyed, London (1954).

Table 2. Movement of Orange II on filter paper

pH of eluent	Treatment of filter paper	Movement of dye spot
6	Treated with nylon	4.65 cm
	Untreated	4.65
1	Treated with nylon	0.75
	Untreated	1.75

compared with that obtained for untreated filter paper. The results are shown in Table 2. With an eluent of pH 6 no difference was found in the distance travelled by the spot on the filter papers treated and not treated with a nylon solution. However with an eluent of pH 1, the distance travelled on the treated paper was less than half the length travelled on the untreated filter paper; this may be interpreted as an indication of a distinct interaction at pH 1.

(3) Solubility. The solubilities of the dyed Nylon 8 in MA and FA were also measured: they are qualitatively listed in Table 3. As can be seen in this table, the insoluble nature of the Nylon 8 in MA is not due to dyeing, but is caused merely by the treatment with hydrochloric acid. MA does not dissolve the treated Nylon 8, even at an elevated temperature, while FA is a good solvent for the Nylon 8 at room temperature under any conditions. Such a difference in solubility probably influences the spreadability of the nylon monolayer when these solvents are used, and this in turn probably influences the processes of monolayer dyeing, as has been mentioned already.

Table 3. Solubility of Nylon 8

Solvent	Undyed	Treated with HCL	Neutral dyeing	Acid dyeing
HCOOH	Soluble	Soluble	Soluble	Soluble
CH_3OH	Soluble	Insoluble	Soluble	Insoluble

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