Sorption of Monobasic Dye-acid by Nylon-6 Fibre

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(Received December 27, 1956)

Introduction

Much quantitative information has been published in regard to the mechanism accounting for the uptake of acid dyes by the polyamide fibres (wool, nylon-66). It is generally agreed that the dye molecule is held by means of a salt-type linkage between the sulphonic acid groups of the dye and the basic amine ends of the fibre 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 fibre[1-5].

The pH isotherms obtained by dyeing nylon-6(polycapramide) fibre from baths of varying pH containing a large amount of dye salt have been described in the previous paper[6] and it was found that at moderate pH levels, adsorption was in close agreement with available end groupings. Moreover, additional evidence has been presented for this conclusion by determining the saturation adsorption of the typical monobasic acid dye onto hydrolysed nylon-6 samples which had various amounts of free amino-groups.

The objectives of the present investigation were to elucidate the mechanism of the combination of monobasic dye-acid with nylon-6 fibre under normal dyeing conditions and to calculate the magnitude of the forces involved.

Experimental

Materials.—The nylon-6 sample employed for dyeing was 3 denier semidull staple fibre which had an end amino-group analysis of 0.043 milliequivalent per g. of fibre by DNFB method[*][6-9]. Before use, the fibres were scoured at 60°C for 20 min. in a bath containing 5 g. soap per l. and then thoroughly rinsed and dried. Distilled water was used throughout.

Dye Purification.—The dyes used were the free acids of Orange II (β-naphthol-azo-p-benzene sulphonic acid, sodium salt, Colour Index No. 151) and Metanil Yellow YK (diphenyl-azo-m-benzene sulphonic acid, sodium salt, Colour Index No. 138).

Two dyes were first isolated as sodium salts free from inorganic electrolytes by the method

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1) E. Elöd and T. Schachowsky, *Melliand Textilber.*, **23**, 437 (1942), ibid., **25**, 237 (1914).

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

3) P. W. Carlene, A. S. Fern and T. Vickerstaff, ibid., **63**, 388 (1947).

4) F. C. McGrew and A. K. Schneider, *J. Am. Chem. Soc.*, **72**, 2547 (1950).

5) W. R. Remington and E. K. Gladding, ibid., **72**, 2553 (1950).

6) M. Yoshida, and M. Nishio, Scientific Reports of Toyo Rayon Co. **9**, 85 (1954) (in Japanese).

[*] This is a simple method which is carried out chemically with the aid of dinitrofluorobenzene for the precise determination of the primary amine content of the polyamide.

7) F. Sanger, *Biochem. J.*, **39**, 507 (1945).

8) J. H. Bows and J. A. Moss, ibid., **55**, 735 (1953).

9) H. Zahn and P. Rathgeber, *Melliand Textilber.*, **34**, 239 (1953).

of Robinson and Mills[10] which involved three or fourfold salting out with sodium acetate followed by repeated extraction with ethyl alcohol until an aqueous solution containing a known amount of dye salt gave a constant optical density as shown in Fig. 1 (Orange II).

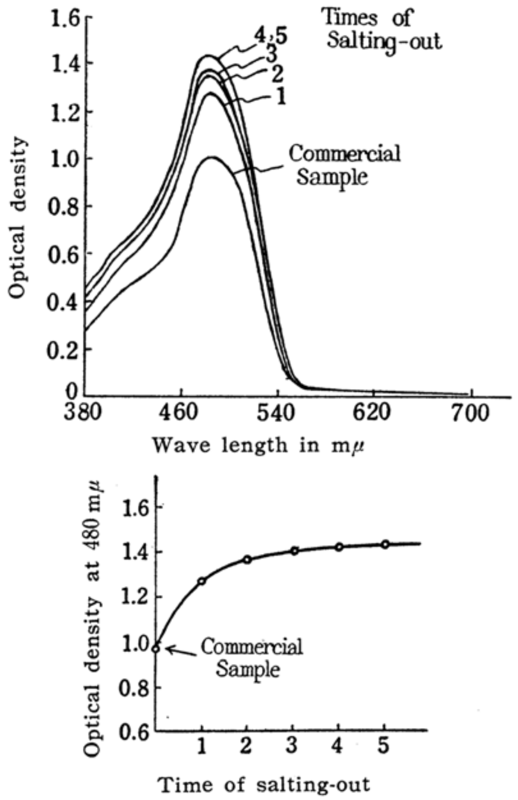

Fig. 1. Variation of absorption spectrum and optical density at 480 mμ of dye solution with time of salting-out. (Orange II, 50 mg./l.).

The free acid of Orange II was then precipitated from the concentrated solution of sodium salt of dye obtained above by means of concentrated hydrochloric acid, filtered off, washed with dilute hydrochloric acid, and finally dried in vacuo over caustic soda flakes until free from chloride ions.

In the case of Metanil Yellow YK, ion exchange resin was employed to obtain electrolyte-free dye-acid. Two % aqueous solution of the above-obtained dye-salt was allowed to run through a column of Amberlite IR-120 (strongly acidic ion exchange resin of Rohm & Hass Co.) previously washed with water and methanol and then activated by treatment with 10% hydrochloric acid.

The pure dye-acid, isolated from the effluent on evaporation and washed with water to remove any inorganic acid, was obtained as bright black sparingly soluble needles.

The ash content of both samples were almost nil and analytical values according to titanous chloride method indicated high purity of at least 98 %. They were dried to constant weight at 105°C before use.

Procedure.—One gram samples of nylon-6 fibre were dyed in a 200 : 1 liquor ratio at 60°C (±0.1°)C for a period of 3 to 6 days (i. e. to equilibrium) in the absence of any acids. The acidity was adjusted by varying concentrations of the dye-acid and the pH values reported were those at the end of the dyeing, at room temperature. Glass electrode pH meter was used for pH determination. After dyeing the dyed sample was removed from the dye liquor, rinsed rapidly with a minimum quantity of distilled water and then air-dried.

TABLE I

ADSORPTION OF FREE DYE-ACIDS BY NYLON-6 FIBRE AT 60°C

Dye in Solution (m.eq./l.)	Final pH of Dye-bath	Dye in Fibre (m.eq./g.)	θ_D	$-\Delta\mu^\circ$HD (kcal./mole)
Orange II				
4.16	2.85	0.083	—	—
1.17	3.15	0.068	—	—
0.77	3.38	0.060	—	—
0.49	3.65	0.055	—	—
0.22	5.53	0.048	0.89	16.9
0.12	5.72	0.037	0.69	15.8
0.060	5.83	0.029	0.54	16.0
0.031	5.72	0.024	0.45	15.4
0.024	5.69	0.014	0.26	14.6
0.002	5.69	0.007	0.13	15.2
	$[S]_F=0.054$		Average:	15.7
Metanil Yellow YK				
0.782	2.05	0.117	—	—
0.597	3.02	0.104	—	—
0.597	3.08	0.104	—	—
0.441	3.12	0.102	—	—
0.229	3.30	0.101	—	—
0.229	3.31	0.097	—	—
0.444	3.34	0.093	—	—
0.229	3.56	0.092	—	—
0.441	3.10	0.091	—	—
0.229	3.59	0.090	—	—
0.229	3.28	0.088	—	—
0.206	3.20	0.087	—	—
0.449	3.87	0.083	—	—
0.096	3.20	0.072	—	—
0.081	3.58	0.071	—	—
0.115	4.93	0.062	—	—
0.022	5.97	0.059	—	—
0.049	4.75	0.049	0.94	17.6
0.048	6.07	0.049	0.94	17.5
0.017	6.07	0.043	0.83	18.8
0.011	6.07	0.038	0.73	18.3
0.003	5.90	0.028	0.54	17.8
0.002	5.65	0.020	0.38	16.4
~0	6.07	0.015	—	—
~0	6.50	0.010	—	—
	$[S]_F=0.052$		Average:	17.8

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[10] C. Robinson and H. A. T. Mills, *Ptoc. Roy. Soc.* (*Lndon*), **A131**, 576, 596 (1931).

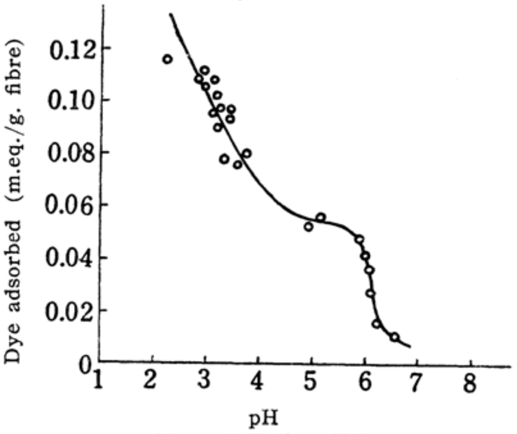
Measurements of dye adsorbed on nylon-6 were made by dissolving the dyed fibre in 80% formic acid and determining the quantity of dye in solution by means of the photoelectric spectrophotometer (Beckman type) on the basis of the application of Beer's law.

Concentrations of dye-acid in aqueous bath were likewise measured spectrophotometrically.

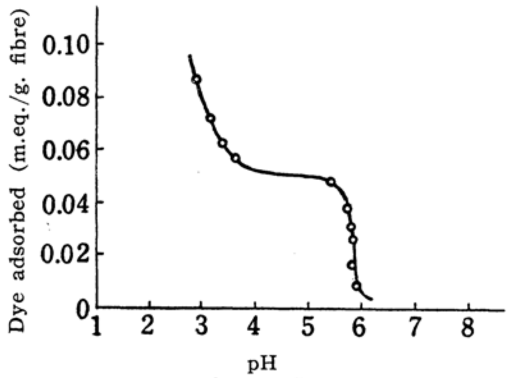
Results and Discussion

Isotherms were determined for varying concentration of the free dye-acids.

The results obtained are given in Table I, illustrated by Fig. 2.



Metanil Yellow YK



Orange II

Fig. 2. Adsorption of monobasic free dye-acids on nylon-6 fibre at 60°C.

The amount of dye adsorbed at equilibrium has been plotted against the final pH of the dyebath. The curves are similar to those in the case of sodium salt of dye which was reported in the previous paper⁶⁾, being sigmoid in shape and reaching a fairly constant value (about 0.05 milliequivalent of dye-acid per g. of fibre) corresponding to saturation of the end amino-groups. Such correspondence has been found to exist generally for acid dyes¹⁻⁶⁾.

As the pH is further decreased, there is another sharp increase in the uptake which corresponds to adsorption of the dye onto weakly basic amide-groups of the polymer chain (amide-dyeing) and new primary amine groups liberated by the occurrence of dye-catalysed hydrolysis. Such a phenomenon has been observed in the case of acid dyes and referred to as "overdyeing"¹¹,¹²⁾.

The uptake of monobasic dye-acid by nylon may be represented schematically as

$$-\mathrm{OOC{-}N_y-NH_3^+ + H^+ + D^-} \longrightarrow \mathrm{HOOC{-}N_y{-}NH_3^+ \cdot D^-}$$

where Ny is the polyamide chain separating the end amino and carboxyl groups and D^- is a dye anion. On immersion of the fibre in a dyebath containing free dye-acid, hydrogen ions are first adsorbed onto carboxyl groups and the more slowly diffusing dye anion is then able to attach itself to the positively charged amino-groups. This mechanism is now accepted as accounting for the adsorption of acid dyes by nylon.

Gilbert and Rideal¹³,¹⁴⁾ first proposed a method of analysis of the adsorption forces of acids and acid dyes on wool, which has been extended to the case with free dye-acids by Lemin and Vickerstaff¹⁵⁾ and later applied to nylon-66 by American workers⁴,⁵⁾, by the use of the equation

$$-\frac{0.434}{RT}(\Delta\mu^\circ_{\mathrm{H}}+\Delta\mu^\circ_{\mathrm{D}}) = 2\log\left(\frac{\theta_{\mathrm{D}}}{1-\theta_{\mathrm{D}}}\right)-\log[\mathrm{D}]_s+\mathrm{pH} \qquad (1)$$

in which $[\mathrm{D}]_s$ represents the molar concentration of the free dye-acid in solution and θ_{D} the fraction of the available basic sites of the fibre which are occupied by dye anion. The notations $\Delta\mu^\circ_{\mathrm{H}}$ and $\Delta\mu^\circ_{\mathrm{D}}$ represent the standard changes in chemical potential (partial molal free energy) for the hydrogen ion and for the monobasic dye anion involved in the sorption of the ions from the solution by the fibre, and the negative of their sum represents the

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11) C. D. O'Briain and R. H. Peters, *J. Soc. Dyers and Colourists*, **69**, 435, (1950).

12) E. Atherton, D. A. Downey and R. H. Peters, *Text. Res. J.*, **25**, 977 (1955).

13) G. A. Gilbert and E. K. Rideal, *Proc. Roy. Soc.*, **A182**, 335 (1944).

14) G. A. Gilbert, ibid., **A183**, 167 (1944).

15) D. R. Lemin and T. Vickerstaff, *J. Soc. Dyers and Colourists*, **63**, 405 (1947).

standard affinity of the acid form of the dye for the fibre ($\Delta\mu^\circ_{HD}$).

This quantity gives a measure of the tendency of the dye acid to move from its standard state in solution to its standard state on the fibre. On this basis calculations were carried out by use of equation (1) and the affinity values obtained are given in the last column of Table I.

In order to evaluate θ_D, the fractional saturation of the fibre sites, it is necessary to determine the saturation value $[S]_F$ which is the concentration of dye in the fibre when all the available sites, end amino-groups, are occupied.

Equation (1) may be converted into the form—

$$-\frac{0.434}{RT}\Delta\mu^\circ_{HD} = \log\left(\frac{\theta_D}{1-\theta_D}\right)^2 \cdot \frac{1}{[H]_S\cdot[D]_S} \qquad (2)$$

where, $\mathrm{pH} = \log 1/[H]_S$

$$\theta_D = [D]_F/[S]_F$$

Removing logarithms,

$$\left[\frac{\theta_D}{1-\theta_D}\right]^2 = \left(\frac{[D]_F}{[S]_F-[D]_F}\right)^2 = K[H]_S\cdot[D]_S \qquad (3)$$

Where K is a constant, $[D]_F$ and $[H]_S$ refer to the concentrations of dye in the fibre and hydrogen ions in solution respectively. Inverting both sides of the equation, and dividing by $[S]_F$,

$$\frac{1}{[D]_F} - \frac{1}{[S]_F} = \frac{1}{\sqrt{K}\cdot[S]_F} \cdot \frac{1}{[H]_S\cdot[D]_S} \qquad (4)$$

A plot of the reciprocal of $[D]_F$ against the reciprocal of the mean molarity of the dye-acid in solution, $\sqrt{[H]_S\cdot[D]_S}$, should yield a straight line as is shown in Fig. 3, the intercept of which on "$1/[D]_F$" axis gives the reciprocal of the saturation value $[S]_F$. The values obtained by extrapolation in this way are 0.054 milliequivalent per g. of nylon-6 fibre for Orange II free acid and 0.052 for Metanil Yellow YK free acid, which were used for calculation of dye affinity.

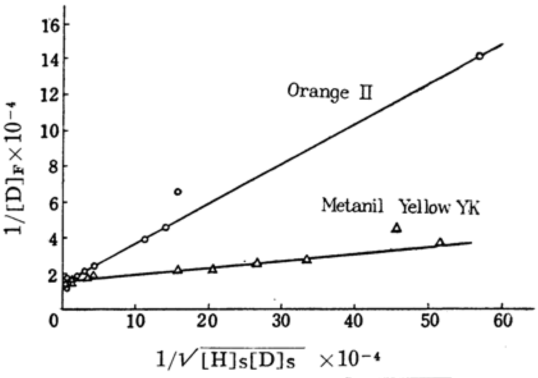

Fig. 3. $1/[D]_F$ against $1/\sqrt{[H]_S[D]_S}$ plot for adsorption of monobasic dye-acid by nylon-6 fibre at 60°C.

Assuming the affinity of hydrogen ion for nylon at 80°C to be −11.9 kg. cal.[16] and the heat of reaction to be negligible as temperature appears to have little effect on adsorption of hydrochloric acid by wool[15] anion affinities have been calculated for two monobasic dyes, with the results shown in the last column of Table II.

TABLE II

AFFINITY OF MONOBASIC DYE ANIONS FOR NYLON-6 FIBRE AT 60°C

Dye-Acid	(Affinity kcal./mole)		
	$\Delta\mu^\circ_{HD}$	$\Delta\mu^\circ_H$	$\Delta\mu^\circ_D$
Orange II	−15.7	−11.9	−3.8
Metanil Yellow YK	−17.8		−5.9

The value for Metanil Yellow YK anion is in good agreement with values for nylon-66 obtained by McGrew and Schneider of −6.1 and −5.9[4], by Remington and Gladding of −6.1 kcal./mole[5,16], being somewhat higher than the affinity value of this dye anion for wool of −5.0 ~ −5.3 kcal./mole[15]. The affinity of acid dye is generally known to be higher for nylon than for wool.

With Orange II, McGrew and Schneider also determined the affinity for nylon-66 of −3.3~−3.9 kcal./mole by adsorption of the sodium salt of the dye from neutral solution in presence of salt at 98°C.

Judging from these results it seems to be possible to conclude that the affinities of two monobasic dye anions are approximately the same on two fibres, nylon-66 and nylon 6.

Thus, the fundamental energetics of dyeing process and the mode of dye attachment are the same on these two fibres and some slight differences in dyeing behavior—for instance, the rate of dyeing and levelness etc. as is often said—must be accounted for by purely physical differences due to the production process of the fibre. Under practical dyeing conditions, however, it is evident that the amine content is of course the controlling factor for building acid dyes upon nylon.

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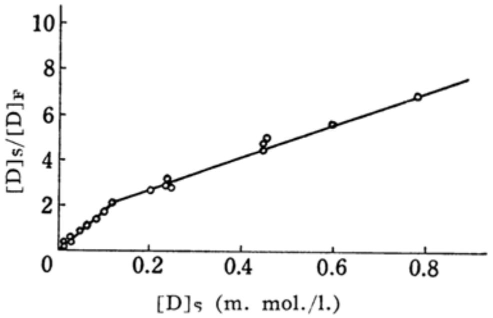
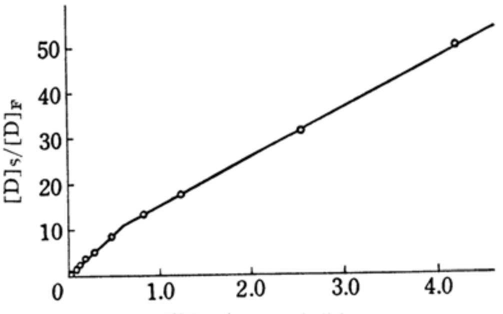
[16] T. Vickerstaff, "The Physical Chemistry of Dyeing", 2nd edition, Oliver and Boyd, London (1954), p. 471.

Finally, the adsorption isotherms already determined give straight lines, when $[D]_S/[D]_F$ is plotted against $[D]_S$ according to the Langmuir's equation:

$$[D]_F = \frac{a[D]_S}{1+b[D]_S} \tag{5}$$



Free acid of Metanil Yellow YK



Free acid of Orange II

Fig. 4. $[D]_S/[D]_F$ against $[D]_S$ plot for adsorption of monobasic dye-acid by nylon-6 fibre at 60°C.

The curves of Fig. 4 consist really of two straight lines with an abrupt change of slope. It therefore appears that the type of site on which dye is adsorbed is different between these two portions. The line at higher concentration has already been discussed and can mainly be attributed to the adsorption of dye on weakly basic amide-groups of the polymer chain. The line of different slope at lower concentration must refer to the primary adsorption of dye on terminal amino-groupings which should also obey the Langmuir adsorption isotherms.

The point at which this change takes place corresponds to $[D]_F$ value of 0.054 m. eq. dye per g. of fibre for Orange II and 0.052 for Metanil Yellow YK which are in good agreement with the values obtained by extrapolation illustrated in Fig. 3 and also close to the number of free amino end groupings (0.043 m. eq./g. fibre) determined by DNFB method. The difference might be due to the substantivity of these dye-acids for nylon or attributed to the fact that overdyeing occurs to a slight extent even at moderate pH levels.

Summary

The equilibrium uptake of two typical monobasic dye-acids by nylon-6 (polycapramide) fibre has been measured for varying concentrations and additional evidence was given to confirm the mechanism of dye attachment to nylon as consisting of (1) combination with basic amine ends at normal dye bath pH and (2) combination mainly with the weakly basic nonterminal amide groups of the polymer chain at lower pH values. The Langmuir equation can well be applied to both regions of adsorption.

It is well known that the thermodynamic affinity of a dye for the fibre represents a fundamental characteristics of the dyeing process. The anion affinities of dye-acids for nylon-6, calculated from data on the equilibrium distribution of dye-acid between bath and fibre in terms of the change in standard chemical potential of the dye sorption process using the equation for wool developed by Gilbert and Rideal, were in good agreement with values for nylon-66 obtained by other workers.

Thus, the fundamental energetics of dyeing process and the mode of dye attachment are the same on these two fibres and some slight differences in dyeing behaviour must arise solely from differences in their physical structure due to the production process.

The author wishes to express his sincere thanks to Dr. K. Hoshino and Mr. M. Yoshida for their kind encouragement and for permission to publish this paper.

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