

Diffusion of Dyes in Adsorptive Dyeing

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Synopsis

The concentration dependence derived from both steady-state permeation and unsteady-state dyeing runs for a system of acid dye C. I. Acid Blue 182–nylon 6 film was analyzed in terms of parallel diffusion with simultaneous multimodal adsorption proposed in the previous paper. The present dyeing process was governed by the surface diffusion incorporating three kinds of Langmuirean adsorption modes. The concentration dependence of the diffusion coefficient of the cationic dye C. I. Basic Red 22 in the anionically modified polyester fiber Dilana measured by Ostrowska et al. [B. Ostrowska, A. Narebska, and H. Krzystek, *J. Appl. Polym. Sci.*, **26**, 463 (1981)] was satisfactorily interpreted by the parallel diffusion incorporating two kinds of Langmuirean adsorption modes.

INTRODUCTION

More than a few studies have been done on the diffusion of acid dyes in nylon. It has been well known that the diffusion coefficients of the dyes in the nylon substrate strongly depend upon the concentration of the dyes in the substrate. In most cases, the diffusion coefficient of the dyes has been derived from the concentration profiles in the polymer film or filament, but little mention has been made of the mechanism of intrapolymer diffusion and the significance of the derived diffusion coefficient. The dependence of the intrapolymer diffusion coefficient on the dye concentration can be simply interpreted as either diffusion in the pores with simultaneous adsorption or diffusion along the pores (i.e., surface diffusion). It was pointed out in the previous paper¹ that the parallel transport comprising pore and surface diffusions with simultaneous multimodal adsorption should be incorporated to follow the variation of the diffusion coefficient over a wide range of fractional uptake. Existing experimental results on the concentration dependence of the diffusion coefficient for various acid dye–nylon systems, which were measured by different techniques, could be rationally interpreted via the parallel transport comprising pore and surface diffusions with simultaneous bimodal Langmuir adsorption.¹ The concentration dependence of the diffusion coefficient appearing in the previous work was measured only by a single method, so that it did not always cover the whole range of uptake. Particularly, there seems to be no experimental investigation on the concentration dependence of the diffusion coefficient near the full uptake.

In the present work, the concentration dependence derived from both steady-state permeation and unsteady-state dyeing runs for a system of acid dye–nylon film² was analyzed in terms of parallel diffusion with simultaneous multimodal adsorption proposed in the previous paper.¹ It was found that the present dyeing process was governed by the surface diffusion incorporating three kinds of Langmuirean adsorption modes.

Recently, Ostrowska et al.³ measured the diffusion profiles of the cationic dye C. I. Basic Red 22 in the anionically modified polyester fiber Dilana with a microspectrophotometer and determined the diffusion coefficients of the dye in the fiber. The experimentally derived concentration dependence of the diffusion coefficient was satisfactorily interpreted by the parallel diffusion incorporating two kinds of Langmuirean adsorption modes.

THEORETICAL BACKGROUND

The theoretical background which can be applicable to analysis of experimental results on permeation of acid dyes in the nylon film will be described in the following.

The flux of diffusion of the acid dye in the nylon film can be expressed as

$$J = -D_C(C) \frac{dC}{dx} \quad (1)$$

provided the process of permeation of the dye in the film follows Fick's diffusion law. After integrating eq. (1) over C from C_l to C_h with J constant under the steady-state, one gets

$$Jd = \int_{C_l}^{C_h} D_C(C) dC = \bar{D}_C(C_h - C_l) \quad (2)$$

where \bar{D}_C denotes the integral diffusion coefficient defined by

$$\bar{D}_C = \frac{1}{C_h - C_l} \int_{C_l}^{C_h} D_C(C) dC \quad (3)$$

It is assumed that the process of permeation of acid dyes in the nylon film is governed by parallel transport comprising pore and surface diffusions with bimodal adsorption of Langmuir and Nernst types, so that the diffusion coefficient in the film can be given by⁴

$$D_C = D_p + K_N D_N^0 + \frac{K_L S D_L^0}{1 + K_L C} \quad (4)$$

In the limit when C approaches zero, eq. (4) reduces to

$$D_C = D_p + K_N D_N^0 + K_L S D_L^0 \quad (5)$$

After substituting eq. (4) into eq. (3) and integrating the resultant equation over C from C_l to C_h , one gets

$$\bar{D}_C = D_p + K_N D_N^0 + \frac{D_L^0 S}{C_h - C_l} \ln \frac{1 + K_L C_h}{1 + K_L C_l} \quad (6)$$

When C_h is much greater than C_l and C_l is nearly equal to zero, eq. (6) reduces to

$$\bar{D}_C = D_p + K_N D_N^0 + \frac{D_L^0 S}{C_h} \ln(1 + K_L C_h) \quad (7)$$

which predicts a linear relationship between \bar{D}_C and $\ln(1 + K_L C_h)$.

When the driving force for diffusion is based on a gradient of the concentration of dye in the adsorbed phase, the diffusive flux can be written by

$$J = -D_q \frac{\partial q}{\partial x} \quad (8)$$

The diffusion coefficient D_q appearing in this equation can be expressed by

$$D_q = \frac{D_p + K_N D_N^0 + K_L S(1 - \theta) D_L^0}{K_N + K_L S(1 - \theta)^2} \quad (9)$$

in terms of the parallel diffusion mentioned above. Here, θ denotes the coverage of Langmuirean adsorption sites and given by

$$\theta = K_L C / (1 + K_L C) \quad (10)$$

There exists an obvious relationship between D_C and D_q as

$$D_C = \frac{\partial q}{\partial C} D_q \quad (11)$$

EXPERIMENTAL—DIFFUSION OF ACID DYE IN NYLON FILM

The acid dye used was Sandolan Blue E-HRL (C. I. Acid Blue 182, molecular weight = 0.589 kg/mol, basicity = 1), which was purified by successive recrystallization from ethanol proposed by Robinson and Mills.⁵ The nylon 6 film was used as nylon substrate. The nylon film kindly supplied by Unichika Co., Ltd., Japan, was biaxially drawn of 41 μm (density = 1.14 g/cm³). The permeation cell with two identical compartments was employed for the steady state diffusion experiments. The permeation area was 17.3 cm², and each compartment of the permeation cell had ca. 1000 cm³ in volume. The unsteady state dyeing experiments were followed by the film roll method developed by Sekido and Matsui.⁶ The volume of dyeing liquor was about 1000 cm³ to guarantee that the concentration of dyeing liquor can be regarded as being constant during the run.

The dyeing temperature was maintained at 353 K and pH of the dyeing liquor was adjusted at 2.1 by adding concentrated H₂SO₄. The concentration of the dye in the permeated solution for the permeation runs was determined by UV spectrophotometry at 594 nm. The concentration of dye adsorbed on the nylon film from the film roll runs was determined by UV spectrophotometry at 494 nm after dissolving the dyed nylon film in formic acid.

RESULTS AND DISCUSSION

Adsorption Isotherm

The concentration of dye inside the nylon, which can be determined experimentally, comprises the concentration of dye in the pores and the adsorbed phase. When the adsorption equilibrium is established, the amount of dye in the pores is negligibly little compared to that of adsorbed dye (less than 0.4% judging from the observed adsorption equilibria in Fig. 1). Thus, the total uptake of dye at the adsorption equilibrium can be regarded as the total amount of adsorbed dye.

The adsorption equilibria were shown in Figure 1. The adsorption isotherm can be expressed by the sum of (i) normal Langmuir-type adsorption, (ii) irre-

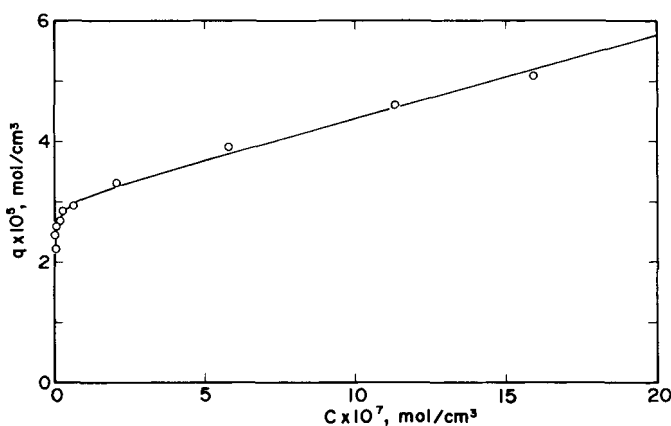


Fig. 1. Adsorption isotherm of C.I. Acid Blue 182 on nylon 6.

versible adsorption, and (iii) Nernst-type adsorption, i.e.,

$$q = \sum_{i=1}^3 \frac{K_{L_i} S_i C}{1 + K_{L_i} C} \quad (12)$$

$$= \frac{K_{L_1} S_1 C}{1 + K_{L_1} C} + S_2 + K_N C \quad (13)$$

The above isotherm is equivalent to the trimodal Langmuir adsorption equation in the limit when $K_{L_2} C \gg 1$ and $K_{L_3} C \ll 1$. The solid curve in Figure 1 represents the calculated relationship by eq. (13) with the parameters set equal to $K_N = 13.8$, $K_{L_1} = 1.48 \times 10^8 \text{ cm}^3/\text{mol}$, $S_1 = 1.1 \times 10^{-5} \text{ mol}/\text{cm}^3$, and $S_2 = 1.9 \times 10^{-5} \text{ mol}/\text{cm}^3$, and agrees with all the experimental data to within 6% of error.

Diffusion Mechanism

The values of the integral diffusion coefficient derived from the steady-state permeation runs were plotted against $\ln(1 + K_{L_1} C_h)/C_h$ on the basis of eq. (7) as shown in Figure 2. It was assumed here that the dyestuff adsorbed on the sites 2 were completely immobilized (i.e., $D_{L_2}^0 = 0$) since these sites might be regarded as being almost saturated. The plots in Figure 2 give an essentially straight line. The slope of the straight line yields $D_{L_1}^0$ as $9.32 \times 10^{-10} \text{ cm}^2/\text{s}$. The intercept of the line gives $D_N^0 = 6.52 \times 10^{-10} \text{ cm}^2/\text{s}$ when the process of intrapolymer diffusion is completely governed by the surface diffusion. There seems no contribution of pore diffusion because the derived value of $D_{L_1}^0$ is comparable to that of D_N .

The values of diffusion coefficient in the nylon film were calculated from observed concentration profiles in the film roll by Matano's method.⁷ The concentration of dye inside the film comprises the concentrations of dye in the pores and the adsorbed phase, where the adsorption equilibrium prevails at any point of the pore wall. But, the amount of dye in the pores is very little as compared to that in the adsorbed phase as stated in the previous section (<0.4%). Thus, the diffusion coefficient determined by that method means D_q , which is defined

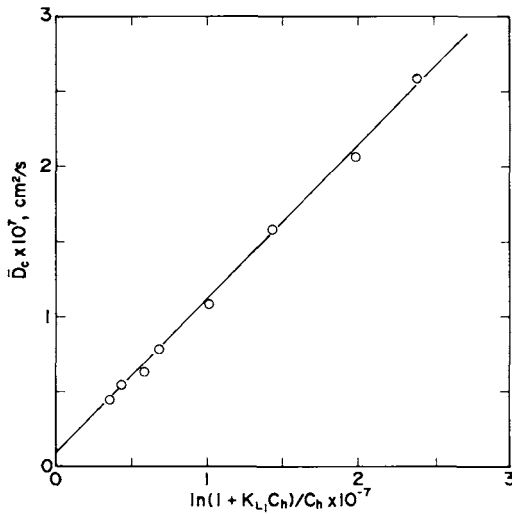


Fig. 2. Integral diffusion coefficients of C.I. Acid Blue 182 in the nylon 6 film.

by eq. (8). The squares in Figure 3 represent the values of D_q as a function of the dye concentration C , which can be easily converted from q by using the adsorption isotherm equation. The circles represent the values of D_q which are converted from \bar{D}_C derived from the steady state permeation runs as follows: The integral diffusion coefficient \bar{D}_C is converted to D_C by

$$D_C = \bar{D}_C + C \frac{d\bar{D}_C}{dC} \tag{14}$$

and the resultant diffusion coefficient D_C is further converted to D_q by eq. (11). Here, from the adsorption isotherm of eq. (12)

$$\begin{aligned} \frac{\partial q}{\partial C} &= K_N + \frac{K_{L_1} S_1}{(1 + K_{L_1} C)} + \frac{K_{L_2} S_2}{(1 + K_{L_2} C)} \\ &= K_N + K_{L_1} S_1 (1 - \theta_1)^2 + K_{L_2} S_2 (1 - \theta_2)^2 \end{aligned} \tag{15}$$

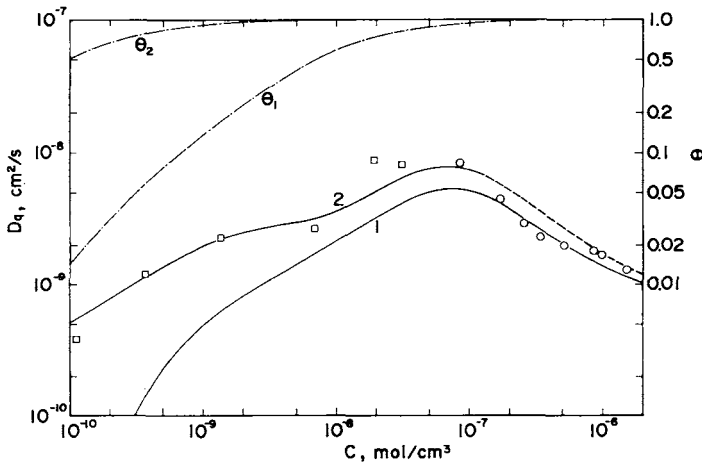


Fig. 3. Dependence of apparent diffusion coefficient of C.I. Acid Blue 182 on its concentration in the dyebath: (O) permeation cell; (□) film roll.

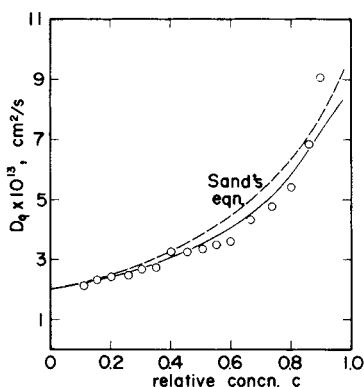


Fig. 4. Dependence of apparent diffusion coefficient of C.I. Basic Red 22 on its relative concentration in the modified polyester fiber.

was employed for $\partial q/\partial C$ in eq. (11). K_{L2} was approximated by a value greater than 2 orders of magnitude than the value of K_{L1} ($= 1.48 \times 10^8 \text{ cm}^3/\text{mol}$) and was replaced with $10^{10} \text{ cm}^3/\text{mol}$.

Let eq. (9) be extended to the case where two kinds of Langmuirean adsorption modes prevail:

$$D_q = \frac{D_p + K_N D_N^0 + K_{L1} S_1 (1 - \theta_1) D_{L1}^0 + K_{L2} S_2 (1 - \theta_2) D_{L2}^0}{K_N + K_{L1} S_1 (1 - \theta_1)^2 + K_{L2} S_2 (1 - \theta_2)^2} \quad (16)$$

The curve 1 in Figure 3 represents the theoretical line calculated by eq. (16) with the diffusion parameter derived from the steady-state permeation runs and $D_{L2}^0 = 0$. The calculated values of D_q were much greater than the observed values in low concentrations of dye. This is because the assumption that the adsorption site 2 is essentially saturated and the dyestuff adsorbed on the site is immobilized does not hold in small C . The chain lines represent the calculated relationships between fraction adsorption (θ_1 and θ_2) and dye concentration C . The surface diffusion of the dyestuff adsorbed on the site 2 should be taken into account in small C . The curve 2 is the theoretical relation calculated by eq. (16) with D_{L2}^0 equal to $2.50 \times 10^{-10} \text{ cm}^2/\text{s}$. The theoretical curve is close to the observed values in the film roll method and in the permeation method for small C . The broken part of the curve 2 is the calculated relation on the concept that the dye adsorbed upon sites 2 can migrate even when θ_2 exceeds 0.999. In such extremely high fractional adsorption, the dyestuffs adsorbed on the sites 2 are immobilized and, accordingly, the curve 2 may gradually move onto the curve 1.

Diffusion Coefficients of C. I. Basic Red 22 in the Anionically Modified Polyester Fiber

Recently, Ostrowska et al.³ measured the diffusion profiles of the cationic dye C.I. Basic Red 22 in the anionically modified polyester fiber Dilana with a microspectrophotometer and determined the diffusion coefficients of the dye in the fiber by analyzing the dye concentration profiles. In their paper,³ diffusion of the cationic dye in fibers made of the anionically modified polyesters (but not normal polyesters) was treated as being accompanied by immobilization of the

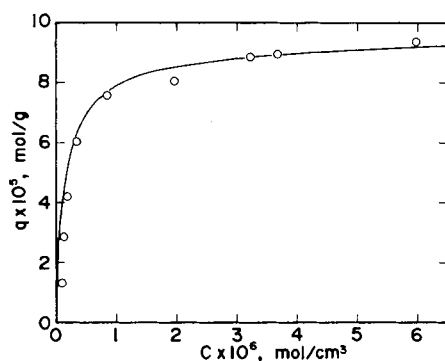


Fig. 5. Adsorption isotherm of C.I. Basic Red 22 on modified polyester.

diffusion species resulting from interaction of dye molecules with active groups of polymers, just as diffusion of ionic dyes in fibers made of polyamides and polyacrylics. Then, the experimentally derived concentration dependence of the diffusion coefficient in Figure 4 was satisfactorily interpreted by Sand's equation⁸:

$$D_q = \frac{(1 + K_{L_1}S_1)D_0}{1 + K_{L_1}S_1(1 - \alpha c)^2} \quad (17)$$

which was developed by the pore diffusion concept. Here α denotes the ratio of q_∞ to S , where q_∞ is the equilibrium dye concentration attained in a fiber dyed in infinite dye bath and $S (= S_1 + S_2)$ the concentration of binding groups in the same fiber, and is approximated by 0.55. c denotes the relative concentration defined by $q/\alpha(S_1 + S_2)$.

In what follows, the concentration dependence will be interpreted by parallel diffusion incorporating two kinds of Langmuirean adsorption modes based on measured equilibrium adsorption data. Figure 5 shows the adsorption isotherm, which can be described by

$$q = q_1 + q_2 = \frac{K_{L_1}S_1C}{1 + K_{L_1}C} + \frac{K_{L_2}S_2C}{1 + K_{L_2}C} \quad (18)$$

The solid curve represents the theoretical relationship by eq. (18) with the adsorption parameters set as follows: $K_{L_1} = 7310 \text{ dm}^3/\text{mol}$, $K_{L_2} = 173 \text{ dm}^3/\text{mol}$, $S_1 = 0.088 \text{ mol/kg}$, and $S_2 = 0.0112 \text{ mol/kg}$.

The diffusion coefficient D_q in the parallel diffusion with simultaneous bimodal Langmuir adsorption can be given by¹

$$D_q = \frac{D_p + K_{L_1}S_1(1 - \theta_1)D_{L_1}^0 + K_{L_2}S_2(1 - \theta_2)D_{L_2}^0}{K_{L_1}S_1(1 - \theta_1)^2 + K_{L_2}S_2(1 - \theta_2)^2} \quad (19)$$

In the limit when $\theta_1 \rightarrow 0$ and $\theta_2 \rightarrow 0$ (i.e., $c \rightarrow 0$), eq. (19) reduces to

$$D_q|_{q=0} = \frac{D_p + K_{L_1}S_1D_{L_1}^0 + K_{L_2}S_2D_{L_2}^0}{K_{L_1}S_1 + K_{L_2}S_2} \quad (20)$$

From Ostrowska et al.'s observation that $D_p = 6.4 \times 10^{-11} \text{ cm}^2/\text{s}$ and $D_q|_{q=0} = 2.0 \times 10^{-13} \text{ cm}^2/\text{s}$ and the assumption that $D_{L_1}^0 = D_{L_2}^0$, the value of $D_{L_1}^0 (= D_{L_2}^0)$ is derived to be $1.0 \times 10^{-13} \text{ cm}^2/\text{s}$. Table I shows the values of D_q calculated by

TABLE I
Estimated Diffusion Coefficients of C.I. Basic Red 22 in Modified Polyester

Relative concn c	$\theta (= \alpha c)$	θ_1	θ_2	$D_q \times 10^{13}$ (cm^2/s)
0.1	0.055	0.06	0.0019	2.19
0.2	0.110	0.119	0.0033	2.42
0.3	0.165	0.182	0.0052	2.71
0.4	0.220	0.243	0.0078	3.06
0.5	0.275	0.309	0.0106	3.53
0.6	0.330	0.371	0.0139	4.10
0.7	0.385	0.434	0.0180	4.86
0.8	0.440	0.493	0.0228	5.82
0.9	0.495	0.554	0.0291	7.30
0.95	0.523	0.583	0.0328	8.05

eq. (19) and fractional adsorption (θ_1 and θ_2) with the adsorption and diffusion parameters estimated above. Here, the values of K_{L_1} and S_1 were taken from the findings of Ostrowska et al. The values of K_{L_2} and S_2 were determined by the plots of $1/(q - q_2)$ against $1/C$. The concentration dependence of the diffusion coefficient is indicated by the solid curve in Figure 4, which is closer to experimental data than the broken curve (Sand's equation⁸).

CONCLUSION

The concentration dependence of the diffusion coefficients of the acid dye (C. I. Acid Blue 182) in the nylon 6 film and the cationic dye (C. I. Basic Red 22) in the anionically modified polyester fiber Dilana was analyzed in terms of the parallel diffusion with simultaneous multimodal adsorption. The former system was governed by the surface diffusion incorporating three kinds of Langmuirean adsorption modes, whereas the latter system was governed by the parallel transport of pore and surface diffusions incorporating two kinds of Langmuirean adsorption modes.

APPENDIX: NOMENCLATURE

c	relative concentration of dye appearing in eq. (17)
C	concentration of dye in pore
C_h	concentration of dye on high concentration side of film
C_l	concentration of dye on low concentration side of film
d	thickness of film
D_C	diffusion coefficient of dye defined by eq. (1)
\bar{D}_C	integral diffusion coefficient of dye defined by eq. (3)
D_p	pore diffusion coefficient of dye
D_q	diffusion coefficient of dye defined by eq. (11)
D_L^0	surface diffusion coefficient of dye adsorbed on Langmuir site at the initial stage of adsorption (i.e., $\theta \rightarrow 0$)
D_N^0	surface diffusion coefficient of dye adsorbed on Nernst site
J	diffusive flux
K_L	Langmuir-type adsorption constant
K_N	Nernst-type adsorption constant
q	concentration of adsorbed dye
S	saturated concentration of adsorbed dye
x	distance coordinate

- α fraction of sites accessible to adsorption appearing in eq. (15)
 θ fractional site saturation
 i subscript, refers to adsorption site i

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