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Reaction and Simultaneous Diffusion in Cellulose of Reactive Dyes Containing a Mixed Bifunctional Reactive System

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ABSTRACT

*The reaction with cellulose and simultaneous diffusion into cellulose for two reactive dyes containing a 4-chloro-2-(*m*-vinylsulfonylanilino)-1,3,5-triazinyl group were investigated at 40–80°C, pH 7–11 and ionic strength 0·3, using the cylindrical cellophane roll method. The experimental diffusion profiles of the active and fixed species were fitted with the theoretical profiles. The relationship between* $\log k_c$ *(the pseudo-first-order rate constant of reaction with cellulose) and pH gave a straight line of unit slope below pH 10·5 for both dyes at 40, 60 and 80°C, the slope decreasing at pH values above 10·5. The surface concentration decreased with increase in pH for the red dye and remained nearly constant for the orange dye, whilst their diffusion coefficients were constant. Activation energies of the reaction with cellulose were 93–95 kJ mol*$^{-1}$ *and those of the diffusion into cellulose were 41–44 kJ mol*$^{-1}$*. These values are within the general range for vinylsulfonyl dyes, and the adsorption behavior of the dyes was similar to that of monochlorotriazinyl dyes.*

NOTATION

C	Concentration of the active species of reactive dyes in cellulose (mol kg^{-1})
C_i	Mean concentration of the active species in the *i*th layer (mol kg^{-1})
C^*	Concentration of the fixed species in cellulose (mol kg^{-1})

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C_i^*	Mean concentration of the fixed species in the ith layer ($\mathrm{mol\,kg^{-1}}$)
C_0	Surface concentration of the active species ($\mathrm{mol\,kg^{-1}}$)
C_s	Dye concentration in the dyebath ($\mathrm{mol\,dm^{-3}}$)
D	Diffusion coefficient of the active species in cellulose ($\mathrm{cm^2\,min^{-1}}$)
E_d	Activation energy of the diffusion in cellulose ($\mathrm{kJ\,mol^{-1}}$)
E_i	C_i/C_0
E_r	Activation energy of the reaction with cellulose ($\mathrm{kJ\,mol^{-1}}$)
G_i	C_i^*/C_0
I	Ionic strength of the dyebath
K_a	Dissociation constant of the hydroxyl group of cellulose ($\mathrm{mol\,dm^{-3}}$)
k_c	Pseudo-first-order rate constant of reaction of the active species with cellulose ($\mathrm{min^{-1}}$)
K_w	Ionic product of water ($\mathrm{mol^2\,dm^{-6}}$)
k_w	Pseudo-first-order rate constant of hydrolysis of the active species in cellulose ($\mathrm{min^{-1}}$)
n_a	Number of data for the calculation of V_a
n_f	Number of data for the calculation of V_f
n_t	Number of data for the calculation of V_t
V_a	Variance of the active species
V_f	Variance of the fixed species
V_t	Variance of the active and fixed species

1 INTRODUCTION

In 1980 the Sumitomo Chemical Co. introduced the first four Sumifix Supra dyes, these dyes containing a mixed bifunctional moiety, viz. the 4-chloro-2-[*m*-{2-(hydroxysulfonyloxy)ethylsulfonyl}anilino]-1,3,5-triazinyl group as the reactive system.[1,2] Since the vinylsulfonyl (VS) and monochlorotriazinyl (MCT) groups complement each other's reactivity, the dyes have a high reactivity and also a high affinity due to the triazine ring. Hoechst AG and the Mitsubishi Chemical Corp. later introduced similar reactive dyes, and Ciba–Geigy AG[3] recently marketed Cibacron C dyes, which are similar but have a fluorotriazine moiety and different VS groups, the dyes being suitable for exhaust and continuous dyeing.

The dyeing properties of the Sumifix Supra dyes has been described,[4–9] and an investigation of the practical dyeing processes, together with disclosure of the chemical structure of the dyes, has been made.[9] The dyes have a combined advantage of two reactive systems and can be used in exhaust dyeing in the temperature range 50–80°C.

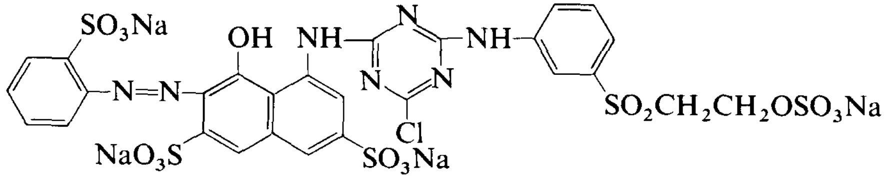
The diffusion and reaction behavior of various reactive dyes using the cylindrical film roll method has been described,[10–12] and in this present study the reaction and the simultaneous diffusion in cellulose of reactive dyes with the above bifunctional reactive system are investigated using the same method. Adsorption, diffusion and reaction characteristics for typical bifunctional reactive dyes containing VS and MCT groups are compared with those for other dyes with different reactive groups.

2 EXPERIMENTAL

2.1 Reactive dyes

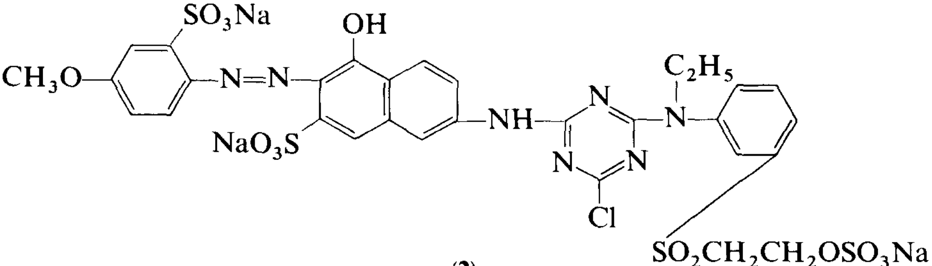
The two reactive dyes employed in this study were:

C.I. Reactive Red 194[9]



(1)

Orange dye



(2)

The dyes were supplied by Sumitomo Chemical Co. Ltd and were used for the diffusion experiments without further purification. The molar concentration of the dyes was determined on the basis of hydrolyzed samples; hydrolyzed samples of both the dyes were also supplied by Sumitomo Chemical Co. Ltd and were purified following a previously described procedure.[13]

2.2 Diffusion experiments

The experimental procedure used was as previously described,[10-12] using the cylindrical cellophane roll method. The thickness of the swollen cellophane was 3·75 x 10^{-3} cm. The experimental conditions are shown in

TABLE 1
Dyeing Conditions

Dye	*Concn of dyebath* ($g\,dm^{-3}$)	*pH*	*Ionic strength*	*Temperature* (°*C*)	*Dyeing time* (*min*)
1[a]	0·50	7–11	0·3	40–80	30–120
2	0·25				

[a] Dye **1** = C.I. Reactive Red 194.

Table 1. In order to minimize the effect of hydrolyzed species in the dyebath on the diffusion of the active species into cellulose and to maintain a constant surface concentration of the active species, a constant feed of stock solutions of the reactive dye and of buffer, with concentrations twice those of the dyebath liquor, was effected using a pump system, and maintaining a constant volume of dyebath liquor. After a prescribed time, the dyed film roll was opened and cut in half. One of the films was immediately scoured in aqueous 50% dimethylformamide at 50°C, renewing the solution to remove any unfixed dyes completely from the cellulose; the films were then treated with boiling water to remove residual dimethylformamide.

The optical densities of the scoured and unscoured films, measured after drying, correspond to the concentration of fixed and total dyes on the films. From these optical density differences between the scoured and unscoured films the sum (mobile species) of active and hydrolyzed species was obtained. The measured optical densities of the ith layer for the fixed and active species are denoted by G_i and E_i, respectively. Buffer solutions were used to adjust the pH of the dyebath, and sodium sulfate was used to adjust the ionic strength (I). The pH of the dyebath was measured by means of a Hitachi–Horiba M-8E pH meter equipped with suitable glass electrodes for high-temperature measurements.

In order to convert the sulfatoethylsulfonyl dye into the VS type, aqueous sodium hydroxide was added at each dyeing temperature and the liquor then immediately neutralized. The ionic strength (0·3) and the concentration of the dye in solution were adjusted by adding Na_2SO_4 and water as appropriate.

3 RESULTS AND DISCUSSION

3.1 Diffusion with simultaneous reaction in cellulose

The diffusion coefficients [D ($cm^2\,min^{-1}$)] and surface concentrations [C_0 ($mol\,kg^{-1}$)] of the VS type for both dyes were measured at pH 6·8, $I = 0·3$,

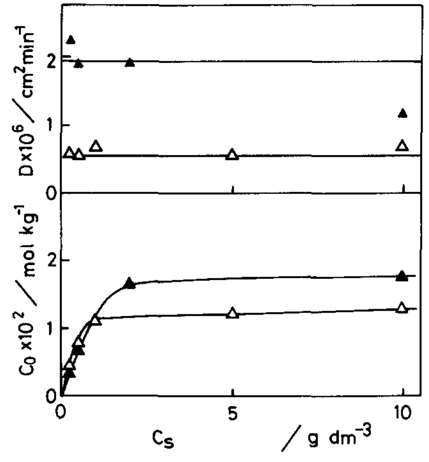


Fig. 1. Relationship between the surface concentration, C_0 (mol kg^{-1}), or the diffusion coefficient, D (cm^2 min^{-1}), and the dyebath concentration, C_s (g dm^{-3}), for C.I. Reactive Red 194 (dye **1**) (▲) and dye **2** (△) at pH 6·89, $I = 0·3$ and 60°C.

and at various dye concentrations, i.e. under conditions where no reaction with cellulose occurred (Fig. 1). The diffusion coefficients were constant within the experimental conditions used. A suitable dyebath concentration for the diffusion experiments was determined from Fig. 1, i.e. 0·50 g dm^{-3} for dye **1** and 0·25 g dm^{-3} for dye **2**.

The diffusion of a reactive dye in cellulose, accompanied by simultaneous reaction with the substrate, can be described by the diffusion equation:[10–12]

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

where C (mol kg^{-1}) is the concentration of the active species of the dye; k_c and k_w (min^{-1}) are the pseudo-first-order rate constant for the reaction of dye with cellulose and dye with water in cellulose, respectively; t (min) is the time; and x (cm) is the distance. If either of the two reactive groups reacts with cellulose, the dye is fixed on the cellulose, and the other reactive group may then later react with cellulose or sometimes with water. Thus the rate constant, k_c, may be the sum of the rate constants in the reaction with cellulose for the VS and MCT groups under the experimental conditions used, in which care was taken to minimize the hydrolysis in the dyebath of the active species.

3.1.1 Diffusion without reaction

The sulfatoethylsulfonyl groups of dyes **1** and **2** were readily converted into VS groups by the addition of alkali to the dye solution. Immediately after the alkali addition the dye solution was neutralized. The diffusion experiments of the VS types in cellulose were carried out from a dyebath at 50°C and pH 6·8. The dyed species on cellophane were almost completely removed by scouring in 50% aqueous dimethylformamide solution. The amount of undesorbed dye from the dyed films, whose absorbance $\geq 1{\cdot}0$, was less than 0·5%. In cases where no reaction with cellulose was observed the values of D and C_0 were determined by the least mean squares method[14] so that the theoretical diffusion profiles of Fick's diffusion equation [$k_c = 0$ and $k_w = 0$ in eqn (1)] fitted with the experimental profiles.

3.1.2 Diffusion accompanied by reaction

The concentration profiles for the active and fixed species are derived from eqn (1).[15,16] In the cylindrical film roll method the mean concentrations of active and fixed species, C_i and C_i^*, in the ith layer are theoretically calculated and are compared with the experimental ones, E_i and G_i, respectively. The experimental concentration profiles for the fixed and active species were in good agreement with the theoretical ones, because the differences $G_i - C_i^*$ and $E_i - C_i$ became negligible by minimizing the variance, v_t or v_f, with the change in the values of the kinetic parameters and in the values of C_0.[17,18]

A typical example is shown in Table 2. During the diffusion dye **1** or **2** may be fixed on cellulose by the reaction of either of the two reactive groups. The hydrolyses of both the reactive groups may thus be considered to be negligible in the substrate, prior to the reaction with cellulose. It was also confirmed that the experimental concentration profiles for the fixed and

TABLE 2

Least Mean Squares Calculation of the Kinetic Parameters for Reactive Dyeing with C.I. Reactive Red 194 (Dye **1**)

Number of layers, i	*Absorbance observed*		*Theoretical concn*		*Differences in optical density*	
	Fixed, G_i	*Mobile,* E_i	*Fixed,* C_i^*/C_0	*Active,* C_i/C_0	*Fixed,* $G_i - C_i^*$	*Active,* $E_i - C_i$
1	0·125	0·283	0·349	0·796	−0·001	−0·004
2	0·060	0·175	0·159	0·474	0·003	0·004
3	0·024	0·095	0·067	0·259	0·000	0·001
4	0·009	0·043	0·026	0·128	0·000	−0·003
5	0·001	0·018	0·009	0·057	−0·002	−0·003
6	0·000	0·008	0·003	0·022	−0·001	0·000
7	0·000	0·000	0·001	0·008	0·000	−0·003

Data were obtained by the cylindrical cellophane roll method under the following conditions: 0·50 g dye dm^{-3}, 40°C, 60 min, pH 9·90, $I = 0{\cdot}3$ and thickness of a swollen layer $= 3{\cdot}75 \times 10^{-3}$ cm.

Results: $D = 7{\cdot}66 \times 10^{-7}$ cm^2 min^{-1}, $k_c = 8{\cdot}25 \times 10^{-3}$ min^{-1}, $k_w = 0$, $C_0 = 0{\cdot}361$ Abs., $V_t(n_t = 10) = 1{\cdot}5$, $V_f(n_f = 4) = 0{\cdot}71$, $V_a(n_a = 6) = 2{\cdot}3$ (cf. Refs 17, 18).

mobile species at different diffusion times were in agreement with the theoretical profiles for identical values of the kinetic parameters.

Under strongly alkaline conditions and at high temperature, where reactive dyes have a large k_c value, the effect of the hydrolysis of the reactive groups was observed. No set of parameters could be determined which gave experimental profiles which were coincident for both the species and with the theoretical profiles. In this case the kinetic parameters were selected by minimizing the variance V_f and also by minimizing the variance V_a within the range of no significant difference in V_f, though the value of V_a became considerable (Table 3). The agreement between the experimental and theoretical profiles at different diffusion times was confirmed by the same set of values for the parameters.

Under these severe dyeing conditions the values of $E_i - C_i$ for the active species were always positive for all the layers, i.e. the experimental concentrations for the mobile species at each layer were larger than those for the theoretical values for the active species. This may indicate that species in which either or both of the reactive groups were hydrolyzed diffused into the inner layers. The experimental profiles for the fixed species at the inner layers were also a little larger (although not significantly so) than those for the theoretical profiles, implying that species in which either of the reactive groups was hydrolyzed diffused into the inner layers and also reacted with cellulose.

The diffusion coefficients and surface concentrations for both dyes at

TABLE 3

Least Mean Squares Calculation of the Kinetic Parameters for Reactive Dyeing with Dye **2**

Number of layers, i	*Absorbance observed*		*Theoretical concn*		*Differences in optical density*	
	Fixed, G_i	*Mobile,* E_i	*Fixed,* C_i^*/C_0	*Active,* C_i/C_0	*Fixed,* $G_i - C_i^*$	*Active,* $E_i - C_i$
1	0·589	0·147	2·320	0·585	0·006	0·000
2	0·150	0·045	0·603	0·178	−0·001	0·000
3	0·036	0·021	0·152	0·054	−0·002	0·007
4	0·009	0·012	0·037	0·016	0·000	0·008
5	0·005	0·007	0·007	0·004	0·003	0·006
6	0·003	0·004	0·000	0·000	0·003	0·004
7	0·000	0·003	0·000	0·000	0·000	0·003

Data were obtained by the cylindrical film roll method under the following conditions: 0·25 g dye dm^{-3}, 80°C, 30 min, pH 9·65, $I = 0·3$ and thickness of a swollen layer = 3·75 × 10^{-3} cm. Results: $D = 1·40 \times 10^{-6}$ cm^2 min^{-1}, $k_c = 0·140$ min^{-1}, $k_w = 0$, $C_0 = 0·251$ Abs., $V_t(n_t = 10) = 4·9$, $V_f(n_f = 5) = 1·4$, $V_a(n_a = 5) = 9·6$ (cf. Refs 17, 18).

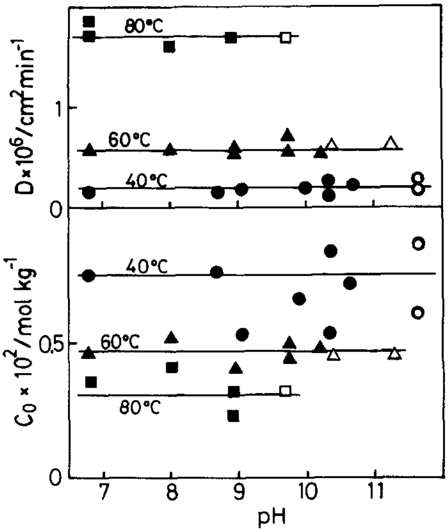


Fig. 2. Relationship between the diffusion coefficient, D (cm^2 min^{-1}), or the surface concentration, C_0 (mol kg^{-1}), for C.I. Reactive Red 194 (dye **1**) and pH at 40°C (●), 60°C (▲) and 80°C (■) (0·5 g dye dm^{-3}, I = 0·3). Data indicated by the corresponding open symbols were determined only from the profiles of the fixed species at the same temperatures.

various pH values are shown in Figs 2 and 3, in which the closed symbols correspond to the cases in Table 2 and the open symbols to those of Table 3. The values of D were constant over the pH range examined. The values of C_0 for dye **1** were constant, showing a similar behavior to VS dyes,[12] whilst those for dye **2** decreased with increase in pH, like MCT dyes.[11] The surface concentration of dye **2** is of a higher order than that of dye **1** under the conditions examined, and since dye **1** has higher affinity for cellulose than dye **1**, dye **2** thus shows similar behavior to that of MCT dyes.

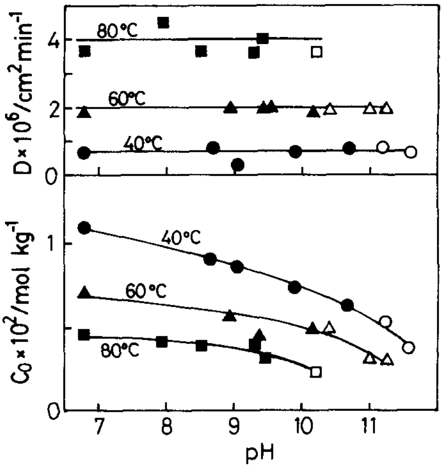


Fig. 3. Relationship between the diffusion coefficient, D (cm^2 min^{-1}), or the surface concentration, C_0 (mol kg^{-1}), for dye **2** and pH at 40°C (●), 60°C (▲) and 80°C (■) (0·5 g dye dm^{-3}, I = 0·3). Data indicated by the corresponding open symbols were determined only from the profiles of the fixed species at the same temperatures.

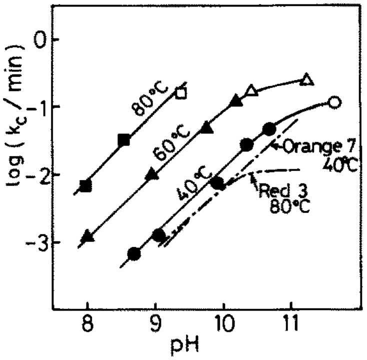


Fig. 4. Relationship between log k_c and pH for C.I. Reactive Red 194 (dye **1**) at 40°C (●), 60°C (▲) and 80°C (■) (0·5 g dye dm^{-3}, $I = 0{\cdot}3$). Data indicated by the corresponding open symbols were determined only from the profiles of the fixed species at the same temperatures.

3.2 Reaction with cellulose

The values of k_c for both dyes are shown in Figs 4 and 5, which demonstrate the relationships between log k_c and pH. Two examples of VS and MCT dyes are shown, viz. C.I. Reactive Orange 7 and Red 3. The plots of log k_c and pH for both dyes seem to show a linear relationship with a slope of unity below pH 10·5, deviating into a curve above pH 10·5. The increase in the pseudo-first-order rate constant in the reaction for both dyes with increase in pH corresponds to the increase in the concentration of cellulosate ion with pH. Since the VS dyes always show a linear plot,[12] the slight curvature of the plots for dyes **1** and **2** in Figs 4 and 5 may be attributed to the decrease in the second-order rate constant of the reaction with cellulose with the MCT groups,[11] as is also shown in the plot for Red 3 in Figs 4 and 5. The decrease can be attributed to the ionization of the imino bridge group between the chromophore and the triazine group.[19] The appearance of such curvature in the plots shows that the value of k_c for the MCT groups may be very similar to that for VS groups, since no curvature is observed if the value for the MCT groups is much lower than that for VS ones.

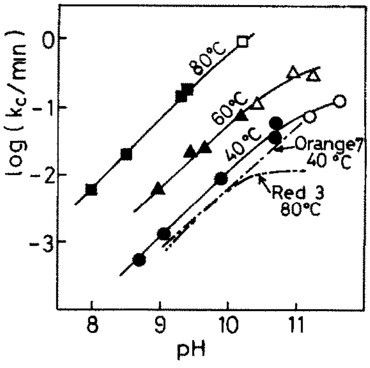


Fig. 5. Relationship between log k_c and pH for dye **2** at 40°C (●), 60°C (▲) and 80°C (■) (0·25 g dye dm^{-3}, $I = 0{\cdot}3$). Data indicated by the corresponding open symbols were determined only from the profiles of the fixed species at the same temperatures.

The values of the second-order rate constant of the hydrolysis for the VS and MCT groups of dye **1** were estimated to be 1·5 and 0·4 $dm^3\ mol^{-1}\ min^{-1}$, respectively, at 50°C (Morita, Z., Miura, K. & Motomura, H., unpublished). The latter value tends to decrease with increase in pH. The value for the VS group is almost four times larger than that of the MCT group. Some previous measurements of the rates of hydrolysis for some model bifunctional reactive dyes have shown an estimated ratio of the reaction rates for VS groups to those for MCT ones to be 2–4,[20] although other studies have indicated a larger ratio.[9]

3.3 Comparison of diffusion and adsorption behavior between different reactive dyes

The values of k_c for dyes **1** and **2** at pH 10·5 and 40°C were 1·8 times larger than that for C.I. Reactive Orange 7 (VS dye), which has the largest value of k_2 in VS dyes,[12] whilst those at pH 9·5 and 80°C were 110 times larger than that for C.I. Reactive Red 3 (MCT dye) (Table 4). The values of the rate constants for individual VS and MCT groups, as mentioned above, are also larger than the values for conventional VS and MCT dyes.[11,12] The MCT groups of dyes **1** and **2** may be highly activated by the metanilic acid residue and by the chromophore. The VS groups may also be activated by the chromophore and by the substituted triazine ring.

TABLE 4
Kinetic Parameters for Reactive Dyeing

Dyes or dye classes	*Conditions*	*Rate of reaction with cellulose*		*Activation energies*	
		k_c (*min*$^{-1}$)	k_2[a] (*dm*^{3} *mol*$^{-1}$ *min*$^{-1}$)	E_r (*kJ mol*$^{-1}$)	E_d (*kJ mol*$^{-1}$)
Red 194 (dye **1**)	40°C, pH 10·5	0·0316	1·7	95	41
	80°C, pH 9·5	0·224	—	(pH 10·0)	
Dye **2**	40°C, pH 10·5	0·0331	1·8	93	44
	80°C, pH 9·5	0·240	—	(pH 10·0)	
Monochlorotriazinyl[11]		—	—	130–197	19–113
C.I. Reactive Red 3[11]	80°C, pH 9·5	0·00200	—	197	113
	40°C, pH 9·5[b]	$3{\cdot}77 \times 10^{-7}$	$2{\cdot}0 \times 10^{-4}$		
Vinylsulfonyl[12]		—	—	88–127	33–50
C.I. Reactive Orange 7[12]	40°C, pH 10·5	0·0178	0·98	118	38
Dichlorotriazinyl[10]		—	—	26–81	28–57

[a] Calculated by $[\text{Cell—O}^-] = 20[\text{OH}^-]\ mol\ dm^{-3}$ and $K_w(40°C) = 2{\cdot}92 \times 10^{-14}(mol^2\ dm^{-6})$.
[b] The k_c value at 40°C was estimated by use of E_r from the value at 80°C.

In order to estimate the values of the second-order rate constant, k_2 (dm^3 mol^{-1} s^{-1}), of the reaction with cellulose, it is necessary to know the dissociation constants, K_a, of cellulose. The values of the ionic products (K_w) of water have been determined at high temperatures, but no value of K_a of cellulose at such temperatures have been reported. An estimation at 25°C has been made,[21] and from this value of K_a Sumner *et al.*[22,23] estimated the ratio of [Cell—O^-]/[OH^-] to be 20 at 20°C at pH below 11. Neglecting the temperature effect on the K_a of cellulose, values of k_2 for dyes **1** and **2** were calculated by use of this ratio and the value of K_w at 40°C (Table 4).

The k_2 value thus obtained for dye **1** is nearly equal to the sum of the second-order rate constants of the hydrolysis for VS and MCT groups.[20] The MCT groups in dyes **1** and **2** make a considerable contribution to the reaction with cellulose, the reactivity of the MCT group in dye **1** being very much higher than in C.I. Reactive Red 3, which has a similar chemical structure.

The activation energies of the reaction with cellulose and the diffusion in cellulose thus calculated are shown in Table 4. The values for dyes **1** and **2** are similar, and are within the range expected for VS dyes, i.e. the Sumifix dyes have similar temperature dependence with respect to diffusion and reaction behavior. No comparison of the adsorption behavior can be made between these dyes and other ranges of dyes, because they are applied at different temperatures, but dyes **1** and **2** show high affinity on cellulose at 40–60°C and an adsorption behavior similar to that of MCT dyes at higher temperature.

4 SUMMARY

The reactive dyes studied, having a mixed bifunctional reactive system, showed a very high reactivity and the same temperature effect of reaction and diffusion into cellulose. The values of the diffusion coefficients are, however, dependent on the chemical structure of the dye and its substituents. The dyes exhibit a high affinity for cellulose due to the relatively moderate temperature of application.

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