Diffusion of Dyes in Polyester Fibers. II. Diffusion Coefficients from the Radial Distribution Curves

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Synopsis

The computational method of a concentration-dependent diffusion coefficient $D(C)$ of dyes in fibers has been presented. This method is based on concentration profiles determined with the microphotometric technique and the numerical solution of Fick's second law of diffusion for the cylindrical system. Exploiting the grid method and data of experimental concentration profiles, diffusion coefficients of disperse dye Synthene Scarlet P3GL in the anionically modified polyester fiber have been calculated. The results have been compared with those obtained by the Boltzmann–Matano method. It was stated that (1) in the investigated polymer–dye system the relation between D and C is of the form $D(C) = D_0 \exp(\delta C)$; (2) the allowance for the cylindrical symmetry of the fiber leads to the lower values $D(C)$ in the total concentration range than those obtained by the Boltzmann–Matano method; and (3) values of D_0 calculated with both methods are coincident.

INTRODUCTION

Detailed investigations of the diffusion of dyes in fibers prove that for many polymer–dye systems the diffusion coefficients of dyes are concentration dependent and sometimes, time or distance dependent. Such information may be found, among others, from the concentration profiles of dyes in fibers determined by scanning with microphotometer of the cross sections of the dyed fibers. Concentration profiles obtained in this way permit calculation of the true diffusion coefficients instead of the apparent or average; however, the proper calculation methods are required.

The relation between a diffusion coefficient and the dye concentration can be investigated carrying calculations based on the Fick's second law of diffusion. Regarding the cylindrical symmetry of the fiber this law may be expressed as follows:

$$\frac{\partial c}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r D(c) \frac{\partial c}{\partial r} \right) \tag{1}$$

Equation (1) is, however, a nonlinear differential equation of a parabolic type and it has no solution in an analytical form. It can be solved using numerical methods only.

In some earlier publications diffusion coefficients $D(c)$ of dyes in fibers were calculated applying the Boltzmann–Matano method.[1,2] This method is based, however, on the solution of Fick's second law for infinite or semi-infinite plane sheets (foils or membranes).[3] Its application to cylindrical systems (fibers) is acceptable only for a short time of dyeing, i.e., when the diffusion is effectively

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confined to the surface layers and the cylinder curvature can be neglected. At longer dyeing times it is in some way erroneous.

The aim of this article is to present the numerical method of computation of the concentration-dependent diffusion coefficient based on the solution of Fick's law for cylindrical system and the experimental concentration profiles. The exponential relation between the diffusion coefficient and the dye concentration has been assumed at the beginning. The $D(c)$ values calculated according to Boltzmann–Matano method and the method proposed in this publication have been compared.

THEORETICAL:

Numerical Solution of Fick's Second Law for Cylindrical Symmetry Using the Grid Method

In the solution of eq. (1) the following initial and boundary conditions were assumed:

$$
\begin{aligned}
C &= 0, \quad 0 < r < a, \quad t = 0 \\
C &= 1, \quad r = a, \qquad t \geq 0, \\
C &= 0, \quad r = 0, \qquad t \geq 0
\end{aligned}
\tag{2}
$$

It has been also assumed that the relation between diffusion coefficient and the dye concentration is of the type

$$
D(C) = D_0 \exp(\delta C) \tag{3}
$$

With relation (3), eq. (1) can be transformed to the form

$$
\frac{\partial C}{\partial t} = D_0 e^{\delta C} \left[\frac{1}{r} \frac{\partial C}{\partial r} + \left(\frac{\partial C}{\partial r} \right)^2 + \frac{\partial^2 C}{\partial r^2} \right] \tag{4}
$$

Partial derivatives appearing in formula (4) can be approximated by the corresponding finite differences as follows[4]:

$$
\frac{\partial C_{i,k}}{\partial t} = \frac{C_{i,k+1} - C_{i,k}}{l} \tag{5}
$$

$$
\frac{\partial C_{i,k}}{\partial r} = \frac{C_{i+1,k} - C_{i,k}}{h} \tag{6}
$$

$$
\frac{\partial^2 C_{i,k}}{\partial r^2} = \frac{C_{i+1,k} - 2C_{i,k} + C_{i-1,k}}{h^2} \tag{7}
$$

where

$$
\begin{aligned}
r &= ih, \quad i = 0,1,2,\ldots,n \\
t &= kl, \quad k = 0,1,2,\ldots,m
\end{aligned}
\tag{8}
$$

With these relations the finite difference approximation of eq. (4) gets the form

$$
C_{i,k+1} = z \left[C_{i,k} \left(\frac{1}{z} + \delta - \frac{1}{i} - 2 \right) + C_{i+1,k} \left(\frac{1}{i} + 1 - 2\delta \right) \right.
$$
$$
\left. + C_{i-1,k} + \delta (C_{i+1,k})^2 (C_{i,k})^{-1} \right] \tag{9}
$$

where

$$z = lh^{-2} D_0 \exp(\delta C_{i,k}) \tag{10}$$

If constants D_0 and δ are known or can be assumed, then starting from the initial row ($k = 0$) of the grid, for which $C_{i,k}$ are determined by the initial conditions

$$\begin{aligned} C(r_i,0) &= 0, \quad i = 0,1,2,\ldots,n-1 \\ C(r_i,0) &= 1, \quad i = n \end{aligned} \tag{11}$$

and using the $C_{i,k}$ values at limiting grid points determined by the boundary conditions

$$C(0,t_k) = 0, \quad C(a,t_k) = 1, \quad k = 0,1,2,\ldots,m \tag{12}$$

it is possible to calculate successively all the crosspoints of the grid. The values of $C_{i,k}$ obtained for the row $k = m$ are the numerical solution of the problem and determine simultaneously the theoretical concentration profile $C(r,t)_{\text{theor}}$.

Values of D_0 and δ for which the theoretical profile is consistent with the experimental one define the looked-for relation between a diffusion coefficient and the concentration of dye in the fiber. This method has been used in this article to calculate the diffusion coefficient of the disperse dye Synthene Scarlet P3GL in the polyester fiber.

EXPERIMENTAL

Characteristics of Fiber and Dye

The investigations of the dye diffusion have been carried out with the anionically modified polyester fiber (supplied by the Institute of Chemical Fibers in Lódź, Poland). The nonannealed fiber and the annealed ones at 388, 393, and 403 K were examined. The fiber containing no delustering agent had a draw ratio of 4.3.

Before dyeing, samples of fibers were purified by washing at 343–353 K with an aqueous solution containing a nonionic detergent Rokaphenol (2 g/dm³) and sodium carbonate (1 g/dm³). To stabilize the fiber structure, the samples were then annealed in a blank dye bath at boiling temperature for 12 hr. Disperse dye Synthene Scarlet P3GL produced by Zachem (Poland) was used for dyeing. According to Color Index this dye corresponds to Disperse Red 54.

Method of Dyeing

The fibers were dyed in water baths of the following compositions:

bath 1:	dye	2 g/dm³
	dispersing agent NNO	3 g/dm³
	(Rokita, Poland)	
bath 2:	dye	2 g/dm³
	dispersing agent NNO	3 g/dm³
	carrier Dilatin OD	2 g/dm³
	(Sandoz, Basel)	

Acetate buffer was added to the dye solution to maintain a constant pH of 5.0. Because of the low solubility of Synthene Scarlet P3GL in water it was used as

a commercial product in stabilized form.   The content of the dye in the product
was determined spectrophotometrically.   The concentration of dye in dye bath
(2 g/dm^3) and the ratio of the volume of the dye liquor to weight of the fiber
(1000:1) secured stability of the bath composition during the dyeing.   After
dyeing, the samples were cooled rapidly and washed with distilled water.   To
remove the dye adhering to the surface the fibers were washed additionally with
acetone at 278 K.

Determination of Concentration Profiles

   The concentration profiles (radial distribution curves) were determined by
scanning the cross sections of the dyed fibers with a microphotometer devised
especially for this purpose.   The cross sections were prepared by cutting polymer
blocks containing bundles of dyed fibers.   The cuttings were placed on micro-
scope slides and the embedding medium was removed by dissolution in acetone.
Then the immersion liquid (α-bromonaphthalene mixed with medicinal paraffin)
with a refractive index close to that of the studied fiber was added.   The cross
sections were photometered at a magnification of 250× using a suitable filter.[5]
The dye distribution curves were recorded automatically in coordinates:
transmitted light intensity versus distance.   To eliminate the instrumental and
optical distortions, the curves were corrected and extrapolated.   The correction
on a slit width was performed according to Navratil.[6]   The optical distortions
were eliminated graphically.   The extrapolation technique was based on the
distribution curve of the uniformly dyed fiber, i.e., that one in which the dye
concentration approached an equilibrium in a total volume.   Figure 1 presents
such a curve.   This curve is drawn in a coordinate system: light absorption (E)
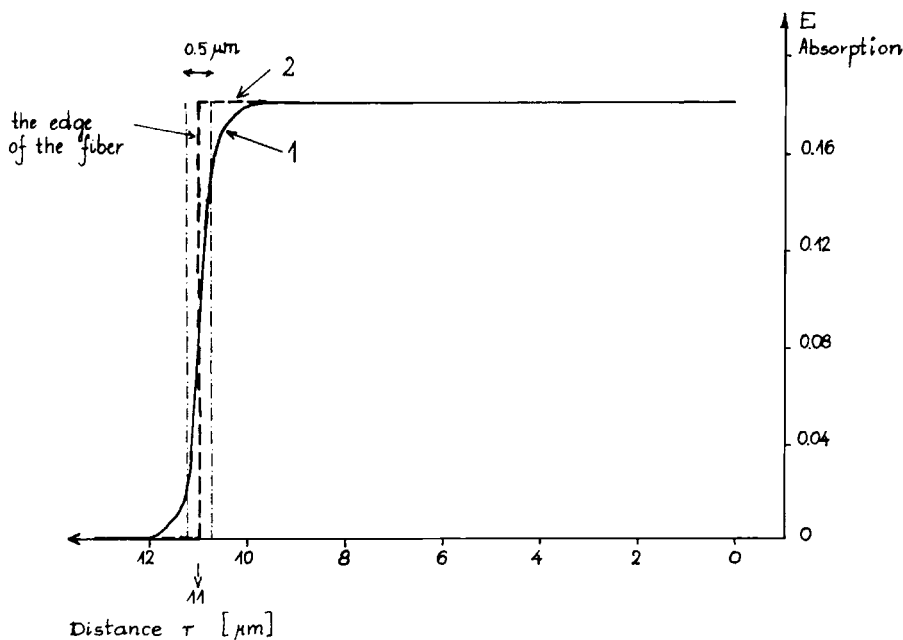

Fig. 1. Distribution curve of Synthene Scarlet P3GL in the uniformly dyed polyester fiber.
(1) Experimental curve, (2) extrapolated curve.   Fiber nonannealed, dyed with a carrier.

versus distance (r), measured from the center of the fiber. Since the diameter of a fiber can be measured with the accuracy ± 0.5 μm, it is possible to determine a position of the geometrical edge of the fiber on this curve and to draw the undistorted profile curve 2, Figure 1. The distribution curves obtained at early stages of dyeing were extrapolated to the fiber edge thus determined. The diameters of all the compared fibers and the thicknesses of the cross sections were the same.

CALCULATIONS AND RESULTS

The distribution curves were measured on different stages of the dyeing process. Figure 2 presents such curves obtained for Synthene Scarlet P3GL in the nonannealed fiber (full lines). The extrapolated curves are marked with the broken lines. After extrapolation, the curves were transformed to the profiles presenting the relative concentration of the dye (C) versus distance (r). Examples of such profiles are presented in Figure 3. The profiles suggest the time dependence of the concentration of the dye on a surface of the fiber. The rate-of-dyeing curves $[c_t/c_\infty = f(t^{1/2})]$ measured for the same fibers confirmed the relation. This problem will be discussed in the next article.[7] The shape of the profiles implies the concentration dependence of the dye diffusion coefficient. It is in agreement with statements of other authors.[8–10] With regard to some arbitrariness in the extrapolation at short times in the following calculations only the curves with surface concentration corresponding to the equilibrium ($c_s = c_\infty$) were exploited (curve 3, Fig. 2). Such profiles and eq. (9) were applied for the calculations of the diffusion coefficients $D(C)$ with the numerical method.
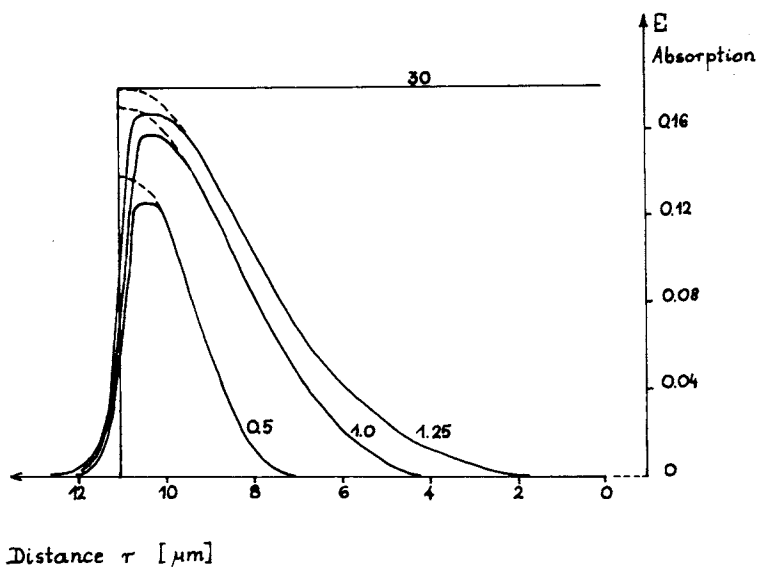

Fig. 2. Distribution curves of Synthene Scarlet P3GL in the nonannealed polyester fiber after different time of dyeing: (—) experimental curve, (—-) extrapolated curve. Fibers dyed with a carrier. The numbers indicate time of dyeing in hr.
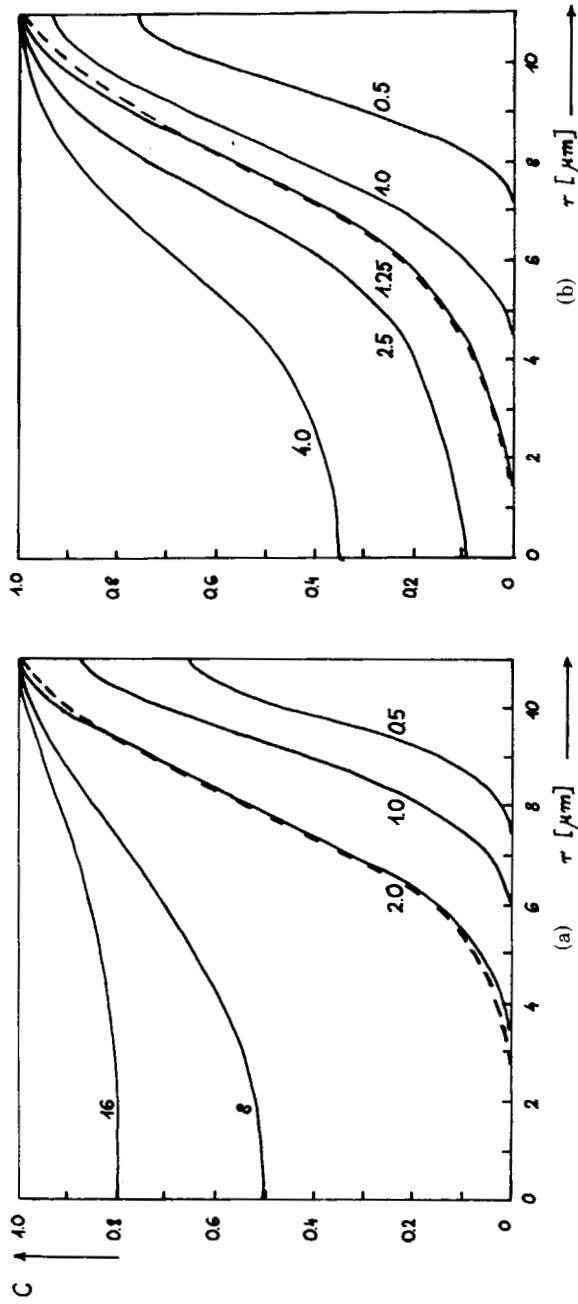
Fig. 3. Concentration profiles of Synthene Scarlet P3GL in the nonannealed polyester fiber, dyed (a) without a carrier and (b) with a carrier, after different times of dyeing: (—) experimental profile, (- - -) numerically calculated profile.

Preliminary Calculations of the Constants D_0 and δ by the Boltzmann–Matano Method

From eq. (9) it is shown that to determine the theoretical profile consistent with the experimental one the constants D_0 and δ should be suitably selected. These constants can be calculated with an appropriate algorithm and a computer of considerably great storage capacity. In this work the preliminary values of the constants have been calculated applying the Boltzmann–Matano method described by Crank[3] et al. In the computations the experimental profiles were exploited. The calculated diffusion coefficients $D(C)$ were plotted in a coordinate system: $\ln D(C) - C$. Extrapolation of the obtained straight line to $C = 0$ defines the diffusion coefficient D_0, whereas the slope of the line defines the exponential constant δ. Both constants found for the dye in fibers dyed with and without a carrier are listed in Table I. Having the preliminary values of the constants the computations of $D(C)$ with the described numerical method have been performed.

Calculation of $D(C)$ Regarding the Cylindrical Symmetry of the Fiber

The numerical computations of the diffusion coefficient $D(C)$ have been performed under the following conditions:

$$
\begin{aligned}
&\text{(i)} \quad \xi = D_0 l h^{-2} \leqslant 0.2 \\
&\text{(ii)} \quad h = 1 \times 10^{-4} \text{ cm}
\end{aligned}
\tag{13}
$$

Preliminary testing proved that condition (i) provides stability to the computations and that the internal spacing h equal to 1×10^{-4} cm [distance axis; condition (ii)] produces deviations of the $C_{i,k}$ points of the last calculation row below the experimental error encountered in the determination of the concentration profiles. It has also been stated that the diffusion coefficient D_0 obtained by the Boltzmann–Matano method corresponds to the one found with the numerical calculations. With this diffusion coefficient and eq. (9) the theoretical profiles were calculated for successively changed δ. The computations were continued until the theoretical and experimental profiles were consistent. The accuracy reached in the determination of the experiment profiles has been accepted as the admissible deviation between the computed and experimental ones. The numerical calculations of the profile of Synthene Scarlet P3GL in the fiber an-

TABLE I
Diffusion Coefficients D_0 and δ Constants Calculated by the Boltzmann–Matano Method and the Numerical Method

Temperature of fiber annealing (K)	Dyeing without a carrier			Dyeing with a carrier		
	Diffusion coefficient D_0 ($\text{cm}^2\text{sec}^{-1} \times 10^{11}$)	Constant δ		Diffusion coefficient D_0 ($\text{cm}^2\text{sec}^{-1} \times 10^{11}$)	Constant δ	
nonannealed fiber	0.36	1.56	1.45[a]	0.83	1.14	1.00[a]
388	0.30	1.60	1.55	0.75	1.23	1.00
393	0.28	1.63	1.40	0.73	1.28	1.10
403	0.23	2.05	1.65	0.60	1.60	1.35

[a] Numerical method.

nealed at 403 K and dyed with the carrier are presented as an example in Table II. They were performed at the following conditions:

$$D_0 = 0.60 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}, \qquad h = 1 \times 10^{-4} \text{ cm}$$
$$\delta = 1.35, \qquad\qquad\qquad\qquad l = 300 \text{ sec} \qquad\qquad (14)$$
$$a = 11 \times 10^{-4} \text{ cm}, \qquad\qquad m = 15$$

The fifteenth row of Table II presents the theoretical profile $C(r,t)$, whereas the sixteenth presents the experimental one. The calculated profile shows some deviations from those experimentally determined in vicinity of the fiber surface. These deviations may result in part from a decrease in precision of calculations caused by the discontinuity of the initial and boundary conditions. In Table I (columns 4 and 7) are listed the δ constants corresponding to the theoretical profiles consistent with experimental ones. The calculated and experimental profiles are presented in Figure 3. Computations were performed on an Odra 1204 digital computer using Algol algorithmic language.

An important problem that should be considered at this point is an elimination from the computational procedure the profiles corresponding to the early stages of dyeing. To some extent it may imply an elimination of the possible time instability of the system. To demonstrate that the observed non-Fickian shape of the profiles is not a consequence of the time dependence of the boundary conditions, additional computations have been performed. For that purpose the diffusion coefficient D, assumed constant, has been calculated exploiting the experimental rate-of-dyeing curve of the fiber and the following equation[3]:

$$\frac{c_t}{c_\infty} = 1 - \frac{2J_1[(\beta a^2/D)^{1/2}]e^{-\beta t}}{(\beta a^2/D)^{1/2}J_0[(\beta a^2/D)^{1/2}]} + \frac{4}{a^2}\sum_{n=1}^{\infty}\frac{e^{-D\alpha_n^2 t}}{\alpha_n^2[\alpha_n^2/(\beta/D)-1]} \qquad (15)$$

The variation in the surface dye concentration described by the formula

$$c_s = c_\infty[1 - \exp(-\beta t)] \qquad (16)$$

has been regarded. Then, knowing the diffusion coefficient D, the theoretical profiles have been calculated with the equation[3]

$$\frac{c_t}{c_\infty} = \frac{J_0(\beta r^2/D)e^{-\beta t}}{J_0(\beta a^2/D)} + \frac{2\beta}{aD}\sum_{n=1}^{\infty}\frac{J_0(r\alpha_n)e^{-D\alpha_n^2 t}}{\alpha_n J_1(a\alpha_n)(\alpha_n^2 - \beta/D)} \qquad (17)$$

They are presented in Figure 4. Such profiles should be observed if diffusion is governed by a constant D and the time-dependent surface concentration. The profiles differ from those experimentally determined (Fig. 3).

DISCUSSION AND CONCLUSIONS

The presented data allow us to draw the following conclusions:

(1) The calculations confirmed that the diffusion coefficient of the disperse dye Synthene Scarlet P3GL in the anionically modified polyester fiber is an exponential function of the dye concentration $D(C) = D_0 \exp(\delta C)$.

(2) The allowance for the cylindrical symmetry of fiber leads to the lower values of $D(C)$ in the total concentration range relative to those obtained by the Boltzmann–Matano method.

(3) The diffusion coefficients D_0 calculated from eq. (9) regarding cylindrical symmetry and that calculated by the Boltzmann–Matano method are coincident.

TABLE II

Numerical Calculations of the Profile of Synthene Scarlet P3GL in the Fiber Annealed at 403 K, Dyed with the Carrier[a]

k							i					
	0	1	2	3	4	5	6	7	8	9	10	11
0	0	0	0	0	0	0	0	0	0	0	0	1.000
1	0	0	0	0	0	0	0	0	0	0	0.441	1.000
2	0	0	0	0	0	0	0	0	0	0.135	0.636	1.000
3	0	0	0	0	0	0	0	0	0.032	0.299	0.670	1.000
4	0	0	0	0	0	0	0.001	0.007	0.101	0.388	0.732	1.000
5	0	0	0	0	0	0	0.001	0.027	0.171	0.465	0.755	1.000
6	0	0	0	0	0	0	0.007	0.058	0.240	0.513	0.785	1.000
7	0	0	0	0	0	0.002	0.017	0.097	0.296	0.560	0.799	1.000
8	0	0	0	0	0	0.005	0.033	0.138	0.348	0.590	0.818	1.000
9	0	0	0	0	0.001	0.010	0.054	0.180	0.389	0.623	0.827	1.000
10	0	0	0	0.001	0.003	0.019	0.078	0.219	0.428	0.643	0.841	1.000
11	0	0	0	0.002	0.006	0.030	0.105	0.257	0.459	0.668	0.847	1.000
12	0	0	0.001	0.004	0.011	0.044	0.132	0.291	0.490	0.683	0.859	1.000
13	0	0	0.001	0.007	0.017	0.060	0.160	0.324	0.514	0.703	0.862	1.000
14	0	0	0.002	0.010	0.025	0.078	0.189	0.352	0.539	0.713	0.872	1.000
15	0	0.001	0.003	0.010	0.034	0.097	0.216	0.380	0.558	0.731	0.874	1.000
16	0	0	0	0.010	0.025	0.090	0.205	0.370	0.530	0.765	0.915	1.000

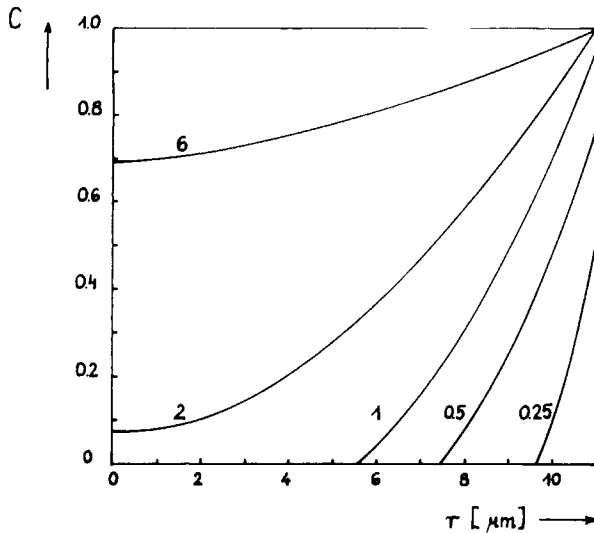[a] Computational conditions: $D_o = 0.60 \times 10^{-11}$ cm²sec⁻¹, $\delta = 1.35$, $t = 4500$ sec, $a = 11 \times 10^{-4}$ cm.

Fig. 4. Theoretical concentration profiles of dye in the fiber calculated from eq. (17): D = const, $c_s = c_\infty$ [1-exp($-\beta t$)]. The numbers indicate time of dyeing in hours. Fiber nonannealed, dyed with a carrier.

To illustrate the difference in $D(C)$ arising from the method of calculations, the data of diffusion coefficient drawn versus relative dye concentration (C), obtained from both methods, are presented in Figure 5.

The data of Table I indicate also that constants D_0 and δ depend on annealing temperature of the fiber and differ for the fibers dyed with a carrier.

The same results have been found by Ruzicka et al.[8] in investigations of dyeing of polyester fibers with C.I. Disperse Red 83. Blacker and Patterson[9] proved that the concentration profiles of C.I. Disperse Red 1, C.I. Disperse Red 15, and C.I. Disperse Yellow 1 in Terylene fibers (dyed without a carrier) are of the non-Fickian shape. In Cometto's[10] opinion, such a shape may suggest that during initial stages of dyeing the dye penetrating into fiber acts as its own carrier.
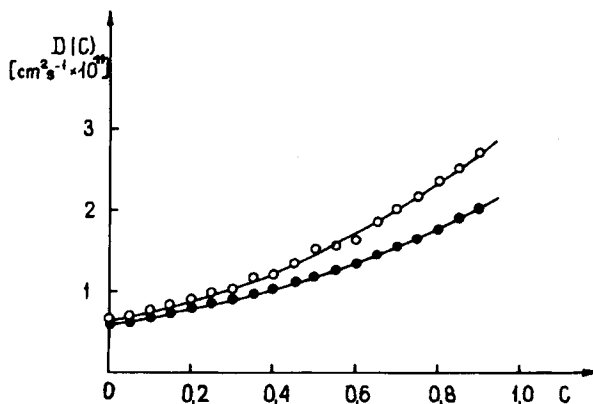

Fig. 5. Concentration dependence of the diffusion coefficient of Synthene Scarlet P3GL in the polyester fiber calculated regarding cylindrical symmetry of fiber (●) and disregarding it (○). Fiber annealed at 403 K and dyed with a carrier.

It loosens the fiber structure and makes diffusion of successive molecules penetrating into polyester easier. Different in some way is the explanation by Iijima.[11] According to him the dependence of the diffusion coefficient on the concentration may be caused by a different accessibility of amorphous regions to the dye molecules. The concentration dependence of the dye diffusion coefficient may also be partially explained if one assumes an interaction between the disperse dyes and polyester. It has been suggested by Athale and Padhye[12] that the disperse dyes are sorbed by the fiber on so-called specific sites, similar to those reacting with a polymer.

NOMENCLATURE

a radius of fiber
r cylindrical coordinate
c concentration of dye at distance r from the center of fiber at time t
C relative concentration of dye at distance r from the center of fiber at time t
c_∞ equilibrium concentration of dye in fiber
$D(c)$ concentration-dependent diffusion coefficient
D_0 diffusion coefficient at zero concentration of dye in fiber
t time of dyeing
δ constant in equation $D(C) = D_0 \exp(\delta C)$
l internal spacing on time axis
h internal spacing on distance axis
n number of internal spacings on distance axis
m number of internal spacings on time axis
c_s surface concentration of dye in fiber, at time t
c_t total concentration of dye in fiber, at time t
β constant in equation $c_s = c_\infty [1 - \exp(-\beta t)]$
D average diffusion coefficient
$J_0(x)$ Bessel function of the first kind of order zero
$J_1(x)$ Bessel function of the first order
α_n positive root of equation $J_0(a\alpha_n) = 0$

References

1. J. P. Bell, W. C. Carter, and D. C. Felty, *Text.Res.J.*, **37**, 512 (1967).
2. H. Morizane, Y. Suda, and F. Nakajima, *Colour.Annu.*, **26**, (1970).
3. J. Crank, *The Mathematics of Diffusion*, Clarendon, Oxford, 1956.
4. B. P. Demidowicz, I. A. Maron, and E. Z. Szuwałowa, *Metody Numeryczne*, Part II, PWN, Warszawa 1965.
5. A. Narębska, G. Lemańska, and B. Ostrowska, *Polimery*, **19**, 374 (1974).
6. J. Navratil, F. Gartner, and B. Milicevic, *Melliand Textilber.*, **55**, 463 (1974).
7. A. Narębska and B. Ostrowska, in preparation.
8. J. Ruzicka, F. Kreici, J. Prsikril, and L. Burgert, Preprints of International Symposium on Man-Made Fibers, Kalinin 1974, Part V, p. 84.
9. J. G. Blacker and D. Patterson, *J.Soc.Dyers Colour.*, **85**, 598 (1969).
10. C. Cometto, M.Sc.thesis, University of Leeds, 1971.
11. T. Iijima and D. J. Chung, *J.Appl.Polym.Sci.*, **17**, 663 (1973).
12. A. M. Athale and M. R. Padhye, *J.Appl.Polym.Sci.*, **20**, 403 (1976).