Concentration-Dependent Diffusion of Dye in Reactive Dyeing Systems

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SYNOPSIS

The physical model of the reactive dyeing system proposed by Sada et al. is extended in this communication to the case with a concentration-dependent diffusion coefficient of dye. The present model with an exponential concentration dependence of the diffusion coefficient is shown to predict the observed data better than did the previous one with a constant diffusion coefficient. Effects of the concentration dependence of the diffusion coefficient, dye reaction rate, degree of mixing, and volume ratio of fiber substrate to the dyebath on the rate of fractional fiber fixation and the dye concentration in the dyebath are investigated parametrically. It has been found that the effect of the volume ratio of the fiber substrate to the dyebath on the fractional fiber fixation is not of the same order of magnitude as those of the other three factors.

INTRODUCTION

The diffusion of dye in natural or man-made fibers has been a process of continuous interest to researchers in the textile industries. The process is important in that understanding of the dye diffusion and reaction phenomena in the fiber permits better control of the desired tone of color in the fiber by optimal selection of operating conditions.

Depending on the type of dye employed, the dyeing process can either be a reactive type or an adsorptive type. In the adsorptive dyeing process, the dye (cationic, acid, or direct type) is adsorbed onto the fiber substrate, obeying either the Langmuir or Freundlich adsorption isotherm. In the reactive dyeing process, the reactive dyes form covalent bonds with the reactive sites of the fiber substrate. In many previous investigations,[1-17] both types of dyeing processes have been examined. A common assumption of the physical models adopted by the previous investigators is that the diffusion coefficient of dye is a constant. This assumption allows simplification of the physical models in numerical predictions of the behaviors of dye diffusion in the fiber substrate and the rate of dye fixation. However, there has been experimental evidence[3,6,7,9,10] that the

diffusion coefficient of the dye in the fiber substrate is not a constant, but, rather, a strong function of the dye concentration. Therefore, to faithfully predict the dye diffusion process, consideration of the concentration dependence of the diffusion coefficient is necessary. The purpose of this study is to extend the physical model of Sada et al.[11-15,17] for reactive dyeing systems by including the concentration dependence of dye diffusion inside the fiber substrate. As will be shown later, the present extended model appears to predict significantly better the experimental dye concentration profiles than did the previous model with a constant diffusion coefficient.

CONCENTRATION-DEPENDENT DIFFUSION COEFFICIENT OF DYE

Two of the most widely used expressions for the concentration-dependent diffusion coefficient are represented by[18]

$$D(C_a) = D_0 \frac{C_a}{C_0} \tag{1a}$$

and

$$D(C_a) = D_0 \exp\left(a_1 \frac{C_a}{C_0}\right) \tag{1b}$$

where C_a is the dye concentration in the liquid; C_0, a reference dye concentration; D_0, the base diffusion coefficient; and a_1, a constant parameter. Although they are relatively easy to use, the above equations may not be able to represent well some complicated concentration dependence of the diffusion coefficient. Hence, the following more general functional relationship is suggested here:

$$D(C_a) = D_0\exp\left[a_1\left(\frac{C_a}{C_0}\right) + a_2\left(\frac{C_a}{C_0}\right)^2 + \cdots\right] \quad (2)$$

in which a_i are constant parameters to be determined. To demonstrate the applicability of eq. (2), two sets of experimental data of Ostrowska et al.[9,10] were employed to determine the parameters. The results of the least-square curve fitting are shown in Figures 1 and 2. Although a simple exponential function is seen to represent well the diffusion coefficient of Synthene Scarlet P3GL in polyester fiber (Fig. 1), a more complicated form of eq. (2) is needed to fit well the diffusion coefficient of Anilana Red BL in polyester fiber (Fig. 2). The diffusion coefficient of Synthene Scarlet P3GL increases relatively mildly with an increase in its dimensionless concentration, as seen in Figure 1. But that of Anilana Red BL in Figure 2 appears to increase very rapidly
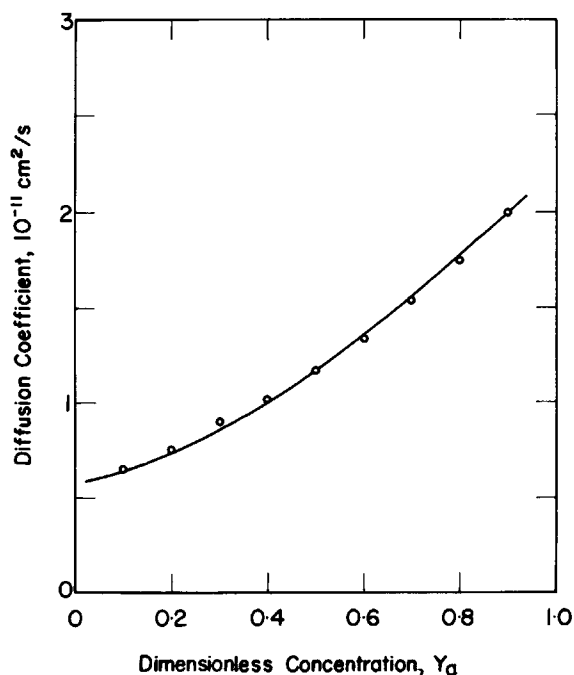
Figure 1 Concentration-dependent diffusion coefficient of Synthene Scarlet P3GL in polyester fiber: (———) $D(Y_a)$ = $0.585 \times 10^{-11}\exp(1.378 Y_a)$ cm^2/s.
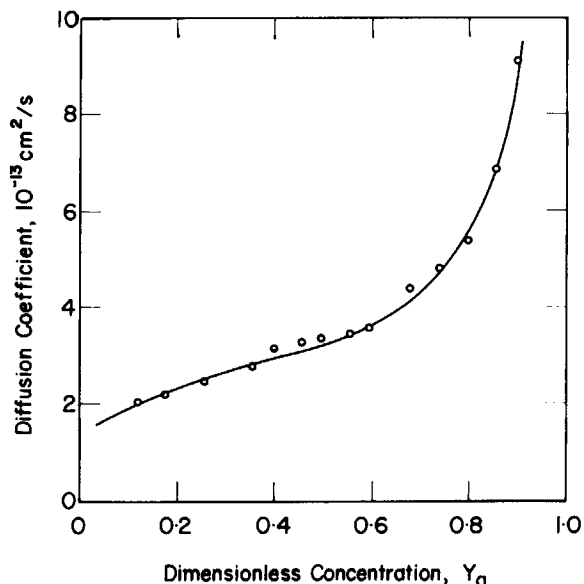
Figure 2 Concentration-dependent diffusion coefficient of Anilana Red BL in polyester fiber: (———) $D(Y_a)$ = $1.313 \times 10^{-13}\exp(4.5 Y_a - 8.64 Y_a^2 + 6.63 Y_a^3)$ cm^2/s.

when its dimensionless concentration is larger than 0.6. It is suspected that there may be significant changes in the physical or chemical properties of the polyester fiber at that high dye concentration level.

With an appropriate number of terms in the exponential polynomial function, eq. (2) is capable of fitting a wide variety of highly complicated diffusion coefficients. As an alternative, a straight polynomial of the following form can also be used:

$$D(C_a) = a_0 + a_1\left(\frac{C_a}{C_0}\right) + a_2\left(\frac{C_a}{C_0}\right)^2 + \cdots. \quad (3)$$

However, eqs. (2) and (3) are, in essence, the same, since expansion of eq. (2) in the Taylor series will automatically lead to eq. (3). For the present study, eq. (2) is adopted.

PHYSICAL MODEL OF REACTIVE DYEING PROCESS

Beside the dye diffusion in the dyebath and the fiber substrate, there are two other major processes occurring in a reactive dyeing system: the dye fixation in the fiber substrate and the dye hydrolysis in the liquid phase. Dye hydrolysis is caused by the reaction of dye with water, rendering less dye being available for fixation in the reactive sites of the fiber substrate.

Hence, the control of proper dyeing conditions is necessary to ensure that the majority of dye in the dyebath is consumed by fiber fixation rather than by hydrolysis. However, no quantitative relationships between the dye fixation and hydrolysis processes have been available. Hence, the simulation approach seems to offer the most effective means for understanding the reactive dyeing system.

The dye reaction in the fiber substrate is assumed to be a second-order reaction with respect to the concentrations of dye and reactive sites, whereas the dye hydrolysis is assumed to obey a first-order kinetics.[15,17] With this assumption, the dye diffusion/reaction system then can be represented by

$$\frac{\partial C_a}{\partial t} = \frac{\partial}{\partial x}\left[D(C_a)\frac{\partial(C_a)}{\partial x}\right] - kC_aC_s - k_wC_a \quad (4)$$

where C_a is the dye concentration in the liquid phase; C_s, the concentration of reactive sites in the fiber substrate; $D(C_a)$, the concentration-dependent diffusion coefficient; k and k_w, the reaction and hydrolysis rate coefficients; x, the spatial coordinate; and t, the time. The rate of reactive site disappearance or the rate of fiber fixation is given by

$$\frac{\partial C_s}{\partial t} = -mkC_aC_s \quad (5)$$

in which m is the stoichiometric coefficient for the reaction between dye and the fiber substrate. In addition to the two above equations, a third equation governing the dye consumption in the dyebath can be written as

$$V\frac{\partial C_b}{\partial t} = A\left[D(C_a)\frac{\partial C_a}{\partial x}\bigg|_{x=L}\right] - k_wC_bV \quad (6)$$

which is simply the dye balance in the dyebath. In eq. (6), C_b is the dye concentration in the dyebath; V, the bath volume; and A, the total cross-sectional area of the fiber substrate.

The initial and boundary conditions for the above governing dye balance equations are given by

$$t = 0; \quad C_a = 0, \quad C_s = C_{s0}, \quad C_b = C_{b0} \quad (7a)$$

$$x = 0; \quad D(C_a)\frac{\partial C_a}{\partial x} = k_L(C_s - C_b) \quad (7b)$$

$$x = L; \quad \frac{\partial C_a}{\partial x} = 0 \quad (7c)$$

where C_{s0} and C_{b0} are, respectively, the initial concentration of reactive sites in the fiber substrate and the initial dye concentration in the dyebath; k_L, the external mass transfer resistance of dye; and L, the thickness of the fiber substrate layer. Note that the concentration-dependent diffusion coefficient $D(C_a)$ in eqs. (4), (6), and (7b) is represented by eq. (1b) or (2).

To facilitate the numerical computations, the above differential equations and inital and boundary conditions are rendered into the following dimensionless form:

$$\frac{\partial Y_a}{\partial \theta} = f(Y_a)\frac{\partial^2 Y_a}{\partial X^2} + \frac{df(Y_a)}{dY_a}\left(\frac{\partial Y_a}{\partial X}\right)^2$$
$$- MY_a(Y_a + S) \quad (8a)$$

$$\frac{\partial Y_s}{\partial \theta} = -\alpha MY_aY_s \quad (8b)$$

$$\frac{\partial Y_b}{\partial \theta} = -\beta\left[f(Y_a)\frac{\partial Y_a}{\partial X}\bigg|_{x=1}\right] - SMY_b \quad (8c)$$

subject to

$$\theta = 0; \quad Y_a = 0, \quad Y_s = 1, \quad Y_b = 1 \quad (9a)$$

$$X = 0; \quad \frac{\partial Y_a}{\partial X} = 0 \quad (9b)$$

$$X = 1; \quad f(Y_a)\frac{\partial Y_a}{\partial X} = Sh(Y_b - Y_a) \quad (9c)$$

The above set of nonlinear differential equations was solved by the orthogonal collocation method[19] in the present study. The essence of this method is to approximate the spatial differential terms by the orthogonal Legendre polynomial at certain "optimized" points[19] (i.e., the roots of the n-th-order Legendre polynomial). With such an approximation, the partial differential equations were transformed into a set of ordinary differential equations that was simultaneously integrated by the Runge–Kutta–Gill method with precision.

Two items of particular interest in the physical simulation are the local and total fractional fixations of the fiber substrate. The local fractional fixation is defined as

$$W = 1 - Y_s \quad (10)$$

and the total fixation is given by

$$W_{tot} = \int_0^1 W(\theta, X)\, dX$$

$$= 1 - \int_0^1 Y_s(\theta, X)\, dX \qquad (11)$$

These quantities represent the extent of the fiber substrate that has been dyed or "fixed" at a particular depth of fiber and at any time during the dyeing period.

DISCUSSION

Reactive dyeing experiments of cellophane films by C.I. Reactive Orange I have been conducted by Motomura and Morita.[7] Those investigators carried out the cellulose dyeings in a very large dyebath that was kept essentially at a constant dye concentration throughout the dyeing period. In addition, the bath was maintained well mixed during the experimental runs, reducing the external mass transfer resistance of dye to a minimum, i.e., $Sh = \infty$. The experiment thus represents a simplification of the reactive dyeing system modeled in the above section. Under these conditions, eq. (8c) reduces to

$$\frac{\partial Y_b}{\partial \theta} = -SM Y_b$$
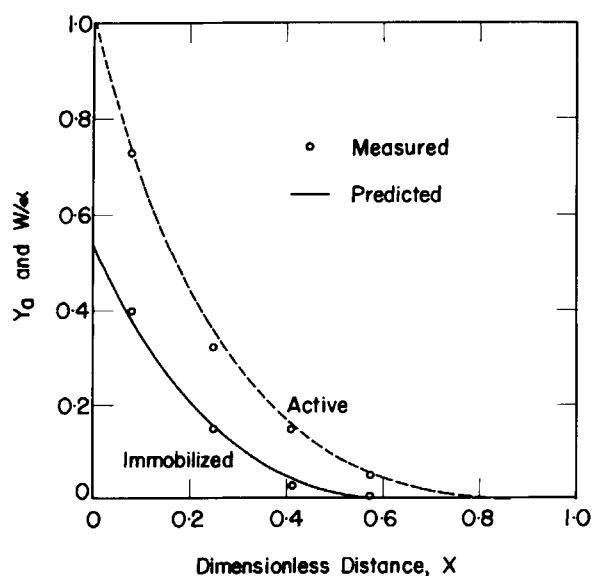
Figure 3 Comparison of predicted and experimental concentration profiles of active and immobilized C.I. Reactive Orange I at pH = 8.8, θ = 0.06, and $f(Y_a)$ = exp$(0.075 Y_a)$.
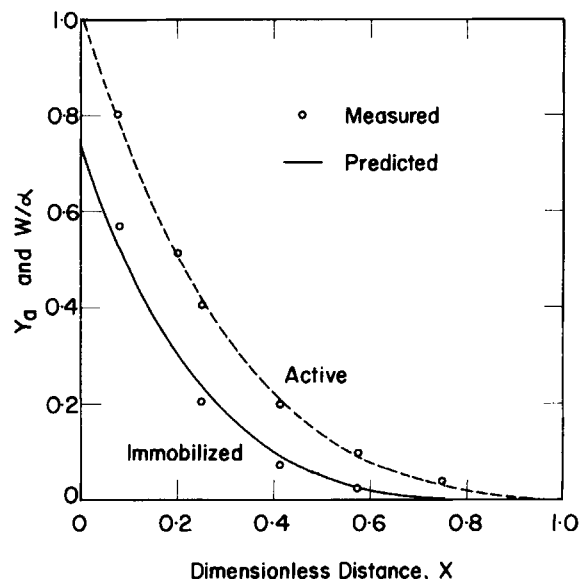
Figure 4 Comparison of predicted and experimental concentration profiles of active and immobilized C.I. Reactive Orange I at pH = 8.8, θ = 0.085, and $f(Y_a)$ = exp$(0.075 Y_a)$.

or

$$Y_b = \exp(-SM\theta) \qquad (12)$$

and the boundary condition (9c) becomes

$$X = 1; \quad Y_a = Y_b \qquad (13)$$

Equations (8a) and (8b) along with the initial and boundary conditions of eqs. (9a), (9b), and (13) then could be integrated for this special case. Figures 3 and 4 compare the predictions by the present model with a exponential concentration-dependent diffusion coefficient and the observed data of Motomura and Morita.[7] The agreement between the predicted and measured values are excellent for both dimensionless times, significantly better than the similar comparison of Sada et al.[11] using a model with a constant diffusion coefficient. This reveals the concentration dependence of the dye diffusion coefficient in this particular reactive dyeing system.

Figure 5 demonstrates the effect of the concentration dependence of the diffusion coefficient on the total fractional fixation W_{tot} and the dimensionless dye concentration in the bath Y_b. It is apparent that an increase in the diffusion coefficient at high dye concentration strongly promotes the total fractional fixation and depresses the dye concentration in the bath. Hence, the concentration dependence of the dye diffusion coefficient tends to positively benefit the dyeing process.
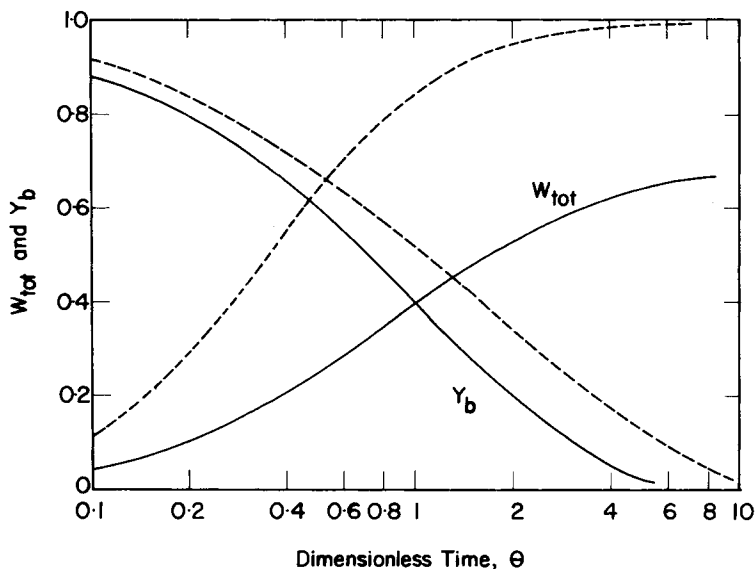
Figure 5 Effect of concentration dependence of the diffusion coefficient on W_{tot} and Y_b
with $M = 10$, $Sh = 5$, $S = 0.001$, $\beta = 0.5$, and $\alpha = 0.5$: (- - - - -) $a_1 = 1.378$; (———) $a_1 = 0$.

The factor M represents the ratio of the dye re-action rate to the internal dye diffusion rate. The effect of this parameter on the total fractional fixation and the dye concentration in the dyebath is displayed in Figure 6. An increase in M corresponds to a higher dye reaction rate or a lower internal dye diffusion, both of which yield a higher W_{tot} and a lower Y_b. Similar effects of M were also observed by Sada et al.[15] for the case with a constant diffusion coefficient. The effects appear to be more pronounced for the present case with the concentration-dependent diffusion coefficient, due primarily to the reduced internal mass transfer resistance of the dye.

In practice, a mixer is provided in the dyebath in most dyeing processes. Mixing not only provides more uniform dye concentration in the dyebath (thus avoiding uneven dyeing of the fiber substrate), but also reduces the external dye transfer resistance. The extent of mixing is represented by the Sherwood number. Complete and no mixings in the dyebath are the two extreme cases with infinite and zero Sherwood numbers. In most practical situations, the
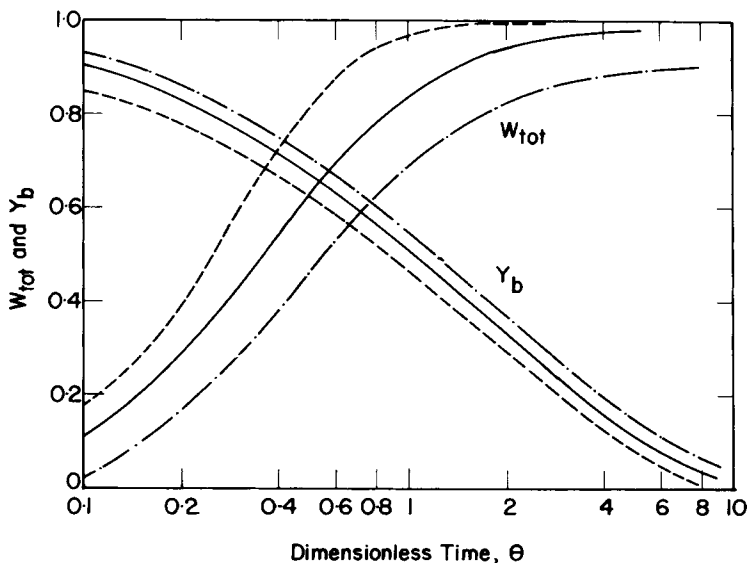
Figure 6 Effect of M on W_{tot} and Y_b with $Sh = 5$, $S = 0.001$, $\beta = 0.5$, $a_1 = 1.378$, and α
$= 0.5$: (- · - · -) $M = 1$; (———) $M = 10$; (- - - - -) $M = 100$.
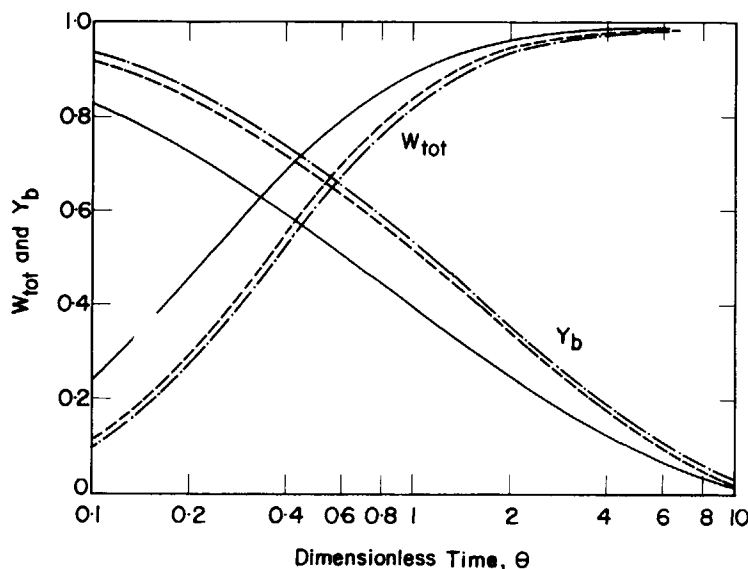
Figure 7   Effect of the Sherwood number on W_{tot} and Y_b with M = 10, S = 0.001, β = 0.5, a_1 = 1.378, and α = 0.5: (— · — · —) Sh = ∞; (-----) Sh = 50; (———) Sh = 5.

Sherwood number will be between these two extremes. Figure 7 shows the effect of the Sherwood number (Sh) on W_{tot} and Y_b. The effect appears to diminish with an increase in Sh. Lin[20] has shown that the external mass transfer resistance becomes negligible when Sh is larger than 100. This is also evident in Figure 7 because of the closeness of both the W_{tot} and Y_b curves for Sh = 50 and Sh = ∞.

The volume ratio of the fiber substrate to the dyebath is represented by the parameter β. A small β implies a small amount of fiber substrate immersed in a large dyebath. Hence, the dye concentration in the dyebath will decrease slowly at a small β, as seen

in Figure 8. A slow decrease of Y_b helps maintain a relatively high concentration gradient across the liquid/fiber interface and indirectly benefits the total fractional fixation. But as seen in Figure 8, such a benefit is not of the same order of magnitude as are the other factors, like the bath mixing, dye reaction rate, and the concentration dependence of the diffusion coefficient.

CONCLUSIONS

An extended dye diffusion model for the reactive dyeing process is presented in this study by consid-
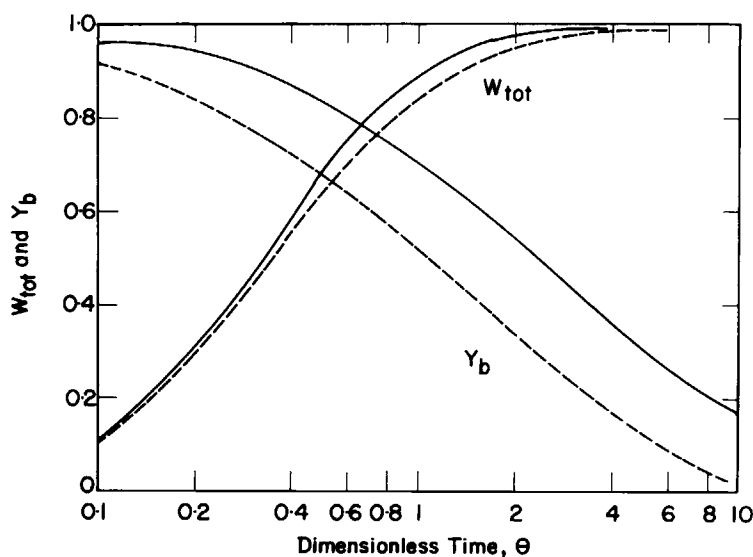
Figure 8   Effect of fiber substrate ratio on W_{tot} and Y_b with M = 10, Sh = 5, S = 0.001, a_1 = 1.378, and α = 0.5: (———) β = 0.5; (-----) β = 0.2.

ering the effect of a concentration-dependent diffusion coefficient. A general exponential polynomial function is suggested to represent the concentration dependence of the diffusion coefficient of the dye. The present model is shown to predict significantly better the experimental dye concentration profiles than did the previous model with a constant diffusion coefficient. The physical model is employed to examine the effects of the concentration dependence of the diffusion coefficient, mixing in the dyebath, dye reaction rate, and volume ratio of fiber substrate to dyebath on the total fractional fixation of the fiber substrate and the dye concentration in the dyebath. It is observed that the effect of the volume ratio of the fiber substrate to the dyebath on the fractional fiber fixation is not of the same order of magnitude as those of the other three factors.

NOMENCLATURE

a_i	constants in the concentration-dependent function of the diffusion coefficient
A	cross-sectional area of the fiber substrate
C_a	dye concentration in the fiber substrate
C_b	dye concentration in the dyebath
C_{b0}	initial dye concentration in the dyebath
C_s	concentration of reactive sites in the fiber substrate
C_{s0}	initial concentration of reactive sites in the fiber substrate
$D(C_a)$	concentration-dependent diffusion coefficient of the dye
D_0	reference diffusion coefficient of the dye
$f(Y_a)$	concentration-dependent diffusion coefficient function
k	reaction rate of the dye in the fiber substrate
k_L	external mass transfer coefficient
k_w	rate of dye hydrolysis
L	thickness of the fiber substrate
m	stoichiometric constant of dye reaction
M	ratio of dye reaction rate to dye diffusion rate, $kC_{s0}L^2/D_0$
M_k	ratio of dye hydrolysis rate to diffusion rate, $k_w L^2/D_0$
S	Ratio of dye hydrolysis to dye reaction rates, $k_w/(kC_{s0})$
Sh	Sherwood number, $k_L L/D_0$
t	time
V	volume of dyebath
W	local fractional fixation of the fiber substrate, defined by eq. (10)

W_{tot}	total fractional fixation of the fiber substrate, defined by eq. (11)
x	spatial coordinate
X	dimensionless spatial coordinate, $(L - x)/L$

Greek Symbols

α	dimensionless initial dye concentration, mC_{b0}/C_{s0}
β	ratio of fiber substrate volume to dyebath volume, AL/V
θ	dimensionless time, tD_0/L^2

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