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The Sorption of Acid Dyes on Nylon[1]

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Much has been learned in recent years of the mechanisms by which the acid dyes are sorbed by the natural polyamides, wool and silk. It is generally agreed that salt linkages between the dye anions and the $-NH_3^+$ cations of the protein are formed in stoichiometric amounts and that the process of formation of these linkages constitutes much of the driving force for the penetration of dyes into the protein fiber.[2,3,4] A close similarity between wool and a synthetic polyamide such as nylon in the sorption of dyes has been shown by several workers.[5,6,7] They have postulated the sorption of acid dyes to take place by the same mechanism as on wool, with, in addition, a weaker bonding at low *p*H between the acidic dye and the weakly basic amide groupings of the polymer chain. Peters[6] in particular has produced evidence to support these mechanisms. He has concluded that adsorption on amino end groupings accounts for dye sorption at *p*H values of about 3 and above, and that the recurring amide linkages are sufficiently basic to account for the very greatly increased adsorption at high acidity. The possibility of an increased end-group adsorption at such low *p*H caused by a dye-catalyzed hydrolysis of the polymer chain, which was rejected by Elöd and Schachowsky, now has fresh support.[8]

This paper presents additional evidence to support the idea of adsorption of acid dyes on amino end groupings at moderate *p*H levels, and quantitative data which permit calculation of the magnitude of the forces involved. The measurement of these forces involves the application to nylon of principles and techniques developed for the study of wool by English workers.[9,10,11,12,13] The key to this approach lies in the concept of affinity as the molal standard free energy change of the dye sorption process. The affinity is calculated from data on the equilibrium distribution of dye between bath and fiber.

Experimental Procedures and Results

Materials and Analytical Methods.—The dyes were obtained from the Organic Chemicals Department of E. I. du Pont de Nemours and Company, and were carefully purified by the method of Robinson and Mills[14] which involved a threefold salting out with sodium acetate followed by repeated extraction with ethyl alcohol until the analytical values indicated at least 95% purity. Measurements of dye adsorbed on the nylon were made by dissolving the dyed fiber in *o*-chlorophenol and determining the quantity of dye in solution by means of the Beckman spectrophotometer on the basis of the application of Beer's law. Concentrations of dye in aqueous baths were likewise measured spectrophotometrically.

The nylon samples, supplied by the du Pont Rayon Department, were polyhexamethylene adipamide, prepared by the polymerization of hexamethylenediammonium adipate. Staple fiber, 3.0 denier per filament, was employed. Before use, the fibers were scoured in an olive oil soap–trisodium phosphate bath and stored in distilled water. Free amino and carboxyl groups terminating the polymer chains were determined by titration.[15,16,17]

Mechanism of Attachment.—The first objective was to establish firmly the relationship between the quantity of dye sorbed by the fiber and the basic character of the fiber as conferred by the terminal amine groupings.

Procedure.—One-gram samples of nylon were dyed at 98° for a period of four hours in the presence of at least a two-fold excess of purified dye. The acidity was adjusted with phosphoric acid and the *p*H values reported were those existing at the conclusion of the dyeing, at room temperature. Preliminary experiments demonstrated that equilibrium of diffusion of dye into the fiber structure and of attachment to any sites available under the initial basicity of the fiber could be obtained under these conditions. A longer dyeing period was avoided in order to prevent errors in end-group stoichiometry resulting from amide hydrolysis.

In Fig. 1 are plotted sorption isotherms of several typical acid dyes on nylon fiber over a *p*H range of 1 through 4. The particular nylon used had, by titration, 0.038 millieq./g. of free amino groups and 0.064 millieq./g. of free carboxyl groups.[18] It is to be expected that if the dye molecule is held by means of a salt linkage between the acid groups of the dye and the amine groups of the fiber, the amount of dye sorption in the *p*H range over which this mech-

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(1) Presented in part before the Textile Section, Chemical Research Conferences, New London, New Hampshire, July 10, 1947.

(2) Steinhardt, Fugitt and Harris, *Bur. Standards J. Res.*, **25**, 519 (1940); **26**, 293 (1941); **28**, 191, 201 (1942).

(3) Speakman and Elliott, "Fibrous Proteins," The Society of Dyers and Colourists, London, 1946, p. 116.

(4) Alexander, "Colloid Chemistry," Vol. 6, Chap. 29; "Physical Chemistry of Dyeing," by E. I. Valko, Reinhold Publishing Corp., New York, N. Y., 1946.

(5) Elöd and Schachowsky, *Melliand Textilber.*, **23**, 437 (1942); **25**, 237, 309 (1944).

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

(7) Carlene, Fern and Vickerstaff, "Recent Advances in the Theory and Practice of Dyeing," The Society of Dyers and Colourists, London, 1947, p. 24.

(8) Gladding and Remington, THIS JOURNAL, **72**, 2553 (1950).

(9) Gilbert and Rideal, *Proc. Roy. Soc.* (*London*), **182A**, 335 (1944).

(10) Gilbert, *ibid.*, **183A**, 167 (1944).

(11) Lemin and Vickerstaff, "Fibrous Proteins," The Society of Dyers and Colourists, London, 1946, p. 129.

(12) Meggy, *Trans. Faraday Soc.*, **43**, 502 (1947).

(13) Lemin and Vickerstaff, "Recent Advances in the Theory and Practice of Dyeing," The Society of Dyers and Colourists, London, 1947, p. 41.

(14) Robinson and Mills, *Proc. Roy. Soc.* (*London*), **131A**, 576 (1931).

(15) Taylor, THIS JOURNAL, **69**, 635 (1947).

(16) Waltz and Taylor, *Anal. Chem.*, **19**, 448 (1947).

(17) Our thanks are due to Dr. L. F. Salisbury and Miss R. E. MacFarlane for the samples and the end-group analyses.

(18) These analyses for available acid and basic groups terminating the polymer chains are in good agreement with measurements of polymer molecular weight and of inactive end groupings composed primarily of nitrogen substituted acetamides (ref. 15).

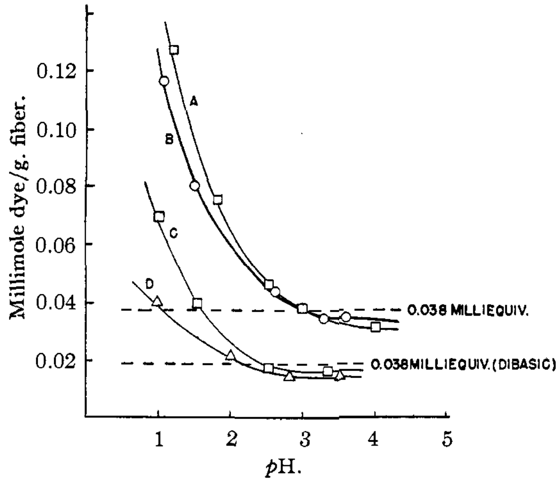

Fig. 1.—Saturation adsorption of acid dyes on nylon, monobasic dyes: A, Anthraquinone Blue RXO; B, Orange RO; Dibasic dyes: C, Pontacyl Carmine 2G; D, Anthraquinone Blue B.

anism is effective should be of the same order as the amine content. It is apparent from Fig. 1 that within the *p*H range of 3.0–4.0 a plateau of such nature exists in the curves of both monobasic and dibasic dyes. Such correspondence has been found to exist generally for acid dyes.

It is possible to obtain additional evidence for this conclusion. By variation of polymerization conditions and by the addition of chain terminating stabilizers, both acidic and basic in nature, it is possible to control both the chain length and the nature of the end groupings of the polyamide, polyhexamethylene adipamide.[19] A series of such nylons was obtained and adsorption curves determined. Table I shows the saturation adsorption at *p*H 3.5 using the typical monobasic acid dye du Pont Anthraquinone Blue RXO (Color Index No. 1076) and the typical dibasic acid dye Pontacyl Carmine 2G (Color Index No. 31). Under these conditions, adsorption was in close agreement with available end groupings.

TABLE I

ADSORPTION OF DYE ON FIBERS OF VARIED BASICITY

Fiber	Carboxyl[a] ends	Amine ends[a]	Milliequivalents of dye at saturation[b] Monobasic[c]	Dibasic[d]
A	...	0.012	0.004	0.004
B	0.064	.038	.035	.032
C	.023	.064	.066	.060
D	.042	.086	.084	...
E	.007	.375	.340	...

[a] Milliequivalents per gram. [b] At *p*H 3.5. [c] Anthraquinone Blue RXO (C. I. No. 1076). [d] Pontacyl Carmine 2G (C. I. No. 31).

Although it is difficult to visualize penetration of the large dye anions into the dense crystallites of the oriented polyamide, it is logical to conclude that the chain endings on which the basic character resides make up the amorphous areas and are not buried in the crystalline structure of the polymer. A slightly lower adsorption for the dibasic dye in each sample can be related to the greater statistical difficulty in satisfying all the basic sites with a dibasic anion than with a monobasic anion adsorbed at the crystallite surface.

It is observed that insofar as actual quantity of adsorption of dyes by the fiber is concerned, the amine content is the controlling factor and the relative number of carboxyl ends in the polymer is unimportant. This is not the case, however, when the question of the magnitude of the forces is considered, as discussed in the following section.

The cause of rapidly increasing dye adsorption at low *p*H (Fig. 1) was not studied. From the observed variation in behavior by the several dyes it may be concluded that it is dependent in large degree upon the dye structure.

Concept of Dye Affinity.—The similarity in acid dyeing behavior of wool and nylon has impelled us to apply to nylon the concepts and measurements of dye affinity.

Gilbert and Rideal[9,10] proposed a means of analysis of the adsorption forces of acids and acid dyes on wool, employing the equation

$$\frac{-0.434}{RT}(\Delta\mu_H + \Delta\mu_D) = 2\log\frac{\Theta_D}{1-\Theta_D} - \log[D] + pH \qquad (1)$$

in which [D] represents the molar concentration of the dye in solution and Θ_D the fraction of the available basic sites of the fiber which are occupied by dye anions. The notations $\Delta\mu_H$ and $\Delta\mu_D$ represent the standard changes in chemical potential (partial molar free energy) for the hydrogen ion and for the dye anion involved in the sorption of the ions from the solution by the fiber, and the negative of their sum represents the standard affinity of the acid form of the dye for the fiber. This equation is similar in approach to those earlier employed for titration of wool with acids,[2] based on application of the law of mass action, but differs by allowing for differences in hydrogen ion concentration within and without the fiber.

This equation (1) was originally devised for the study of wool fiber in which the carboxyl and amine groups are essentially equal in number. Application to nylon, in which this ratio may vary considerably, is dependent upon the use of nylons which do not have an amine titer in excess of the carboxyl titer.

The method has been applied to wool[11,12,13] despite considerable hydrolysis of the wool by the free dye acid. Separation of the affinity values assignable to the dye anion and to the hydrogen cation was made from data on hydrochloric acid in which the affinity of chloride ion for wool was arbitrarily taken as zero. By this establishment of a comparative scale the contribution of the dye anion in the dyeing of the free acid dye was

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[19] Peterson, U. S. Patent 2,174,527.

easily obtained. In the present paper the affinity of chloride ion for nylon has similarly been taken as zero to provide a relative measure of affinity. Application of this method to nylon, however, was found to be impracticable because an abnormally high proportion of dye acid was adsorbed at the low *p*H prevailing. It was, therefore, necessary to use the alternative approaches outlined below.

Determination of Affinity

I. By Desorption of Dye from Fiber.—This technique is based on desorption of dye-anion caused by chloride ion. This involves determination of the fraction of basic sites occupied at equilibrium by approach from the high side rather than the low. Equation (2) modified from Gilbert and Rideal is applicable

$$\frac{-0.434}{RT}\,(\Delta\mu_D - \Delta\mu_{Cl}) = \log \frac{\Theta_D}{1 - \Theta_D} - \log[D] + \log[Cl] \quad (2)$$

TABLE II

DESORPTION OF DYE FROM NYLON AT 98°, *p*H 3.2

Dye	Equiv./liter dye in soln. ($\times 10^{-4}$)	Chloride ion, mole/liter	Θ	($\Delta\mu_D - n\,\Delta\mu_{Cl}$) kcal./mole
Metanil yellow[a]	0.197	0.041	0.638	6.1
	.110	.041	.538	6.2
	.074	.011	.659	5.9
	.030	.041	.317	6.3
	.022	.041	.281	6.5
	.011	.011	.358	6.3
Anthr. Blue RXO[a]	.171	.041	.625	6.1
	.127	.021	.625	5.8
	.0705	.011	.663	5.9
	.0383	.041	.316	6.3
	.0156	.011	.327	6.0
Orange RO[a]	.329	.041	.594	5.5
	.105	.041	.406	5.8
	.0975	.041	.400	5.8
	.0283	.041	.197	6.0
	.0110	.011	.238	5.9
Orange II[a]	.487	.041	.493	4.9
	.271	.011	.593	4.7
	.250	.041	.358	5.0
	.120	.021	.430	5.3
	.104	.011	.414	5.4
Anthr. Green G[b]	.0747	.101	.566	4.8
	.0532	.101	.522	4.9
	.0121	.041	.508	4.6
	.0096	.101	.309	5.0
	.0095	.041	.564	5.0
Anthr. Blue B[b]	.228	.041	.540	2.6
	.172	.021	.651	2.3
	.137	.041	.354	2.0
	.070	.011	.722	2.4
Pontacyl Carmine 2G[b]	.103	.011	.648	1.7
	.087	.041	.328	2.1
	.067	.041	.259	2.1
	.030	.021	.281	1.6
	.0157	.011	.366	1.7
Pontacyl Light Yellow GX[b]	.0788	.011	.576	1.6
	.0386	.101	.207	1.5
	.0234	.041	.344	1.5
	.0127	.021	.422	1.4

[a] Monobasic, $n = 1$. [b] Dibasic, $n = 2$.

Desorption was accomplished through the use of a large excess of chloride ion to displace an appreciable fraction of the dye anion. The fiber was kept saturated as completely as possible with hydrogen ions so that the basic sites would be combined with either chloride or dye ion at all times. The measurements were carried out at *p*H 3.2, chosen on the basis of a study of the effect of *p*H upon the affinity values obtained, in which it was observed that in the range of *p*H 2.5–4.5 the values were quite consistent, while at higher and lower acidities distinct variations occurred (Fig. 2). Such changes could be attributed at *p*H below 2.5 to the interference of secondary attachment processes or to hydrolysis of the fiber. At a higher *p*H, variations result from the presence of insufficient acid to saturate the desorbed basic sites. Insofar as $\Theta_{Cl} + \Theta_D < 1$, the equation would require correction for extreme precision, but we have followed Lemin and Vickerstaff[11] in proceeding without this refinement.

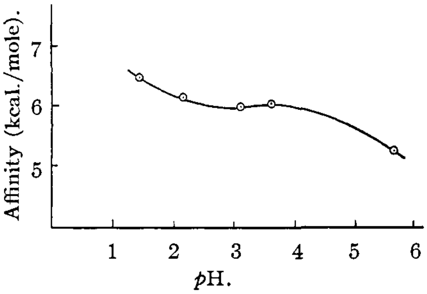

Fig. 2.—Effect of *p*H on affinity as measured by desorption (Procedure 1).

Procedure.—One gram of fiber was placed in 50 ml. of a bath containing between 0.01 and 0.10 *N* chloride ion and sufficient hydrochloric acid to produce a *p*H of 3.2 at the conclusion of the desorption. After thirty minutes at 98°, the fiber was removed, blotted to remove surface liquid, and reimmersed in an identical solution for sixty minutes. Orienting studies demonstrated the adequacy of the sixty-minute period. The dye in the fiber and in the second bath was then determined.

Concentrations have been used in place of activities throughout this work. The lack of activity coefficients for most of the ions involved has necessitated this approximation, which is considered to be adequate for the accuracy intended. In these experiments, fiber dyed to between 0.2 and 0.7 of its capacity (Θ value) was employed. Very large and very low values for Θ were excluded because calculations based on them magnified experimental errors.

The data acquired by use of this procedure (Table II) show good consistency. This method was not applicable to certain dyes whose affinity was so great that insufficient desorption could be brought about.

II. By Sorption of Sodium Salts

Since it was desirable to obtain order of magnitude measurements on dyes having such high attraction for the fiber that they were not readily desorbed, another procedure was tested. The fiber was dyed with the sodium salt of the dye, applied in a neutral bath in the presence of sodium chloride.

Procedure.—This work was carried out at 98° since equilibrium was not reached at lower temperatures before deterioration of certain of the dyes took place. A period of twelve hours at this temperature and essentially at neutrality gave equilibrium without such deterioration and without change in the end-group titers of the nylon.

One-gram portions of staple fiber were dyed at 98° for twelve hours at a fiber–liquid ratio of 1–100 in the presence of sodium chloride, the concentration of which was varied from 0.02 to 0.4 *N*. The dye was present in considerable excess over that required for saturation of the fiber. At the conclusion of the dyeing the volume of the dye bath, quantity of dye on the nylon, and the quantity of dye remaining in the bath were determined.

Calculations were carried out by use of equation (3).

$$\frac{-0.434}{RT}(\Delta\mu_{\mathrm{Na}} + \Delta\mu_{\mathrm{D}}) = \log\frac{\Theta_{\mathrm{D}}}{(1-\Theta_{\mathrm{D}})} + \log\frac{\Theta_{\mathrm{Na}}}{(1-\Theta_{\mathrm{Na}})} - \log\,[\mathrm{D}] - \log\,[\mathrm{Na}] \quad (3)$$

Θ_{Na} for the nylon employed was equal to 0.406 Θ_{D}, based on the difference between the carboxyl and amine titers of the polyamide

$$\Theta_{\mathrm{Na}} = (64 - 38)\,\Theta_{\mathrm{D}}/64$$

This has less justification than equations (1) or (2), since it implies that as dye anions enter the fiber they are accompanied by Na^+ ions exclusively. Use of added sodium chloride helps to make the approximation valid by supplying sufficient Na^+ ions to diminish H^+ adsorption. The data obtained by this method (Table III) do not have a rigorous theoretical basis, and are presented solely because they show generally the same order of increasing affinity as measurements by the more acceptable desorption procedure. The exception of Anthraquinone Green G (Table IV) to this observation is to be attributed to the questionable nature of the procedure. However, the method does permit the convenient extension of the investigation to dyes of high affinity.

The contribution of the Na^+ ions toward the measured affinity was considered to be small in comparison with that of the dye anion; in any case, it contributes substantially equally to all affinity values determined by this procedure, so that their relative validity is unaffected.

TABLE III

DYEING WITH DYE SALT AT 98°

Dye	Equiv./liter dye in soln. ($\times 10^{-4}$)	Sodium ion, mole/liter	Θ	($\Delta\mu_{\mathrm{D}} + n\,\Delta\mu_{\mathrm{Na}}$) kcal./mole
Milling Yellow G[a]	23.1	0.0816	0.438	12.4
	21.55	.0427	.371	11.3
	13.08	.0510	.327	10.7
	11.70	.0908	.392	11.0
Milling Red SWB[a]	30.40	.0728	.352	10.0
	20.95	.0940	.387	10.45
	14.64	.0704	.314	10.0
	9.85	.0474	.319	11.0
	7.01	.1322	.326	9.8
	6.93	.0688	.323	10.7
	1.51	.0444	.183	10.7
Metanil Yellow[b]	25.4	.1040	.597	5.5
	19.5	.0797	.546	5.7
	13.3	.2470	.685	5.8
	11.6	.0511	.473	5.9
	9.5	.1760	.658	6.3
	7.72	.0880	.524	6.2
	5.74	.0424	.309	5.8
Anthr. Blue RXO[b]	19.25	.0946	.466	5.2
	17.4	.1712	.526	5.1
	8.36	.0414	.263	5.2
	8.0	.0802	.310	5.1
Orange RO[b]	20.7	.1590	.372	4.25
	17.1	.0685	.287	4.5
	7.5	.1340	.294	4.5
	6.51	.0674	.203	4.6
	6.33	.0673	.222	4.6
	3.04	.0670	.165	4.8
Orange II[b]	40.1	.0717	.231	3.5
	39.7	.1780	.308	3.3
	19.9	.0732	.167	3.4
	12.66	.0476	.154	3.9
	9.23	.1400	.145	3.7
	7.53	.0950	.156	3.8
Anthr. Green G[a]	6.67	.1760	.116	6.7
	6.71	.4500	.159	5.9

[a] Dibasic, $n = 2$. [b] Monobasic, $n = 1$.

Affinity of Dibasic Dyes.—The foregoing procedures were also applied to dibasic acid dyes. An equation of Gilbert and Rideal was adapted for desorption

$$\frac{-0.434}{RT}(\Delta\mu_{\mathrm{D}} - 2\,\Delta\mu_{\mathrm{Cl}}) = \log\left(\frac{\Theta_{\mathrm{D}}}{1-\Theta_{\mathrm{D}}}\right)^2\left(\frac{\Theta_{\mathrm{D}}}{2-\Theta_{\mathrm{D}}}\right) - \log\,(\mathrm{D}) + 2\log\,(\mathrm{Cl}) \quad (4)$$

This equation is dependent upon maintenance of electroneutrality, and the other assumptions of (2).

The measurement of affinity for dibasic dyes having too great an attachment to nylon for desorptive processes, was attempted using equation (5).[20]

$$\frac{-0.434}{RT}(\Delta\mu_{\mathrm{D}} + 2\Delta\mu_{\mathrm{Na}}) = \log\left(\frac{\Theta_{\mathrm{D}}}{1-\Theta_{\mathrm{D}}}\right) + \log\left(\frac{B/A - 1 + 2D}{1 - 2\Theta}\right)^2 - \log D - 2\log \mathrm{Na} \quad (5)$$

where "*B*" represents the total carboxyl titer, "*A*" the total amine titer of the nylon fiber, and

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(20) We are indebted to Drs. E. K. Gladding and W. R. Remington for suggesting this approach.

TABLE IV

AFFINITY OF ACID DYES FOR NYLON (98°)

Color index	Dye	Sulfonic acids	Mol. wt.	Affinity (kcal./mole) Equation 2		Equation 3	
				a	*b*	*a*	*b*
365	Milling Yellow G	2	680	*c*	*c*	11.35	9.75
430	Milling Red SWG	2	831	*c*	*c*	10.4	8.8
138	Metanil Yellow	1	375	6.2	5.4	5.9	5.1
1076	Anthraquinone Blue RXO	1	444	6.0	5.2	5.15	4.35
161	Orange RO	1	364	5.8	5.0	4.5	3.7
151	Orange II	1	350	5.1	4.3	3.6	2.8
1078	Anthraquinone Green G	2	622	4.9	3.3	6.3	4.5
1054	Anthraquinone Blue B	2	474	2.3	0.7	*d*	*d*
31	Pontacyl Carmine 2G	2	509	1.8	0.2	*d*	*d*
639	Pontacyl Light Yellow GX	2	551	1.5	−0.1	*d*	*d*

[a] At the theoretical *p*H of 0.0. [b] Corrected to *p*H 3.0. [c] Not applicable because of insufficient dye desorption. [d] Not applicable because of insufficient dye adsorption.

Θ_D is in terms of *moles* of dibasic dye. This procedure suffers in common with (3) from neglect of the action of H^+ in the adsorption process. Data in Tables III and IV may be taken as presenting an order of magnitude only.

In accordance with the definition of standard affinity, the values obtained by these routes represent the actual affinity that would be realized at "standard" conditions, namely, unit activity of all reactants and $\Theta = {}^1/_2$. To permit comparison of dye affinity toward a fiber at a *p*H normally used for application, and particularly comparisons of the mono- and divalent anions, it becomes necessary to add a term of $-RT \ln 1/H$ and $-RT \ln 1/H^2$, respectively. These corrections have been inserted as columns 6 and 8 in Table IV to correspond to *p*H 3.0 at 98°. Table IV contains a summary of averaged affinities on nylon for a group of typical monobasic and dibasic acid dyes by the procedures I and II.

Rates of Dye Sorption.—Though the work reported in this paper was primarily concerned with the static question of affinity, a limited number of observations were made on the dynamic behavior of the dyes involved to demonstrate the distinction between these aspects of the sorption process. In one series of experiments, the rates of exhaustion from solution of several of these dyes were measured by well-known methods.[21,22] These measurements, presented in Fig. 3, were carried out at 85° on nylon fiber in dye solutions containing equivalent proportions of dye present in amount insufficient to saturate the fiber.

A second comparison was made by measuring the rate of penetration into the nylon. This was accomplished by placing nylon monofilaments in the dye bath for a specified period, removing, cross-sectioning, and measuring the depth of penetration. Sharply defined colored rings were obtained which permitted accurate comparisons. As demonstrated in Fig. 4, there was no definite correlation of this rate with the rate of sorption nor with the order of affinity. Each involves a separate phenomenon.

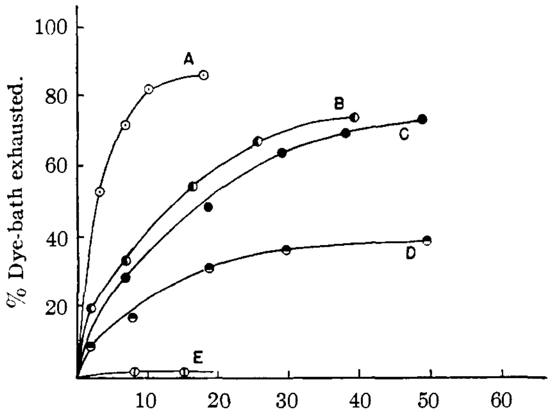

Fig. 3.—Rate of exhaustion on nylon staple at 85°, *p*H 3.5: Metanil Yellow (A); Anthraquinone Blue RXO (B); Orange RO (C); Anthraquinone Green G (D); Milling Yellow G (E).

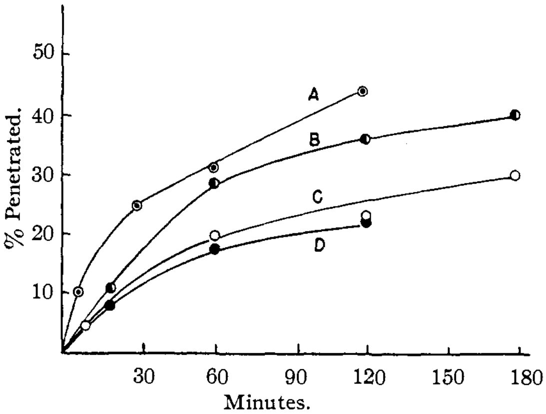

Fig. 4.—Rate of penetration into monofilament, 98°, *p*H 2.0: Orange RO (A); Anthraquinone Blue RXO (B); Anthraquinone Green G (C); Milling Yellow G (D).

Discussion

Explanations of the data involve speculation about the nature of the affinity of polymeric

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(21) Davenport, *J. Sci. Instruments*, **21**, 84 (1944).

(22) Boulton, *J. Soc. Dyers Colourists*, **60**, 5 (1944).

materials such as nylon for dyes. We believe that for the most part the affinity measures bonding forces between dye molecules and the abundant amide groups of the polymer. These forces may consist of hydrogen bonds, dipole–dipole interactions, and other sources of energy loosely classifiable as secondary valence associations.

It is evident from Table IV that there is no simple correlation between affinity and dye structure in regard to molecular weight, the number of sulfonic acid groups, or the molecular structure (both azo and anthraquinone types are represented). This we believe is the result of our use of aqueous solutions of the dyes as their reference states. In this approach, each affinity figure represents the difference between the standard free energy of the dye on the fiber and in water. Since secondary valence forces undoubtedly play a substantial part in the free energy of the dye in water, the affinity is probably a difference between two relatively large quantities. For translation of the results to applied research, however, the affinities as we have determined them are useful as a measure of the free energy changes when *polymer* replaces *water* in the association with dye molecules.

There is also, as expected, no correlation between affinity (*i. e.*, *free energy* of sorption) and *rate* of sorption or penetration of dyes. The work reported herein clarifies the distinction between these two aspects of the sorption process—a distinction that has not been recognized in much of the literature on dyeing. Affinity is but one factor in sorption rate together with density (or porosity) of the polymer and the molecular size of the dye molecules. A complete rationalization of the dynamic problem requires consideration of all these factors and probably analysis of the activation energy involved in diffusion through the polymer.

The affinity values provide an explanation for some well-known phenomena in the behavior of mixtures of acid dyes toward nylon.[6,23,24] Certain dyes are known to inhibit adsorption of others, and even to replace these other dyes on predyed fiber. For example, fiber dyed with Anthraquinone Blue B dye can be made yellow by digestion in a solution of Milling Yellow G, but the reversal cannot be carried out. We now see that this is the result of virtually complete replacement of a low-affinity dye by a high-affinity dye. It has been possible to establish a sequence in which each dye will replace any dye of lower order, but cannot readily be replaced in turn by any of these lower order dyes. This sequence coincides exactly with the arrangement of dyes in diminishing magnitude of affinity. The affinity values therefore account for the situation to be expected at *equilibrium* when two dyes are in competition for the limited number of sites for sorption in the fiber (amine ends).

While, as noted above, rate of dyeing with single dyes is not governed simply by affinity, relative rates of sorption of two dyes in competition shows prominently the effect of affinity. When Milling Yellow G and Anthraquinone Blue B (representing an extreme difference in affinity) are both present in solution, only the yellow dye is adsorbed, with complete exclusion of the blue. On the other hand, dyes of nearly equal affinity tend to be sorbed from mixed solutions in the same ratio as their concentrations.

These results indicate why the adsorption of dyes on nylon from mixed solutions is accompanied by more irregularities than is the case with a polymer like wool. The smaller number of available basic sites in nylon leads to such competition between dyes.

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Summary

1. Evidence has been presented to confirm the mechanism of attachment of acid dyes to nylon at moderate *p*H levels as consisting of a salt-type linkage between the basic amine ends of the polymer chain and the sulfonic acid groups of the dye.

2. The quantitative measurement of affinity of dye for the fiber, previously applied to wool, has been successfully extended to nylon. The procedure has been modified to permit its application to dyes with high affinity.

3. The affinities for nylon have been measured for ten representative acid dyes.

4. The affinity has been shown to provide a quantitative basis for the explanation of competitive effects in the sorption of acid dyes by nylon from mixed solutions.

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[23] Stott, *Am. Dyestuff Reptr.*, **29**, P641 (1940).

[24] Fidel, Royer and Millson, *ibid.*, **37**, P166 (1948).