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The Reactions of Dichlorotriazinyl Reactive Dyes with Cellulose and Simultaneous Diffusion in Cellulose

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The diffusion coefficients and rate constants of the reactions of C. I. Reactive Yellow 4, Orange 1, and Red 1 were measured at 30 °C by means of a cylindrical cellophane film roll. The diffusion coefficients of the three hydrolyzed dyes were nearly constant at all the pH values examined. The apparent diffusion coefficients of all the active species of Orange 1 and Red 1 except Yellow 4 were gradually decreased with an increase in the pH of the dyebath; this decrease was due to the hydrolysis of the active species in the cellulose substrate. The rate constants of the reactions with cellulose were of a pseudo-first-order; *i.e.*, the second-order rate constants of reactions with cellulose were constant up to a certain pH, and thereafter they decreased with an increase in the pH of the dyebath. The pH dependence of the reactivity with cellulose was similar to that of the hydrolysis reported previously. The concentration profiles of the removed and immobilized species in cellulose dyed from a weakly alkaline dyebath agreed with the theoretical profiles of active and reacted species respectively. From a highly alkaline dyebath, those of the immobilized species agreed with the theoretical profiles of reacted species, while those of the removed ones did not agree with theoretical profiles of active species because of hydrolysis.

Only a few works on the reaction of reactive dyes with cellulose have been reported,[1–3] though there have been many studies of the mechanisms on the reactive dyeing.[4,5] The reactivities of mono- and dichlorotriazinyl reactive dyes have been examined through reactions with water[6–15] and with alcohols as a model for cellulose.[1,7,10–13] The rate of the reaction of reactive dyes with cellulose must be derived from the theory of the diffusion with a simultaneous reaction in solid cellulose. Preston and Fern have obtained the diffusion coefficients and the rate constants of reactions with cellulose from Danckwart's equation by measuring the total amount of reactive dye on the substrate.[1]

In a previous paper, the theoretical equations which described the concentration profile of the immobilized species of reactive dyes in the substrate were derived from the diffusion equation with a chemical reaction of the first-order or pseudo-first-order.[3] A new method by which the reaction-rate constants of dye with cellulose could be obtained from the concentration profiles of reactive dyes was presented, though the basic diffusion equation used was the same as that of Preston and Fern. The profiles were measured from the cylindrical-film-roll method, where, after the diffusion, the immobilized profile was experimentally obtained by removing the active and hydrolyzed species by scouring; it corresponded to the theoretical distribution of reactive dyes fixed by the chemical reaction with cellulose.

In the present paper, the reaction-rate constants of dichlorotriazinyl reactive dyes will be obtained from the concentration profiles of the immobilized species by using the same method as in the previous paper[3] and will be discussed in comparison with those of hydrolysis and alcoholysis.[6–15] The diffusion coefficients of active and hydrolyzed species will also be measured.

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 h. The thickness of a swollen film was measured to be 3.68×10^{-3} cm. The cylindrical film roll was made by the usual method.

Reactive Dyes and Reactive Dyeing. Three reactve dyes manufactured and supplied by the Nippon Kayaku Co., Ltd., were used, and the dyeing was performed at 30 °C under the dyebath conditions shown in Table 1. The reagents for the buffer solutions used in order to adjust the pH of the dyebath were KH_2PO_4 and $Na_2B_4O_7$ from pH 6.8 to 9.0, $Na_2B_4O_7$ and Na_2CO_3 from 9.2 to 11.0, and Na_2HPO_4 and NaOH at pH 12. NaCl was added to adjust the ionic strength of the dyebath.

In order to exclude the influence of the hydrolyzed species in the dyebath, a constant feed of the stock solutions of both the reactive dye and the buffer was carried out by the use of a quantitative pump, and the same amount of solutions used as feed was allowed to overflow. A cylindrical cellophane roll was dipped into the dyebath for a prescribed time. After the dyeing, it was immediately opened and the layers from the surface were cut off in halves. One film cut off was promptly scoured in boiling water for 20 min to remove the unreacted dye with cellulose and was dried after scouring. The other one was also dried, but without scouring.

Table 1. Dyeing conditions

C. I. Reactive	Mikacion dyes	Ionic strength	Concentration of dyebath (mol/dm^3)	Concentration of dyebath (g/dm^3)	Dyeing time (h)
Yellow 4	Yellow RS	0.15	1.93×10^{-4}	0.15	1—12
		0.15	3.86×10^{-4}	0.30	
Orange 1	Brilliant Orange GS	0.15	5.36×10^{-4}	0.60	1— 6
Red 1	Brilliant Red 2BS	0.15	6.45×10^{-4}	1.0	1— 4
		0.50	6.45×10^{-4}	1.0	

Dyeing with Hydrolyzed Dyes at Various pHs and with Reactive Dyes at pH 6.8. As the reactions with cellulose were not observed, the diffusion coefficients of the reactive dye at pH 6.8 and those of the hydrolyzed one at various pHs were measured by the Sekido-Matsui method using a cylindrical cellophane film roll, as the concentration profiles in this case were Fickian.[16] The concentration profiles obtained in these experiments or the dyes adsorbed could be completely removed by the scouring of the films dyed with the hydrolyzed species and the active ones at pH 6.8. A purified sample of the hydrolyzed species was prepared by the hydrolysis of the reactive dyes and by salting-out with sodium acetate.[3]

Concentration Profiles of Immobilized and Removed Dyes and Determination of Reaction-Rate Constants, k. The concentrations of the dyes in the films were obtained by measuring the optical densities at the wavelength of the maximum absorption of the dye by means of a Shimadzu 40S spectrophotometer. The calibration curves of the reactive dyes in the film were made with the hydrolyzed and purified dye as the reference in molar concentration. The concentration profile of the immobilized dyes was obtained from the scoured film after dyeing, and that of the removed dyes, from the difference between the concentrations of the scoured and unscoured films at each layer. The former corresponds to the concentration of reactive dye reacted with cellulose, and the latter, theoretically to the active species not yet reacted with cellulose if there were no or little reaction with water in cellulose. The dyes reacted with cellulose were not removed, as was confirmed by no coloration of the renewed scouring solution and by no hydrolysis of the dye-fiber bond under all the dyeing conditions.

The reaction rate-constant, k, was approximately determined from the relation between k and the ratio of the fixed dye to the total dye in the first layer (*cf.* Ref. 3, Fig. 6). The surface concentration, C_0, could be obtained by the extrapolation of the profile of the removed dye. The diffusion coefficients, D, k, and C_0, obtained above were modified so as to fit the experimental profile to the theoretical one by means of a trial-and-error method with a computer. Under highly alkaline conditions, they were obtained from the fitting of the experimental profile for the immobilized species to the theoretical one. In order to avoid the contrary modification of C_0 and obtain a highly reliable value of C_0, several experiments were carried out for different dyeing times under certain dyebath conditions. The most satisfactory values of C_0, k, and D especially were evaluated from the experimental profiles for different dyeing times.

Results and Discussion

Diffusion of Reactive Dyes. Some experimental profiles of the immobilized and removed species in cellulose are shown in Figs. 1—3. As has been mentioned previously, the concentration profiles of immobilized and active species for reactive dyes in cellulose could be described by theoretical equations derived from the diffusion equation with a chemical reaction of a pseudo-first-order:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - kC, \tag{1}$$

where C(mol/kg) was the concentration of active species, t(min) was the time, x(cm) was the distance, and k (min^{-1}) was the pseudo-first-order rate constant of the reaction with cellulose, provided that the diffusion coefficient, D(cm^2/min), of the active species was constant. This equation was solved under the conditions of an infinite dyebath, *i.e.*, a constant surface concentration, C_0.[3] The theoretical profiles of the fixed and active species are also shown in the figures.

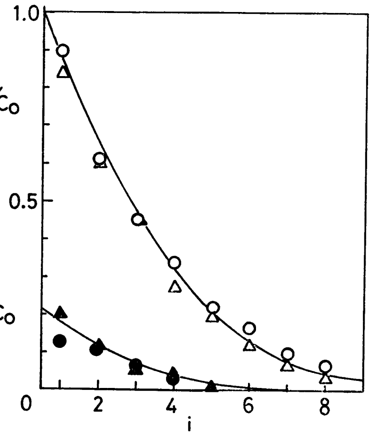

Fig. 1. Concentration profiles of the active (○, △) and immobilized species (●, ▲) of C. I. Reactive Red 1 at pH 7.6 (I=0.5), 30 °C and for 2 h. Results from two experiments under the same condition are shown. The lines in figure are the theoretical ones for $D=8.2\times10^{-7}$ cm^2/min and $k=2.0\times10^{-3}$ min^{-1}.

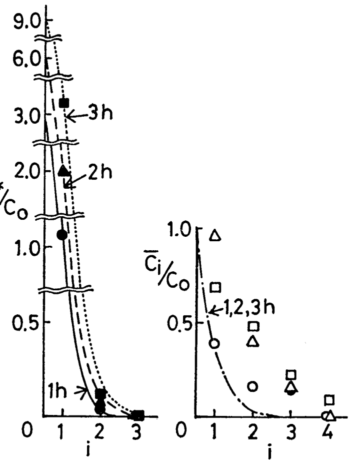

Fig. 2. Concentration profiles of the active (○ at 1 h, △ at 2 h, and □ at 3 h) and immobilized species (● at 1 h, ▲ at 2 h, and ■ at 3 h) of C. I. Reactive Orange 1 at pH 11.6 (I=0.15) and 30 °C. The lines in figure are the theoretical ones for $D=1.0\times10^{-7}$ cm^2/min and $k=5.0\times10^{-2}$ min^{-1}.

The concentration profiles obtained experimentally are classified into three types by comparing them with the theoretical profiles of the immobilized and active species. Type 1 consists of profiles dyed from a weakly alkaline dyebath; a typical example is shown in Fig. 1, where the agreements between the experimental profiles of the immobilized and removed species and the theoretical profiles of fixed and active species, and their reproducibility are fairly good. Type 2 consists of profiles dyed from a moderately alkaline dyebath; it is shown in Fig. 2, where the experimental immobilized profiles for different diffusion times are in agreement

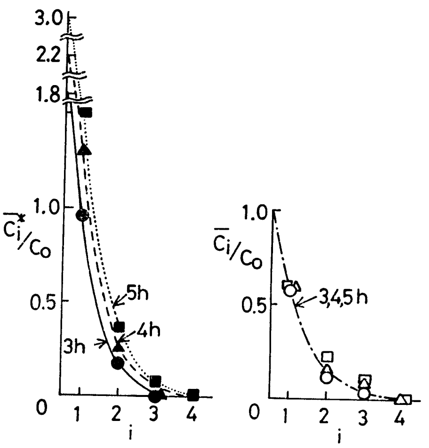

Fig. 3. Concentration profiles of the active (○ at 3 h, △ at 4 h, and □ at 5 h) and immobilized species (● at 3 h, ▲ at 4 h, and ■ at 5 h) of C. I. Reactive Yellow 4 at pH 9.2 ($I=0.15$) and 30 °C. The lines on figure are theoretically described by Eqs. 7 and 8 of Ref. 3 ($D=9.0\times10^{-8}$ cm²/min, $k=1.0\times10^{-2}$ min^{-1}).

with the theoretical profiles for the fixed species, but the removed ones are not in agreement with that for the active species. Type 3 is intermediate between them and is shown in Fig. 3, where the profiles of the immobilized species for different diffusion times are in agreement with the theoretical profiles of the fixed species, but the experimental profiles of the removed species penetrated more deeply than the theoretical ones. The theoretical profiles for the active species shown in Figs. 2 and 3 are asymptote and show that no active species can penetrate more deeply than the line. Theoretically, all the active species adsorbed from the dyebath are reacted with cellulose, and the distribution of active species is in the equilibrium state. The experimental profiles of the removed species shown in Fig. 2, however, penetrated the more deeply, the longer the diffusion times. As the penetrations of fixed and active species must be theoretically in agreement with each other,[3] there should be inactive or hydrolyzed species in cellulose during diffusion. There would be other reasons for the minor possibility that the hydrolyzed dyes in the alkaline dyebath were also adsorbed, though the concentration of active species in the dyebath was kept constant and the surface concentration of active species was not varied during the dyeing, or that the species immobilized by the reaction with cellulose were mobilized again by the hydrolysis of the dye-fiber bond. The last possibility was experimentally confirmed to be so small that the reaction-rate constant, k, was not practically influenced at 30 °C below pH 12.0 under the experimental conditions of the present study.

Because of the agreement between the experimental and theoretical profiles for the immobilized species, and because of the disagreement between the removed or experimental profile and the active or theoretical one under highly alkaline conditions, the D and k of active species were determined from the immobilized profiles. The D and C_0 at various pHs are compared with those

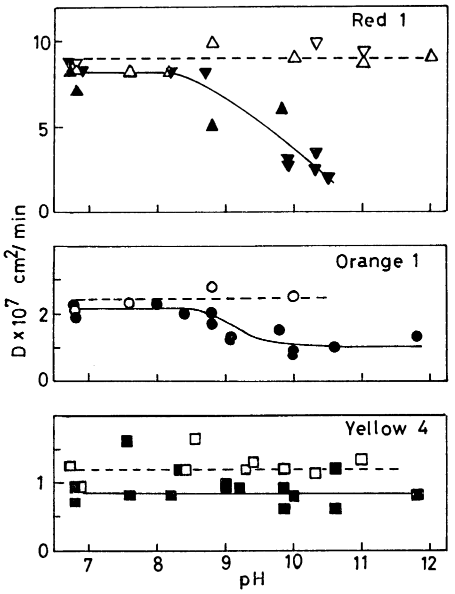

Fig. 4. Apparent diffusion coefficients of the active (solid symbols) and hydrolyzed species (open symbols) at 30 °C and $I=0.15$. In the case of Red 1, results for $I=0.15$ (▽ and ▼) and for $I=0.5$ (△ and ▲) are shown.

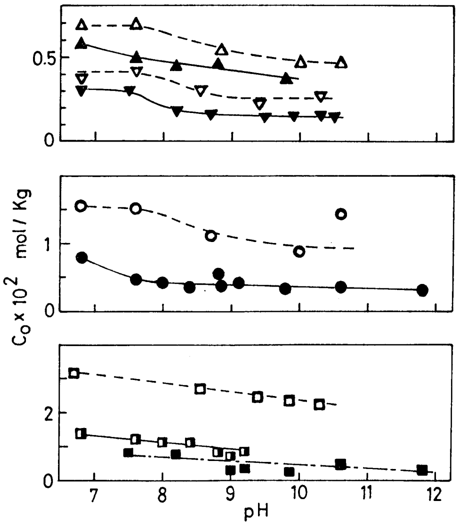

Fig. 5. Surface concentrations of the active and hydrolyzed species at 30 °C.

Dye	Species	Symbol	Ionic strength I	Concentration (mol/dm³)	(g/dm³)
Red 1	H	△	0.50	8.14×10^{-4}	(0.5)
		▽	0.15	1.63×10^{-3}	(1.0)
	A	▲	0.50	6.45×10^{-4}	(1.0)
		▼	0.15		
Orange 1	H	○	0.15	8.64×10^{-4}	(0.5)
	A	●	0.15	5.36×10^{-4}	(0.6)
Yellow 4	H	□	0.15	1.56×10^{-3}	(0.9)
	A	◨	0.15	3.86×10^{-4}	(0.3)
		■	0.15	1.93×10^{-4}	(0.15)

H=Hydrolyzed, A=Active.

of hydrolyzed species in Figs. 4 and 5. Though the C_0 of the hydrolyzed species were slightly decreased with an increase in the pH, the C_0's of the active species were almost constant under the alkaline conditions above pH 8. This shows that C_0 can actually be kept constant at a highly alkaline pH if a sufficient amount of electrolytes is added to the dyebath. Sumner and Taylor have reported, after using the dye base and diamino derivatives of three Procion dyes, the complicated findings that the affinities of Yellow 4 were constant over the whole pH range between 8 and 13, while those of Red 1 were constant up to pH 10 and then decreased slightly with an increase in the pH.[17] Although the standard affinities of reactive dyes for cellulose could not be calculated, as no alkaline adsorption by cellulose was measured in the present study, the adsorption behavior of the active and hydrolyzed species for the three reactive dyes used all appeared to have the same pH dependence.

At pH 6.8, the D values of the hydrolyzed species for the three dyes were slightly larger than those of the active species (Fig. 4). Sumner and Taylor also observed that the D values of the dye bases for three Procion dyes were larger than those of diamino derivatives and estimated that those of active species were intermediate.[17] Although they reported the complicated diffusional behavior of three Procion dyes at various pH values between 8 and 13, the D values of the hydrolyzed species for the three reactive dyes used in the present study appeared to be constant over the whole pH range examined (Fig. 4). However this behavior for Yellow 4 appeared to be in accordance with their results.

On the other hand, the D values of the active species for Orange 1 and Red 1, as estimated from the diffusion profiles of the immobilized species, apparently decreased with an increase in the pH, and that for Yellow 4 was nearly constant over the whole pH range examined. The decreasing tendency of the D for Red 1 was larger than that for Orange 1. As was mentioned in the previous paper (*cf.* Ref. 3, Fig. 1), some combinations of D and k described theoretically the concentration profiles of the immobilized and active species obtained from a diffusion experiment. Because the k values of active species could be estimated by various methods, because their obtained values coincided with each other, and because the pH dependence of k was similar to that of the rate constants of hydrolysis (*cf.* Fig. 6), the values of k obtained can be considered reasonable. If the D of an active species was estimated from the profile of the immobilized species with the value of k obtained above, however, it was smaller than the D of the hydrolyzed species under highly alkaline conditions. It is notable that the dyes with larger D values of the active species have a larger decreasing tendency than those with smaller ones do. It has been also shown in the previous paper that the larger the D of the active species and the smaller the k, the deeper was the penetration of immobilized and active species of reactive dyes into the substrate.[3] Thus, the dyes with larger k values are hindered in penetrating into the substrate. In spite of the fact that the D in the present study was estimated considering this effect, a cosiderably large rate of reaction with water in cellulose would be expected under highly alkaline conditions if the D of active species was constant over the whole pH range and was equal to that at pH 6.8. However, the detailed studies of the mechanism of the pH dependence for D and of the differences among the reactive dyes are now under way.

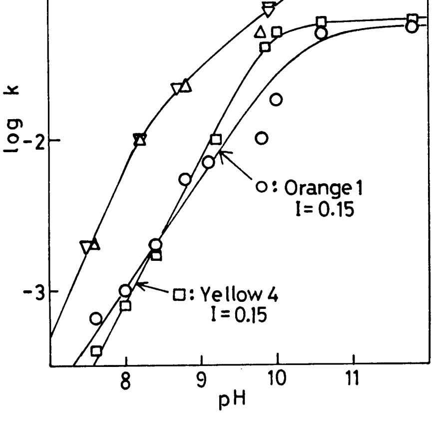

Fig. 6. Effect of pH on the rate constants of reaction with cellulose at 30 °C.

Reaction with Cellulose. The reaction-rate constants, k, determined from the immobilized profiles at various pHs are shown as relationships between log k and pH in Fig. 6. The relationships were similar to that of hydrolysis measured by Ingamells *et al.* at 20 °C.[7] They observed two kinds of relations between the rate of hydrolysis and the pH. Such a relation is also found in Fig. 6; *i.e.*, the effect of the pH on the reactivity for Yellow 4 and Orange 1 is different from that for Red 1. In the cases of Yellow 4 and Orange 1, log k had a constant slope up to pH 11. The rate constants of the hydrolysis for Yellow 4 and Red 1 were measured to be 0.016 and 0.060 min^{-1} respectively by Sumner and Vickerstaff at pH 11 and 30 °C.[18] According to Dawson *et al.*, they were 0.0175 min^{-1} for Yellow 4 and 0.055 min^{-1} for Red 1.[6] Comparing the rate constants of the reaction with cellulose for Yellow 4 in the present study with those of hydrolysis quoted above, the former value was about 5 times larger than the latter at pH 11, though the ionic strength and the kind of buffer solution were different. Although the k of Red 1 at pH 11 was too large to be obtained by measuring the optical densities of the immobilized species on cellophane, it was estimated by extrapolation of the k-pH relationship in Fig. 6 and thus found to have the value of 0.6—1.0 min^{-1}, 10—17 times larger than that of the hydrolysis. The rate constants of the reaction with cellulose for Red 1 measured by Preston and Fern at 20 °C were 25—11 times larger than those of the hydrolysis over the pH range between 9.5 and 12.8.[1] The ratio of the constants of the reaction with cellulose to those of hydrolysis may differ with the kind of reactive dye. On the other hand, the effect of the ionic strength on the rate of reaction with cellulose for Red 1 was investigated by changing the salt concentration added to the dyebath. As is shown in Fig. 6, no influences on the rate constants by the ionic strength were observed within the range of experimental error.

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