

## Diffusion with Simultaneous Reaction of Reactive Dyes in Cellulose

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### Synopsis

The theoretical equations which described the concentration profile of immobilized species of reactive dyes in the substrate were derived from the diffusion equation with the chemical reaction of first-order or pseudofirst-order. The theoretical profiles in the substrate described by the equations were discussed. The larger the diffusion coefficient  $D$  of active species and the smaller the reaction rate constant  $k$ , the deeper is the penetration of the immobilized and active species of reactive dyes into the substrate. The method of estimating  $D$  and  $k$  from the diffusion profiles of both species obtained by means of the method of the cylindrical cellophane film roll was described. The diffusion coefficients of the hydrolyzed species of C.I. Reactive Orange 1 and Red 1 were nearly constant in all the pH values examined. The concentration profiles of both the species of Orange 1 at pH 8.8 were identical with the theoretical ones; while the profiles of immobilized species of Red 1 at pH 10 and of Orange 1 at pH 12 agreed with the theoretical ones and those of active species did not because of the hydrolysis. The diffusion coefficients of active species of these dyes at these pH ranges were smaller than those of the hydrolyzed species.

### INTRODUCTION

There still seem to remain some theoretical problems in reactive dyes about the diffusion in polymer with simultaneous reaction in spite of the great development and many fundamental studies in the last two decades. These results have been summarized in two books published recently.<sup>1,2</sup> The diffusion problem of reactive dyes in cellulose has mainly been treated by the so-called Danckwerts' equation,<sup>3-11</sup> while that in protein fiber has also been studied by the same equation.<sup>12</sup>

In these reports, the diffusion coefficients of reactive dyes have been obtained from the total adsorption, not from the concentration profile in the substrate.<sup>3-9,12</sup> Some experiments have been carried out under conditions without the simultaneous reaction.<sup>9-11</sup> The first study which obtained the diffusion coefficients from the diffusion profile of reactive dye in cellulose has recently been reported by Karasawa et al.<sup>13</sup> However, they treated the diffusion profile of "active" species. The theoretical distribution of immobilized dye, which was practically of importance in reactive dyeing, has not yet been reported.

In the present paper, the equations which describe the diffusion profile of

immobilized species in the substrate will be derived, and the theoretical diffusion profiles will be calculated by the equations and will be discussed from a practical point of view in reactive dyeing. A method to obtain the reaction rate constant by means of the cylindrical film roll method will be described and some experimental results will be reported.

## THEORETICAL

### Derivation of Equations

The diffusion of reactive dyes in the substrate may be regarded as a problem in diffusion where some of the dyes become immobilized when the diffusion proceeds. If the reactive dyes are immobilized by a first-order or pseudofirst-order reaction whose rate constant is  $k$ , the diffusion equation for the "active" species of the dyes in one-dimensional semiinfinite media is

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - kC \quad (1)$$

where  $C$  is the concentration of active species,  $t$  is the time, and  $x$  is the distance, provided that the diffusion coefficient  $D$  is constant.

In the diffusion from an infinite dye bath, the initial and boundary conditions are

$$\begin{aligned} C &= 0, & x &> 0, & t &= 0 \\ C &= C_0, & x &= 0, & t &> 0 \end{aligned} \quad (2)$$

According to Danckwerts,<sup>14</sup> the solution of eq. (1) is

$$\begin{aligned} \frac{C}{C_0} &= \frac{1}{2} \exp\left(-x\sqrt{\frac{k}{D}}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} - \sqrt{kt}\right) \\ &\quad + \frac{1}{2} \exp\left(x\sqrt{\frac{k}{D}}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + \sqrt{kt}\right) \end{aligned} \quad (3)$$

where

$$\operatorname{erfc} z = 1 - \operatorname{erf} z = \frac{2}{\sqrt{\pi}} \int_z^\infty e^{-\eta^2} d\eta \quad (4)$$

The total quantity  $M_t'$  of reactive dye adsorbed in time  $t$  is obtained from eq. (3) as follows:

$$\begin{aligned} M_t' &= \int_0^t -D \left(\frac{\partial C}{\partial x}\right)_{x=0} dt \\ &= C_0 \sqrt{\frac{D}{k}} \left\{ \left(kt + \frac{1}{2}\right) \operatorname{erf} \sqrt{kt} + \sqrt{\frac{kt}{\pi}} \exp(-kt) \right\} \end{aligned} \quad (5)$$

As eq. (3) represents the concentration distribution of active species in the substrate, that of "immobilized" ones in time  $t$  by the reaction with substrate is obtained by the integration of eq. (3) with time:<sup>15</sup>

$$\begin{aligned} \frac{C^*}{C_0} &= \int_0^t kC dt \\ &= \frac{k}{2} \left\{ \left( t - \frac{x}{2\sqrt{Dk}} \right) \exp \left( -x \sqrt{\frac{k}{D}} \right) \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} - \sqrt{kt} \right) \right. \\ &\quad \left. + \left( t + \frac{x}{2\sqrt{Dk}} \right) \exp \left( x \sqrt{\frac{k}{D}} \right) \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} + \sqrt{kt} \right) \right\} \quad (6) \end{aligned}$$

where  $C^*$  denotes the concentration of immobilized species.

In order to obtain the concentration profile of reactive dyes in the present study, the cylindrical film roll method is used. The film roll can be regarded as a semiinfinite medium made of successive film layers. The respective dyed layers are optically measured to obtain the total quantity of adsorption on the film or the mean adsorption on the film. The theoretical adsorption of active species on the  $i$ th layer  $M_i$  is given by integrating eq. (3) with  $x$ ,<sup>13</sup>

$$\begin{aligned} M_i &= C_0 \int_{(i-1)\epsilon}^{i\epsilon} C dx \\ &= -\frac{C_0}{2} \sqrt{\frac{D}{k}} \left[ \exp \left( -x \sqrt{\frac{k}{D}} \right) \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} - \sqrt{kt} \right) \right. \\ &\quad \left. - \exp \left( x \sqrt{\frac{k}{D}} \right) \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} + \sqrt{kt} \right) \right]_{(i-1)\epsilon}^{i\epsilon} \quad (7) \end{aligned}$$

where  $\epsilon$  denotes the thickness of a layer, while that of the immobilized species on the  $i$ th layer  $M_i^*$  is similarly given from eq. (6):

$$\begin{aligned} M_i^* &= C_0 \int_{(i-1)\epsilon}^{i\epsilon} C^* dx \\ &= \frac{C_0}{2} \left[ \left\{ \frac{x}{2} - \sqrt{\frac{D}{k}} \left( kt - \frac{1}{2} \right) \right\} \exp \left( -x \sqrt{\frac{k}{D}} \right) \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} - \sqrt{kt} \right) \right. \\ &\quad \left. + \left\{ \frac{x}{2} + \sqrt{\frac{D}{k}} \left( kt - \frac{1}{2} \right) \right\} \exp \left( x \sqrt{\frac{k}{D}} \right) \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} + \sqrt{kt} \right) \right. \\ &\quad \left. - \frac{2\sqrt{Dt}}{\sqrt{\pi}} \exp \left( -\frac{x^2}{4Dt} - kt \right) \right]_{(i-1)\epsilon}^{i\epsilon} \quad (8) \end{aligned}$$

Then, the total adsorption of reactive dyes on the  $i$ th layer  $M_i'$  is

$$M_i' = M_i + M_i^* \quad (9)$$

The total quantity  $M_t^*$  of immobilized species is obtained from eq. (8):

$$\begin{aligned} M_t^* &= C_0 \int_0^\infty C^* dx \\ &= C_0 \sqrt{\frac{D}{k}} \left\{ \left( kt - \frac{1}{2} \right) \operatorname{erf} \sqrt{kt} + \sqrt{\frac{kt}{\pi}} \exp(-kt) \right\} \quad (10) \end{aligned}$$

Similarly, that of active species  $M_t$  is obtained from eq. (7):

$$\begin{aligned} M_t &= C_0 \int_0^\infty C dx \\ &= C_0 \sqrt{\frac{D}{k}} \operatorname{erf} \sqrt{kt} \quad (11) \end{aligned}$$

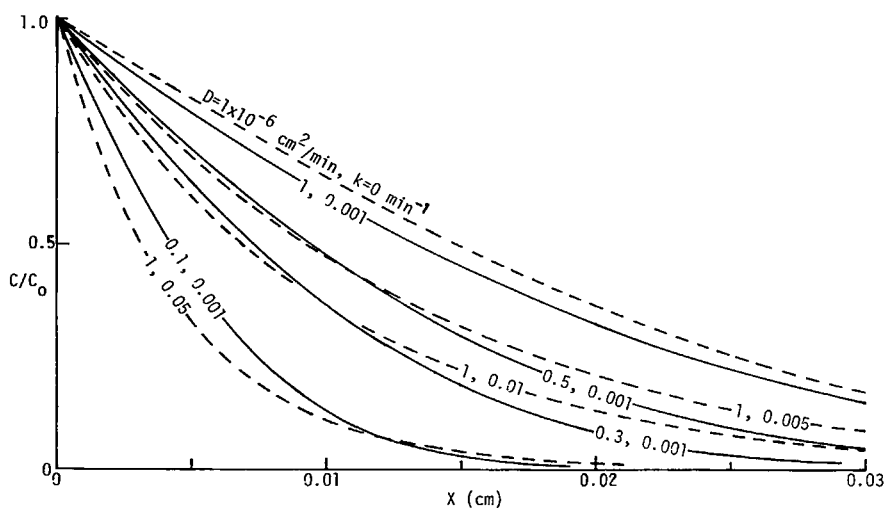


Fig. 1. Theoretical concentration profiles of active species described by eq. (3) at  $t = 240$  min.

The total quantity of immobilized and active species (i.e., total adsorption)  $M_t'$  given by eq. (12) is equal to eq. (5):

$$M_t' = M_t + M_t^* \quad (12)$$

### Diffusion Profiles

The concentration profiles of the "active" species described by eq. (3) are shown in Figure 1 for the various diffusion coefficients  $D$  and the reaction rate constants  $k$ , and in Figure 2 for the various diffusion times  $t$ . Since a general concentration profile of reactive dyes can not be drawn, some profiles for proper values of  $D$ ,  $k$ , and  $t$  within the range of the present study are shown. The diffusion of active species into substrate increases with increase in the diffusion coefficients as expected (solid lines in Fig. 1) and decreases with increase in the rate constants (dotted lines). There are similar diffusion profiles of active species between the quite different combinations of the values of  $D$  and  $k$  due to the duplicate dependence of the diffusion on the parameters of  $D$  and  $k$ .

If  $\sqrt{kt} \geq 3$ ,  $\exp(-x/\sqrt{k/D})$  in the first term on the right-hand side of eq. (3) approximates to  $10^{-3}$  as  $x \rightarrow 5\sqrt{D/k}$ . At this range of  $x$ , the value of the error function complement in the first term is nearly equal to 2 as  $x/2\sqrt{Dt} - \sqrt{kt} \lesssim -2$  and  $\operatorname{erfc} z \lesssim 5 \times 10^{-3}$  when  $z \geq 2$ ; while the second term on the right-hand side approximates to zero as the second term converges faster than the first one. Thus, eq. (3) has an asymptote described by eq. (13), which has no dependence on  $t$  and is shown as a chain line in Figure 2:

$$\frac{C}{C_0} = \exp\left(-x \sqrt{\frac{k}{D}}\right) \quad (13)$$

On the other hand, the concentration profiles of the immobilized species described by eq. (6) are shown in Figures 3 and 4. They are largely dependent on  $k$  as expected. Because on the surface,  $C^*/C_0 = kt$  from eq. (6), the surface concentration of immobilized species is determined by  $t$  and  $k$ .

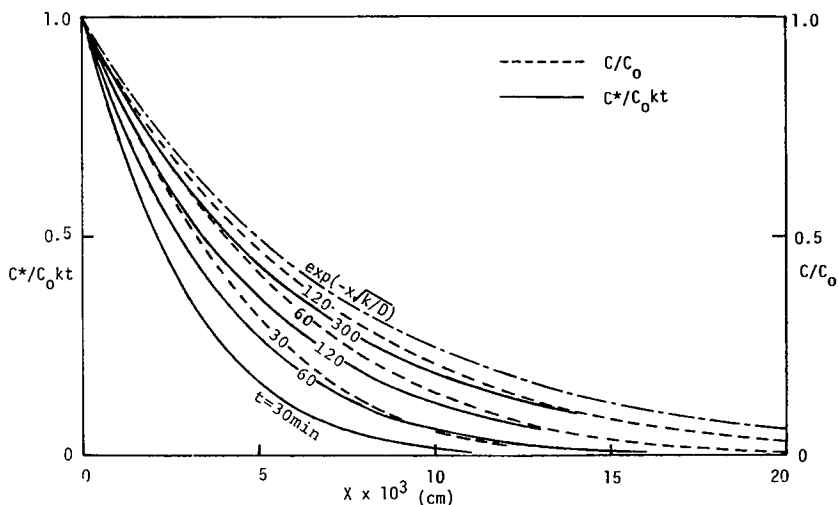


Fig. 2. Theoretical concentration profiles of active (dotted line) and immobilized species (solid line) for the various diffusion times described by eqs. (3) and (6) divided by  $kt$  ( $D = 5 \times 10^{-7}$  cm<sup>2</sup>/min,  $k = 0.01$  min<sup>-1</sup>). Both profiles approach a common asymptote (chain line) as time proceeds.

If  $\sqrt{kt} \gtrsim 3$ , eq. (6) has an asymptote described by eq. (14) in the same manner as the relation between eqs. (3) and (13):

$$\frac{C^*}{C_0} = k \left( t - \frac{x}{2\sqrt{Dk}} \right) \exp \left( -x\sqrt{\frac{k}{D}} \right) \tag{14}$$

The time dependence in the diffusion profiles of immobilized species described by eq. (14) appears exclusively near the surface (cf. Fig. 4). Because the rate of convergence of eq. (14) to zero is dependent on  $\sqrt{k/D}$  in the exponential term, the penetration distance of immobilized species has practically no dependence on  $t$  as in the active species. If  $C^*/C_0kt$  and  $C/C_0$  versus  $x$  relations described by eqs. (3) and (6) are drawn in order to compare both the profiles of immobilized and active species for the various diffusion times, both the penetration distances are identical with each other (Fig. 2). The right-hand side of eq. (14) divided by  $kt$  is equal to that of eq. (13) when  $t \rightarrow \infty$ , so that both profiles have a common asymptote. However, the approach of the profile of active species to the common asymptote is faster than that of the immobilized one. Thus, the penetration of both species does not practically occur as  $\sqrt{kt} \gtrsim 3$ .

In general, both the concentration profiles of immobilized and active species are dependent on the magnitudes of  $D$  and  $k$  of active one as well as of  $t$  shown in Figures 1-4. In the case of a small rate constant, the diffusion profiles approach the Fickian ones. In the reverse case, such as  $\sqrt{kt} \gtrsim 3$ , they approach their asymptotes described by eqs. (13) and (14).

The rate of convergence of eqs. (3) and (6) is dependent on the magnitude of  $D$ . The larger the diffusion coefficients, the deeper the penetration. As the second term on the right-hand side of eqs. (3) and (6) converges faster than the first one, the penetration of dyes depends upon the value of  $\sqrt{k/D}$ . The larger the rate constant, the larger the amount of immobilized species near the surface and the smaller the penetration.

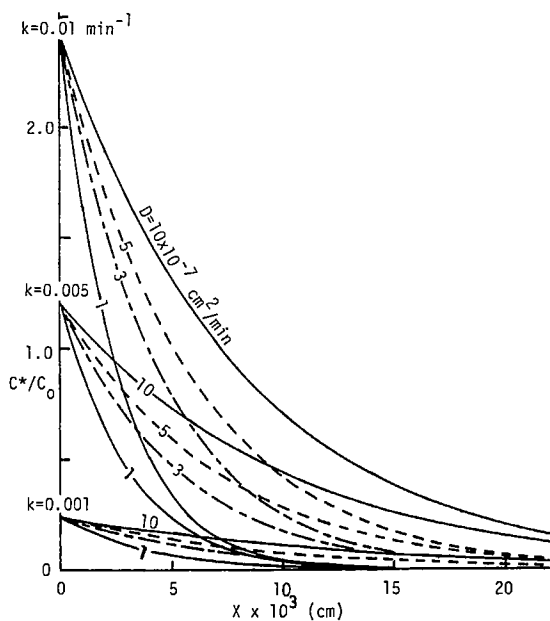


Fig. 3. Theoretical concentration profiles of immobilized species described by eq. (6) at  $t = 240$  min. The larger the  $D$  of active species and the smaller the  $k$ , the deeper the penetration of the immobilized species into the substrate.

A special case has conditions such as  $k > 1/t$  and  $\sqrt{kt} \lesssim 3$  at a short diffusion time. The above discussions do not hold in this case.

## EXPERIMENTAL

### Films

Cellophane films (#300, Tokyo Cellophane Sheet Co., Ltd.) were cut 5 cm wide and 60 cm long and scoured several times in boiling water for 2 hr. The thickness of a swollen film was measured by a thickness dial gauge (Ozaki Seisakusho) to be  $3.68 \times 10^{-3}$  cm. The cylindrical cellophane film roll was made by the usual method.<sup>16,17</sup>

### Reactive Dyes and Reagents

C.I. Reactive Orange 1 (Mikacion Brilliant Orange GS) and C.I. Reactive Red 1 (Mikacion Brilliant Red 2BS), manufactured and supplied by Nippon Kayaku Co., Ltd., were used; 8 g of the commercial samples were dissolved into 100 ml 0.1N NaOH. The solution was kept at 80°C for 2 hr and neutralized by acetic acid. The hydrolyzed dye was recrystallized six times by sodium acetate which was extracted with ethanol after drying. The absence of impurities and reactivity was confirmed by paper chromatography.<sup>18</sup> The purified hydrolyzed dyes thus prepared were used as the reference in molar concentration. The calibration curves of reactive dyes on cellophane were made by use of the purified dyes. The concentrations of the immobilized, active, and hydrolyzed species of these dyes were calculated from the curves on the assumption that the molar extinction

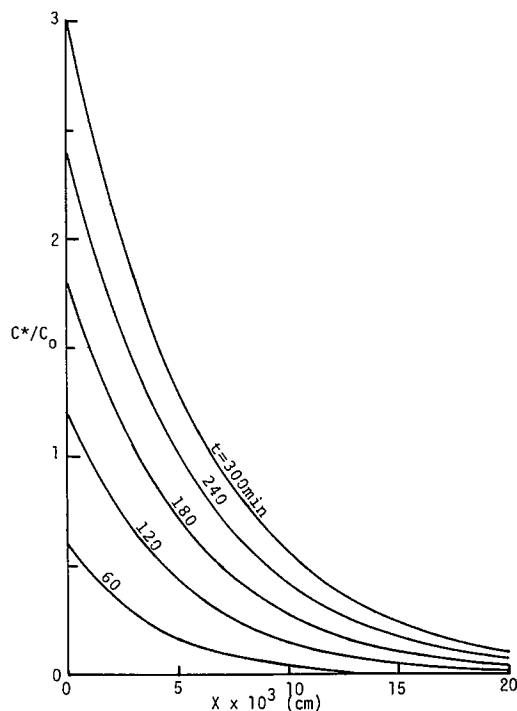


Fig. 4. Theoretical concentration profiles of immobilized species for various diffusion times ( $D = 5 \times 10^{-7} \text{ cm}^2/\text{min}$ ,  $k = 0.01 \text{ min}^{-1}$ ). Though the profiles near the surface gradually increase as time proceeds, the penetration distances do not change appreciably.

coefficients of the three kinds of species on substrate were the same. The other chemicals used were reagent grade.

### Measurement of Diffusion Coefficients

Since the simultaneous estimation of  $D$  and  $k$  from the concentration profiles of immobilized dyes was difficult, the determination of  $D$  was carried out by the use of purified hydrolyzed dyes prior to reactive dyeing. The diffusion coefficients were calculated from the diffusion profiles obtained by the method of cylindrical cellophane film roll.<sup>16,17</sup> In order to adjust the pH of the dyebath, Kolthoff's buffer solutions with  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{B}_4\text{O}_7$  from pH 6.8 to 9.2, with  $\text{Na}_2\text{B}_4\text{O}_7$  and  $\text{Na}_2\text{CO}_3$  from pH 9.2 to 11.0, and with  $\text{Na}_2\text{HPO}_4$  and  $\text{NaOH}$  at pH 12.0 were used, and  $\text{NaCl}$  was added to adjust the ionic strength of the dyebath.

### Reactive Dyeing

In order to keep the concentration of "active" species of dyes in the dyebath constant, a constant feed of both the stock solutions of reactive dye and buffer whose concentrations were twice those of the dyebath was carried out by a quantitative pump, and the same amount of solution as feed was overflowed (Fig. 5). They were mixed just prior to the injection into the dyebath. Each flux of the solutions fed was 1.0 l./hr. The quantities of hydrolyzed species in the

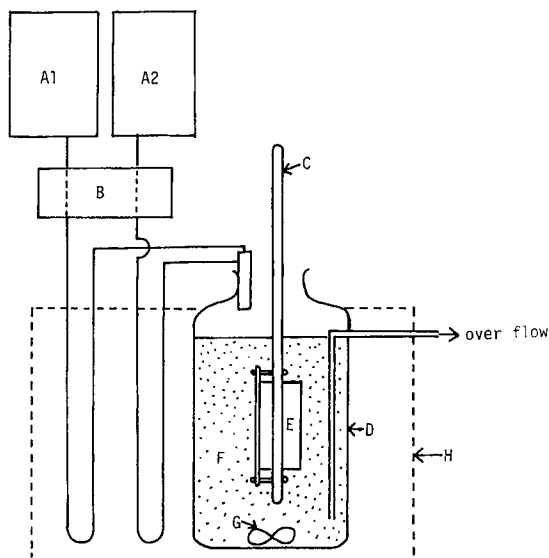


Fig. 5. Experimental apparatus for reactive dyeing: A<sub>1</sub>, A<sub>2</sub>, stock solutions of reactive dyes and buffer; B, quantitative pump; C, glass tubing; D, dyeing vessel; E, film roll; F, dyebath; G, stirrer; H, thermostat.

dyebath were confirmed to be constant by a pyridine–NaOH reagent during the diffusion experiments at all the pH values examined.<sup>18</sup>

Since the hydrolysis of active dyes proceeded considerably in the dyebath at pH 12, the diffusion experiment was carried out after the concentration of hydrolyzed species became constant. The stirring of dyebath was necessary to obtain a level dyeing especially at pH higher than 11. The same buffer solutions as in the dyeing with hydrolyzed dyes were used. The effect of electrolytes contained in the commercial dyes on the ionic strength was neglected, since the concentration of the electrolytes was smaller than that of the buffer solutions.

A cylindrical film roll was inserted into the dyebath for a prescribed time. After the diffusion, it was opened and the layers from the surface were cut in half. The film cut off was immediately scoured in boiling water for 20 min to remove the unreacted dyes with cellulose.

After drying, the optical densities of the respective layers of both the films were measured at the wavelength of maximum absorption of the dyes by a Shimadzu D-40S spectrophotometer. Those of scoured and unscoured films correspond to the concentration of immobilized and total dyes on the films. From the difference between them, the sum of active and hydrolyzed dyes was obtained. The concentration profiles of immobilized and unreacted dyes in the substrate were calculated by the use of calibration curves prepared as above.

### Calculation of Rate Constants and Diffusion Coefficients

The value of  $C_0$  was usually obtained by the extrapolation of the profiles of active species. When  $k$  was large,  $D$  was small, or  $t$  was short, only an approximate value of  $C_0$  was obtained from the experimental profile, since the immo-



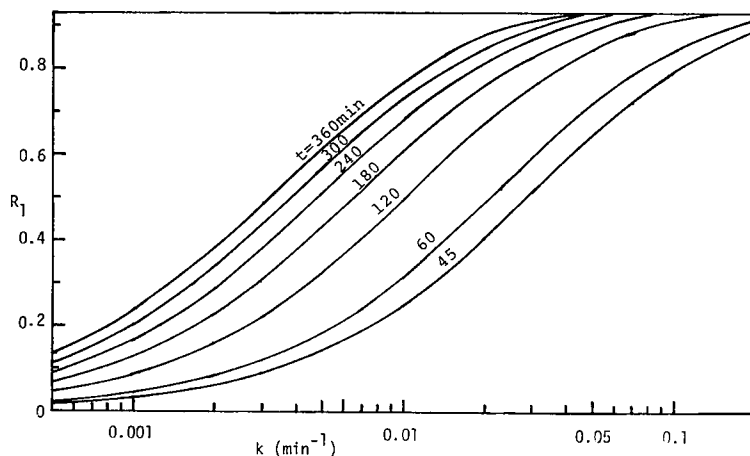


Fig. 6. Relation between  $R_1$  (the ratio of the total adsorption and that of immobilized species in the first layer) and  $k$  at the various diffusion times. Almost the same curves were obtained in the range  $\epsilon = (2-6) \times 10^{-3}$  cm and  $D = 10^{-7}-10^{-6}$  cm<sup>2</sup>/min.

bilized and active species did not penetrate into more than the second or third layers.

The ratios of the total adsorption and that of immobilized species in the first layer,  $R_1 = M_1^*/(M_1^* + M_1)$ , given by eqs. (7) and (8), were calculated for the various  $k$  and  $t$ , and are shown in Figure 6.  $R_1$  is approximately determined by the diffusion time for any values of  $D$  and  $\epsilon$  (the thickness of a film). However,  $R_i$  for  $i \geq 2$  was not the case. Thus, the value of  $k$  was estimated from the experimental value of  $R_1$  for the various diffusion times. By the use of  $D$ ,  $C_0$ , and  $k$  thus obtained, the calculations of theoretical profiles of both species given by eqs. (7) and (8) were carried out by a computer. The theoretical profiles were compared with the experimental ones. Then, the values of  $D$ ,  $k$ , or  $C_0$ , if necessary, were changed slightly, and the calculation and comparison were repeated to obtain the optimum values. Under a strongly alkaline condition, the calculation of the theoretical profiles of immobilized species given by eq. (8) was carried out because of the hydrolysis of active species. The value of  $D$  at first, then  $k$  and  $C_0$ , if necessary, were changed, and the calculation and comparison were repeated.

## RESULTS AND DISCUSSION

### Diffusion of Hydrolyzed Species

The diffusion coefficients of the hydrolyzed species in cellulose measured at 30°C from the dye bath of various pH values are shown in Figure 7. They were nearly constant at all the pH values examined and were confirmed to be Fickian. Those of C.I. Reactive Red 1 was much larger than those of Orange 1. No effect of the ionic strength in the diffusion coefficients of Red 1 was observed. It was also confirmed that the diffusion coefficient of active species of Red 1 at pH 6.8 was similar to that of hydrolyzed species.

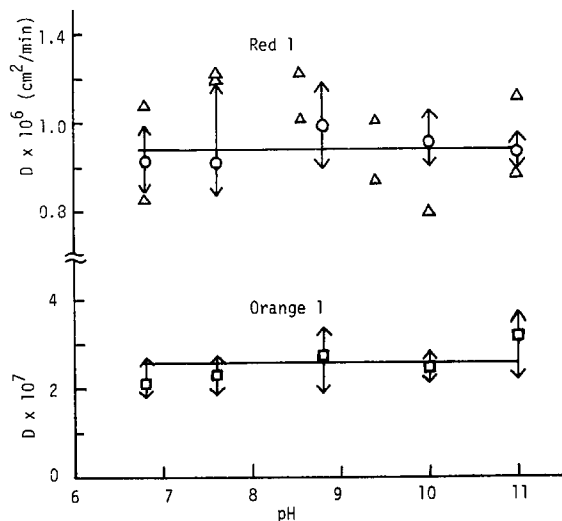


Fig. 7. Diffusion coefficients of the hydrolyzed species of C.I. Reactive Orange 1 ( $I = 0.15$  ( $\square$ ) mean value) and Red 1 ( $I = 0.15$  ( $\Delta$ ) and  $0.5$  ( $\circ$ ) mean value) at  $30^\circ\text{C}$ .

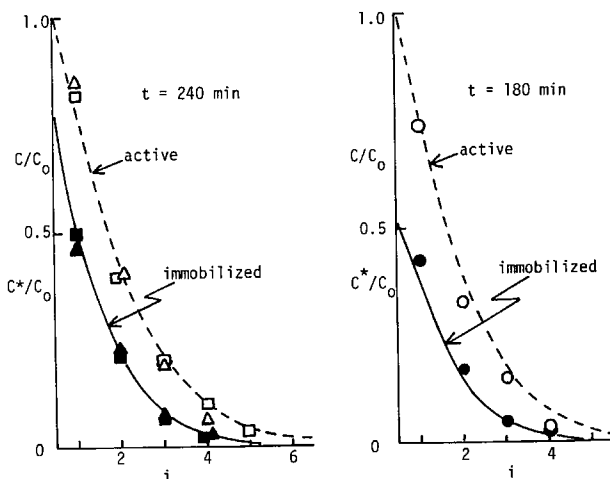


Fig. 8. Concentration profiles of active ( $\Delta$  and  $\square$  at 240 min, and  $\circ$  at 180 min) and immobilized species ( $\blacktriangle$  and  $\blacksquare$  at 240 min, and  $\bullet$  at 180 min) of C.I. Reactive Orange 1 at pH 8.8 ( $I = -0.15$ ) and  $30^\circ\text{C}$ . Dotted (active species) and solid lines (immobilized species) were described by eqs. (7) and (8), respectively ( $D = 1.7 \times 10^{-7} \text{ cm}^2/\text{min}$ ,  $k = 0.0032 \text{ min}^{-1}$ ). Results from two experiments under the same condition at  $t = 240 \text{ min}$  are shown.

### Concentration Profiles of Reactive Dyes in Substrate

The concentration profiles of the active, immobilized, and total species are shown in Figure 8. The surface concentration of active species,  $C_0$ , was obtained on extrapolating the profile of active species to the surface.  $M_i^*/C_0\epsilon$  and  $M_i/C_0\epsilon$  versus  $i$  are plotted in the figure in which the solid lines are the theoretical profiles given by the eqs. (7) and (8). The agreement between the experimental and theoretical curves was fairly good, as shown in the figure. Though  $C_0$  obtained

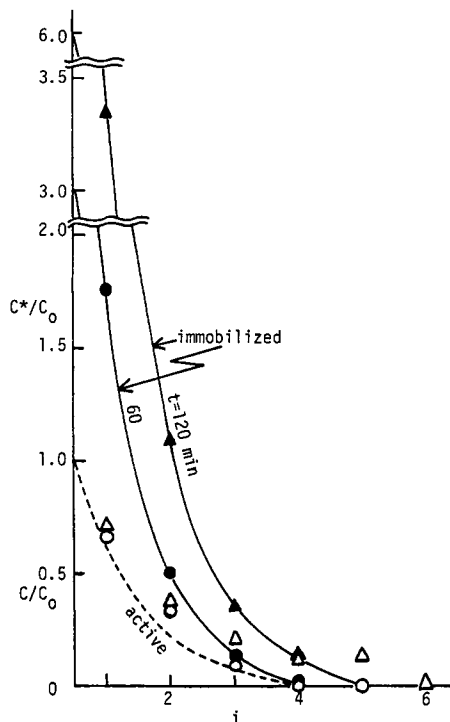


Fig. 9. Concentration profiles of active and immobilized species of C.I. Reactive Red 1 at pH 10 ( $l = 0.5$ ) and  $30^{\circ}\text{C}$ . Dotted (active species:  $\circ, \Delta$ ) and solid (immobilized species:  $\bullet, \blacktriangle$ ) lines were described by eqs. (7) and (8), respectively ( $D = 6.0 \times 10^{-7} \text{ cm}^2/\text{min}$ ,  $k = 0.05 \text{ min}^{-1}$ ).

from the experiments of various diffusion times showed some scatter, the reproducibility of  $k$  obtained from  $R_1$  was considerably good. According to Preston and Fern, since the ratio of the rate constants of dyes for cellulose and those for water is constant, some proportions of reactive dyes would become hydrolyzed besides the covalent binding with cellulose.<sup>4</sup> Below pH 8.8, however, it was observed that the contribution of hydrolyzed species was practically negligible and that the diffusion coefficients of active species obtained from the experimental profiles were identical with those of the hydrolyzed species.

Under weakly alkaline conditions, the quantity of immobilized species was more or less the same order as the adsorption of active ones in the present diffusion times, and the profiles of both species were identical with the ones described by the theoretical equations.

On the other hand, the concentration profiles of Red 1 at pH 10 and of Orange 1 at pH 12 are shown in Figures 9 and 10. Under such strongly alkaline conditions, the immobilized species penetrated into only the first or second layer near the surface, i.e., ring dyeing, and the species unreacted with substrate diffused deeply into the inner layers. In this case, the rate constant was also estimated from the surface concentration of immobilized species for the various diffusion times. The profile of immobilized species obtained experimentally was nearly identical with the theoretical one (solid line) given by eq. (8), and that of active species was not at all identical with the one (dotted line) given by eq. (7) (Figs. 9 and 10). Moreover, the diffusion coefficients of active species obtained from

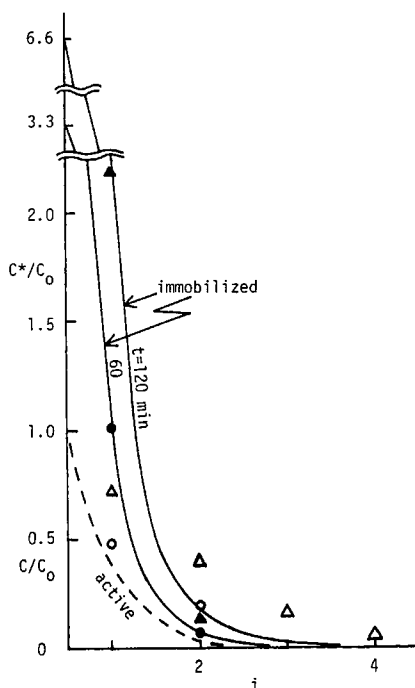


Fig. 10. Concentration profiles of the active and immobilized species of C.I. Reactive Orange 1 at pH 12 ( $l = 0.15$ ) and  $30^{\circ}\text{C}$ . Dotted (active species:  $\circ$ ,  $\Delta$ ) and solid (immobilized species:  $\bullet$ ,  $\blacktriangle$ ) lines were described by eqs. (7) and (8), respectively ( $D = 1.3 \times 10^{-7} \text{ cm}^2/\text{min}$ ,  $k = 0.055 \text{ min}^{-1}$ ).

the experimental profiles of immobilized species by the use of eq. (8) were smaller than those of the hydrolyzed species obtained above. An increase in the concentration of hydrolyzed species in comparison with that of lower pH examined by the pyridine-NaOH reagent was observed at the pH in spite of the constant feed of fresh solution of reactive dyes. Therefore, the hydrolyzed species would be contained in the concentration profile of unreacted species. At higher pH, there may remain also a possibility of hydrolysis of active and immobilized species in the substrate. In spite of these circumstances at higher pH, the value of  $k$  could be determined only by the use of the profiles of immobilized species.

From these results, it is concluded that the assumptions introduced into the calculations of  $D$  and  $k$  are practically reasonable. Since the presence of hydrolyzed species disturbs the estimation of  $D$  and  $k$  from the Danckwartz' eq. (4) and especially that from eqs. (7) or (3), the present method would be more useful than the former methods. The concentration profiles of immobilized species of reactive dyes in cellulose in the wide pH range can be described by the theoretical equations with chemical reaction derived in the present paper. Besides reactive dyeing, the equations which describe the concentration profiles of immobilized species in the substrate will also be useful in the polymer reactions, especially such as textile finishing.

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