

Kinetic Aspects of Dyeing Processes

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Synopsis

The dyeing of textiles was classified into two main categories: reactive and adsorptive dyeing. A mathematical model for each case was developed on the basis of a pore model concept. The validity of the proposed models was confirmed by comparison with existing experimental data on dyeing of reactive dyes in cellulose and acid dyes in nylon. It was further desired that the proposed models be checked by experimental results in high fixation regimes. The overdyeing phenomenon may be simulated by intrafiber diffusion with simultaneous multimodal adsorption.

INTRODUCTION

The dyeing of textiles is a process in which the dye molecule diffuses into the interior of the textile polymer and then combines with the polymer substrate either physically or chemically. In general, it is required that the textile materials be uniformly dyed in a desired tone of color throughout the fiber because the value is recognized only after the dyestuff has been immobilized in the fiber phase. To obtain a criterion for the level of dyeing, it is necessary to clarify the interplay between intrafiber diffusion of the dye and chemical reaction of the dye with the textile substrate. At present, in order to obtain information on the diffusion of dyes in polymer textile materials, the diffusion coefficients of the dye within polymer films and filaments have been determined from the dye-concentration profiles within polymers measured by means of film roll, microdensitometric, and microspectrophotometric methods.

In these experiments, however, only the initial periods of dyeing are covered and the intrapolymer diffusion coefficients are determined. Little work has been done on whether the diffusion coefficients experimentally obtained are applicable to the dye-immobilization process in high fixation regimes or on modeling the dyeing process by the common transfer theories.

Consider a hydrophilic textile fiber. When a dyestuff diffuses into a fiber phase, there are two main categories from the standpoint of dyeing kinetics. Category 1: Diffusion in the pore accompanied by a chemical reaction (reactive dyeing). Category 2: Diffusion in the pore accompanied by adsorption (adsorptive dyeing).

The objective of this paper is to classify the various mechanisms encountered in dyeing systems, to develop a mathematical model for each case based on the pore model, and to kinetically discuss the dye-immobilization process.

FORMULATION OF THE DYE-IMMOBILIZATION PROCESS

Reactive Dyeing

Consider a system in which a dyestuff "A" diffuses into a fiber substrate "S" uniformly. The reaction between the dyestuff and the substrate is assumed to be second order with respect to the two species. The diffusion of reactive dyes within the fiber can be expressed by Fick's second law in the same manner as the diffusion of reactant species within a porous pellet. Then, the conservation equation of the reactive dye in the fiber is described as:

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k C_A C_S \quad (1)$$

If the stoichiometric factor for the reaction between the dyestuff and the substrate is equal to ν , the rate of consumption of the substrate can be expressed as:

$$\frac{\partial C_S}{\partial t} = -\nu k C_A C_S \quad (2)$$

The dye bath is assumed to be infinite and the fiber can be regarded as a slab with thickness $2L$. The initial and boundary conditions to be imposed are as follows:

$$t = 0, \quad x > 0; \quad C_A = 0, \quad C_S = C_{S0} \quad (3)$$

$$t > 0, \quad x = 0; \quad C_A = C_{A0} \quad (4)$$

$$t > 0, \quad x = L; \quad \partial C_A / \partial x = 0 \quad (5)$$

After introducing such dimensionless variables as $Y_A = C_A / C_{A0}$, $Y_S = C_S / C_{S0}$, $\xi = x / L$, and $\theta = D_A t / L^2$, the basic mass balance equations [eqs. (1) and (2)] can be put into the following dimensionless form:

$$\frac{\partial Y_A}{\partial \theta} = \frac{\partial^2 Y_A}{\partial \xi^2} - M Y_A Y_S \quad (6)$$

$$\frac{\partial Y_S}{\partial \theta} = -M \gamma Y_A Y_S \quad (7)$$

with the initial and boundary conditions

$$\theta = 0, \quad \xi > 0; \quad Y_A = 0, \quad Y_S = 1 \quad (8)$$

$$\theta > 0, \quad \xi = 0; \quad Y_A = 1 \quad (9)$$

$$\theta > 0, \quad \xi = 1; \quad \partial Y_A / \partial \xi = 0 \quad (10)$$

Here the parameter M is defined by $k C_{S0} L^2 / D_A$ and is equivalent to the square of the Thiele modulus in catalytic reactions or the square of the reaction-diffusion modulus in gas absorption with chemical reactions. The parameter γ is a dimensionless concentration of dye in the dye bath defined as $\nu C_{A0} / C_{S0}$.

Equations (6) and (7) include a nonlinear reaction term. Hence, the simul-

taneous differential equations with the initial and boundary conditions were numerically solved by using the quasilinearization technique proposed by Lee,¹ whose validity was confirmed by previous work on chemical absorption.^{2,3}

A more convenient way to present the computational results is in terms of fractional fixation. The local and total fractional fixations are defined as:

$$f = 1 - Y_S \quad (11)$$

and

$$f_{\text{tot}} = 1 - \int_0^1 Y_S d\xi \quad (12)$$

respectively.

When the effect of diffusion within the fiber on the overall dyeing rate is neglected, Y_A is always equal to unity and the rate of consumption of substrate is given by:

$$\frac{dY_S}{d\theta} = -M\gamma Y_S \quad (13)$$

in the dimensionless form. Equation (13) is solved with the initial condition: $\theta = 0$; $Y_S = 1$ to yield

$$Y_S = \exp(-M\gamma\theta) \quad (14)$$

In this case the local fixation agrees with the total fixation and is given as:

$$f = f_{\text{tot}} = 1 - \exp(-M\gamma\theta) \quad (15)$$

Therefore, the effect of diffusion within the fiber phase on the overall dyeing rate is assessed by the ratio of dimensionless dyeing time required to reach a fractional fixation f calculated from eq. (15), $\theta_{f,\text{id}}$, to that required to reach the same fractional fixation calculated from eq. (12), θ_f . That is,

$$\eta = \theta_{f,\text{id}}/\theta_f \quad (16)$$

The factor η is a quantity analogous to the catalytic effectiveness factor and is called the diffusion factor by Rys.⁴

Adsorptive Dyeing

The rate of adsorption of the dye in the fiber can be expressed by $k_a C_A (q_A^0 - q_A)$, while the rate of desorption of the adsorbed dye can be expressed by $k_d q_A$. The diffusion of dye in the pores of fiber is controlled by Fick's second law. Then, the mass balances in the pore and adsorbed phase are described by:

$$\epsilon \frac{\partial C_A}{\partial t} + (1 - \epsilon) \frac{\partial q_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} \quad (17)$$

$$\frac{\partial q_A}{\partial t} = k_a C_A (q_A^0 - q_A) - k_d q_A \quad (18)$$

The reactive dyeing developed in the previous section is equivalent to the case where $k_d = 0$, i.e., the adsorption process is irreversible. The dyebath is infinite and the fiber is regarded as a slab with thickness $2L$. The initial and boundary conditions are

$$t = 0, \quad x > 0; \quad C_A = q_A = 0 \quad (19)$$

$$t > 0, \quad x = 0; \quad C_A = C_{A0} \quad (20)$$

$$t > 0, \quad x = L; \quad \partial C_A / \partial x = 0 \quad (21)$$

The conservation equations in the dimensionless form reduce to:

$$\frac{\partial^2 Y_A}{\partial \xi^2} - \epsilon \frac{\partial Y_A}{\partial \theta} = M_a \left(Y_A (1 - \omega_A) - \frac{\omega_A}{K_A C_{A0}} \right) \quad (22)$$

$$\frac{\partial \omega_A}{\partial \theta} = \frac{M_a \gamma}{1 - \epsilon} \left(Y_A (1 - \omega_A) - \frac{\omega_A}{K_A C_{A0}} \right) \quad (23)$$

subject to:

$$\theta = 0, \quad \xi > 0; \quad Y_A = \omega_A = 0 \quad (24)$$

$$\theta > 0, \quad \xi = 0; \quad Y_A = 1 \quad (25)$$

$$\theta > 0, \quad \xi = 1; \quad \partial Y_A / \partial \xi = 0 \quad (26)$$

The local and total fractional fixations are given by:

$$f = (1 + 1/K_A C_{A0}) \omega_A \quad (27)$$

$$f_{\text{tot}} = \left(1 + \frac{1}{K_A C_{A0}} \right) \int_0^1 \omega_A d\xi \quad (28)$$

respectively.

When the effect of intrafiber diffusion on the overall dyeing rate is neglected, eq. (18) reduces to:

$$\frac{dq_A}{dt} = k_a C_{A0} (q_A^0 - q_A) - k_d q_A \quad (29)$$

because C_A is always equal to C_{A0} . Solution of eq. (29) subject to the initial condition: $t = 0; q_A = 0$, gives:

$$\frac{q_A}{q_A^0} = \frac{K_A C_{A0}}{1 + K_A C_{A0}} \left\{ 1 - \exp \left[-M_a \gamma \left(1 + \frac{1}{K_A C_{A0}} \right) \theta \right] \right\} \quad (30)$$

Therefore, the fractional fixation is given by the following equation:

$$f = f_{\text{tot}} = 1 - \exp[-M_a \gamma (1 + 1/K_A C_{A0})] \quad (31)$$

The effect of diffusion within the fiber on the dyeing rate can be assessed by the diffusion factor:

$$\eta = \theta_{f,\text{id}} / \theta_f \quad (32)$$

as in reactive dyeing. Here $\theta_{f,\text{id}}$ is a dimensionless dyeing time required for a fractional fixation f calculated from eq. (31), whereas θ_f is a dimensionless dyeing time required for the same fractional fixation calculated from eq. (28).

When the adsorption equilibrium is instantaneously established, ω_A is related to Y_A by the following equation (Langmuir adsorption isotherm):

$$\omega_A = K_A C_{A0} Y_A / (1 + K_A C_{A0} Y_A) \quad (33)$$

Then, the mass balance in the fiber can be written

$$\frac{\partial^2 Y_A}{\partial \xi^2} - \left(\epsilon + \frac{(1 - \epsilon) K_A C_{A0}}{\gamma(1 + K_A C_{A0} Y_A)^2} \right) \frac{\partial Y_A}{\partial \theta} = 0 \quad (34)$$

subject to eqs. (24)–(26).

If the adsorption surface is nonuniform, the adsorption isotherm equation can be expressed by

$$q_{A_i} = K_{A_i} q_{A_i}^0 C_A / (1 + K_{A_i} C_A)$$

For dual adsorption sites, the concentration of dye in the adsorbed phase is expressed by:

$$q_A = \frac{K_{A_1} q_{A_1}^0 C_A}{1 + K_{A_1} C_A} + \frac{K_{A_2} q_{A_2}^0 C_A}{1 + K_{A_2} C_A} \quad (35)$$

The mass balance in the fiber is given by

$$\frac{\partial^2 Y_A}{\partial \xi^2} - \left(\epsilon + \frac{(1 - \epsilon) K_{A_1} C_{A0}}{\gamma_1 (1 + K_{A_1} C_{A0} Y_A)^2} + \frac{(1 - \epsilon) K_{A_2} C_{A0}}{\gamma_2 (1 + K_{A_2} C_{A0} Y_A)^2} \right) \frac{\partial Y_A}{\partial \theta} = 0 \quad (36)$$

DISCUSSION

Typical examples of computational results on reactive dyeing are shown as solid and broken curves (Figs. 1 and 2) where the concentration of movable dye in the pores and the fractional fixation are plotted against dimensionless position in the fiber. The experimental results on reactive dyeing of cellophane film obtained by Motomura and Morita⁵ are also plotted in Figures 1 and 2. The experiments were performed by use of a roll film method. The parameters “ M ” and “ θ ,” required for computation of solid and broken curves, are evaluated from the values of the reaction rate constant and diffusivity obtained in the reactive dyeing experiments⁵ as well as dyeing time. Only the value of the parameter γ is selected so as to fit the experimental points. The reactive dyeing model proposed here satisfactorily simulates the process of dyeing of cellulose by reactive dyes. However, the experimental points (Figs. 1 and 2) are taken in the

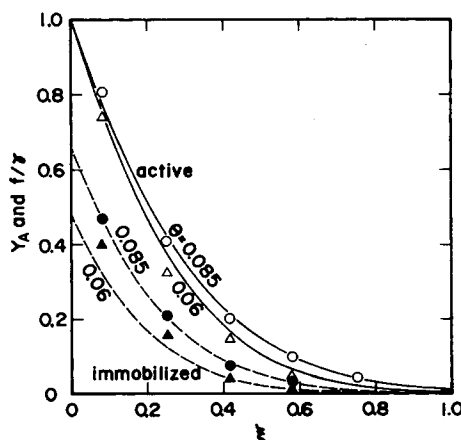


Fig. 1. Comparison of theoretical and experimental concentration profiles of (O, Δ) active and (●, ▲) immobilized species of C.I. Reactive Orange I at pH 8.8. t (min): (Δ, ▲) 180, (O, ●) 240; $M = 9.2$; $\gamma = 0.5$. θ : (O) 0.085; (Δ) 0.06; (●) 0.085; (▲) 0.06.

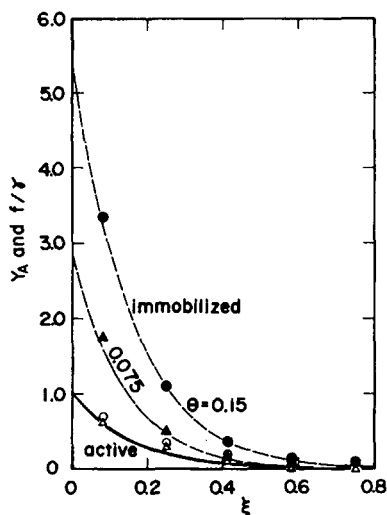


Fig. 2. Comparison of theoretical and experimental concentration profiles for C.I. Reactive Red I at pH 10. t (min): (Δ, \blacktriangle) 60, (O, \bullet) 120; $M = 40.6$; $\gamma = 0.05$. (\bullet, \blacktriangle) Immobilized; (O, Δ) active.

initial periods of dyeing. Experimental data taken in high fixation regimes can check the validity of the reactive dyeing model.

Figure 3 is a plot of the diffusion factor versus modulus in reactive dyeing. The relationship between diffusion factor η and modulus " M " depends upon the total

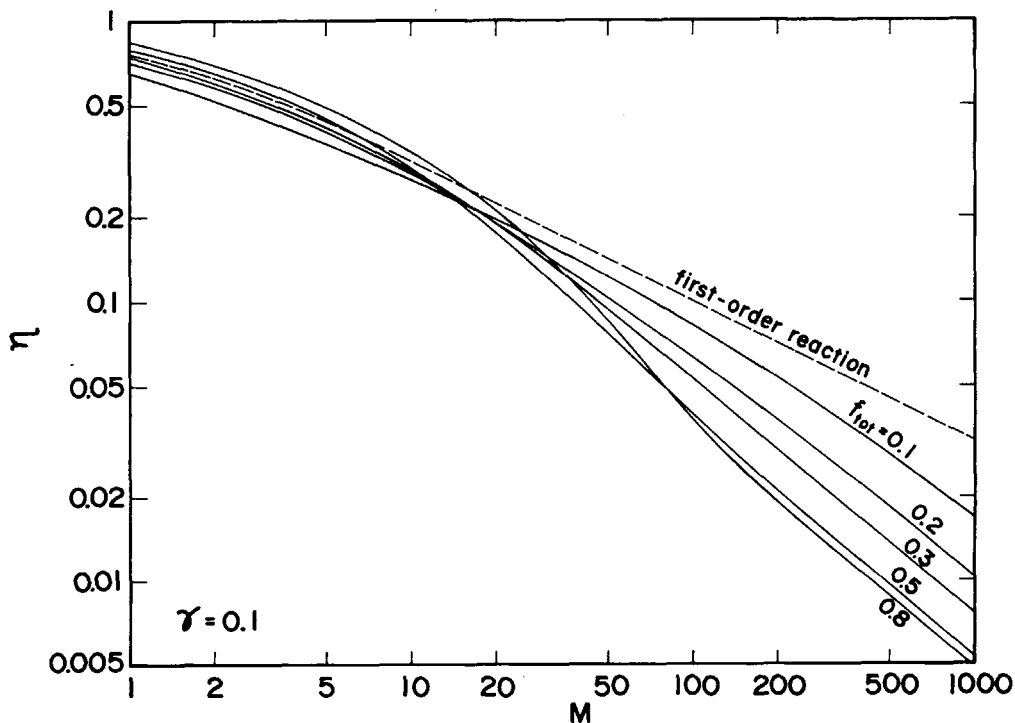


Fig. 3. Relation of diffusion factor η vs. modulus M with fractional fixation as a parameter for reactive dyeing.

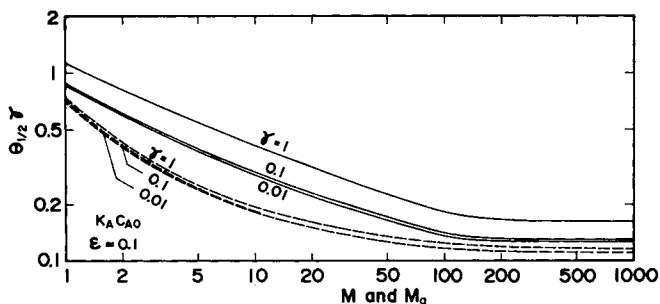


Fig. 4. Relation of $\theta_{1/2}\gamma$ vs. M or M_a . (—) Reactive dyeing; (---) adsorptive dyeing.

fixation and the concentration of dye in the dyebath. The value of the diffusion factor for the experiments (Figs. 1 and 2) are evaluated as 0.14 and 0.15, respectively.

The half-dyeing time which is defined as the time required to reach a fixation of 50% of its final or equilibrium value, is widely used as a measure of the overall dyeing rate. Figure 4 shows the relationship between dimensionless half-dyeing time, $\theta_{1/2}$, and modulus M . For $M > 200$, $\theta_{1/2}\gamma$ remains almost constant, where the dyeing is completely governed by intrafiber diffusion. For $\gamma < 0.1$, the relation of $\theta_{1/2}\gamma$ to M is almost independent of γ . That is, the half-dyeing time is inversely proportional to the concentration of dye in the dyebath.

A plot of the diffusion factor versus modulus for adsorptive dyeing (adsorption rate finite) is shown in Figure 5. The effect of γ in the η - M_a chart is small as compared to that in reactive dyeing. For $\gamma < 0.1$, the effect is negligibly small. The relation of half-dyeing time to modulus M_a is revealed as broken curves in Figure 4. γ has a very small influence on the relation of $\theta_{1/2}\gamma$ vs. M_a . For $\gamma < 0.1$, the influence is negligible. Also, the half-dyeing time is inversely proportional to the dye concentration in the dyebath.

Figure 6 shows a typical example for adsorptive dyeing where the Langmuir adsorption equilibrium is instantaneously attained, as a plot of local fixation

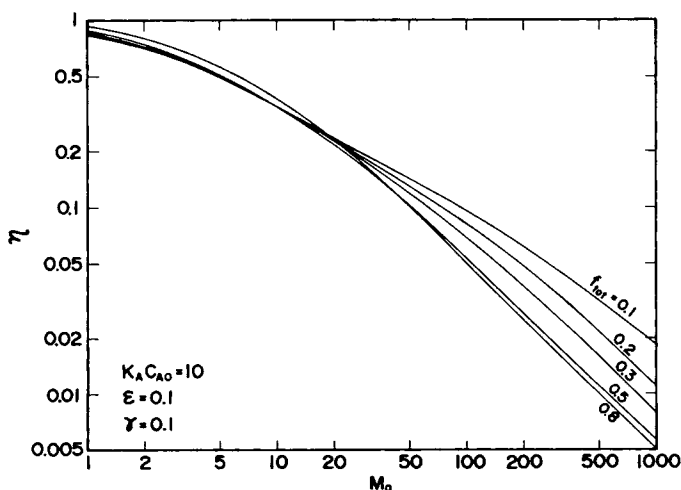


Fig. 5. Relation of diffusion factor η vs. modulus M_a with fractional fixation as a parameter for adsorptive dyeing.

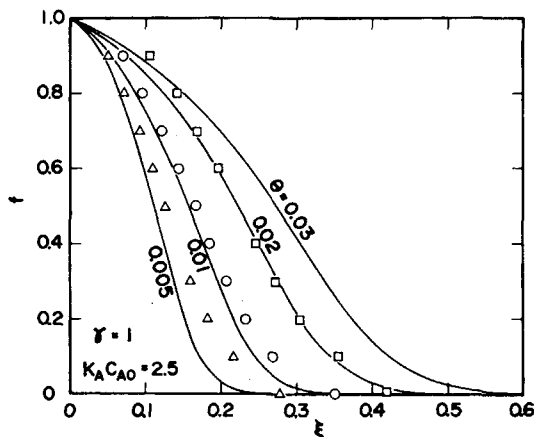


Fig. 6. Comparison of theoretical and experimental fractional fixations for naphthalene Fast Orange 2GS. t (min): (Δ) 80, (\circ) 160; (\square) 320.

versus dimensionless position in the fiber. In the same figure are also plotted the experimental data obtained by Morizane et al.,⁶ who measured the concentration profile of acid dye (naphthalene Fast Orange 2GS) in nylon 6 monofilaments of ca. 900 μm in diameter by means of a microspectrophotometric method. The parameters $K_A C_{A0}$ and γ required for calculation of the solid lines are selected so as to fit the experimental data at a dyeing time of 320 min. The value of voidage ϵ is put at 0.1 as a typical value. The agreement of computed lines with experimental data at 160 and 180 min does not seem to be satisfactory, because the parameters to be deduced are too numerous. In future studies, examination of adsorption isotherms and comparison with experiments during high fixations would be desirable to confirm the applicability of the adsorptive dyeing model.

Figure 7 indicates the dependence of adsorption equilibrium constant on half-dyeing time. γ and $K_A C_{A0}$ have a small influence on the relation $\theta_{1/2}\gamma$ vs. $K_A C_{A0}$. For $\gamma < 0.1$ and $K_A C_{A0} > 10$, the influence can be ignored. That is, the half-dyeing time is inversely proportional to the dye concentration in the dyebath.

The dyeing process during overdyeing will be governed by intrafiber diffusion with simultaneous multimodal adsorption. Figure 8 shows computational results for adsorptive dyeing incorporating dual adsorption compared with experimental data by Tak et al.⁷ on dyeing of C.I. Food Yellow 3 in nylon films at pH 2.2 and 50°C. By comparing computed and experimental results, the dyeing time of 24 h corresponds to the dimensionless dyeing time of $\theta = 1.1$, and the diffusion coefficient in the pores is evaluated to be $2.59 \times 10^{-11} \text{ m}^2/\text{s}$.

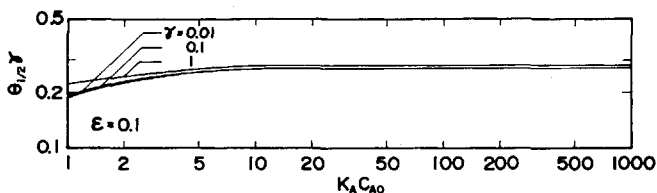


Fig. 7. Relation of $\theta_{1/2}\gamma$ vs. $K_A C_{A0}$ for Langmuir-type dyeing.

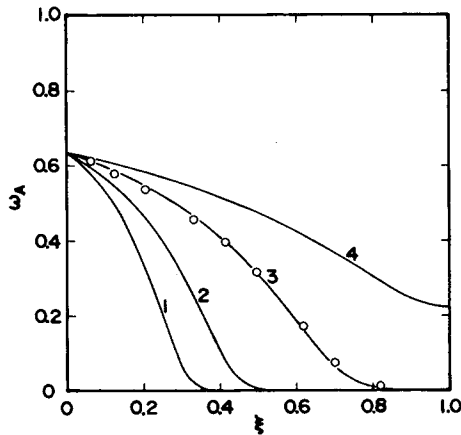


Fig. 8. Comparison of experimental data with theoretical predictions for over dyeing. 1, $\theta = 0.2$; 2, $\theta = 0.4$; 3, $\theta = 1.1$; 4, $\theta = 2.6$; (O) $t = 24$ h.

CONCLUSION

The kinetic models for reactive and adsorptive dyeing proposed in this paper satisfactorily simulated the processes of dyeing of reactive dyes in cellulose and acid dyes in nylon, respectively, in their initial periods. It is desirable to compare the results with experiments in high fixation regimes. There is a small influence of γ on the relation $\theta_{1/2}\gamma$ vs. M (or M_a) in either reactive or adsorptive dyeing. Especially, for $\gamma < 0.1$, the relation is almost independent of γ . That is, the half-dyeing time is inversely proportional to the dye concentration in the dyebath. In adsorptive dyeing in which the Langmuir adsorption equilibrium is instantaneously attained, the effects of γ and $K_A C_{A0}$ on the relation $\theta_{1/2}\gamma$ vs. $K_A C_{A0}$ are rather small. For $\gamma < 0.1$, the effect of γ is negligibly small and the half-dyeing time is inversely proportional to the dye concentration in the dyebath. The over dyeing phenomenon may be simulated by intrafiber diffusion with simultaneous adsorption on multimodal sites.

NOMENCLATURE

C_A	concentration of dye in pore (mol/m ³)
C_S	concentration of substrate in fiber (mol/m ³)
D_A	diffusion coefficient of dye in pore (m ² /s)
f	local fractional fixation in fiber
f_{tot}	total fractional fixation in fiber
k	second-order reaction rate constant (m ³ /mol s)
k_a	adsorption rate constant (m ³ /mol s)
k_d	desorption rate constant (1/s)
K_A	adsorption equilibrium constant (m ³ /mol)
L	half-width of fiber (slab) (m)
M	$= kC_{S0}L^2/D_A$
M_a	$= k_aq_A^0L^2/D_A$
q_A	concentration of adsorbed dye (mol/m ³)
q_A^0	saturated concentration of adsorbed dye (mol/m ³)
t	dyeing time (s)
x	distance from surface of fiber (m)
Y_A	dimensionless concentration of dye in pore $= C_A/C_{A0}$

Y_S dimensionless concentration of substrate in fiber = C_S/C_{S0}

Greek symbols

γ	$\nu C_{A0}/C_{S0}$ in reactive dyeing and C_{A0}/q_A^0 in adsorptive dyeing
ϵ	voldage in fiber
η	diffusion factor defined as eq. (16) or eq. (32)
θ	dimensionless time = $D_A t/L^2$
θ_f	dimensionless time required to reach a given fractional fixation "f"
ν	stoichiometric factor appearing in $A + \nu S \rightarrow P$
ξ	dimensionless distance from surface of fiber = x/L
ω_A	dimensionless concentration of adsorbed dye = q_A/q_A^0

Subscripts

A	dye
S	substrate
0	initial value or value in dyebath

References

1. E. S. Lee, *AIChE J.*, **14**, 490 (1968).
2. E. Sada, H. Kumazawa, and M. A. Butt, *AIChE J.*, **22**, 196 (1976).
3. E. Sada, H. Kumazawa, and M. A. Butt, *Chem. Eng. J.*, **13**, 225 (1977).
4. P. Rys, *Text. Res. J.*, **43**, 24 (1973).
5. H. Motomura and Z. Morita, *J. Appl. Polym. Sci.*, **21**, 487 (1977).
6. H. Morizane, Y. Suda, and T. Shirota, *Sen'i Gakkaishi*, **27**, 113 (1971).
7. T. Tak, J. Komiyama, and T. Iijima, *Sen'i Gakkaishi*, **35**, T486 (1979).

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