Chemical Engineering Aspects of Reactive Dyeing

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Synopsis

The process of dyeing with reactive dyes was formulated on the basis of diffusion of dye species in the pores of polymer phase accompanied by fixation reaction with fiber substrate on the pore wall incorporating hydrolysis of dye species. The effect of the hdyrolysis on the fractional fixation was numerically analyzed under various levels of bath ratio and degree of mixing in the dyebath. The simulation model was presented to yield the unlevelness arisen from lack of uniformity of degree of mixing in the dyebath.

INRODUCTION

The dyeing of textiles is regarded as a combined process comprised of intrafiber diffusion of dye molecule or ion and chemical reaction with or adsorption on to the fiber substrate. In reactive dyeing, further, the reaction of the reactive dye with water (hydrolysis) normally competes with the dye fixation reaction. As the hydrolyzed dye cannot react with the substrate, dyeing conditions should be chosen so that good exhaustion of the dye on the substrate is assured before hydrolysis in the dyebath takes place.[1] However, quantitative relationships have not yet been given between the efficiency of reactive dyeings and all the operating parameters. In view of the fact that any systematic experiments of reactive dyeings have not been performed, one of the most convenient and effective tools to do this seems to be a simulation approach. That is, the simulation model of reactive dyeing is first established on the basis of multiphase transport theory, and, then, numerical analyses are made under a wide variety of practical conditions. Modeling of dye-immobilization process in the fiber is an essential basis for control of dyeing processes, because conditions in the fiber cannot be observed and directly controlled though conditions in the dyebath can be rather readily followed and controlled through sensors and electronic techniques. Our earlier work[2,3] has been done from such standpoints.

In our earlier article,[2] the process of dyeing of hydrophilic textile fiber was formulated on the basis of diffusion of dye in pores within the fiber accompanied by chemical reaction or adsorption, and the validity of the proposed model was confirmed by comparison with existing experimental data on dyeings of reactive dyes in cellulose[4] and acid dyes in nylon.[5,6] In another paper,[3] the previous treatment on reactive and adsorption dyeings[2] was extended to that for a finite dyebath and the influence of the bath ratio on the dyeing rate or time variation of fractional uptake or fixation was mainly discussed. In reactive dyeing, however, hydrolysis of reactive dyes which normally takes place in the dyebath as well as in the fiber, has been

neglected, though the bath ratio plays an important role on the time variation of fixation and the final fixation.

In the present work, the process of dyeing with reactive dyes was formulated on the basis of diffusion of dye in the pores of polymer phase with chemical reaction incorporating hydrolysis of dye, and the time variation of fractional fixation was mainly discussed under various combinations of the bath ratio and the degree of mixing in the dyebath. Further, the simulation model was presented to give the unlevelness arisen from the lack of uniformity of degree of mixing.

FORMULATION OF REACTIVE DYEING INCORPORATING HYDROLYSIS OF DYE

The dyeing with reactive dyes can be regarded as a process in which a dyestuff diffuses in a pore of polymer phase, simultaneously reacting with the textile substrate distributing uniformly on the pore wall. Only the substrates on the pore wall will take part in the fixation reaction. In the reactive dyeing to be considered here, the dyestuff is assumed to suffer hydrolysis in both the pore liquid and the dyebath with the first-order kinetics ($r_w = k_w C_A$). The reaction between the dye and the substrate is assumed to be of second order in both reactants ($r_c = k C_A C_S$).

Then, the conservation equation of the dye in the pore of the polymer phase can be written as[1,2]

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k C_A C_S - k_w C_A \tag{1}$$

If the stoichiometric coefficient for the reaction between the dye in the pore liquid and the textile substrate on the pore wall is v, viz., $A + vS \rightarrow$ products, the rate of consumption of the substrate can be written as

$$\frac{\partial C_S}{\partial t} = -v k C_A C_S \tag{2}$$

The dyebath is operated in a finite volume of dye liquor and the fiber phase is regarded as a slab with thickness $2L$. The initial and boundary conditions to be imposed are[2,3]

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

$$t = x = 0; \quad C_A = C_{A0} \tag{4}$$

$$t > 0, \quad x = 0; \quad C_A = C_{Ai} \text{ (variable)}$$

$$-v \frac{\partial C_{Ai}}{\partial t} = v k_w C_{Ai} + \left(-D_A \frac{\partial C_A}{\partial x} \bigg|_{x=0} \right) \tag{5}$$

$$t > 0, \quad x = L; \quad \partial C_A / \partial x = 0 \tag{6}$$

Here, v represents the volume of dye liquor per unit surface area of the polymer phase. Equation (5) implies that the reduced amount of dye in the bath is equal to the total amount of diffusion into polymer phase. Hydrolysis takes place in the dyebath as well as in the pore liquid. So the bath ratio plays an important role on the efficiency of reactive dyeings.

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 (1) and (2) are rewritten in the dimensionless form as

$$\frac{\partial Y_A}{\partial \theta} = \frac{\partial^2 Y_A}{\partial \xi^2} - MY_A Y_S - M_w Y_A \tag{7}$$

$$\frac{\partial Y_S}{\partial \theta} = -M\gamma Y_A Y_S \tag{8}$$

subject to

$$\theta = 0, \quad \xi > 0; \quad Y_A = 0, \quad Y_S = 1 \tag{9}$$

$$\theta = \xi = 0; \quad Y_A = 1 \tag{10}$$

$$\theta > 0, \quad \xi = 0;$$

$$Y_A = Y_{Ai}, \quad \frac{\partial Y_{Ai}}{\partial \theta} = M_w Y_{Ai} - \frac{L}{v}\frac{\partial Y_A}{\partial \xi}\bigg|_{\xi=0} \tag{11}$$

$$\theta > 0, \quad \xi = 1; \quad \frac{\partial Y_A}{\partial \xi} = 0 \tag{12}$$

Here, the parameters M and M_w are defined by $kC_{S0}L^2/D_A$ and $k_w L^2/D_A$, respectively, and the parameter γ is the initial dimensionless concentration of dye in the dyebath which is given by vC_{A0}/C_{S0}. v/L is equivalent to the bath ratio.

A convenient way to express the computational results is in terms of fractional fixation. The local and total fractional fixations are defined by

$$f = 1 - Y_S \tag{13}$$

and

$$f_{tot} = 1 - \int_0^1 Y_S \, d\xi \tag{14}$$

respectively.

COMPUTED RESULTS AND DISCUSSION

Effect of Bath Ratio

The moduli M and M_w in the basic mass balance equations (7) and (8) represent the ratios of the rates of the fixation reaction and the hydrolysis of dye, respectively, to the rate of diffusion within the pore. Let s $(= k_w/$

kC_{S0}) be referred to the selectivity of hydrolysis to fixation reaction, then M_w equates sM.

Figure 1 shows the time variations of the total fixation and the concentration of dye in the bath as a parameter of bath ratio, where the rate of fixation reaction is as low as $M = 10$, that is, the process is reaction-controlled. The final fixation, when the dye in the bath is completely consumed, is found to be almost independent of the bath ratio. Such a situation corresponds to the low-temperature dyeing. When the rate of fixation reaction goes up (e.g., the dyeing temperature goes up) while the selectivity s is as small as 0.001, the final fixation decreases with the bath ratio as shown in Figure 2. Such a trend becomes remarkable when s is as large as 0.01, as shown in Figure 3. As the hydrolysis takes place in the dyebath as well as in the pore liquid, hydrolysis has much more influence on the efficiency of reactive dyeings than would be expected from a magnitude of s. In solid-catalyzed reactions, even when s amounts to 0.01, the catalyst particles seem to be highly selective.

The temperature dependence of k is smaller than that of k_w because the constant k usually contains the adsorption equilibrium constant, and the value of s increases with the dyeing temperature. Thus, to suppress the loss of dye due to hydrolysis, it is desirable that the dyeing temperature is maintained as low as possible as would be expected.

As a reference, the profiles of fixation in the fiber at the final stage of dyeing were indicated for the dyeing conditions as depicted in Figures 3–5. The spatial distribution is not dependent on v/L at $M = 10$, because the process is reaction-controlled.

It is evident from the above computational results that the value of combined parameter $\gamma(v/L)$ should be increased beyond unity in order to increase the final fixation to a realistic level even when the selectivity s is as small as 0.001. Figures 6 and 7 show the time variations of the total fixation and the concentration of dye in the bath, when the value of $\gamma(v/L)$ equates 1.2, while the other dyeing conditions are the same as in Figures 1 and 2, respectively. The amount of dye required to gain a certain final fixation is reduced as the bath ratio is decreasing.
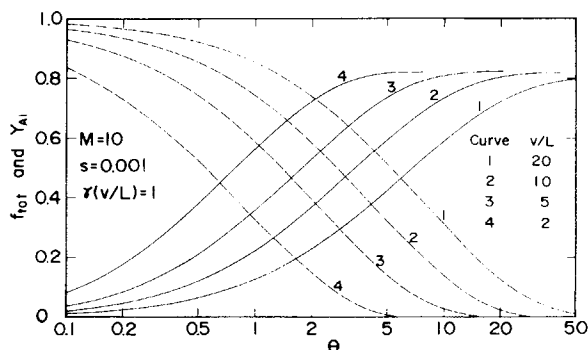

Fig. 1. Fractional fixation and dimensionless concentration of dye in the bath as a function of dimensionless time at $M = 10$ and $s = 0.001$.
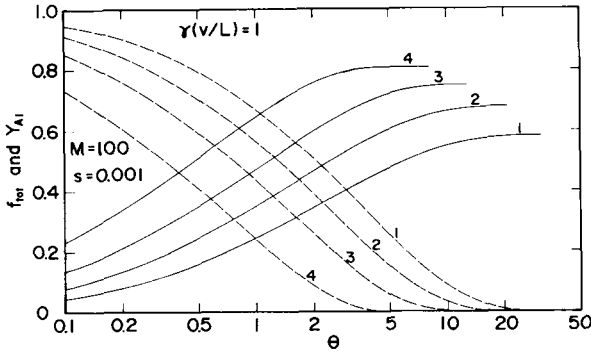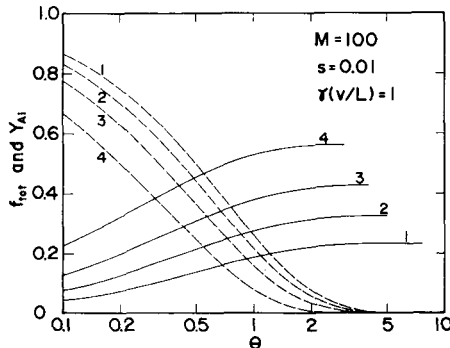
Fig. 2. Fractional fixation and dimensionless concentration of dye in the bath as a function of dimensionless time at $M = 100$ and $s = 0.001$.

Effect of Mixing in the Dyebath

When the mixing in the dyebath is insufficient and hence the concentration of dye on the surface of fiber cannot be replaced with the concentration in the bulk of dyebath, the concentration of dye on the surface is determined so that the rate of diffusion of dye through the liquid film next to the outer surface of fiber may just match with that of diffusion into the fiber. When this case is met, the boundary conditions on the surface of fiber should be altered as follows:

$$\text{at } x = 0; \quad t > 0, \quad C_A = C_{Ai}$$

$$k_f(C_{Ab} - C_{Ai}) = - D_A \frac{\partial C_A}{\partial x}\bigg|_{x=0} \tag{15}$$

$$- v \frac{\partial C_A}{\partial t} = v k_w C_A + \left(- D_A \frac{\partial C_A}{\partial x}\bigg|_{x=0} \right)$$

Fig. 3. Fractional fixation and dimensionless concentration of dye in the bath as a function of dimensionless time at $M = 100$ and $s = 0.01$.
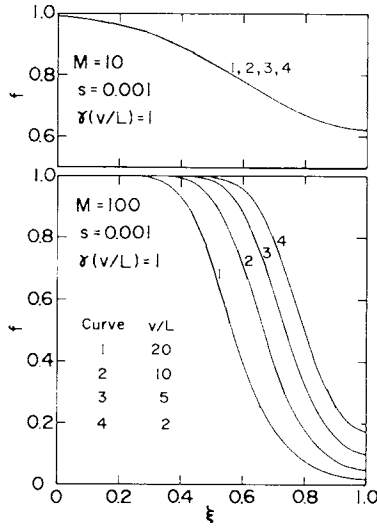
Fig. 4. Spatial distribution of fixation in the fiber at the final stage of reactive dyeing under the conditions depicted in Figures 1 and 2.

or in the dimensionless form,

$$\text{at } \theta = 0, \quad \xi > 0; \quad Y_A = Y_{Ai}$$

$$Y_{Ab} - Y_{Ai} = -\frac{1}{B_I}\frac{\partial Y_A}{\partial \xi}\bigg|_{\xi=0} \tag{16}$$

$$-\frac{\partial Y_A}{\partial \theta} = M_w Y_{Ab} - \frac{L}{v}\frac{\partial Y_A}{\partial \xi}\bigg|_{\xi=0}$$

Here, the parameter B_I is the Biot number which is defined by $k_f L / D_A$ and represents the ratio of resistance to diffusion within the fiber to that
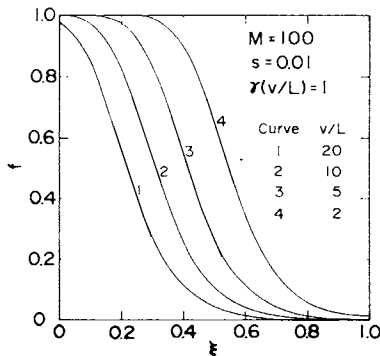

Fig. 5. Spatial distribution of fixation in the fiber at the final stage of reactive dyeing under the conditions depicted in Figure 3.
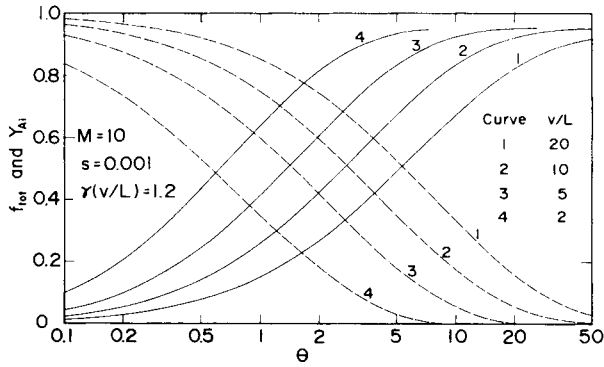
Fig. 6. Fractional fixation and dimensionless concentration of dye in the bath as a function of dimensionless time at $M = 10$, $s = 0.001$ and $\gamma(v/L) = 1.2$.

to liquor-to-fiber mass transfer. Large B_l implies vigorous mixing in the dyebath. Infinitely large B_l corresponds to complete mixing.

The effects of mixing on the time variations of the total fixation and the concentration of dye in the bath at high and low bath ratios were shown in Figures 8 and 9, respectively. It is apparent that the higher the bath ratio is, the fixation is the more influenced by mixing in the bath. When the fixation reaction is slow, however, the final fixation is not almost affected by the mixing as depicted in Figure 10. Thus, the final fixation is almost independent of both the bath ratio and the degree of mixing in the bath for a slow fixation reaction.

If the mixing in the bath is not completely uniform, a great majority of dye is consumed by the reaction with the substrate lying in the violent mixing environment. So the fixation in the violently mixing region may greatly differ from that in the calmly mixing region. If n kinds of mixing environment exist on the surface of fiber and the corresponding surface fraction is designated as f_i $(i = 1, 2, \ldots, n)$, then the boundary conditions to be imposed on the surface of fiber can be given in the dimensionless form
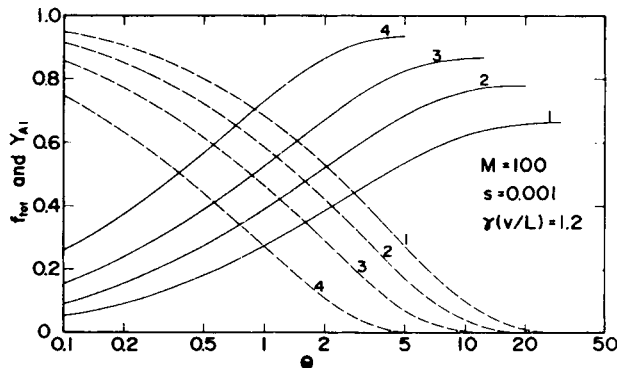

Fig. 7. Fractional fixation and dimensionless concentration of dye in the bath as a function of dimensionless time at $M = 100$, $s = 0.001$, and $\gamma(v/L) = 1.2$. The number beside each curve is the same as in Figure 6.
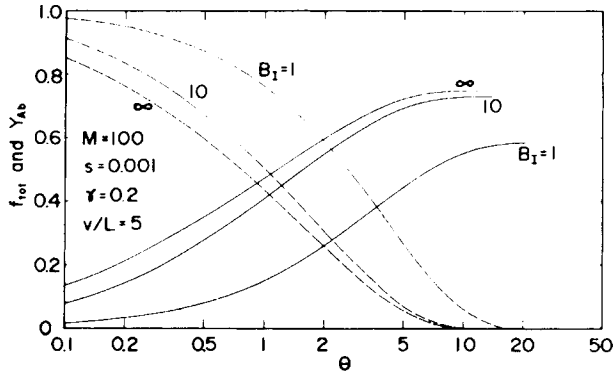
Fig. 8. Effect of liquid-to-fiber mass transfer on total fixation at a low bath ratio.
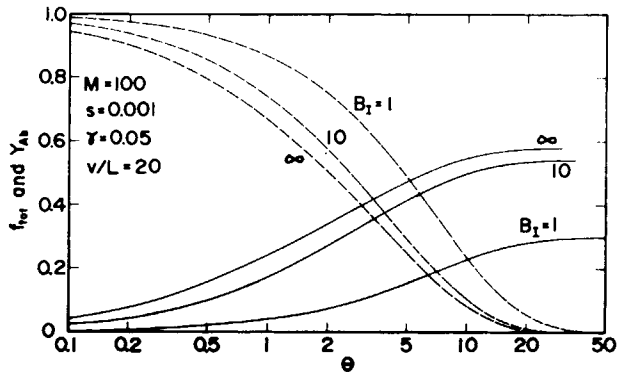

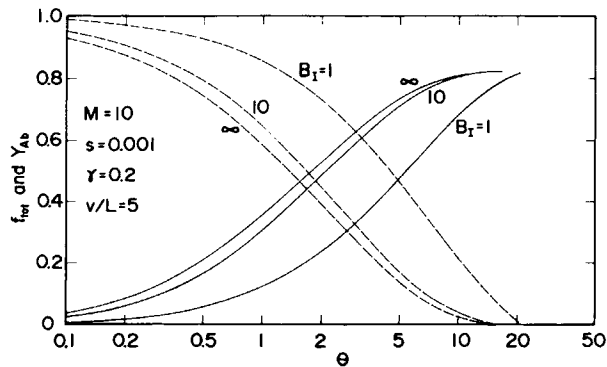Fig. 9. Effect of liquid-to-fiber mass transfer on total fixation at a high bath ratio.

Fig. 10. Effect of liquid-to-fiber mass transfer on total fixation under the slow reaction regime.

as

at $\xi = 0$, $\theta > 0$; $Y_A^{(i)} = Y_{Ai}^{(i)}$

$$Y_{Ai} = Y_{Ab} + \frac{1}{B_{Ii}}\left(\frac{\partial Y_A^{(i)}}{\partial \xi}\bigg|_{\xi=0}\right) \tag{17}$$

$$-\frac{\partial Y_{Ab}}{\partial \theta} = M_w Y_{Ab} - \frac{L}{v}\sum_{i=1}^{n}\left(\frac{\partial Y_A^{(i)}}{\partial \xi}\bigg|_{\xi=0}\right)f_i$$

The mixing environment on the surface of fiber is not fixed at all during the whole dyeing process, but alters every moment. The correspondence of the mixing environment specified by B_{Ii} to the fractional surface area f_i should not be fixed during the whole dyeing process. But, due to convenience of computation, the mixing environment on the surface of fiber was classified into two groups: violently mixing region and calmly mixing region,* and the time variation of fractional fixation was calculated.

Figures 11 and 12 are typical examples of computational results on the time dependence of fixation in the two mixing environments for slow and rapid fixation reactions, respectively. It is apparent from these figures that the final fixation values in the two environments are strikingly different, and lack of uniformity of mixing in the dyebath essentially induces uneven dyeing.

Nonisothermal Dyeing

The practical dyeing is usually undertaken at the nonisothermal conditions. The time–temperature dyeing program is one of the most important operating factors in practical dyeings. Then, the numerical analyses thus far will be extended to the nonisothermal case. As a typical example, the

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* It is further assumed that no exchange is made between two mixing regions. Therefore, this simulation is based on one extreme condition that the surface of fiber is exposed to the most uneven situation.
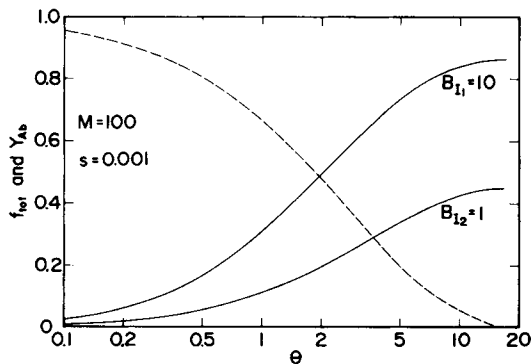

Fig. 11.   Time variation of total fixation of two regions of fiber lying in violent and calm mixing environments at $M = 10$, $s = 0.001$, $v/L = 5$, $\gamma = 0.2$, and $f_1 = 0.9$.
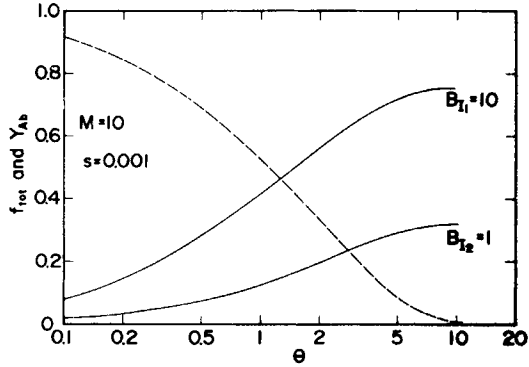
Fig. 12. Time variation of total fixation of two regions of fiber lying in violent and calm mixing environments at $M = 100$, $s = 0.001$, $v/L = 5$, $\gamma = 0.2$, and $f_1 = 0.9$.

time–temperature dyeing curve will be given by a linear function of dyeing time:

$$T = T_0 + at \quad \text{for } t < t_E$$
$$T = T_E \qquad \text{for } t \geq t_E \tag{18}$$

where $a = (T_E - T_0)/t_E$. The Arrhenius equation describes the relationship between the rate parameter and temperature, i.e.,

$$k = k_0 \exp\left[-\frac{E_R}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{19}$$

$$k_w = k_{w0} \exp\left[-\frac{E_w}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{20}$$

$$D_A = D_{A0} \exp\left[-\frac{E_D}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{21}$$

Thus, the moduli, M and M_w, and the dimensionless time θ, which are included in the basic mass balance equations and boundary conditions, take the temperature–dependent form

$$M = M_0 \exp\left[-\frac{E_R - E_D}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{22}$$

$$M_w = M_{w0} \exp\left[-\frac{E_w - E_D}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{23}$$

$$\theta = \frac{D_{A0}t}{L^2} \exp\left[-\frac{E_D}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{24}$$

Figures 13 and 14 indicate typical examples of computational results on the time dependences of fixation and the concentration of dye in the bath at a nonisothermal condition, where the values of parameter M and M_w at the initial temperature T_0 ($=298$ K) (i.e., M_0 and M_{w0}) are replaced with the same values as in Figures 1 and 6 and $B_I = 10$. The values of combined parameter $\gamma(v/L)$ are replaced with 1.0 in Figure 13 and 1.5 in Figure 14, respectively. The chain lines in both figures represent the time-temperature curve defined by eq. (18) with $T_0 = 298$ K, $T_E = 343$ K, and $a = 0.025$ K/s. As the values of activation energy for reactions and diffusion are replaced with $E_R = 40$ kJ/mol,* $E_w = 80$ kJ/mol,* and $E_D = 40$ kJ/mol, there is an increased influence of hydrolysis of dye with an increase in temperature (i.e., $s = s_0 = 0.001$ at $T = T_0 = 298$ K, while $s = 0.0083$ at $T = T_E = 343$ K). Therefore, the dyestuff is rapidly consumed at the final stage of dyeing process suffering from increased hydrolysis. Both Figures 1 and 2 showed that there is a negligible influence of the bath ratio on the final fixation when $M = 10$ and $s = 0.001$ under an isothermal dyeing, whereas the final fixation under the nonisothermal dyeing strikingly affected by the bath ratio in Figures 13 and 14. It is obvious from both figures that as the bath ratio decreases, the final fixation increases and besides the time required to reach the final fixation becomes short.

CONCLUSION

The simulation model for reactive dyeing with hydrolysis of dye in a finite bath was presented, and numerical analyses were made for typical isothermal and nonisothermal conditions. Consequently, the following findings were obtained. The lower the bath ratio, the less the decrease of the final fixation due to hydrolysis of dye and, accordingly, the higher is the final fixation. The lower the bath ratio, the less the influence of mixing in the dyebath on the fixation. When the rate of fixation reaction is low, the final

* As noted before, it is reasonable to assume that $E_w > E_R$, because the reaction rate constant k usually contains the adsorption equilibrium constant.
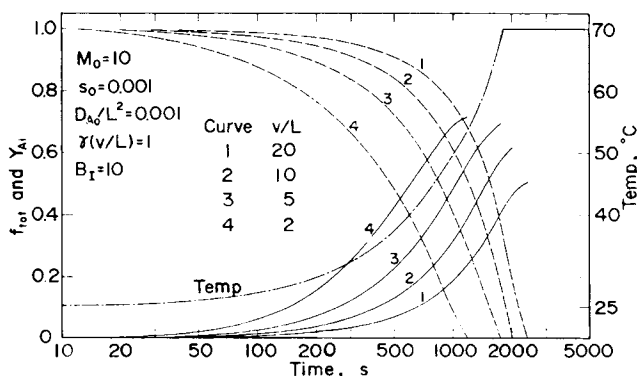

Fig. 13. Time dependences of fractional fixation and dimensionless concentration of dye in the bath under the nonisothermal condition for $\gamma(v/L) = 1$.
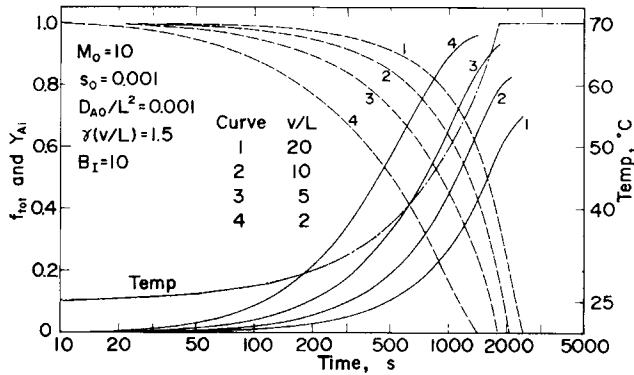
Fig. 14. Time dependences of fractional fixation and dimensionless concentration of dye in the bath under the nonisothermal condition for $\gamma(v/L) = 1.5$.

fixation is almost independent of the bath ratio and the degree of mixing in the dyebath. Uneven dyeing is essentially induced by lack of uniformity of mixing in the dyebath.

NOMENCLATURE

a	coefficient in eq. (18)
B_I	Biot number $= k_f L / D_A$
C_A	concentration of dye in the pore liquid (kmol/m³)
C_S	concentration of reactive site on the pore wall (kmol/m³)
D_A	diffusion coefficient of dye in the pore liquid (m²/s)
E_D	activation energy of diffusion in the pore liquid (kJ/mol)
E_R	activation energy of fixation reaction (kJ/mol)
E_w	activation energy of hydrolysis reaction of dye (kJ/mol)
f_i	fractional surface area of polymer phase lying in a mixing environment specified by B_{Ii}
f_{tot}	total fractional fixation in polymer phase
k	rate constant of second order fixation reaction [m³/(kmol s)]
k_f	liquid-to-polymer phase mass transfer coefficient (m/s)
k_w	rate constant of hydrolysis reaction (s⁻¹)
L	half width of polymer phase (m)
M	$= k C_{s0} L^2 / D_A$
M_w	$= k_w L^2 / D_A$
R	gas constant [kJ/(mol K)]
s	selectivity $= k_w / k C_{S0}$
T	dyeing temperature (K)
t	dyeing time (s)
v	dyeing liquor volume per unit surface area of polymer phase (m³/m²)
x	distance from surface of polymer phase (m)
Y_A	dimensionless concentration of dye in the pore liquid $= C_A / C_{A0}$
Y_S	dimensionless concentration of reactive site on the pore wall $= C_S / C_{S0}$

Greek Symbols

γ	$= v C_{A0} / C_{S0}$
θ	dimensionless dyeing time $= D_A t / L^2$
v	stoichiometric coefficient appearing in fixation reaction $A + vS \rightarrow$ Products
ξ	dimensionless distance from surface of polymer phase $= x / L$

Subscripts

A   dye
b   bulk of liquid
i   surface of polymer phase
S   reactive site
0   initial value or initial condition

Superscript

(i)   mixing environment specified by B_{I_i}

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