

Diffusion of Dyes in Polyester Fibers. III. Time Delay in Establishment of the Equilibrium Concentration of Dye at Fiber Surface

ANNA NARĘBSKA and BARBARA OSTROWSKA-GUMKOWSKA,
Nicholas Copernicus University, Institute of Chemistry, ul. Gagarina 7, 87-100 Toruń, Poland, and HENRYK KRZYSZEK, *Institute of Chemical Fibers, ul. M. Skłodowskiej-Curie 19/27, 90-570 Łódź, Poland*

Synopsis

In the dyeing process of the copolyester fiber Dilana with the disperse dye Synthene Scarlet P3GL, a deviation from the simple model of Fickian sorption occurs. It manifests itself as a time delay in establishment of the equilibrium dye concentration at the fiber surface. As has been stated, the variation of c_s (the surface dye concentration) with time of dyeing fits the equation: $c_s = c_\infty (1 - e^{-\beta t})$. Regarding the relation of c_s to t , the diffusion coefficient of the dye in the studied fiber has been calculated by the theoretical equation reported in Crank's monograph. It has been proved that the experimental data on kinetics of dyeing the fiber Dilana with Synthene Scarlet P3GL fit considerably better the tested equation than the classical Hill's equation.

INTRODUCTION

Isothermal rate-of-dyeing curves relating a total concentration of dye within a fiber c_t to time of dyeing t are often employed in the investigations of the dyeing kinetics of fibers. Such curves are the basis for calculations of diffusion coefficients D and equilibrium concentrations c_∞ of dyes within fibers. If dyeing occurs in an infinite dye bath, Hill's equation is most frequently used in the calculations¹:

$$\frac{c_t}{c_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} e^{-D \alpha_n^2 t} \quad (1)$$

Equation (1) is a solution of Fick's second law of diffusion. It has been derived assuming that: (1) diffusion proceeds radially in an isotropic infinitely long cylinder of radius a , (2) the diffusion coefficient D is constant, and (3) a concentration of a penetrant at the surface of a cylinder c_s is constant. Assumption (3) implies that the concentration c_s attains immediately the value corresponding to the saturation equilibrium concentration of dye within a fiber $c_s = c_\infty$.

In the really met fiber-dye systems not all of the above assumptions are obeyed. Investigations performed with the method proposed by Blacker and Patterson² or by photometration of cross sections of dyed fibers³ led to the conclusion that, in some systems, the dye concentration at the fiber surface is not constant but it changes with time of dyeing $c_s = f(t)$. Blacker and Patterson^{2,4} observed time dependence of c_s on dyeing of polyester and polyamide fibers with C. I. Disperse Red 1, C. I. Disperse Red 15, C. I. Disperse Yellow 1; Cometto,³

on dyeing of the polyester fiber with C. I. Disperse Blue 24; and Bell et al.⁵ on the range of relatively short times of dyeing the polyamide fiber with C. I. Acid Red 1. The same observations found experimentally on dyeing the copolyester fiber Dilana with the disperse dye Synthene Scarlet P3GL we have reported earlier.⁶

In the present paper we have attempted to find a mathematical relation which describes the changes of dye concentration c_s occurring during the dyeing process. Then, having this relation and the rate constant β of attaining the equilibrium dye concentration at the fiber surface, a theoretical equation reported in Crank's monograph¹ has been tested. Crank's equation has not been verified experimentally yet. The calculations performed in this paper prove that the experimental data on kinetics of dyeing fit considerably better the tested equation than the classical Hill's equation.

EXPERIMENTAL

Fiber. The experiments were carried with the copolyester fiber Dilana. The copolymer and preparation and properties of the fiber have been described in details in the previous paper.⁷ Before dyeing, the samples of the fiber were extracted with a mixture of methanol and distilled water (3:1) in a Soxhlet apparatus. Then the samples were immersed in a blank bath and allowed to equilibrate at boiling for 12 h.

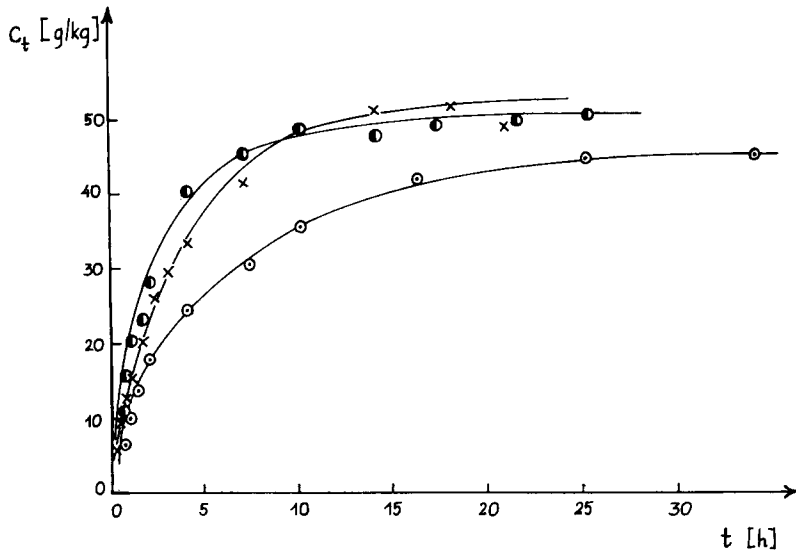
Dye. The disperse dye Synthene Scarlet P3GL (C. I. Disperse Red 54), produced by ZACHEM, Poland, was used for dyeing experiments. Owing to the difficulty met in preparing a stable dispersion from the purified dye, the commercial product was used for dyeings.

Dyeing Conditions. The fibers (0.5 g) were dyed at boiling in aqueous baths (0.5 dm³) of the following composition:

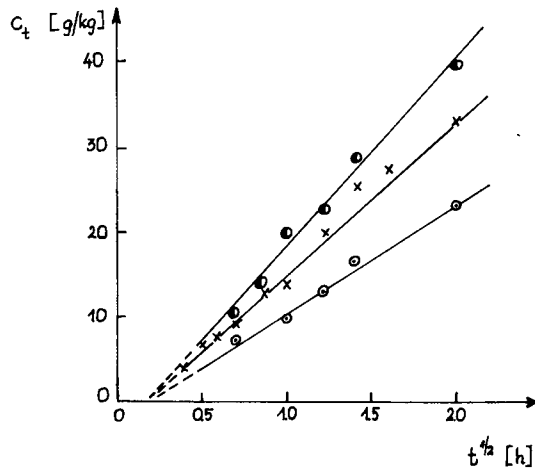
	bath 1	bath 2
dye	2.0 g/dm ³	2.0 g/dm ³
dispersing agent NNO (produced by NZPO "Rokita" Poland)	3.0 g/dm ³	3.0 g/dm ³
carrier Dilatin OD (produced by Sandoz, Switzerland)	—	2.0 g/dm ³
acetic acid	0.6 g/dm ³	0.6 g/dm ³
sodium acetate	0.9 g/dm ³	0.9 g/dm ³

Due to an excess of the dye, the concentration of the bath remained practically constant during the whole dyeing process. The time of dyeing ranged from 10 min to 36 h. After dyeing, the fibers were withdrawn from the bath and immersed into ice-water to stop the further diffusion. Then they were dried and washed with cold acetone (278 K) to remove the dye adhering to the surface. The amount of the dye present in the fiber was determined colorimetrically (Specol Spectrophotometer, C. Zeiss Jena) after extraction with the solution composed of *N,N*-dimethyl formamide (40%), ethylene glycol (59%), and formic acid (1%).

Dye Concentration Profiles. The dye concentration profiles were measured by scanning the cross sections of the dyed fibers with a microphotometer devised specially for this purpose. The technique of preparing the cross sections and



(a)



(b)

Fig. 1. Rate-of-dyeing curves of the fiber Dilana dyed with Synthene Scarlet P3GL. Experimental data plotted in coordinates: dye concentration in fiber vs. time of dyeing (a) and square root of dyeing time (b). Nonannealed fiber dyed without a carrier (\odot), and with a carrier (\bullet); fiber annealed at 403 K, dyed with a carrier (x).

the method of measurements of the radial distribution curves have been described in details in the previous papers.^{6,7}

CALCULATIONS AND RESULTS

Some typical rate-of-dyeing curves of the copolyester fiber Dilana with Synthene Scarlet P3GL are shown for example in Figure 1(a). These curves seem to fit Hill's equation. However, when the dye concentration within the fiber c_t is plotted vs. the square root of dyeing time $t^{1/2}$, some deviations from the simple model of the Fickian sorption become visible [Fig. 1(b)]. As it results from Figure

TABLE I
 Constants of Equation: $c_t = At^{1/2} + B$ and Correlation Coefficients R

Dyeing method	Temperature of annealing of the fibers (K)	A	B	R
Without a carrier	Nonannealed	12.75	-1.99	0.998
With a carrier	Nonannealed	22.25	-4.57	0.995
	338	19.31	-1.43	0.994
	394	18.44	-1.01	0.995
	403	19.20	-3.41	0.993

1(b), at the initial stage of dyeing the relation c_t to $t^{1/2}$ is a straight line, but this line does not meet the origin of coordinates when it is extrapolated to zero time. The following equation describes the experimental data:

$$c_t = At^{1/2} + B \quad (2)$$

where A and B are constants. The negative values of constant B (Table I) prove that there is so-called "time delay" before the dye uptake curves become linear. The deviations from the simple model of dyeing are even more pronounced if one takes into consideration the concentration-distance curves of Synthene Scarlet in the fiber [Fig. 2(a)]. These curves make evident that the dye concentration at the fiber surface increases with time of dyeing long after the diffusion into the fiber begins. As follows from Figure 2(b), in which the time dependence of c_s , resulting from the measured concentration-distance curves has been graphically presented, the time required for c_s to approach the equilibrium value c_∞ is about 2 h when the carrier is present in the dye bath. When the fiber is dyed in the absence of carrier, the time is about 3 h.

It has been also proved that the kinetics of attaining the equilibrium dye concentration at the fiber surface can be described by the equation

$$c_s = c_\infty(1 - e^{-\beta t}) \quad (3)$$

which is formally an equation of the first-order reaction. Constant β is a rate constant with the dimension s^{-1} or h^{-1} . The numerical values of β , calculated

TABLE II
 Diffusion Coefficients D and Equilibrium Concentrations c_∞ of Synthene Scarlet P3GL in Dilana, Calculated by Eq. (4)

Dyeing method	Temperature of annealing of the fibers (K)	D ($cm^2 \cdot s^{-1} \times 10^{11}$)	c_∞ ($g \cdot kg^{-1}$)	β^a (h^{-1})	$V^2 b$
Without a carrier	Nonannealed	0.7	44.1	2.15	0.0018
With a carrier	Nonannealed	1.7	49.4	2.85	0.0009
	388	1.4	48.6	2.80	0.0026
	393	1.6	47.3	2.85	0.0022
	403	1.3	50.6	2.95	0.0044

^a Rate constant calculated by eq. (3).

^b Relative variance calculated by eq. (5).

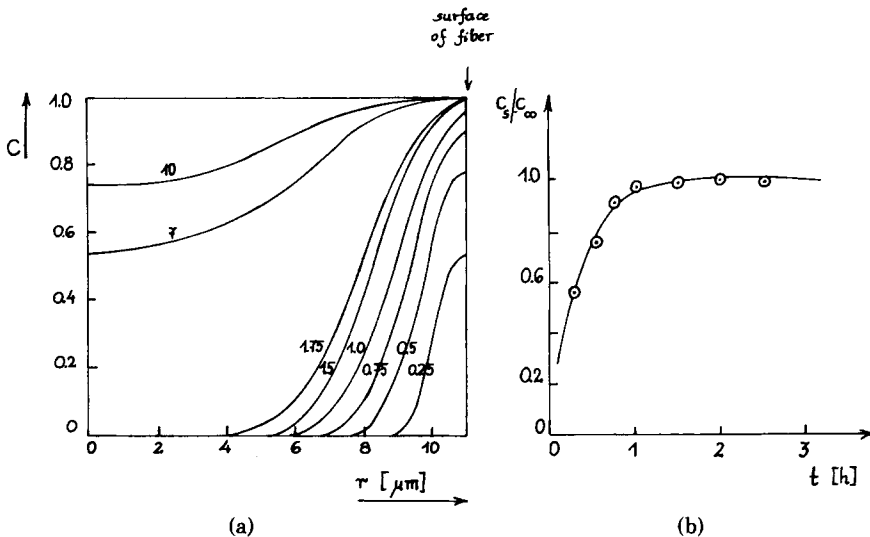


Fig. 2. Concentration profiles (a) and variations of the relative surface concentration (b) of Synthene Scarlet P3GL in Dilana. Fiber annealed at 403 K, dyed with a carrier. Numbers on curves of Figure 2(a) represent the dyeing times in h.

on the basis of the measured concentration profiles and eq. (3), are presented in Table II.

Diffusion Coefficients with Regard to Time-Dependence of c_s . Having the functional relation c_s to t [eq. (3)], the earlier mentioned theoretical equation reported in Crank's monograph was applied to calculate the diffusion coefficient of Synthene Scarlet P3GL in Dilana. This is as follows:

$$\frac{c_t}{c_\infty} = 1 - \frac{2J_1[(\beta a^2/D)^{1/2}]e^{-\beta t}}{(\beta a^2/D)^{1/2} J_0[(\beta a^2/D)^{1/2}]} + \frac{4}{a^2} \sum_{i=1}^n \frac{e^{-D\alpha_n^2 t}}{\alpha_n^2(\alpha_n^2/\beta/D - 1)} \quad (4)$$

Diffusion coefficient and equilibrium concentrations of the dye in the investigated fibers calculated by the equation are inserted in Table II. In the same table the values of a relative variance of the experimental points (c_{t_i}, t_i) around the theoretically predicted curve, calculated by the equation⁸

$$V^2 = \frac{\sum_{i=1}^k (c_{t_i} - \hat{c}_{t_i})^2}{k - 1} \times \frac{k}{\sum_{i=1}^k c_{t_i}} \quad (5)$$

are also given. The applicability of the experimental data to the equation can be estimated also on the basis of Figure 3. In the figure, the theoretical uptake curves of Synthene Scarlet P3GL calculated by eq. (4) have been plotted (full lines). The broken lines in the same figure illustrate the rate-of-dyeing curves calculated with Hill's equation. It is easy to see that the experimental data coincide better with the curves predicted by eq. (4) than by eq. (1). The numerical values of the diffusion coefficients derived from the both equations (Tables II and III) do not differ considerably. The appreciable differences are

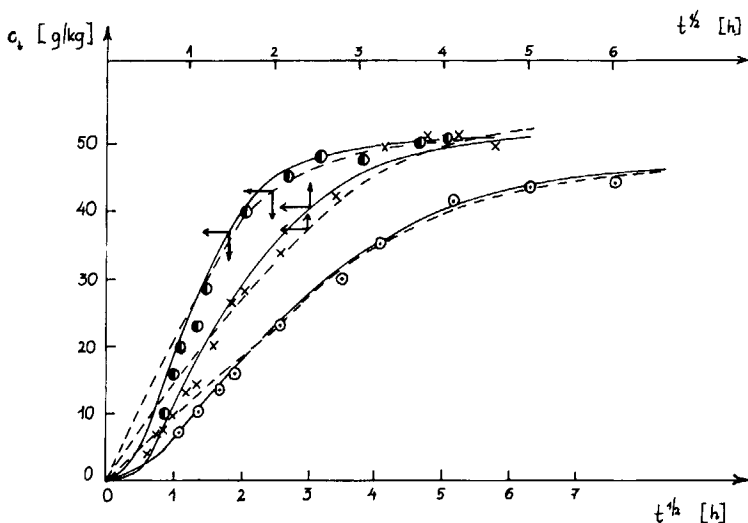


Fig. 3. Rate-of-dyeing curves for the fiber Dilana calculated by theoretical equation (4) (—) and Hill's equation (---). Nonannealed fiber dyed without a carrier (○) and with a carrier (●); fiber annealed at 403 K, dyed with a carrier (x).

observed only for fibers which had been annealed at 403 K, and dyed on the presence of the carrier. In this case, the D and c_{∞} values calculated with eq. (4) are: $1.3 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ and $50.6 \text{ g} \cdot \text{kg}^{-1}$ and with eq. (1), respectively, $0.8 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ and $54.0 \text{ g} \cdot \text{kg}^{-1}$. For the other fibers, the differences in values of D do not exceed 25%, and in the values of c_{∞} are in the range of an experimental error.

The sigmoidal shape of the concentration profiles shown in Figure 2(a) suggests that the diffusion coefficient of Synthene Scarlet in Dilana is not constant. This problem has been discussed in the previous paper.⁶ It has been proved there that the diffusion coefficient of Synthene Scarlet P3GL is an exponential function of its concentration in the fiber $D(c) = D_0 \exp(\delta c)$, where $c = f(r, t)$. It is necessary therefore to treat the diffusion coefficient calculated with eq. (4) as an average diffusion coefficient \bar{D} , and having in mind a heterogeneity of the investigated fiber and a presence of auxiliaries in the dye bath—in principle—as an apparent diffusion coefficient D_{app} .

COMMENTS TO THE RESULTS

The assumption made generally is that on dyeing in infinite dye baths, rigorously agitated, the concentration c_s instantaneously attains the equilibrium concentration equal to that which can be established in a total volume of a fiber after $t \rightarrow \infty$. This assumption and the additional one, i.e., that $D = \text{const}$ or a function of c only are the basis of the Fickian sorption model.⁹ The experimental data prove, however, that in some fiber-dye systems the deviations from this model occur.

In this paper there are too little data to explain the "time delay" in approaching the saturation equilibrium concentration at the fiber surface and to decide what factors are responsible for it, as they can be different in nature. In the opinion

TABLE III
Diffusion Coefficients D and Equilibrium Concentrations c_{∞} of Synthene Scarlet P3GL in Dilana calculated by Eq. (1)

Dyeing method	Temperature of an annealing of the fibers (K)	D ($\text{cm}^2\text{-s}^{-1} \times 10^{11}$)	c_{∞} ($\text{g}\cdot\text{kg}^{-1}$)	V^2 ^a
Without a carrier	Nonannealed	0.6	44.3	0.0033
With a carrier	Nonannealed	1.4	49.8	0.0036
	388	1.2	48.7	0.0045
	393	1.2	48.5	0.0038
	403	0.8	54.0	0.0098

^a Relative variance calculated by eq. (5).

of some authors,^{2,4} there are no reasons for supposing that the rate of sorption at the fiber surface is markedly greater than in its interior. Some other authors^{10,11} suggest that a possible cause of the time delay in approaching c_{∞} is a barrier existing at the fiber surface. The barrier, the nature of which is not known exactly, hinders the transfer of dye molecules into the interior of a fiber. Blacker and Patterson^{2,4} represent the opinion that the surface dye concentration may be a function of duration of dyeing when the rate constant for transfer of dye molecules through the interface fiber-dyebath into a fiber is equal or smaller than the rate constant of the reverse process.

The functional relation c_s to t , observed in this paper [eq. (3)], may be formally regarded as the equation of a first-order reaction. Having this in mind, one can postulate that the diffusion of dye into a fiber is governed by the rate of sorption of single dye molecules. As a colloidal dispersion is the usual state of a disperse dye in a water bath, the sorption of some amount of single molecules may be dependent on kinetics of association-dissociation processes of dye. It cannot be decided if the process concerns the dye in solution or on the fiber surface, after instantaneous sorption of dye associates. When dissociation of the dye associates is slow, the time-dependence of c_s is possible.

Equation (3) may be also regarded as one of pseudo-first-order reaction. It implies that in spite of covering the surface of a fiber with dye in an amount corresponding to c_{∞} , the diffusion proceeds only from strictly defined sites of sorption, localized on the fiber surface. If a completion of the free sites with successive dye molecules is relatively slow, a time dependence of the dye concentration at the fiber surface can be expected.

The structural heterogeneity of the oriented and crystalline fiber causes additionally that the lines of dye flow are not parallel and the diffusion is not strictly isotropic.

The observed deviations from the classical Hill equation may also partially result from the complexity of the investigated fiber-dye system. The used dye bath was itself multicomponent, being composed of water, dye, dispersing agent, carrier, and buffer. The diffusion flux of the dye is then influenced by any other component present in the bath.

Considering the above factors, one can expect that an account of the kinetics of dyeing the copolyester fiber with Synthene Scarlet requires a more complex model of sorption and diffusion than a simple Fickian one.

APPENDIX: NOMENCLATURE

A, B	constants of equation: $c_t = At^{1/2} + B$
a	radius of fiber
c_t	concentration of dye in fiber, at dyeing time t
\hat{c}_t	concentration of dye in fiber, at time t , resulting from theoretical equation
c_∞	equilibrium concentration of dye in fiber
c_s	concentration of dye at surface of fiber, at dyeing time t
D	diffusion coefficient of dye in fiber
\bar{D}	average diffusion coefficient of dye in fiber
D_{app}	apparent diffusion of dye in fiber
$D(c)$	concentration-dependent diffusion coefficient
D_0	concentration-dependent diffusion coefficient at zero concentration of dye in fiber
β	constant of equation: $c_s = c_\infty(1 - e^{-\beta t})$
δ	constant of equation: $D(c) = D_0 e^{\delta c}$
$J_0(x)$	Bessel function of the first kind of order zero
$J_1(x)$	Bessel function of the first order
k	number of experimental points on rate-of-dyeing curve
α_n	positive root of equation $J_0(a\alpha_n) = 0$
R	correlation coefficient
r	distance from center of fiber
t	time of dyeing
V^2	relative variance

References

1. J. Crank, *The Mathematics of Diffusion*, Clarendon, Oxford, 1956.
2. J. G. Blacker and D. Patterson, *J. Soc. Dyers Colour.*, **85**, 598 (1969).
3. C. Cometto, M.Sc. thesis, University of Leeds, 1971.
4. D. Patterson, Diffus. Solutes Solution Fibre Syst., Proceedings of a Symposium, 1973, 1-6, Department of Chemical Technology, University of Bombay, Bombay.
5. J. P. Bell, W. C. Carter, and D. C. Felty, *Text. Res. J.*, **37**, 512 (1967).
6. B. Ostrowska and A. Narębska, *J. Appl. Polym. Sci.*, **25**, 2845 (1980).
7. B. Ostrowska, A. Narębska, and H. Krzyszek, *J. Appl. Polym. Sci.*, **26**, 643 (1981).
8. J. Linnik, *Metoda Najmniejszych Kwadratów i Teoria Opracowywania Obserwacji*, PWN, Warszawa, 1962.
9. R. McGregor, *Diffusion and Sorption in Fibers and Films*, Academic, London and New York, 1974, Vol. 1.

Received February 3, 1983

Accepted October 7, 1983