Diffusion with Simultaneous Reaction of Reactive Dyes in Cellulose. II. Effect of Hydrolysis

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Synopsis

Theoretical equations that describe the concentration profiles of immobilized and active species for reactive dyes were derived from the diffusion equation accompanied by the reaction with cellulose and water in the substrate. The diffusion coefficient D and the rate constant of the reaction with cellulose, k_{cell}, and that with water in cellulose, k_w, were estimated by using the theoretical equations and the cylindrical film roll method. The theory predicted that the apparent diffusion coefficients decreased with the hydrolysis of active species in cellulose. Results from diffusion experiments with C.I. Reactive Yellow 4 and Orange 1 show that the ratio P of k_w to k_{cell} for Orange 1 increased with increase in pH to about pH 13 and that the P for Yellow 4 was smaller than unity. Using an alternative experiment to diffusion, P of Orange 1 was measured to be 1.0–1.5, and that of Yellow 4 was smaller than unity at pH 11.6 at 30°C. It was therefore concluded that the D of active species was constant to a highly alkaline region and that the decrease in the apparent diffusion coefficient of Orange 1 was mainly due to the hydrolysis of active species in cellulose.

INTRODUCTION

The main factors controlling the fixation ratio in the reactive dyeing of cellulose are: the substantivity for substrate, the rate of reaction with cellulose and water in both the dyebath and cellulose substrate, the temperature, the pH, and the concentrations of reactive dye and salt. Preston and Fern have reported that the rate of reaction with sorbitol as a model compound for cellulose and that with cellulose were about 40 times and a few times as large as that of hydrolysis, respectively.[1] Ingamells et al. examined the hydrolysis and alcoholysis of reactive dyes,[2] and others also substantiate that the reaction with cellulose was much faster than that with water in the substrate.[3–6]

In dyeing with reactive dyes, a large quantity of neutral salt is added in order to minimize the loss of dye through the decrease in fixation ratio resulting from the hydrolysis of active species in the dyebath. Thus, the effect of hydrolysis of active species in the substrate is negligible.

In the previous paper, the theoretical equations which describe the diffusion profiles of active and immobilized species for reactive dyes in the substrate were derived, and the diffusion and reaction of reactive dyes in cellulose were studied by the cylindrical film roll method.[7,8] In the theory, only the diffusion which accompanied the pseudofirst-order chemical reaction with cellulose was taken into consideration. Under weak alkaline conditions, the theoretical and experimental profiles of both the species were in agreement. Under highly alkaline conditions, the concentration profiles of immobolized species agreed with the theoretical profile of fixed species. However, the removed species did not agree with the theoretical profile of active species, because the removed species pen-

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etrated more deeply than the theoretical asymptote and the apparent diffusion coefficients of some reactive dyes were decreased with increase in pH. The diffusion coefficients D of hydrolyzed species were constant over the pH range examined. A theory that postulates the hydrolysis of active species in cellulose is developed and verified experimentally in this study. Equations which describe the diffusion profiles of immobilized and active species accompanied by the simultaneous reaction with cellulose and water in the substrate are derived. A method to estimate the D and the rate of reaction with cellulose and water and an alternative method to estimate the rate of hydrolysis of reactive dyes in cellulose are presented herein.

THEORETICAL

When reactive dyes react independently with cellulose and water in cellulose into which they diffuse, the former dyes are immobilized and the latter ones are hydrolyzed and lose their reactivity. If both reactions were first order or pseudofirst order with rate constants of k_{cell} (min^{-1}) and k_w (min^{-1}), respectively, the diffusion equation in one-dimensional semiinfinite media accompanied by the first-order reaction is

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - (k_{cell} + k_w)C \tag{1}$$

where C (moles/kg) is the concentration of active species, D (cm^2/min) is the diffusion coefficient of active species, t (min) is the time, and x (cm) is the distance, provided that D is constant. This has been reported by Rys and Zollinger.[9]

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

$$\begin{aligned} C &= 0 \qquad x > 0 \qquad t = 0 \\ C &= C_0 \qquad x = 0 \qquad t > 0 \end{aligned} \tag{2}$$

where C_0 (moles/kg) is the surface concentration of active species dyed from the infinite dyebath. When the substitution of $k_{cell} + k_w$ for k is made, the solution of eq. (1) is[7,10]

$$\frac{C}{C_0} = \frac{1}{2}\exp\left(-x\sqrt{\frac{k_{cell} + k_w}{D}}\right)\operatorname{erfc}\left\{\frac{x}{2\sqrt{Dt}} - \sqrt{(k_{cell} + k_w)t}\right\} + \frac{1}{2}\exp\left(x\sqrt{\frac{k_{cell} + k_w}{D}}\right)\operatorname{erfc}\left\{\frac{x}{2\sqrt{Dt}} + \sqrt{(k_{cell} + k_w)t}\right\} \tag{3}$$

where

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

The concentration profile of the fixed species immobilized by the reaction with cellulose is calculated as follows[7]:

$$\frac{C^*}{C_0} = \int_0^t k_{cell} C\, dt = \frac{1}{2}\left\{k_{cell}t - \frac{x}{2}\sqrt{\frac{k_{cell}}{(1+P)D}}\right\}\exp\left\{-x\sqrt{\frac{(1+P)k_{cell}}{D}}\right\}$$

$$\times \operatorname{erfc}\left\{\frac{x}{2\sqrt{Dt}} - \sqrt{(1+P)k_{cell}t}\right\} + \frac{1}{2}\left\{k_{cell}t + \frac{x}{2}\sqrt{\frac{k_{cell}}{(1+P)D}}\right\}$$
$$\times \exp\left\{x\sqrt{\frac{(1+P)k_{cell}}{D}}\right\} \operatorname{erfc}\left\{\frac{x}{2\sqrt{Dt}} + \sqrt{(1+P)k_{cell}t}\right\} \quad (5)$$

where $P = k_w/k_{cell}$ and C^* (moles/kg) is the concentration of the fixed species.

In order to use the cylindrical film roll method, it is convenient to transform the concentration of the active and fixed species into the mean ones in each layer. The mean concentrations of active and fixed species, $\overline{C}_i$ and $\overline{C}_i{}^*$ (moles/kg), in the ith layer are given by eqs. (6) and (7), respectively[7,11]:

$$\frac{\overline{C}_i}{C_0} = \frac{1}{\epsilon}\int_{(i-1)\epsilon}^{i\epsilon} C\,dx$$
$$= -\frac{1}{2\epsilon}\sqrt{\frac{D}{(1+P)k_{cell}}}\left[\exp\left\{-x\sqrt{\frac{(1+P)k_{cell}}{D}}\right\}\right.$$
$$\times \operatorname{erfc}\left\{\frac{x}{2\sqrt{Dt}} - \sqrt{(1+P)k_{cell}t}\right\}$$
$$\left. - \exp\left\{x\sqrt{\frac{(1+P)k_{cell}}{D}}\right\} \operatorname{erfc}\left\{\frac{x}{2\sqrt{Dt}} + \sqrt{(1+P)k_{cell}t}\right\}\right]_{(i-1)\epsilon}^{i\epsilon} \quad (6)$$

$$\frac{\overline{C}_i^*}{C_0} = \frac{1}{\epsilon}\int_{(i-1)\epsilon}^{i\epsilon} C^*\,dx$$
$$= \frac{1}{2\epsilon}\left[\left\{\frac{x}{2(1+P)} - \sqrt{\frac{D}{(1+P)k_{cell}}}\left(k_{cell}t - \frac{1}{2(1+P)}\right)\right\}\exp\left\{-x\sqrt{\frac{(1+P)k_{cell}}{D}}\right\}\right.$$
$$\times \operatorname{erfc}\left\{\frac{x}{2\sqrt{Dt}} - \sqrt{(1+P)k_{cell}t}\right\} + \left\{\frac{x}{2(1+P)}\right.$$
$$+ \sqrt{\frac{D}{(1+P)k_{cell}}}\left(k_{cell}t - \frac{1}{2(1+P)}\right)\exp\left\{x\sqrt{\frac{(1+P)k_{cell}}{D}}\right\}\operatorname{erfc}\left\{\frac{x}{2\sqrt{Dt}}\right.$$
$$\left.\left.\left. + \sqrt{(1+P)k_{cell}t}\right\} - \frac{2\sqrt{Dt}}{\sqrt{\pi}(1+P)}\exp\left\{-\frac{x^2}{4Dt} - (1+P)k_{cell}t\right\}\right]_{(i-1)\epsilon}^{i\epsilon} \quad (7)$$

where ϵ (cm) is the thickness of a layer and i is the number of layers from the surface.

The total amount of fixed dye in time t, M_t^* (moles), is calculated from eq. (7)[7]:

$$M_t^* = \int_0^\infty C\,dx$$
$$= C_0 k_{cell}\sqrt{\frac{D}{(1+P)k_{cell}}}\left[\left\{t - \frac{1}{2(1+P)k_{cell}}\right\}\operatorname{erf}\sqrt{(1+P)k_{cell}t}\right.$$
$$\left. + \sqrt{\frac{D}{\pi(1+P)k_{cell}}}\exp\{-(1+P)k_{cell}t\}\right] \quad (8)$$

As the total amount of all the species, M_t' (moles), adsorbed from the surface in time t is obtained by eq. (9):

$$M_t' = \int_0^t -D\left(\frac{\partial C}{\partial x}\right)_{x=0} dt \quad (9)$$

The ratio Q, defined by M_t^*/M_t', is given by eq. (10):

$$Q = \frac{1}{1+P}\left[1 - \frac{1 - \operatorname{erf}\sqrt{(1+P)k_{cell}t}}{\left\{(1+P)k_{cell}t + \frac{1}{2}\right\}\operatorname{erf}\sqrt{(1+P)k_{cell}t} + \sqrt{\frac{(1+P)k_{cell}t}{\pi}}\exp\{-(1+P)k_{cell}t\}}\right] \tag{10}$$

When the reaction time elaspses, the ratio becomes

$$\lim_{t\to\infty} Q = \frac{1}{1+P} \tag{11}$$

The Q in eq. (10) is dependent upon the three parameters k_{cell}, P, and t, but is independent of D. The diffusion coefficient of reactive dyes decides the concentration distribution in the substrate but has no relation to the fixation ratio.

On the other hand, eqs. (3) and (5) have the asymptotes described by eqs. (12) and (13), respectively[7]:

$$\frac{C}{C_0} = \exp\left(-x\sqrt{\frac{(1+P)k_{cell}}{D}}\right) \tag{12}$$

$$\frac{C^*}{C_0} = k_{cell}t\exp\left(-x\sqrt{\frac{(1+P)k_{cell}}{D}}\right) \tag{13}$$

When $\sqrt{(1+P)k_{cell}} \geq 3$, eqs. (12) and (13) can be used to describe the diffusion profiles of active and immobilized species within the experimental error of 5%. If $D/(1+P)$ is substituted by the apparent diffusion coefficient D' in eqs. (12) and (13), these asymptotes equal those of the previous paper in which no hydrolysis of active species in cellulose has been considered.[7] The profiles described by these asymptotes clearly show that the larger the rate of hydrolysis of active species in cellulose, the smaller the penetration of reactive dyes into substrate.

Some concentration profiles of the active and fixed species described by eqs. (3) and (5) are shown in Figure 1 for the various P values. Though no condition for the application of eq. (13) is satisfied, the profiles show shallower penetration as P becomes larger. This behavior is similar to that where the apparent diffusion coefficients become smaller with an increase in pH when $P = 0$ (cf. ref. 8, Fig. 4). The larger the k_{cell}, the more profound is the effect of P on the profiles of immobilized species C^* irrespective of the value of P. The larger the values of D and t, the lower the apparent diffusion coefficients. For example, in the case of $k_{cell} = 0.02\ \text{min}^{-1}$, $t = 60$ min, and $D = 10^{-7}\ \text{cm}^2/\text{min}$ as well as in the case of $k_{cell} = 0.02\ \text{min}^{-1}$, $t = 60$ min, and $D = 10^{-6}\ \text{cm}^2/\text{min}$, the lowering effect of D appears distinctly at $P = 0.5$. When $k_{cell} = 0.1\ \text{min}^{-1}$ and $D = 10^{-7}$–$10^{-6}\ \text{cm}^2/\text{min}$, the lowering effect is observed at $P = 0.5$ and at $t = 30$ min. As expected, Figure 2 shows that the larger the P, the smaller the Q. Because all the

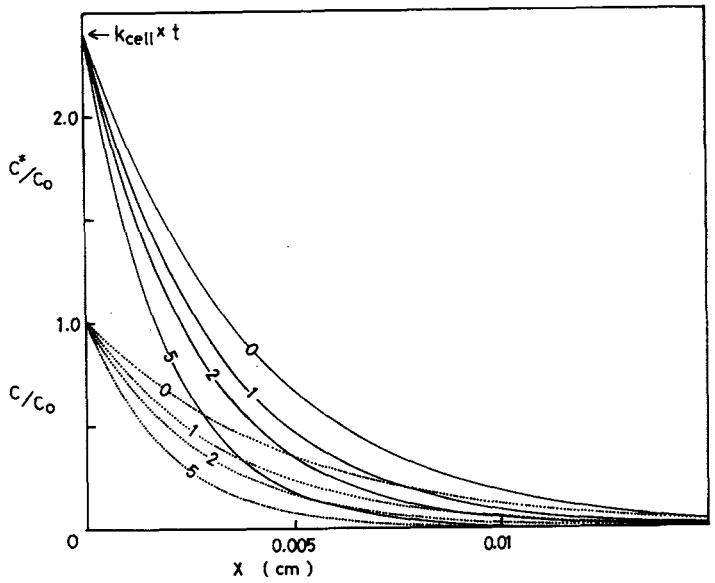

Fig. 1. Theoretical concentration profiles of active (dotted lines) and fixed species (solid lines) described by eqs. (3) and (5) for various P values shown on the lines ($D = 2.3 \times 10^{-7}$ cm^2/min, $k_{cell} = 0.01$ min^{-1}, $t = 240$ min, $P = 0 \sim 5$).

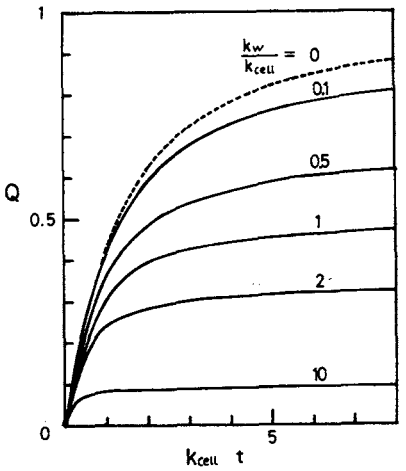

Fig. 2. Relations between fixation ratio Q and $k_{cell}t$ described by eq. (10).

active species do not penetrate into the substrate from the dyebath and hydrolysis occurs simultaneously in the dyebath, the fixation ratio of reactive dyes in practical dyeing must be smaller than Q given by eq. (10).

EXPERIMENTAL

In the estimation of C_0, D, k_{cell}, and P using a computer and eqs. (6) and (7) from the diffusion profiles of immobilized and removed species in cellophane, the D of active species was assumed to be constant over the pH range examined.

The D of hydrolyzed species was constant within the pH range. The values for P were at first estimated from the relation that the apparent diffusion coefficients D' of active species at highly alkaline pH were similar to $D/(1 + P)$. Final values for P were determined by curve fitting between the experimental and theoretical profiles with a computer. The values of k_{cell} and C_0 obtained previously[8] were seldom modified in the present calculations.

RESULTS AND DISCUSSION

Diffusion of Reactive Dyes

If the effects of pH on the diffusion coefficients D of active and hydrolyzed species were similar to the results by Sumner and Taylor,[12] the D for active species for C.I. Reactive Orange 1 would be constant from pH 6.8 to 12. The D for hydrolyzed species is also constant in the same pH region as shown in the previous paper,[8] where the value of D for the hydrolyzed species of Orange 1 at 30°C was estimated to be 2.3×10^{-7} cm^2/min.

When the P was regarded to be minimum, the three parameters D, k_{cell}, and C_0 could be estimated.[7] If the D for active species was assumed to be constant over the pH range examined, and as the values for k_{cell} and C_0 could be estimated, the value for P could be obtained by computer fitting the theoretical profile of fixed species described by eq. (7) for the values of D, k_{cell}, and C_0.

Under weakly alkaline conditions, the experimental profiles of immobilized and removed species agreed with the theoretical within experimental error (Fig. 3). These profiles were also similar to those described by eqs. (6) and (7) for $D = 1.7 \times 10^{-7}$ cm^2/min, $k_{ell} = 3.0 \times 10^{-3}$ min^{-1}, and $P = 0$. There may be no other direct method for measuring the k_{cell} and D of active species under alkaline conditions.

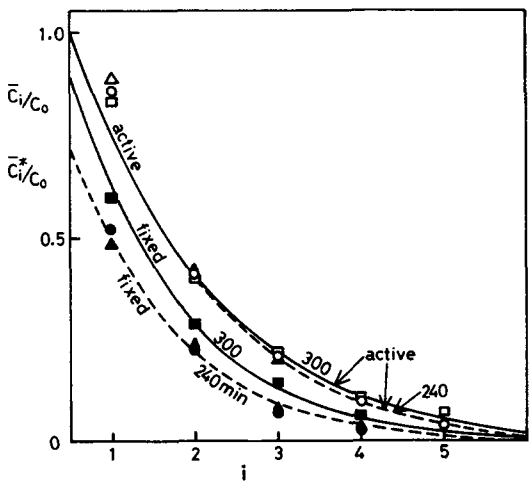

Fig. 3. Concentration profiles of active (○ and △ at 240 min, and □ at 300 min) and fixed species (● and ▲ at 240 min, and ■ at 300 min) of C.I. Reactive Orange 1 at pH 8.8, 30°C, and $I = 0.15$. Lines were described by eqs. (6) and (7), respectively ($D = 2.3 \times 10^{-7}$ cm^2/min, $k_{cell} = 0.003$ min^{-1}, $P = 1.0$). Results from two experiments under the same condition at $t = 240$ min are shown: (- - -) 240 min; (——) 300 min.

Under highly alkaline conditions (Fig. 4), the experimental profile of immobilized species for Orange 1 agreed with the theoretical (lines 1 and 2). The experimental profile for removed species, however, did not agree with the theoretical (line 3). The theoretical profiles for fixed species calculated with two sets of D and P ($D = 2.3 \times 10^{-7}$ cm^2/min, $P = 2.3$; $D = 1.0 \times 10^{-7}$ cm^2/min, $P = 0$) and with the same k_{cell} and C_0 yielded the same curve as that for the experimental profile for immobilized species.

The removed species penetrated more deeply into the substrate than the theoretical profile of active species and, moreover, with the passage of diffusion time (Fig. 4). The dotted lines (lines 4 and 5) in Figure 4 show the difference between the experimental concentration of removed species and the theoretical concentration for the active species. Theoretically, the active species must not diffuse into the substrate more deeply than the immobilized species.[7] The profiles for removed species describe the concentration distribution of reactive dyes which are hydrolyzed during diffusion in cellulose. Remaining mobile, they either diffuse toward the surface, where they are almost desorbed into the dyebath, or diffuse into the inner substrate. The profiles for the removed species are composed of the sum of active and hydrolyzed species (Fig. 4).

The agreement between the experimental and theoretical profiles for immoblized species for different diffusion times was fairly good and the parameters P and k_{cell} obtained were independent of time, over the pH range examined (Figs. 3 and 4).

When P was zero, the D' for active species decreased with increase in pH.[8] This can now be explained quantitatively by introducing the hydrolysis in cellulose concept. The value for P being larger than unity was confirmed by experiments other than diffusion.

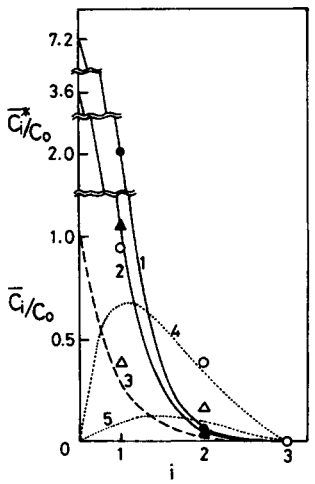

Fig. 4. Concentration profiles of active (removed species △ at 60 min and ○ at 120 min) and fixed species (▲ at 60 min and ● at 120 min) of C.I. Reactive Orange 1 at pH 10.6, 30°C, and $I = 0.15$. Lines 1 and 2 were described by eq. (7) ($D = 2.3 \times 10^{-7}$ cm^2/min, $k_{cell} = 0.06$ min^{-1}, $P = 2.3$, and $t = 60$ or 120 min), and line 3 by eq. (6) with the same parameters (see text).

Hydrolysis in Cellulose

The pH dependence of P for Orange 1 is shown in Figure 5. The values of P for Orange 1 increased with increase in pH and reached pH of about 13. There were few differences between the theoretical profiles for immobilized and active species for the P between 0 and 1 within the pH range 7.6 to 8.4, because the values of k_{cell} were small and t was relatively short. The values for P, therefore, could not be precisely estimated in this experiment. As the D for active species for Yellow 4 was almost constant over the pH range of 6.8 to 12.0, the value for P equals zero. As the removed species of Yellow 4 penetrated to the second layer from the surface due to the small D and large k_{cell}, the reliability for agreement between the experimental and theoretical profiles was inferior for Orange 1.

When the values of P for Yellow 4 above pH 10 were estimated from the immobilized profiles described by eq. (7) for $D = 2.0 \times 10^{-7}$ cm^2/min in the same manner as Orange 1, they were definitely smaller than unity. The experimental profiles for removed species did not agree with the theoretical ones for the active species. Thus, the P for Yellow 4 at highly alkaline pH was smaller than the values for those of Orange 1. The values were between 0 and 1.

The effect of pH on k_{cell} on the rate of hydrolysis measured by Ingamells et al.[2,8] for Yellow 4 and Orange 1 were very similar; the slopes of log k_{cell} to pH were about unity. Since the ionization of cellulose under alkaline conditions is linear below pH 11,[13] the different effects of pH between reactive dyes may be due to the structure and properties of the dyes.

Alternative Estimation of P

The values for P could be obtained *if* reactive dyes adsorbed uniformly in cellulose remained there until reactions with cellulose and water were completed. In order to estimate the value of P by a method other than diffusion, an experiment to satisfy this condition was carried out.

A cellophane film was dyed uniformly by the active species of reactive dye from the neutral dyebath containing sodium sulfate of the same ionic strength. The film was rolled on a glass tubing in several layers. Another film, which was scoured by distilled water and immersed in the same buffer solution, was rolled in three layers on the film roll. The film roll was immediately immersed in a buffer solution at 30°C until the reactive dyes reacted with cellulose and water for a sufficient length of time. After the reaction, it was opened and the layers were cut in half. In the same manner as in the diffusion experiments, unscoured

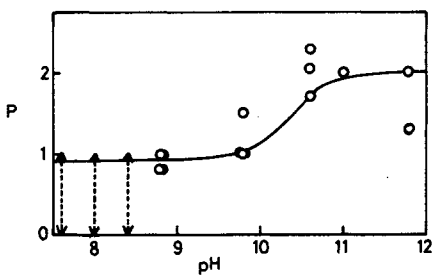

Fig. 5. The pH dependence of P values for C.I. Reactive Orange 1 obtained from diffusion experiments (30°C, $I = 0.15$).

and scoured films were spectrophotometrically analyzed. The results are shown in Figure 6 and Table I. Most of the adsorbed dyes would react in cellophane in the initial state if: (1) the equilibration of hydroxyl ions in the layers of cellophane was far beyond the diffusion of reactive dyes, and (2) the reactions of the active species in cellulose were sufficiently fast.

It was confirmed experimentally that these situations were satisfied only at highly alkaline pH in the case of Yellow 4 and Orange 1 (Fig. 6). The inner layers adsorbed active species, and the total concentration of reactive dyes remained constant, i.e., no diffusion of reactive dyes occurred. Moreover, the reaction with cellulose and water in cellulose may be regarded as complete.

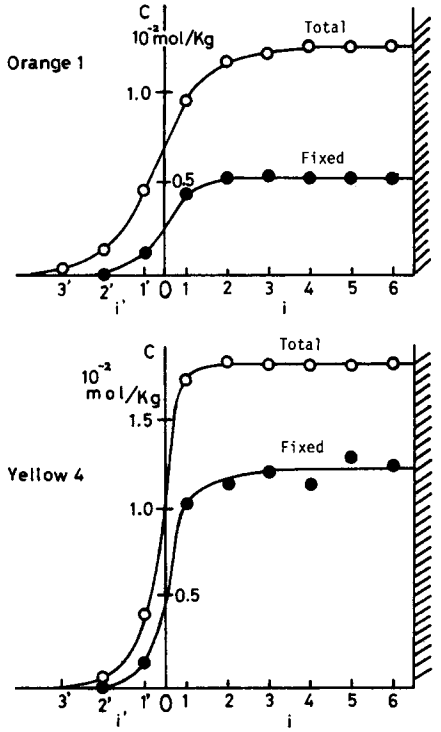

Fig. 6. Concentration profiles of C.I. Reactive Orange 1 and Yellow 4 after the reaction with cellulose and water in substrate at pH 11.6, 30°C, $I = 0.15$, and for 90 min ($Q_1 = 0.424$ for Orange 1 and 0.648 for Yellow 4).

TABLE I
Values of P ($=k_w/k_{cell}$) Obtained from the Fixation Ratios Q_1 at 30°

C.I. Reactive dye	pH	Ionic strength I	P	Film used
Yellow 4	11.0	0.15	0.51	original
	11.6	0.15	0.54	original
	11.6	0.15	0.75	dyed with Red 1 (0.024 mole/kg)
Orange 1	11.6	0.15	1.36	original
	12.6	0.15	1.51	original
	12.6	1.0	1.07	original
	12.6	0.15	1.25	dyed with Yellow 4 (0.013 mole/kg)
	12.6	0.15	1.31	dyed with Blue 4 (0.034 mole/kg)

If the active species remained in the initial state, the rate of reaction with cellulose and water is given by eq. (14),

$$\frac{dC}{dt} = -(k_{\text{cell}} + k_w)C \tag{14}$$

where the notations are the same as before, provided that the reactions are first order or pseudofirst order. As the initial condition at $t = 0$ is $C = C_1$, where C_1 (moles/kg) is the initial concentration of active species in cellophane, the solution of eq. (14) is

$$C = C_1 \exp\{-(k_{\text{cell}} + k_w)t\} \tag{15}$$

The concentration C^*_{cell} (moles/kg) of fixed species having reacted with cellulose during reaction time t is given by

$$C^*_{\text{cell}} = \int_0^t k_{\text{cell}} C \, dt = \frac{C_1}{1+P}\{1 - e^{-(1+P)k_{\text{cell}}t}\} \tag{16}$$

Then, the fixation ratio Q_1 is given by eq. (17) and has a limiting value of eq. (18):

$$Q_1 = \frac{C^*_{\text{cell}}}{C_1} = \frac{1}{1+P}\{1 - e^{-(1+P)k_{\text{cell}}t}\} \tag{17}$$

$$\fallingdotseq \frac{1}{1+P} \qquad [(1+P)k_{\text{cell}}t \gg 1] \tag{18}$$

The Q_1 values can be estimated from the ratios between the concentrations of scoured and unscoured films in Figure 6. The P values for Yellow 4 and Orange 1 are calculated to be 0.54 and 1.36, respectively, at pH 11.6 and 30°C.

The values of P for Orange 1 above pH 11.6 were nearly constant (Table I). Below pH 11, they could not be obtained, since the diffusion of active species occurred until the reactions with cellulose and water were completed. A long time was required because of the small k_{cell} and k_w.

The value for P for Orange 1 decreased with increase in ionic strength. Some dichlorotriazinyl reactive dyes showed the same behavior as Orange 1.[14] On the other hand, a somewhat larger value of P for Yellow 4 was obtained when a deeply dyed film was used.

In any event, the approximate values for P above pH 11 may be regarded to be 0.5 for Yellow 4 and 1.3–1.5 for Orange 1, respectively. The P values of Orange 1 were slightly smaller than those which resulted from the diffusion method. The values of P obtained by both experimental methods in the present study were larger than those reported previously.[1-6] They depended upon the structure and properties of reactive dyes, although the k_{cell} and the rate of hydrolysis had the same pH dependence.[8]

In dyeing and printing with reactive dyes, the fixation ratio demonstrated a decreasing tendency after an increasing one with increase in the alkaline concentration. This phenomenon is due to the increase in hydrolysis of active species in the dyebath or in the printing paste. It is concluded that there are other factors needed to decrease the fixation ratio of reactive dyes.

SUMMARY

1. The rates of hydrolysis of reactive dyes in cellulose are larger than those in bulk water. In particular, the P of C.I. Reactive Orange 1 becomes larger than unity in the highly alkaline region.

2. The apparent diffusion coefficients of active species for some reactive dyes, for example, Orange 1, decrease with increase in pH, although the D values of hydrolyzed species are constant over the pH range.

3. The decrease in the apparent diffusion coefficient of Orange 1 is due mainly to the increase in the hydrolysis of active species in cellulose, i.e., an increase in P with increase in pH.

4. The diffusion with simultaneous reactions in cellulose for Orange 1 can be described by the diffusion equation (1) where the hydrolysis in cellulose is taken into consideration. This effect explains the behavior of dichlorotriazinyl reactive dyes.[14]

5. The apparent diffusion coefficients for active species for some reactive dyes, for example C.I. Reactive Yellow 4, are constant over the pH range examined. The diffusion behavior of the reactive dyes of this type in cellulose can be described by the diffusion equation (1) where P is practically regarded as null. (Some vinylsulfonyl reactive dyes demonstrated this behavior.[15])

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