Diffusion with Simultaneous Immobilization in Polymer–Dye Systems. I. Diffusion of the Cationic Dye Anilana Red BL in the Anionically Modified Polyester Fiber Dilana

BARBARA OSTROWSKA* and ANNA NARĘBSKA,* *Nicholas Copernicus University, Institute of Chemistry, Toruń, Poland,* and HENRYK KRZYSTEK, *Institute of Chemical Fibers, Łódź, Poland*

Synopsis

The diffusion coefficient of the cationic dye Anilana Red BL in the anionically modified polyester fiber Dilana has been calculated regarding a general diffusion-immobilization model. In the model the mobile species are distinguished from the immobilized ones. In computations of Sand's equation and experimentally determined sorption isotherm of the dye in the fiber, the rate-of-dyeing curve and the concentration profiles of the dye in the same fiber were employed. The diffusion coefficient of the mobile species of Anilana Red BL in the fiber is two orders of magnitude higher than the average diffusion coefficient obtained from Hill's equation and the apparent diffusion coefficient calculated by the Boltzmann–Matano method.

INTRODUCTION

Diffusion of ionic dyes in fibers made of polyamides, polyacrylics, and the ionically modified polyesters is accompanied by immobilization of the diffusing species resulting from interactions of dye molecules with the active groups of polymers. The immobilization causes some dye molecules to become partially or completely eliminated from the creation of the diffusion flux.

In a mathematical account of the problem, a partition of the diffusing species into the immobilized and mobile ones required a solution of Fick's second law in its original physical meaning of a material balance.[1-4] For the diffusion in a cylindrical system (fiber), this law is as follows:

$$D_m \left\{ \frac{\partial^2 C_m}{\partial r^2} + \frac{1}{r} \frac{\partial C_m}{\partial_r} \right\} = \frac{\partial C}{\partial t} \tag{1}$$

where $C = C_m + C_{im}$ and D_m denotes diffusion coefficient of the mobile species (assumed constant); C_m, C_{im} stands for concentrations of the mobile and immobilized species within a fiber, respectively; and r, t denotes cylindrical and time coordinates. The left side of eq. (1) represents the difference between fluxes into and out of a volume element in which diffusion occurs, and it is therefore concerned with the concentration of the mobile species (C_m) only. The right side of the equation represents the time-dependent variation of the total concentration (C) of species in that element.

Equation (1) contains one more variable than the classical Fick's law of a pure

* Present address: 87-100 Torun, ul. Gagarina 7, Poland.

diffusion. For this reason its solution is possible when the functional relation $C = f(C_m)$ is known. If the local equilibrium between the mobile and immobilized species is rapidly attained, relative to the overall rate of diffusion, then an immobilization isotherm can provide the required information.[1–5] If not, additional experimental data or assumptions concerning the kinetics of the immobilization process are necessary.

A number of analytical[5–8] and numerical[1,3,4,9,10] solutions of a diffusion accompanied by immobilization, i.e., adsorption or chemical reaction, were presented. This article is one more endeavor to solve this problem with reference to the dyeing process of fibers. The main purpose was to calculate the diffusion coefficient of the mobile species of a cationic dye in the anionically modified polyester fiber Dilana.

THEORETICAL

Diffusion Coefficient of the Mobile Dye Species Within the Fiber

If the diffusion flux J is created by the mobile dye species only, then the following relation exists between an apparent diffusion coefficient $D(C)$, calculated from dye concentration profiles $C = f(r,t)$, and the diffusion coefficient of the mobile dye species D_m[11,12]:

$$D(C) = D_m(\partial C/\partial C_m) \tag{3}$$

With assumptions that (1) an equilibrium between mobile and immobilized dye species is established immediately at each point of the fiber and (2) a Langmuir sorption isotherm is accomplished, eq. (3) may be expressed as follows:

$$D(C) = \frac{D_m}{1 + K_l S(1 - \theta)^2} \tag{4}$$

In the above equation, K_l and S are constants of the sorption isotherm, and θ denotes a fractional saturation of binding groups of the fiber. From eq. (4) it follows that if $\theta = 0$, then

$$D_m = D_0(1 + K_l S) \tag{5}$$

where D_0 is an apparent diffusion coefficient at zero concentration of dye within the fiber.

To allow the possibility that in a complex morphologic fiber structure a part of binding groups may be inaccessible for dye, we introduced a factor α, being the ratio of C_∞ and S, where C_∞ denotes the equilibrium dye concentration attained in a fiber dyed in infinite dye bath and S is the concentration of binding groups in the same fiber. Taking the factor α into consideration, eqs. (4) and (5) acquire the forms

$$D(C) = \frac{D_m}{1 + K_l S \alpha (1 - \alpha \theta)^2} \tag{6}$$

and

$$D_m = D_0(1 + K_l S \alpha) \tag{7}$$

It follows that for computation of the diffusion coefficient of the mobile dye

species within the fiber, the following data are required: (1) partition of dye molecules within the fiber between the mobile and immobilized species, $C_{im} = f(C_m)$; (2) a concentration of binding groups within the fiber accessible for dye molecules (C_∞); and (3) an apparent diffusion coefficient of dye in the fiber (D_0). These data may be determined from the sorption isotherm of dye in the fiber, the rate-of-dyeing curve, and the concentration profiles of dye in the same fiber.

Sorption Isotherm of a Cationic Dye in the Modified Polyester Fiber

If one assumes that in the dyeing process the acidic groups —SO_3^- of the anionically modified polyester fiber exchange counterions K_f^+ for dye cations D_s^+, the reaction may be written in the form[13–15]

$$\text{fiber–}SO_3^-K^+ + D_s^+ \rightleftarrows \text{fiber–}SO_3^-D^+ + K_s^+ \tag{8}$$

An equilibrium constant of this reaction is described by the expression

$$K_K^D = \frac{[D_f][K_s]}{[K_f][D_s]} \tag{9}$$

where $[D_f]$ and $[K_f]$ refer to the concentrations of dye and potassium cations in the fiber, whereas $[D_s]$ and $[K_s]$ refer to those in the external solution. As in a dye bath, hydrogen and sodium ions are present, and the following reactions may also take place:

$$\text{fiber–}SO_3^-H^+ + D_s^+ \rightleftarrows \text{fiber–}SO_3^-D^+ + H_s^+ \tag{10}$$

and

$$\text{fiber–}SO_3^-Na^+ + D_s^+ \rightleftarrows \text{fiber–}SO_3^-D^+ + Na_s^+ \tag{11}$$

with the corresponding constants

$$K_H^D = \frac{[D_f][H_s]}{[H_f][D_s]} \quad \text{and} \quad K_{Na}^D = \frac{[D_f][Na_s]}{[H_f][D_s]} \tag{12, 13}$$

If no other cations are present and an exchange is the only mechanism for dye uptake, then the electrical neutrality condition requires that

$$[D_f] + [K_f] + [Na_f] + [H_f] = S \tag{14}$$

where S is the concentration of acidic groups within the fiber. As the concentration of hydrogen, potassium, and sodium ions can be assumed constant during the dyeing process, the uptake of dye by the fiber can be formally described by the Langmuir isotherm written in the form[14]

$$\frac{[D_f]}{[S - D_f]} = K_l[D_s] \tag{15}$$

where

$$\frac{1}{K_l} = K_D^K[K_s] + K_D^H[H_s] + K_D^{Na}[Na_s] \tag{16}$$

Assuming that the experimentally measured isotherm represents an "intrinsic" sorption, eq. (15) was applied further to determine the relation C_{im} to C_m.

EXPERIMENTAL

Fiber

A copolyester fiber made of poly(ethyleneterephthalate)–monopotassium salt of bis(β-hydroxyethylene)sulfoterephthalate copolymer was used for the experiments. The fiber was formed from the bright copolyester in an extruder spinning machine at a rate of 700 m/min and then drawn in water at 358 K to a draw ratio of 1:4.5 at a rate of 100 m/min.

Samples of the oriented fiber were subjected to heat-setting treatment at temperatures of 388, 393, and 403 K for 15 min. The heat-setting treatment was followed by 12 hr of boiling in a blank dye bath to prevent structural changes of the fiber during subsequent dyeing experiments. To remove finishes, the fibers were extracted with a mixture of methanol and distilled water (3:1) in a Soxhlet apparatus. Additional data on fiber properties and compositions are given in Table I.

Dye

The cationic dye Anilana Red BL (C.I. Basic Red 22) produced by ZPB "Boruta" (Poland) was employed for dyeing. Its chemical structure is as follows:
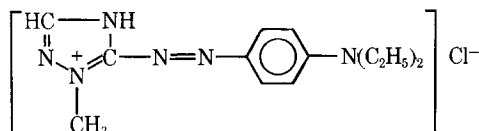
The dye was purified by successive recrystallization from aqueous ethanol until the extinction coefficient was constant. The purity of the dye was controlled additionally by elemental analysis.

Dyeing of Fibers

Fibers (0.5 g) were dyed at boiling in the water dye bath (0.5 liter) containing 2.5×10^{-3} mol/l. Anilana Red BL. To prevent hydrolysis of the copolyester, the buffer (0.010 mole/l. acetic acid, 0.035 mole/l. sodium acetate) and a neutral electrolyte (0.070 mole/l. potassium sulfate) were added to the dyebath. The concentration of the dye secured the stability of the bath composition. After dyeing the fiber samples were removed, immersed in cold water to prevent further diffusion, and then rinsed in acetone at 278 K.

TABLE I
Properties of Copolyester Fiber

Trade name	Linear density, dtex	Tenacity, cN/tex	Elongation, %	—SO$_3$K eq/kg	—COOH eq/kg
Dilana	3.3	31.5	49.6	0.094[a]	0.063[a]

[a] Determined by titration of the dissolved fiber.

Dye Concentration Profiles

The concentration profiles of the dye in the fiber were measured with a microphotometer devised specially for this purpose. The main part of the instrument was a microscope. A synchronous drive was fitted to its stage. During the photometration the cross section was scanned with a narrow slit of known dimensions, using a suitable filter. Intensity of the transmitted light was recorded automatically as a function of distance.

The cross sections were prepared by cutting polymer blocks containing bundles of dyed fibers strictly perpendicularly to the fiber axis.[17] The cross sections were placed on the microscope slides, and the embedding medium was removed by dissolution. Then the liquid (α-bromonaphthalene mixed with medicinal paraffin) of a refractive index close to that of the fiber was added to prevent Becke line effects.

The dye distribution curves obtained by the photometration were corrected for instrumental and optical distortions. The correction for the slit width was performed according to Navratil.[18] The optical distortions were eliminated graphically.[19] The extrapolation technique was based on the distribution curve of the uniformly dyed fiber, i.e., that in which the dye concentration approached the equilibrium value in a total volume of the fiber. The corrected dye distribution curves were then transformed to the profiles presenting the relation of the relative dye concentration to distance. Having thus obtained the profiles, the diffusion coefficient D_0 was calculated by the Boltzmann–Matano method.[5]

Sorption Isotherm

The sorption isotherm of Anilana Red BL was determined using a polymer powder dispersed in the dye bath. This technique makes possible to shorten the time necessary for attainment of the equilibrium dye concentrations in the polymer. To get the powder, the fiber was dissolved at 333 K in freshly distilled m-cresol. The solution was then cooled and the copolyester precipitated with acetone. The sediment was filtered, dried over phosphorus pentoxide, and then milled in a ball mill. The 0.5-g samples of the powder were dyed for 36 hr in 0.5 liter aqueous solution of the dye. The pH of the solution was adjusted to 4.2 with acetate buffer (acetic acid 0.010 mole/l., sodium acetate 0.035 mole/l.) and potassium sulfate (0.070 mole/l.). The dye concentration in the bath ranged from 4.0×10^{-5} to 6.0×10^{-3} mole/l. After dyeing, the powder was filtered, rinsed with cold water, and dried. The amount of the dye sorbed in the polymer was determined colorimetrically.

RESULTS AND DISCUSSION

Sorption Isotherm of Anilana Red BL in the Modified Polyester

The sorption isotherms of Anilana Red BL drawn in coordinates C_p vs. C_s and C_p/C_s vs. C_s are shown in Figures 1(a) and 1(b). As seen from Figure 1(b), the experimental data deviate from linearity predicted by eq. (17), being the transformed Langmuir isotherm:
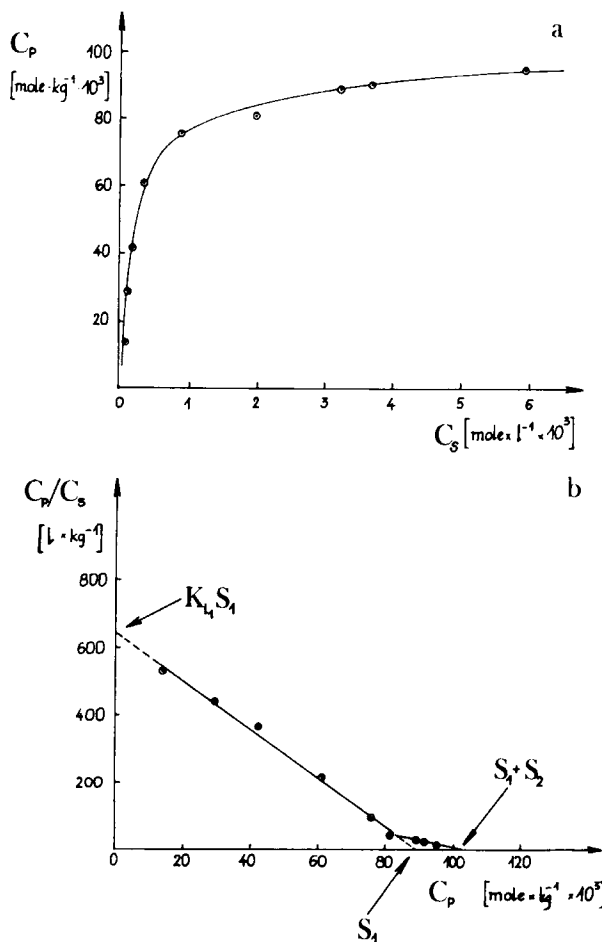
$$C_p/C_s = K_l S - K_l C_p \qquad (17)$$

Fig. 1. Sorption isotherm of Anilana Red BL on modified polyester: (a) experimental sorption isotherm; (b) Langmuir plot of the experimental sorption isotherm. Polymer powder dyed at 373 K in dye baths of pH 4.2.

Harwood et al.[15] attributed a "tail" on an isotherm either to binding of the dye by two kinds of ionic groups present in a fiber or to a solution of dye, in accordance with the Nernst partition law. Regarding the experimental data of Figure 1, it is difficult to decide about the origin of the tail as both mechanisms are possible. In the modified polyester, two kinds of acidic groups—sulfonic and carbox-ylic—are present, and a participation of the carboxylic groups in binding of the cationic dye cannot be rejected. According to some authors,[20] these groups react above pH 6.0, however, Rossbach[21] proved that in the modified polyester the dye may be bound at pH 4.5 already. One also cannot exclude a Nernst-type partition of part of Anilana Red BL between the bath and the polymer. Addi-tional investigations are necessary to decide which factor is responsible. For that reason, in the following discussion the deviation from the Langmuir isotherm has been partially neglected.

The main rectilinear part of the isotherm [Fig. 1(b)] may be expressed by the equation

$$C_p/C_s = K_{l_1} - K_{l_1}C_p \qquad (18)$$

TABLE II
Constants of Experimental Sorption Isotherm

S_1, mole/kg	S_2, mole/kg	K_{l_1}, l./mole
0.088	0.014	7310

The points of intersection of the straight line with the axes give the saturation value S_1 and the equilibrium constant K_{l_1}. Extrapolation of the second part of the isotherm to the abscissa determines the total concentration of immobilization sites in the polymer $(S_1 + S_2)$. The numerical values of S_1, S_2, and K_{l_1} are summarized in Table II. The table lists the contents (mole/kg) of sulfonic and carboxylic groups in the polymer, determined by titration methods according to Stain[22] and Skwarski,[23] respectively. The determined constant K_{l_1} is slightly higher than that which should be obtained taking into account the whole isotherm.

Diffusion Coefficient D_0 and Factor α

The diffusion coefficient D_0 was determined by extrapolation to zero the $D(c)$ curve presenting the dependence of the apparent diffusion coefficient on the total concentration of dye in the fiber. Typical examples of the concentration–distance profiles are seen in Figure 2. The results of calculations of $D(c)$ for Anilana Red BL in the nonannealed fiber are presented in Figure 3. The diffusion coefficient D_0 for all the investigated fibers are summarized in Table III.

As was mentioned earlier, the complex structure of crystalline and oriented fibers is the reason that some of the active groups may be inaccessible to dye. In such a case, the factor α calculated as the ratio of the equilibrium dye concentration (C_∞), determined from the rate-of-dyeing curve, and the concentration of active groups in a polymer (S), determined from the sorption isotherm, differs from unity. The numerical values of the ratio are summarized in Table III (column 3).
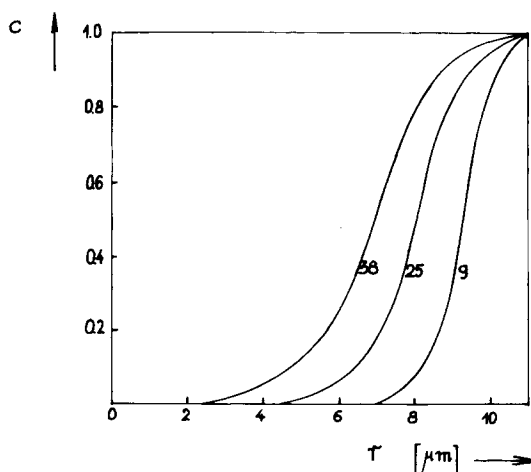

Fig. 2. Concentration profiles of Anilana Red BL in the fiber at various stages of the dyeing process. (Nonannealed fiber dyed at 373 K. Numbers on curves represent the dyeing times in hr.)
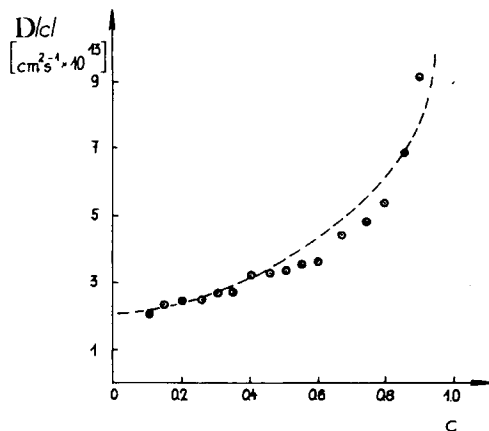
Fig. 3. Dependence of apparent diffusion coefficient of Anilana Red BL on its relative concentration in the fiber, calculated by the Boltzmann–Matano method (⊙) and by Sand's equation (- - -). (Nonannealed fiber dyed at 373 K.)

Diffusion Coefficient of the Mobile Dye Species D_m

To calculate the diffusion coefficient of the mobile species of Anilana Red BL in the fiber eq. (7) and the data summarized in Table II were employed. It has been stated that the diffusion coefficient D_m is of the order 10^{-11} cm^2/sec and varies with temperature of fiber stabilization from 6.4×10^{-11} to 10.8×10^{-11} cm^2/sec. It appears then that the diffusion coefficient of the mobile dye species (D_m) is two orders of magnitude higher than the apparent diffusion coefficient calculated with the Boltzmann–Matano method and the average diffusion coefficient ($\overline{D}$) resulting from Hill's equation; they both are of the order of 10^{13} cm^2/sec (Table III, columns 2 and 5).

To verify the applicability of the assumed model of hindered idffusion to interpretation of the dyeing process of the modified polyester fiber, the theoretical diffusion coefficients calculated with Sand's equation were compared to experimental ones. In the computations of the theoretically predicted relation $D(c) = f(c)$, eq. (6) was used. The same relationship based on the experimental data was obtained with the Boltzmann–Matano method. The results are presented in Figure 3. It is seen that in the range of relative concentrations up to 0.5 the agreement of the experimental data with those predicted theoretically is satisfactory. At higher concentrations some deviations are observed. They are caused presumably by neglecting in the computations the "tail" on the measured isotherm.

TABLE III
Diffusion Coefficients D_0, D_m, and $\overline{D}$ and Factor α of Anilana Red BL in Modified Polyester Fiber

Temperature of annealing, K	D_0, (cm^2/sec) $\times 10^{13}$	α[a]	D_m, (cm^2/sec) $\times 10^{11}$	$\overline{D}$, (cm^2/sec) $\times 10^{13}$
nonannealed	2.0	0.55	6.4	3.4
388	2.2	0.63	9.0	3.5
392	2.4	0.57	8.9	3.8
403	2.7	0.62	10.8	4.2

[a] $\alpha = C_\infty/S_1$.

CONCLUSIONS

The diffusion coefficient of the mobile species (D_m) of the cationic dye Anilana Red BL in the anionically modified polyester fiber is of the order of 10^{11} cm^2/sec, i.e., two orders of magnitude higher than the average $(\overline{D})$ and apparent diffusion coefficients $[D(c)]$. The equilibrium uptake of the dye in the modified polyester follows the Langmuir sorption isotherm in the concentration range up to ~85% of saturation. In that range the dye molecules are sorbed by the ion-exchange mechanism. A small fraction of the dye, ~15%, is taken up by other mechanism, presumably by dissolution. The physical structure of the crystalline and oriented fiber restricts considerably the accessibility of acid groups for dye molecules. At a temperature of 373 K, only about 50% of $-SO_3^-$ groups present in the examined fiber exchange their counterions for the cations of Anilana Red BL.

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