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Equilibria in the Dyeing of Nylon with Acid Dyes

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Introduction

The objectives of the present investigation were to elucidate the mechanism of the combination of monobasic acid dyes with nylon under normal dyeing conditions and to apply the knowledge thereby obtained to an understanding of the phenomena which occur when nylon is degraded by the application of excessive amounts of dye from acid solutions. Acid dyes are highly colored sulfonated organic compounds, substantive to fibers containing basic groups and are usually applied from acidified solutions. At the present time, these are the dyes most frequently used to obtain shades of maximum fastness-to-washing and -to-light on nylon.

Although nylon fiber has been available commercially for about ten years, relatively little quantitative information on its combination with acid dyes has been published. Stott[1] investigated the practical aspects of the problem quite thoroughly and found that the saturation value of the fiber with respect to acid dyes was much less than that of wool. From this result, it seems probable that the dyeing mechanism directly involves the relatively few amino groups present in the nylon.[2] Thus, the very low saturation value of nylon as compared with wool can be explained by the great difference in the amine contents of the two fibers (30–50 millimoles/kilogram for nylon compared to about 800 millimoles/kilogram for wool).

On the other hand, Elöd and Schachowsky[3] reported that when excess dye is available to the fiber the amount taken up increases indefinitely as the *p*H of the dyebath is lowered and that no saturation value exists. The work of Peters[2] confirmed these results. He, however, demonstrated the existence of a *p*H range (roughly, 3 to 6) within which the quantity of dye absorbed by the nylon remained at a nearly constant value, approximately equivalent to the amine content of the fiber as determined by titration with hydrochloric acid. Peters postulated two mechanisms to account for his results: (1) at *p*H values of 3 or higher, combination of dye with the amine end-groups of the fiber occurred and (2) at lower *p*H values, the dye combined with the weakly-basic amide groupings.

The chemical similarity between nylon and wool makes it seem reasonable that the two fibers should interact with acids in similar ways. For wool, this mechanism has been put on a firm theoretical basis by Gilbert and Rideal[4] for the thermodynamically ideal case.[5] The applicability of their treatment to the absorption of monobasic acid dyes by wool has been demonstrated by Lemin and Vickerstaff.[6]

Theoretical.—The following theory is developed on the basis of the arguments advanced by Gilbert and Rideal in the development of their acid-titration equation for fibrous proteins.[4] Thus, the amino and carboxyl end-groups present in nylon are assumed to occupy fixed positions and to ionize (Assumption A) with the consequent production of alkyl ammonium ions ($-NH_3^+$) and carboxyl ions ($-COO^-$). Inasmuch as nylon contains a greater number of carboxyl than amino end-groups, some of the carboxyl end-groups necessarily must be present as unionized –COOH.

In the dyeing process only two reactions are postulated

$$H^+ + -COO^- \rightleftharpoons -COOH$$
$$D^- + -NH_3^+ \rightleftharpoons [-NH_3^+D^-]$$

where D^- represents the anion of a monobasic acid dye. It is assumed further that all of the $-NH_3^+$ sites have identical properties in so far as their ability to combine with dye anions is concerned and that all of them are equally accessible to the dye anions. Similar assumptions hold regarding the properties of the $-COO^-$ sites and their availability for reaction with hydrogen ions. Finally, it is supposed that hydrogen ions and dye anions are absorbed in equal amounts in order to maintain electrical neutrality of the fiber.

The dyed fiber, then, contains besides the –COOH originally present, hydrogen ions in the form of –COOH distributed at random among a limited number of $-COO^-$ sites and an equal number of dye anions in the form of $-NH_3^+D^-$ similarly distributed among a limited number of $-NH_3^+$ sites. Statistical theory leads at once to the following expression for the partial molal free energy of the dye in the fiber[4]

$$\mu(HD)_F = \mu^0(HD)_F + RT \ln \frac{\theta_D}{1-\theta_D} \times \frac{\theta_H}{1-\theta_H} \quad (1)$$

where $\mu(HD)_F$ is the partial molal free energy of

(1) Stott, *Amer. Dyestuff Repr.*, **29**, 646 (1940).

(2) Peters, *J. Soc. Dyers and Colourists*, **61**, 95 (1945).

(3) Elöd and Schachowsky, *Melliand Textilber.*, **23**, 437 (1942).

(4) Gilbert and Rideal, *Proc. Roy. Soc.* (*London*), **A182**, 335 (1944). This reference also reviews critically earlier efforts in this field, notably the work of Speakman and Stott (*Trans. Far. Soc.*, **31**, 1425 (1935)) and Steinhardt (*J. Research Nat. Bur. Standards*, **28**, 191 (1942)).

(5) McGrew and Schneider, THIS JOURNAL **72**, 2547 (1950), measured the absorption of a variety of acid dyes on nylon. The general acid-titration equation for wool of Gilbert and Rideal was utilized in the calculation of the standard free energies of the dyeing process. The free energies thus calculated were found useful in describing the behavior of the dyes when applied to nylon individually or in admixture.

(6) Lemin and Vickerstaff, *J. Soc. Dyers and Colourists*, **63**, 405 (1947).

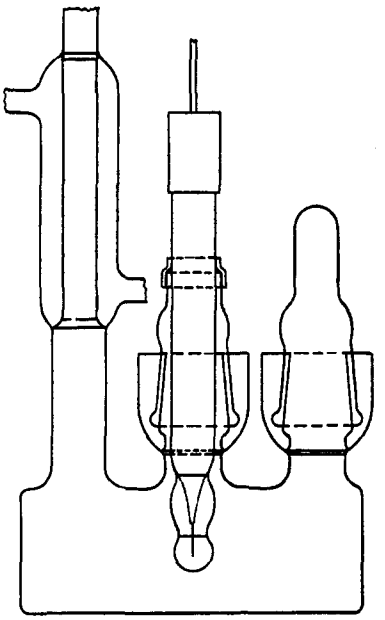

Fig. 1.

he d e in the fiber and $\mu^0(HD)_F$ is the corresponding partial molal free energy of the dye in the standard state defined by

$$\frac{\theta_H}{1-\theta_H} \times \frac{\theta_D}{1-\theta_D} = 1$$

By definition

$$\theta_H = H_F/C \text{ and } \theta_D = D_F/A$$

where H_F is the concentration of -COOH within the fiber, D_F is the concentration of $-NH_3{}^+D^-$ within the fiber and C and A represent, respectively, the carboxyl and amine titers of the undyed fiber. Equation (1) now takes the form

$$\mu(HD)_F = \mu^0(HD)_F + RT \ln \frac{H_F}{C - H_F} \times \frac{D_F}{A - D_F} \quad (2)$$

As equal amounts of dye anions and hydrogen ons are absorbed, $C - H_F$ will be equal to $A - D_F$ and Equation (2) becomes

$$\mu(HD)_F = \mu^0(HD)_F + RT \ln \frac{D_F(C - A + D_F)}{(A - D_F)^2} \quad (3)$$

In the aqueous (dye-bath) phase

$$\mu(HD)_S = \mu^0(HD)_S + RT \ln (H^+)(D^-) \quad (4)$$

where $\mu(HD)_S$ is the partial molal free energy of the dye in solution when its ions are present in molar concentrations of (H^+) and (D^-) and $\mu^0(HD)_S$ is the partial molal free energy of the dye in the customary standard state.

When equilibrium is reached between dye in the fiber and dye in the bath

$$\mu^0(HD)_F - \mu^0(HD)_S = \Delta F^0 = -RT \ln k \quad (5)$$

where k is the equilibrium constant for the dyeing process and is defined by

$$k = \frac{D_F(C - A + D_F)}{(A - D_F)^2(H^+)(D^-)} \quad (6)$$

Analogous expressions are readily obtained for the case when two dyes are simultaneously equilibrated with the fiber, thus

$$\left.\begin{aligned} k_1 &= \frac{(D_F)_1(C - A + (D_F)_1 + (D_F)_2)}{(A - (D_F)_1 - (D_F)_2)^2(H^+)(D_1^-)} \\ k_2 &= \frac{(D_F)_2(C - A + (D_F)_1 + (D_F)_2}{(A - (D_F)_1 - (D_F)_2)^2(H^+)(D_2^-)} \end{aligned}\right\} \quad (7)$$

Results and Discussion.—It has been found useful to test the data by means of Equation (6) rearranged as

$$r \equiv \sqrt{\frac{D_F(D_F + X)}{(H^+)(D^-)}} = A\sqrt{k} - D_F\sqrt{k} \quad (8)$$

In Equation (8), the difference between the carboxyl and amine titer of the fiber, $C - A$, has been designated by X. A plot of r, as defined by Equation (8), *versus* D_F should yield a straight line, the intercept of which on the D_F axis gives the value of A and the slope of which is equal to $-\sqrt{k}$. The position of the intercept on the D_F axis is not affected greatly by variations in the value of X; thus it is possible to determine the value of the important constant A, the saturation value of the fiber with respect to the monobasic acid dyes, from dye absorption measurements.

In Fig. 2 a typical set of data has been plotted according to Equation (8). The straight line has been fitted by a least squares treatment[7] in which all points have been weighted equally and the abscissas have been assumed to be free of error. The latter assumption is justified by the fact that the hydrogen ion activity, the least certain measured quantity, occurs only in the ordinate. The quantity X (the difference between the carboxyl and amine titers) has been

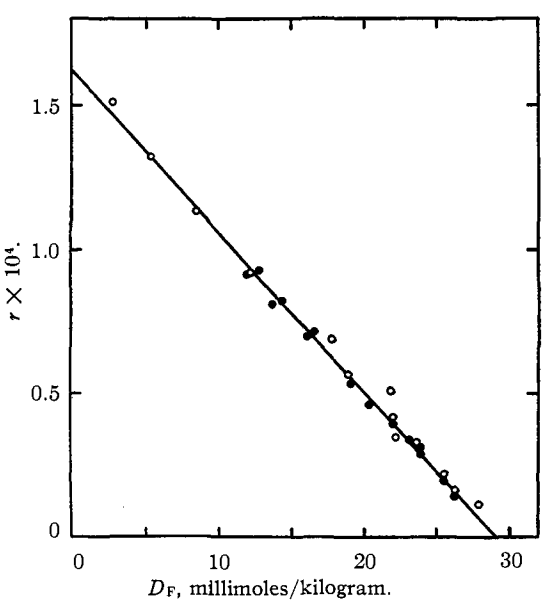

Fig. 2.—Metanil yellow at 80°: O, absorption; ●, desorption.

(7) Birge, *Phys. Rev.*, **40**, 207 (1932).

TABLE I

SUMMARY OF RESULTS

Set	Dye	A (mmoles/kg.)	$k \times 10^{-11}$	ΔF^0 (kcal./mole)	ΔH^0 (kcal./mole)	ΔS^0 (cal./mole°)	Range of D_F	Range of H^+ ($\times 10^5$)	No. of points
1	M. Y.[c]	29.2 ± 1.2	3.0 ± 0.2	18.56 ± 0.05	−9.1	27	2.8–27.9	0.018–1.1	32
2[a]	M. Y.	30.3 ± 1.2	40.0 ± 2	16.96 ± 0.04		27	13.9–28.1	.056–0.34	8
3[b]	M. Y.	94.2 ± 3.4	0.69 ± 0.04	17.52 ± 0.04			9.2–84.3	.014–2.0	15
4	Q. B.[d]	28.3 ± 0.8	2.3 ± 0.1	18.36 ± 0.04	−9.1	26	5.3–23.8	.023–.12	17
5[a]	Q. B.	28.0 ± 2.1	31 ± 4	16.81 ± 0.07		26	16.8–29.7	.027–2.9	24
6[b]	Q. B.	75.7 ± 5.9	1.4 ± 0.2	18.02 ± 0.10			18.6–71.8	.012–1.7	15
7	M. Y. (80%)	30.8 ± 0.9	2.7 ± 0.1	18.48 ± 0.03					
	Q. B. (20%)	30.7 ± 0.8	2.4 ± 0.1	18.40 ± 0.03			9.88–28.0	.015–0.20	16
8	M. Y. (50%)	30.2 ± 1.0	2.5 ± 0.1	18.43 ± 0.04					
	Q. B. (50%)	29.5 ± 1.0	2.4 ± 0.1	18.39 ± 0.04			4.6–27.2	.014–0.22	16
9	M. Y. (20%)	31.3 ± 1.5	2.1 ± 0.2	18.31 ± 0.06					
	Q. B. (80%)	30.0 ± 1.1	2.0 ± 0.1	18.27 ± 0.04			5.91–25.6	.012–0.12	15

[a] These sets at 21°. All others at 80°. [b] These sets with damaged nylon. [c] M. Y. = Metanil Yellow. [d] Q. B. = Quinizarine Blue.

assigned the value obtained by titration[8] (43.4 millimoles/kilogram). All of the data have been subjected similarly to least squares analysis and the results are presented in Table I.

The good agreement between absorption points and desorption points in Fig. 2 constitutes proof that equilibrium was attained in set 1, and similar proof was obtained in set 4. The time allowed for sets 3 and 6–9 was based on these, and its adequacy is, therefore, assured. In set 5 it was clear that equilibrium was not attained; the absorption and desorption points defined separate and apparently parallel lines. However, the lines were close together as borne out by the moderate probable errors. Set 2 also appeared not to have come to equilibrium, and the desorption points were highly erratic. Eight of the twelve absorption points, however, appeared to form a satisfactory straight line, and the constants derived therefrom are included in Table I. In the remaining 4 runs, the nylon contained more than enough dye to saturate the amino groups (see below).

The satisfactory agreement between theory and experiment is shown in Fig. 2, which presents the equilibrium data for Metanil Yellow at 80° plotted according to Equation (8). It is to be noted that the agreement holds over the wide ranges of D_F and H^+ values employed. Similar agreement was obtained with Quinizarine Blue at 80°.

The dye absorption experiments afford a rather precise measure of the saturation value of the fiber. The value for A of 29.2 ± 1.2 obtained with Metanil Yellow agrees within the limits of experimental error with the value of 28.3 ± 0.8 obtained with Quinizarine Blue and the agreement of both of these values with the titrated amine end content of the fiber (21.5, 27.3, 28.7), while not perfect, is good, particularly in view of the difficulty of the titration.

The alternative assumption that the amino and carboxyl groups within the fiber are not ionized (Assumption B) leads to the conclusion that dye anions and hydrogen ions are absorbed on free amino groups according to the reaction

$$-NH_2 + H^+ + D^- \rightleftarrows [-NH_3{}^+D^-]$$

If this is the case, the quantity of dye on the fiber should be related to the concentrations of dye anions and hydrogen ions

$$D_F/(H^+)(D^-) = kA - kD_F \qquad (9)$$

an expression which is analogous to Equation (8). Equation (9) was applied to the data for several of the points on Fig. 2, and the curve marked Equation (9) in Fig. 3 resulted. The marked departure from linearity indicates that Assump-

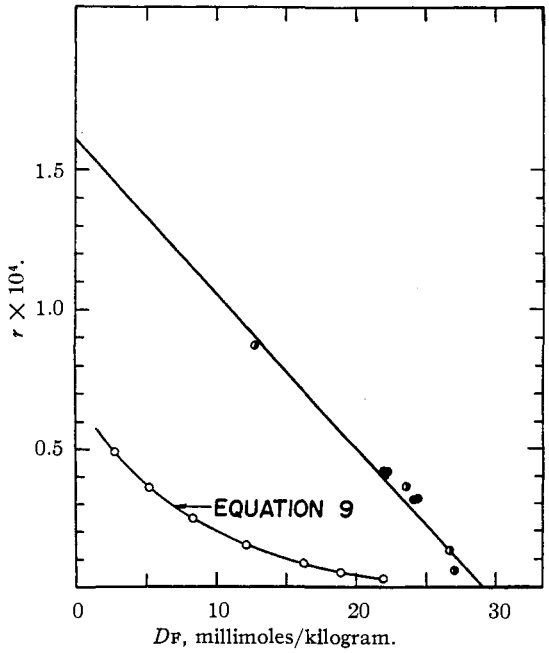

Fig. 3.—●, 5 × 10^{-3} M buffer; ◑, 21°, runs reëquilibrated.

(8) Waltz and Taylor, *Ind. Eng. Chem., Anal. Ed.*, **19**, 448 (1947).

tion A is preferable to Assumption B, that is, the end-groups in the undyed fiber are ionized.

For examination of the data on mixtures of dyes, Equation (7) was rearranged to

$$\sqrt{\frac{D_{F1}(X + (D_{F2}) + (D_{F1})}{(H^+)(D_1^-)}} = A\sqrt{k_1} - ((D_F)_1 + (D_F)_2)\sqrt{k_1} \quad (10)$$

Figure 4 illustrates the manner in which the data on one mixture fit Equation (10). All of the mixtures yielded satisfactorily small probable errors for both A and k (see Table I). No obvious trends appeared in A as the ratio of the dyes was varied, but the value of k for Metanil Yellow decreased slightly as the proportion of Metanil Yellow in the mixture was made smaller.

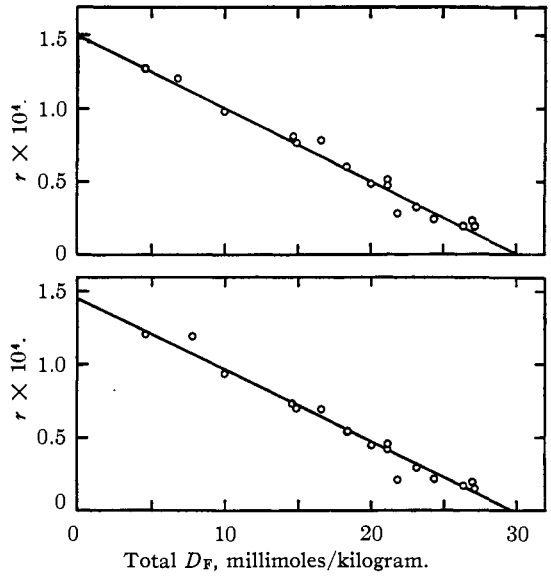

Fig. 4.—Top, 50/50 mix, metanil yellow; bottom, 50/50 mix, quinizarine blue.

An alternate treatment of the data for the mixture dyeings makes it possible to compare the equilibrium constants of the two dyes without requiring any knowledge of the dye-bath pH or the fiber constants, A and X. An expression for the ratio of the two equilibrium constants is obtained by division of one of the equations (7) into the other

$$\frac{k_1}{k_2} = \frac{(D_F)_1}{(D_F)_2} \times \frac{(D_2^-)}{(D_1^-)} \quad (11)$$

Application of Equation (11) to the present data showed that the ratio k_1/k_2 (k_1 = Metanil Yellow, k_2 = Quinizarine Blue) generally increased as the total amount of dye in the fiber increased and as the relative proportion of Metanil Yellow in the fiber decreased. The effect was hardly, if at all, noticeable in the set utilizing Metanil Yellow and Quinizarine Blue in the ratio of 80:20, and was most marked in the set employing the two dyes in the inverse ratio. Results are illustrated in Fig. 5.

The two methods of treating the data lead to conflicting conclusions, since the results obtained by the use of Equation (10) indicated that k_1/k_2 decreased as the relative proportion of Metanil Yellow in the fiber became smaller (see Table I).

It is possible that the apparent inconsistencies in the results would be removed if the original equations were modified to take into account interaction energies between dye anions in the fiber[9] but the present data are not sufficiently precise to test such a modified equation. Nonetheless Equations (8) and (10) appear to afford a useful description of the nylon/dye system for monobasic acid dyes and mixtures thereof.

Because they afford the only available information on the heat of the dyeing reaction, the two low-temperature sets (2 and 5) have been included, even though they suffer from some uncertainty as regards equilibration. For both dyes, lowering the temperature results in a greater proportion of dye on the fiber at equilibrium. Thus, the necessity for high temperatures in the dyeing of acid dyes in heavy shades on nylon appears to be dictated by the sluggishness of the approach to equilibrium at low temperatures, rather than by the unfavorableness of the equilibrium.

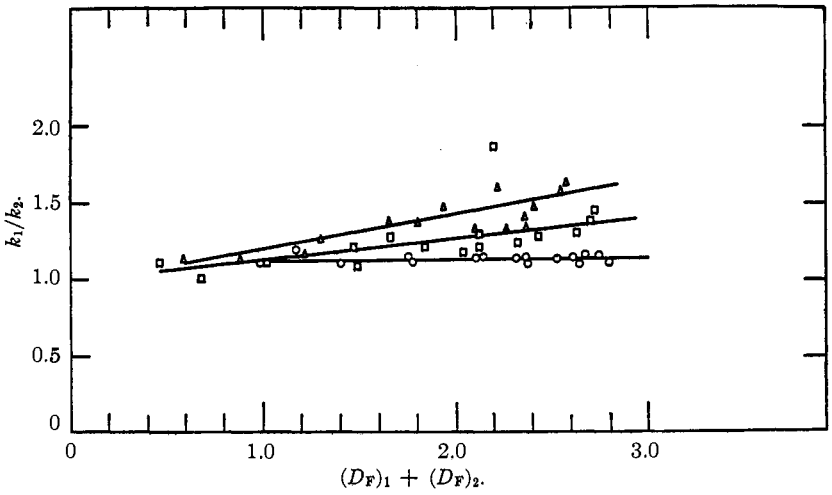

Fig. 5.—Equilibrium constant ratios: O, 20% QB, 80% MY, set 7; □, 50% QB, 50% MY, set 8; △, 80% QB, 20% MY, set 9.

In four instances, at 21°, there was more dye on the fiber than could be accounted for by the number of amino groups present. These "over-

(9) Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge University Press, London, 1939, p. 429 ff.

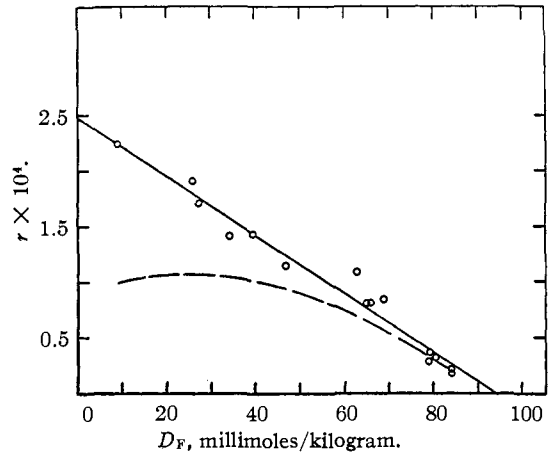

Fig. 6.—Damaged metanil yellow, 80°.

dyed" samples were equilibrated with fresh dye-baths at 80° and the points so determined coincided, within the limits of experimental error, with the previously determined line for the 80° dyeings (the straight line in Fig. 2 has been repeated in Fig. 3, *q.v.*). Evidently the fiber had not been damaged or otherwise changed by its prolonged exposure to the acidic dye-bath at the lower temperature. While there is no direct experimental evidence to confirm the point, we believe that the "over-dyeing" at low temperature was caused by solubility of the dye in the fiber (perhaps as Na^+D^-), a possibility which seems reasonable in view of the known solubility of certain mono-sulfonated dye sodium salts in other organic media.

That the above type of "over-dyeing" was not a significant factor in the acid-dyeing experiments at 80° is indicated by the data presented in Fig. 7. The points defining the upper curve were taken from a typical set of acid-dyeing runs made at *p*H 6.7; those defining the lower curve were obtained in a similar manner, but at *p*H 10. At the latter *p*H only an immeasurably small quantity of dye should have entered the fiber by the acid-dyeing mechanism. Actually, measurable amounts were absorbed, but as may be seen in the figure, the amounts were too small to exert a serious disturbing influence on the results at the lower *p*H's.

The fact that ΔS^0 (see Table I) is positive implies that the entropy change favors the transfer of dye from the aqueous to the nylon phase under standard conditions. However, when practical dyeing conditions ($D^- = 5 \times 10^{-5} M$; $H^+ = 2 \times 10^{-4} M$) are assumed, ΔS becomes -10 cal./mole deg. (It is here assumed that ΔH is independent of concentration.) The negative value is in accord with the idea that a certain degree of order is imposed on the dyed fiber phase with the result that the entropy term opposes the dyeing process.

Possibly the most striking result of this investigation is the clear picture it gives of the

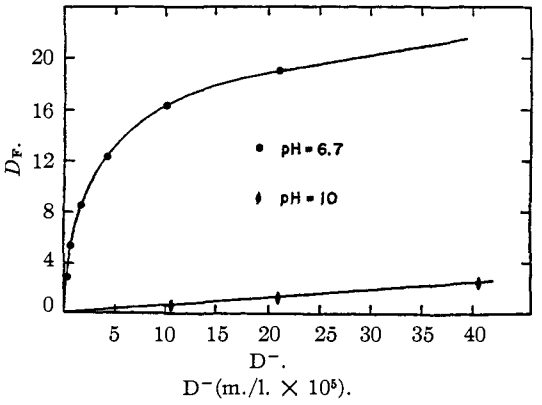

Fig. 7.—Metanil yellow, dyeing at high and low *p*H, 80°.

manner in which nylon can be degraded by the application of excessive dye from acid solution (over-dyeing). Figure 6 shows that fiber which had been dyed to approximately three times the normal saturation level still behaved as did the normal fiber, except that the amine titer, A, was then 94 instead of 29. Similarly (Table I, set 6) over-dyeing with Quinizarine Blue raised A to 76.

In this connection it should be pointed out that Equation (8) affords what appears to be the best possible means of analysis of the data and determination of the value of A for fiber which contains dye. The titration method fails when the fiber has been damaged by over-dyeing, because the dye anions present in the fiber interfere with the analytical procedure.

The new amino groups must have been produced by the hydrolysis of amide groups, but there might still be a question whether preferential hydrolysis of the terminal amide groups ($-NHCOCH_3$) would not take precedence over the hydrolysis of the chain-forming amide groups ($-NHCOCH_2-$). Therefore, two extreme assumptions were made: (1) that no terminal amide groups had been hydrolyzed (solid line, and points, Fig. 6), and (2) that all of the terminal amide groups had been hydrolyzed, *i. e.*, that $X = 0$ (dashed line, Fig. 6). Although the great curvature of the dashed line does not constitute proof that no terminal amide groups had been hydrolyzed, it can be concluded that most of the hydrolysis occurred at non-terminal amide groups, even though the total number of amide groups hydrolyzed slightly exceeded the number of terminal amide groups originally present. In the above discussion we have assumed that all acetic acid formed by hydrolysis would diffuse out of the fiber. While this assumption appears to be eminently reasonable, we cannot exclude the possibility that acetic acid formed by hydrolysis may have remained in the fiber and simulated the behavior of terminal carboxyl groups.

The relative viscosity data given in Table II confirm the fact that the over-dyeing resulted in considerable chain rupture.

TABLE II

EFFECT OF OVER-DYEING ON VISCOSITY

Treatment	Relative viscosity
None	42.4
HCO_2H + No dye	39.1
HCO_2H + Metanil Yellow	16.4
HCO_2H + Quinizarine Blue	18.1

The question may arise as to why so little hydrolysis occurred at low *p*H (2.2) with no dye present. In discussing an equivalent question, Peters[2] seems to have failed to recognize that high acidity in the aqueous phase is no guarantee of high acidity in the polymer phase. If the fiber is to remain electrically neutral, the number of hydrogen ions entering the fiber must be limited by the number of anions entering. Thus the acidity within the fiber might be expressed as $k_X(H^+)(X^-)$. Apparently, k_X is much greater for the dyes examined than for acids such as hydrochloric (used by Peters) or formic (used in this work).

Our finding of hydrolysis promoted by anions and hydrogen ions parallels the extensive experience of Steinhardt on wool.[10]

Further indication that the application of excessive dye from acid solution results in hydrolysis of the amide groups was obtained by examining the rate of dye take-up over very long periods.

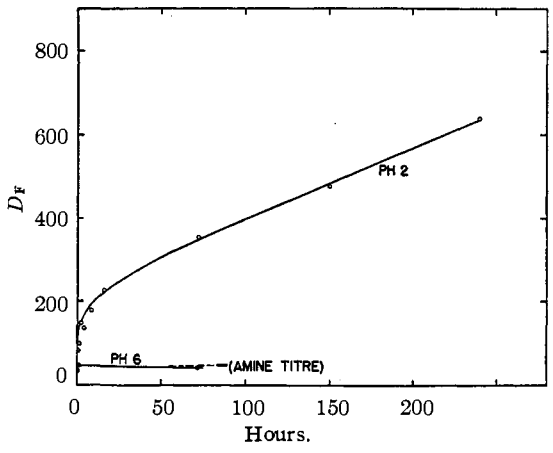

Fig. 8.—Rate of dyeing with anthraquinone dye.

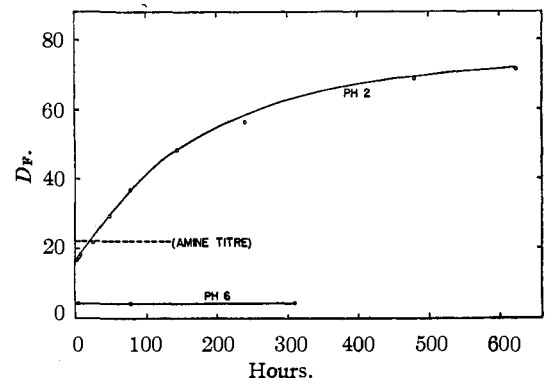

Fig. 9.—Rate of dyeing with azofuchsine.

For these experiments the dyebaths contained phosphoric acid at a concentration of 0.085*M*, adjusted with sodium hydroxide to the selected *p*H at room temperature. Dyeings were carried out under reflux and samples of nylon were removed periodically for analysis. The dyes used were azofuchsine (Colour Index 30) (8-amino-2-phenylazo-1-naphthol-3,6-disulfonic acid disodium salt), and an anthraquinone dye [1-(2-sulfo-*p*-toluino)-4-*p*-toluinoanthraquinone sodium salt]. The initial composition of the dyebaths is tabulated below (the lower *p*H lies well within the range obtained in commercial dyeing practice).

Dye	Dye concn.	Nylon concn.	*p*H
Azofuchsine	2×10^{-4} *M* (100 mg./l.)	0.5 g./l.	2
Azofuchsine	2×10^{-4} *M* (100 mg./l.)	0.5 g./l.	6
Anthraquinone dye	5×10^{-4} *M* (250 mg./l.)	1 g./l.	2
Anthraquinone dye	5×10^{-4} *M* (250 mg./l.)	1 g./l.	6

The amount of dye absorbed has been plotted against time in Figs. 8 and 9. As is immediately evident, the first rapid reaction was complete within less than ten hours. Clearly this was the diffusion of the dye into the fiber to occupy the dyeable sites originally present. It is likewise evident that a much slower reaction followed the first, but only at the lower *p*H. Apparently, the slow reaction was the hydrolysis of the amide groups to produce additional sites for dyeing. The hydrolysis occurred only in the strongly acid solution. So serious was the degradation caused by the anthraquinone dye at the lower *p*H that the fiber could be powdered readily between the fingers.

Our results do not support amide-dyeing of the sort postulated by Peters[2] (see Introduction, mechanism 2). However, it is possible that some combination of this type may precede hydrolysis during over-dyeing.

Curves closely resembling those in Figs. 8 and 9 have been published very recently by Elöd and Fröhlich.[11] Nevertheless these authors have accepted Peters' hypothesis of amide-dyeing at low *p*H's and have predicted that controlled acid hydrolysis of nylon should result in decreased absorption of acid dyes at *p*H's below 2.2.

Experimental

Equilibrium Studies.—The experimental verification of Equation (8) required that $[H]^+$, $[D^-]$ and $[D_F]$ be determined in a system consisting of an aqueous solution of dye anions and hydrogen ions in equilibrium with nylon in the absence of other ions which might compete for the dyeable sites in the nylon. Therefore, the equilibrations were carried out in sodium phosphate buffers, mostly with ionic strength 2×10^{-3} molal, this being about the minimum degree of buffering which would yield adequate *p*H stability. At this ionic strength the activity coefficient

(10) Steinhardt, *J. Research Nat. Bur. Standards*, **29**, 315 (1942).

(11) Elöd and Fröhlich, *Melliand Textilber.*, **30**, 103 (1949).

of the dye was set equal to unity. Since increasing the buffer ionic strength to 5×10^{-3} molal failed to change the equilibrium distribution of the dye (see Fig. 3), we conclude that the phosphate ions do not compete for the dyeable sites, for if the phosphate ions had competed for the sites, the data for 5×10^{-3} molal buffer should have fallen below the straight line in Fig. 3.

The most difficultly measurable activity required was that of the hydrogen ion. Being temperature-dependent, it had to be measured at the temperature at which the dyeing equilibrium had been established and in such a manner as to minimize the disturbance of the lightly buffered system. Accordingly, the *p*H measurements were made in the reaction vessel while the nylon was still present.

The reaction vessel employed is shown in Fig. 1 with one electrode in place. Essentially, it consisted of a horizontal glass cylinder with attached condenser, and ⅋ joints for the electrode assemblies. The cups served to protect the ⅋ joints from contamination by the thermostat bath.

A Beckman Model G *p*H meter was used with standard six-inch calomel electrode and high-temperature glass electrode. The heat-sensitivity of the glass electrode set an effective upper limit of 80°. As the highest possible temperature was desired to minimize the time required for equilibration, the bulk of the experiments were carried out at this temperature. Under these conditions, Metanil Yellow (Colour Index 138, *m*-(*p*-anilinophenylazo)-benzenesulfonic acid, sodium salt) dyeings reached equilibrium within eighteen hours, while Quinizarine Blue (Colour Index 1073, 1-(2-sulfo-*p*-toluino)-4-hydroxyanthraquinone, sodium salt) required forty hours.

For the experiments at 21° four-ounce bottles with mouths wide enough to admit both electrodes served as reaction vessels. The bottles were shaken daily and the progress of the diffusion of the dye was followed by microscopically examining cross sections of the nylon in duplicate runs set aside for this purpose. Metanil Yellow penetrated the fibers completely in thirteen days, while Quinizarine Blue required about thirty days; consequently the former type of runs were terminated after sixty-six days, while the latter were continued for one hundred seven days.

For each run approximately 200 mg. of nylon (3 denier per filament, bright staple) and 85 ml. of buffer were used. In the absorption runs 0.25 to 50 mg. of dye (recrystallized from water until chromatographically pure) was dissolved in the buffer, while in the desorption runs colorless buffer was used with previously dyed nylon.

Immediately after the *p*H measurement, the nylon was removed from the buffer solution, rinsed briefly with distilled water, blotted dry and stored over saturated aqueous sodium chromate (approximately 52% R. H.). For the determination of $[D_F]$, a sample was dissolved in a 90% *o*-chlorophenol–10% pyridine mixture and photometered. Correction was made for light absorption due to the nylon and for the contribution of the dye to the weight of the sample. Beer's law was obeyed.

For the determination of $[D^-]$ the buffer solution (diluted when necessary) was photometered at room temperature after the nylon had been removed. All photometry was done with a Beckman Spectrophotometer Model DU.

The estimation of the individual dyes in mixtures was facilitated by the fact that the maximum absorption by Quinizarine Blue occurs at a wave length where the Metanil Yellow absorption is negligibly small. This made possible the direct measurement of the concentration of Quinizarine Blue which yielded a small correction to be used in the calculation of the concentration of Metanil Yellow.

Although "liquefied phenol" is a convenient solvent for nylon, it could not be used in this investigation because it converted Metanil Yellow partially into the red "acid" form. The addition of pyridine regenerated the normal "alkaline" form of the dye, but the mixed solvent rapidly turned yellow. Fortunately, no such difficulties were encountered with *o*-chlorophenol containing 10% pyridine and the dyed nylon dissolved readily in it to yield solutions whose absorptions were constant for a week.

Over-dyeing.—Nylon (5 g.) was refluxed for ten hours in 500 ml. of 1% aqueous formic acid (final *p*H 2.2). Three samples were treated, one with each dye (about 5 times the amount required to saturate the amino groups), and one with no dye.

Summary

The mechanism proposed by Gilbert and Rideal[4] to explain the absorption of acids by fibrous proteins has been demonstrated to account for the absorption of monobasic acid dyes by nylon. The acid-titration equation for nylon derived on the basis of this mechanism differs from the corresponding equation for wool, as developed by Gilbert and Rideal, by the inclusion of a term which takes account of the excess of carboxyl over amino end-groups. Application of an appropriately rearranged form of the acid-titration equation permits the graphical analysis of the equilibrium absorption data. The experimental data both for single dyes and for mixtures fit the equation in a satisfactory manner.

When graphically analyzed in this way, the absorption data yield a precise value for the amine-end content of the fiber, which is the practical upper limit for dyeing with acid dyes. No other method is known which permits the determination of this quantity for dyed nylon.

By these procedures the nature of the degradation of nylon by the application of excessive amounts of acid dyes from solutions of low *p*H has been elucidated. It has been shown that the absorption of dye in this manner is accompanied by the hydrolytic rupture of principally nonterminal amide groups with the consequent production of additional dyeing sites. These phenomena have been observed at *p*H's within the range of normal dyeing practice.

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