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Diffusion/Adsorption Behaviour of Reactive Dyes in Cellulose

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ABSTRACT

The diffusion/adsorption behaviour in cellulose films of two monochlorotriazinyl (MCT) reactive dyes having high substantivity to cellulose was investigated from the dyebath using a wide concentration range of sodium sulphate at 80°C. Diffusion coefficients for these reactive dyes showed a large concentration dependence at low salt concentration and a smaller dependence with an increase in salt concentration. The concentration dependence of the diffusion coefficient or of the diffusion behaviour for reactive dyes in cellulose was essentially the same as that for direct dyes. From the results obtained the diffusion/adsorption behaviour of reactive dyes in cellulose could be explained by a variable porosity model in the low concentration range of the dyes. In the case of high salt concentration, the diffusion coefficients in cellulose increased with increasing dye concentration at which the saturated adsorption appeared. © *1997 Elsevier Science Ltd*

Keywords: Diffusion, adsorption, reactive dyes, cellulose, diffusion model, pore model.

1. INTRODUCTION

The diffusion of direct dyes in water-swollen cellulose has been explained in terms of a diffusion/adsorption theory based on a pore model [1–5]. Rys and Zolloinger [6,7] proposed a pore model for the diffusion of reactive dyes, although the applicability of this has not yet been fully examined. With the usual types of reactive dye, however, it has been observed that these have a constant diffusion coefficient within experimental errors [8–10].

In order to confirm the applicability of diffusion/adsorption theory to the reactive dye–cellulose system, it is necessary to analyse the experimental diffusion profiles of reactive dyes in cellulose. But since reactive dyes usually have a low substantivity to cellulose, the estimation of diffusion coefficients from the concentration distribution in cellulose may not be possible. In reactive dyeing, large amounts of electrolytes are added to the dyebath in order to minimize the exclusion of polyanion by the fixed dyes. Since usually ionic strengths $\gtrsim 1$ are applied, an analysis of salt effect on the diffusion and adsorption behaviour of reactive dyes may be important.

In a previous paper [11] the adsorption behaviour on cellulose of two monochlorotriazinyl (MCT) reactive dyes with high substantivity, i.e. CI Reactive Red 120 and Red E, was investigated in detail over a wide range of salt concentrations, and the constant values of the standard chemical potential differences between the cellulose and solution phases were obtained at the intermediate concentrations of neutral salt.

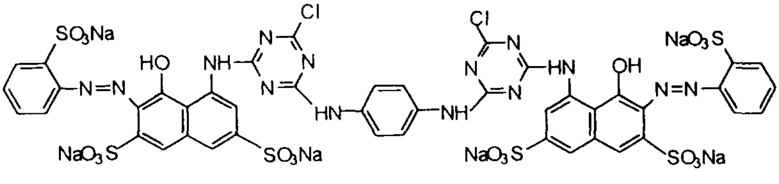
In the present study, the concentration dependence of the diffusion coefficients for reactive dyes with as high a substantivity to cellulose as possible, i.e. CI Reactive Red 120 and Red E, was analysed in order to clarify whether or not the diffusion/adsorption model holds for the diffusion of reactive dyes in cellulose.

2. EXPERIMENTAL

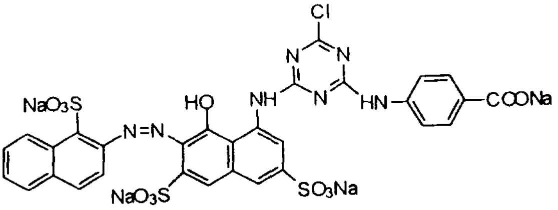
2.1. Materials

The dyes used were a typical reactive dye with high substantivity, (CI Reactive Red 120) and a MCT monoazo red dye (Red E; supplied by Nippon Kayaku Co. Ltd). Their chemical structures and CI generic and constitution numbers, where available, are shown below:

1. CI Reactive Red 120, CI 25810



2. MCT monoazo dye (Red E)



Red E was purified using a method described previously [11], but CI Reactive Red 120 was used without purification for the diffusion experiments.

Cellulose films (Futamura Kagaku Kogyo K. K., #300) 3.0 cm wide and 60 cm long were scoured in boiling distilled water for 2 h. The thickness of the swollen cellophane was 3.47×10^{-3} cm. Ionic strengths were adjusted with sodium sulphate.

2.2. Methods

The diffusion experiments were carried out by the cylindrical film roll method [12] in order to obtain the diffusion profiles in cellulose from the dyebath (500 ml) at 80°C, pH 6.8 and various concentrations of sodium sulphate. After dyeing, the surface of the film roll was quickly washed with distilled water and dried by placing the film between flat leaves of paper. The optical density of each film layer was then measured by a V-550 spectrophotometer (Jasco Corp.). Diffusion profiles were analysed by Matano's method [13] to obtain the differential diffusion coefficients as a function of dye concentration.

3. RESULTS AND DISCUSSION

3.1. Diffusion profiles in cellulose

CI Reactive Red 120 and Red E have high substantivity to cellulose at high ionic strength and low substantivity at low ionic strength, a property typical of reactive dyes. The general diffusion behaviour for reactive dyes, especially the concentration dependence of diffusion, may be discussed by analysing the concentration profiles in cellulose for these dyes, since conventional vinylsulfonyl (VS) and MCT dyes have too low a substantivity to obtain the concentration profiles in order to examine the diffusion behaviour. Figures 1 and 2 show the diffusion profiles for CI Reactive Red 120 and Red E, respectively, in cellulose for different diffusion times at various salt concentrations. As expected from the salt effect on adsorption, the surface concentrations were increased and the penetration of dye into cellulose decreased with an increase in salt concentration, except for the concentration range in which the saturated adsorption appeared [11].

3.2. Experimental diffusion coefficients

Boltzmann plots, or the superimposition of the experimental diffusion profiles in cellulose at different diffusion times, gave the master profile at each concentration of sodium sulphate in the dyebath, as shown in Figs 1 and 2, implying the time-independent diffusion coefficients.

In order to examine whether the diffusion in cellulose is either enhanced or more suppressed with an increase in ionic strength, salt effects on the diffusion of CI Reactive Red 120 and Red E were examined as shown, for example, in Figs 1 and 2. These figures show the suppression of diffusion with an increase in salt concentration, as a result of the increase in apparent substantivity of the dyes by the crossing of diffusion profiles at intermediate dye concentrations. No difference was found in the diffusion behaviour between CI Reactive Red 120 and Red E.

Applying Matano's method [13] to the master profiles, the experimental diffusion coefficients of the dyes as a function of dye concentration were estimated as shown in Figs 3 and 4. These figures have many features similar to those in the results reported by McGregor et al. [14] for CI Direct Blue 1, as well as to those for the diffusion of many anionic dyes in cellulose over wide concentrations of neutral salt [2,4,5]. It may be concluded that the concentration dependence of diffusion or the diffusion behaviour for reactive dyes in cellulose is essentially the same as that for direct dyes. The same smaller concentration dependence of the diffusion coefficients at high ionic strengths, as observed for direct dyes [5,14], was also observed up to the

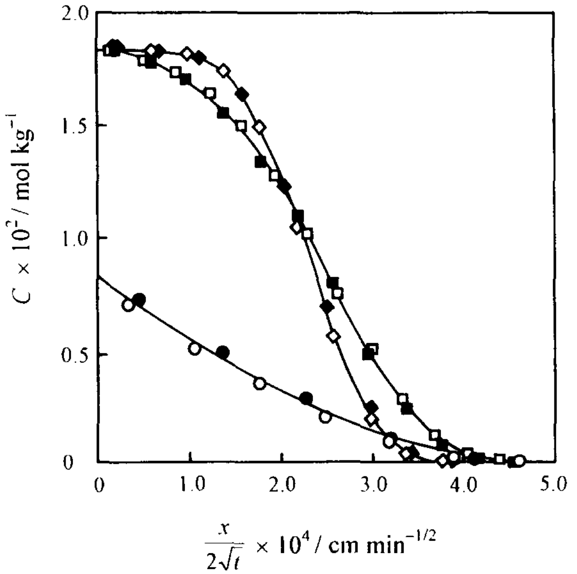


Fig. 1. Boltzmann plots of the concentration profiles in the diffusion of CI Reactive Red 120 in swollen cellophane from the dyebath at 80°C, pH 6.8 and the following concentrations of sodium sulphate: 0.133 mol dm^{-3} ($C_s = 4.33 \times 10^{-5}$ mol dm^{-3}) for 360 min (●) and 600 min (○); 0.333 mol dm^{-3} ($C_s = 2.20 \times 10^{-4}$ mol dm^{-3}) for 1920 min (■) and 2440 min (□); and 0.533 mol dm^{-3} ($C_s = 2.20 \times 10^{-5}$ mol dm^{-3}) for 1440 min (◆) and 1920 min (◇).

intermediate concentration of dye, while at higher dye and salt concentrations the diffusion coefficients were increased. Although it does not appear to have been reported thus far, direct dyes which show saturated adsorption may also exhibit an increase in the diffusion coefficients in the corresponding concentration range of dye and salt.

The common features which have been outlined in the preceding discussion are summarized as follows:

1. The diffusion coefficients had a complex dependence on the concentrations of dye and salt.
2. The diffusion coefficients were increased with an increase in dye concentration.
3. The diffusion coefficients were decreased with an increase in salt concentration except for the dye concentration at which saturated adsorption occurred.
4. A range of constant diffusion coefficients appeared at high sodium sulphate concentrations, for example at 0.533 mol dm^{-3} for CI Reactive Red 120 and at 0.333 mol dm^{-3} for Red E, up to an intermediate concentration of dye.
5. A steep increase in diffusion coefficients appeared in the concentration range of dye and salt where the saturated adsorption occurred.

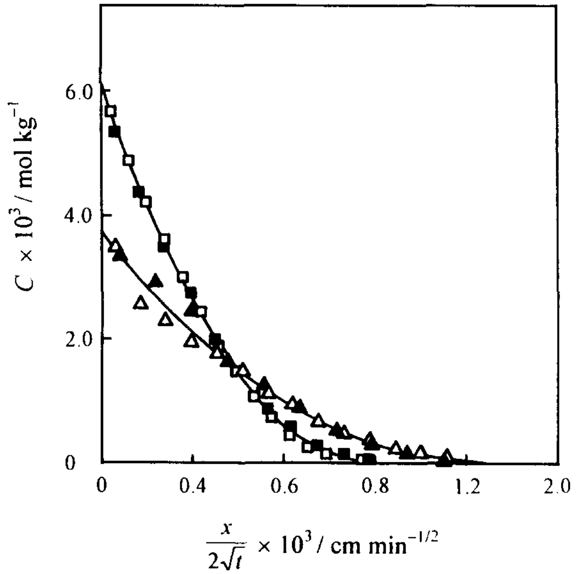


Fig. 2. Boltzmann plots of the concentration profiles in the diffusion of Red E in swollen cellophane from the dyebath at 80°C, pH 6.8 and the following concentrations of sodium sulphate: 0.0333 mol dm^{-3} ($C_s = 3.54 \times 10^{-4}$ mol dm^{-3}) for 120 min (▲) and 240 min (△); and 0.333 mol dm^{-3} ($C_s = 6.86 \times 10^{-5}$ mol dm^{-3}) for 240 min (■) and 480 min (□).

3.3. Diffusion/adsorption theory

As stated earlier, Figs 1 and 2 indicate that an increase in the apparent substantivity makes the diffusion coefficients smaller, implying that the applicability of diffusion/adsorption theory can be applied to the diffusion of direct dyes in cellulose. This may be explained by a variable porosity model [5,15], since the constant diffusion coefficients of direct dyes at high ionic strengths cannot be explained by a constant porosity model.

3.3.1. Diffusion coefficients based on a pore model [1,5]

In a pore model for the diffusion of anionic dyes in water-swollen cellulose, the dye anions diffuse in a pore solution which is regarded to be the same as the external solution. However, the diffusion coefficients may be different because the rotational freedom of the dye molecule may be partially limited due to the narrow diameter of the pore. It is also assumed that an adsorption equilibrium of dye anions is always maintained between the inner solution and the inner cellulose surface.

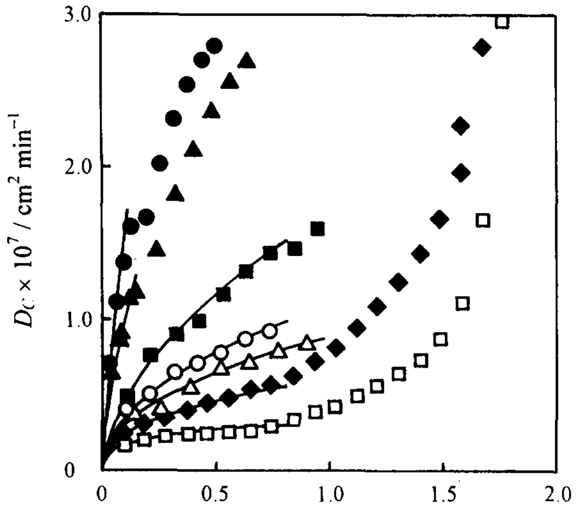


Fig. 3. Experimental diffusion coefficients for CI Reactive Red 120, estimated using Matano's method from the diffusion profiles (see Fig. 1) obtained by the cylindrical cellophane roll method, in swollen cellulose at 80°C, pH 6.8 and at the following concentrations of Na_2SO_4: 0.0167 (●), 0.0333 (▲), 0.133 (■), 0.200 (○), 0.267 (△), 0.333 (◆), and 0.533 (□) mol dm^{-3}; and the theoretical curves (solid lines) of D_c described by eqn 10, the values of the parameters of which are listed in Table 1.

The total concentration of the dye, C (mol kg^{-1}), is described as the sum of the concentrations for mobile dye in the pore solution, C_m (mol dm^{-3}), and adsorbed dye on the pore wall of water-swollen cellulose, C_{im}(mol kg^{-1}):

$$C = PC_m + C_{im} \tag{1}$$

where P (dm^3 kg^{-1}) is a volume of pore solution in the swollen cellulose which is described by the weight of dry cellulose. If the degree of swelling, S (dm^3 swollen cellulose/kg dry cellulose), is introduced the quantity of P/S (–) corresponds to the fraction of accessible water in the total volume of swollen cellulose; this is termed 'porosity'.

In the determination of $\Delta\mu^0$-values, the observed values of the dye concentration on cellulose were assumed to be equal to the values of C_f, since their observed values must be almost equal to the C-values and the value of PC_m may be negligible compared with that of C_f. However, in the diffusion/adsorption theory the relationships between C_f and C_m are again used to describe the instantaneous dynamic equilibrium between them by taking the values of C_m into consideration, which may play an important role in the diffusion in water-swollen cellulose.

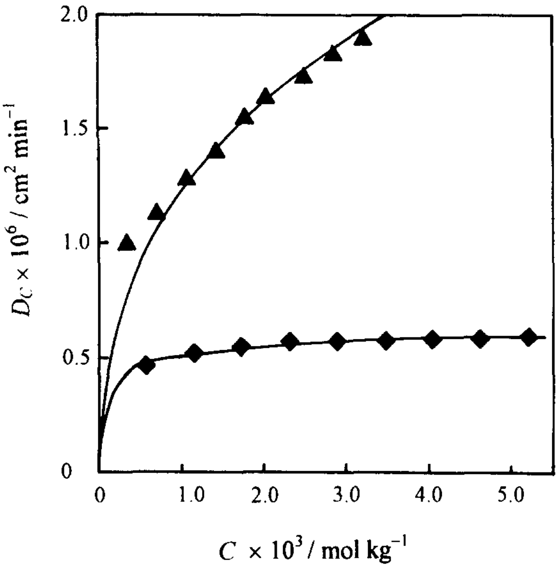


Fig. 4. Experimental diffusion coefficients for Red E, estimated using Matano's method from the diffusion profiles (see Fig. 2) obtained by the cylindrical cellophane roll method, in swollen cellulose at 80°C, pH 6.8 and at the following concentration of Na_2SO_4: 0.0333 (▲) and 0.333 (◆) mol dm^{-3}; and the theoretical curves (solid lines) of D_c described by eqn 10, the values of the parameters of which are listed in Table 2.

When the apparent diffusion coefficient for the total concentration is introduced, D_c (cm^2 min^{-1}), the diffusion equation for the species is given by:

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(D_c\frac{\partial C}{\partial x}\right) \tag{2}$$

Assuming that while maintaining the adsorption equilibrium the mobile and adsorbed species diffuse independently, and substituting eqn 1 for C, the following equation is obtained:

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(\frac{D_m}{b_m}\frac{\partial PC_m}{\partial x}+\frac{D_{im}}{b_{im}}\frac{\partial C_{im}}{\partial x}\right) \tag{3}$$

$$=\frac{\partial}{\partial x}\left[\frac{D_m}{b_m}\left(P\frac{\partial C_m}{\partial C}+C_m\frac{\partial P}{\partial C}\right)+\frac{D_{im}}{b_{im}}\frac{\partial C_{im}}{\partial C}\right]\frac{\partial C}{\partial x} \tag{4}$$

where D_m (cm^2 min^{-1}) denotes the diffusion coefficient of mobile species in the pore solution, D_{im} (cm^2 min^{-1}) denotes the diffusion coefficient of the adsorbed species, and b_m and b_{im} denote the tortuosity factor (–) of mobile and adsorbed species, respectively.

In order to analyse the concentration dependence of diffusion, it is appropriate to introduce the Freundlich isotherm (eqn 5) into the diffusion equation in order to describe the dynamic equilibrium between the mobile and adsorbed species [1–5]:

$$C=KC_S^{1/n} \tag{5}$$

where C (mol kg^{-1}) denotes the total concentration of the dye in cellulose, C_s (mol dm^{-3}) the dye concentration in the dyebath, and K and n the Freundlich constants given by eqn 5.

It is assumed that the adsorption equilibrium of dye anions between the pore solution and the inner surface of cellulose is described by the Freundlich equation (eqn 5). By combining eqn 4 and eqn 5 after substituting C_{im} for C and C_m for C_s, respectively, in eqn 5, D_c may be written as follows:

$$D_C=\frac{D_m}{b_m}\left(P\frac{\partial C_m}{\partial C}+C_m\frac{\partial P}{\partial C}\right)+\frac{D_{im}}{b_{im}}\left[\left(K^nC^{1-n}-P\right)\frac{\partial C_m}{\partial C}-C_m\frac{\partial P}{\partial C}\right] \tag{6}$$

Assuming that $D_{im}=0$, eqn 4 and eqn 6 give eqn 7:

$$D_C = \frac{PD_m}{b_m}\frac{\partial C_m}{\partial C} + \frac{D_m}{b_m}C_m\frac{\partial P}{\partial C} \tag{7}$$

and by substituting eqn 5 for C_m, eqn 7 becomes eqn 8:

$$D_c = \frac{D_m}{b_m}\left(nP + C\frac{\partial P}{\partial C}\right)K^{-n}C^{n-1} \tag{8}$$

In many cases where the dye concentrations are not high, the second term in the right hand side of eqns 7,8 have been assumed to be negligible [1–6]. As is noted below, this assumption may be valid only in the low concentration range of dyes. Thus, the same assumption (eqn 9):

$$\frac{\partial P}{\partial C} = 0 \tag{9}$$

was made to give eqn 10:

$$D_C = \left(\frac{PD_m}{b_m}\right)nK^{-n}C^{n-1} \tag{10}$$

The applicability of eqn 10 to the diffusion of direct dyes in cellulose has been proved by other workers [1–6].

3.3.2. Freundlich isotherm to analyse the concentration-dependent diffusion coefficients

As reported in a previous paper [11], no precise adsorption isotherms for CI Reactive Red 120 and Red E on cellulose have been determined at sodium sulphate concentrations ≤ 0.10 mol dm^{-3} and ≤ 0.008 mol dm^{-3}, respectively. Moreover, it was confirmed in the present study that the Freundlich equation (eqn 5) could not describe the adsorption isotherms over the whole dye concentration range measured.

However, an attempt was made to apply the Freundlich equations to the adsorption isotherms for both the dyes in the lower concentration range of the experimental results measured in the previous study [11], in order to determine the two constants, n and K. When the range of dye concentrations was given, the most appropriate set of n and K could be determined, although the variance between the Freundlich equation and the experimental adsorption isotherm was dependent upon the range. This procedure therefore made the examination of the validity of applying the pore model to the diffusion of reactive dyes in cellulose impossible, since various sets of the fittest values of n and K could be determined, depending on the range of dye concentrations and the variance.

In this study, therefore, the values of n were at first determined from the slope of the linear relationship between log D_c and log C (i.e. the logarithmic plots of the experimental D_c shown in Figs 3 and 4) at dye concentrations of -0.008 mol kg^{-1} for CI Reactive Red 120 and ≤ 0.0035 mol kg^{-1} for Red E by taking the experimental errors of D_c into consideration, as shown in Tables 1 and 2. Then, using these estimated values of n, the values of K were determined from the adsorption isotherms within the same dye concentration range at a given salt concentration, although the ranges of C and C_s differed with the salt concentrations. When the values of n and K were determined, the concentration range of dye, or the upper limit to which the Freundlich equation fitted with the practical adsorption isotherms, could be decided, as shown in Fig. 5 and in Tables 1 and 2. When the values of K of the Freundlich equation were estimated using the n values determined as described previously, the relationships between C and C_s, which gave the corresponding value of $-\Delta\mu^0$, were also used to obtain reasonable values of K in addition to the experimental data [11].

3.3.3. *Applicability of the pore model at low dye concentrations*

When the theoretical diffusion coefficients based on the pore model are drawn by eqn 10 by use of the Freundlich constants, the experimental differential diffusion coefficients, illustrated in Fig. 3 for CI Reactive Red 120 and Fig. 4 for Red E, show a good correlation with the theoretical curve within experimental error. This fact may also indicate that the assumptions of $D_{im} = 0$ and eqn 9 hold under the same conditions. In this case, the average values of PD_m/b_m were determined so that the theoretical curves of eqn 10 coincided with the experimental values of D_c, assuming that the values of PD_m/b_m were only a function of ionic strength. Their average values so estimated are listed in Tables 1 and 2. Although the validity of their values may decide the applicability of the pore model to this system, the problems are discussed in the following section (see section 3.4).

Figure 3, however, shows also the exceptional behaviour for CI Reactive Red 120 at salt concentrations of 0.333 and 0.533 mol dm^{-3}, at which the saturated adsorption of the dyes appears. These problems are also discussed in Section 3.4.

3.3.4. *Extension of the application to low salt concentration*

No precise value of $-\Delta\mu^0$ for these dyes has previoulsy been estimated [11], however, the diffusion profiles, which seemed to be similar to those at higher salt concentrations, were obtained down to 0.0167 mol dm^{-3} of sodium

TABLE 1

Freundlich Constants Combined with Diffusion/Adsorption Model, the Upper Limit of Dye Concentrations and the Values of PD_m/b_m in the Application for the Diffusion of CI Reactive Red 120 in Cellulose Films at 80°C, pH 6.8 and Various Concentrations of Na_2SO_4

Concn of Na_2SO_4 (mol dm^{-3})	*Freundlich constants*		*Upper limit of dye concn for a given set of* n *and* K *(see Fig. 5)*		$\left(\frac{PD_m}{b_m}\right) \times 10^5$ *(cm^2 min^{-1}) (upper limit,* C $\times 10^3$/ *mol kg^{-1}; see Figs 3 and 6)*	*Debye lengths (nm)*
	n *estimated from* D_c *at* C≦ *0.008 mol kg^{-1}*	K *estimated from adsorption for a given value of* n	*On cellulose (mol kg^{-1})*	*In dyebath (mol dm^{-3})*		
0.0167	1.9[a]	0.075	0.002	1.0×10^{-3}	0.03 ± 0.004 (1.3)	1.32
0.0333	1.7[b]	0.47	0.004	3.0×10^{-4}	0.20 ± 0.02 (1.6)	0.94
0.133	1.57	6.13	0.007	2.5×10^{-5}	2.58 ± 0.09 (7.1)	0.47
0.200	1.51	10.6	0.008	1.6×10^{-5}	2.72 ± 0.13 (7.3)	0.38
0.267	1.46	19.0	0.007	1.0×10^{-5}	3.69 ± 0.27 (8.9)	0.33
0.333	1.39	38.6	0.010	1.0×10^{-5}	4.16 ± 0.09 (8.0)	0.30
0.533	1.27	181.0	0.009	3.3×10^{-6}	6.51 ± 0.21 (8.4)	0.23

[a] n estimated from D_c at $C \leq 0.0015$ mol kg^{-1}.

[b] n estimated from D_c at $C \leq 0.005$ mol kg^{-1}.

TABLE 2

Freundlich Constants Combined with Diffusion/Adsorption Model, the Upper Limit of Dye Concentrations and the Values of PD_m/b_m in the Application for the Diffusion of Red E in Cellulose Films at 80°C, pH 6.8 and Various Concentrations of Na_2SO_4

Concn of Na_2SO_4 *(mol* dm^{-3}*)*	*Freundlich constants*		*Upper limit of dye concn for a given set of* n *and* K		$\left(\frac{PD_m}{b_m}\right) \times 10^5$ *(*cm^2 min^{-1}*)* *(upper limit,* C $\times 10^3$/ *mol* kg^{-1}*; see Fig. 4)*	*Debye lengths (nm)*
	n *estimated from* D_c *at* C≦ *0.0035 mol* kg^{-1}	K *estimated from adsorption for a given value of* n	*On cellulose* *(mol* kg^{-1}*)*	*In dyebath* *(mol* dm^{-3}*)*		
0.0333	1.39	1.15	6.3×10^{-3}	7.2×10^{-4}	1.59 ± 0.02 (3.2)	0.94
0.333	1.10	38.0	1.8×10^{-2}	2.1×10^{-4}	5.06 ± 0.10 (5.5)	0.30

sulphate. However, at lower salt concentrations the accuracy of the profiles may be low due to the small range of concentration. The experimental diffusion coefficients estimated by the same method for CI Reactive Red 120 are shown in Fig. 3.

Here, it is necessary to consider the surface concentrations, C_0 (mol kg^{-1}), estimated by the cylindrical film roll method; the values are summarized in Table 3. The equilibrium adsorption of CI Reactive Red 120 dye on cellulose at low salt concentrations was larger than that calculated from the corresponding values of $-\Delta\mu^0$ (Table 3) [11]. The value of C_0 was smaller than the adsorption at equilibrium at 0.133 mol dm^{-3} of sodium sulphate, while they were the same at higher salt concentrations, as expected. At very low salt concentrations the values of C_0 were smaller than the experimental values of C at equilibrium. Therefore, the concentration profiles of the whole concentration range may not be used for analysis under these conditions.

In this case, attempts were made to analyse the profiles in the concentration ranges where the profiles were not influenced by additional factors. Using the calculated amounts of adsorption under the given conditions (see Table 3), the ranges were estimated to be ≤ 0.0015 mol kg^{-1} at 0.0167 mol dm^{-3} of Na_2SO_4 and ≤ 0.005 mol kg^{-1} at 0.0333 mol dm^{-3} of Na_2SO_4, respectively.

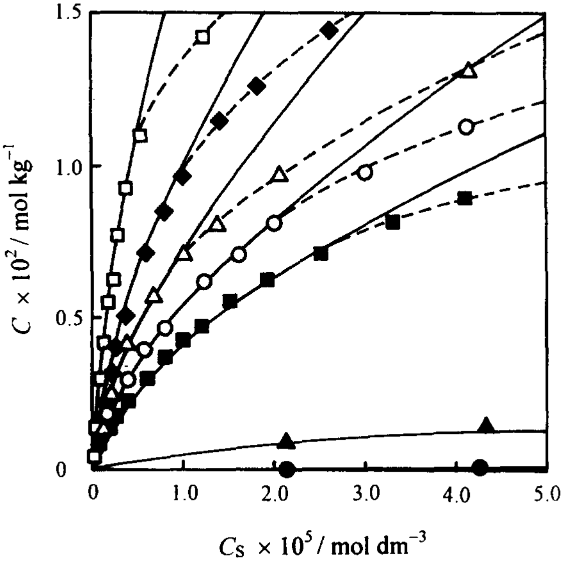


Fig. 5. Applicability of Freundlich equation to the adsorption isotherms for CI Reactive Red 120 on cellulose film at 80°C, pH 6.8 and at various concentrations of Na_2SO_4: 0.0167 (●), 0.0333 (▲), 0.133 (■), 0.200 (○), 0.267 (△), 0.333 (◆) and 0.533 (□) mol dm^{-3}. Freundlich equations are represented by solid lines using the values of n and K in Table 1 and the experimental adsorption isotherms are represented by broken lines.

Initially, the values of n were estimated from the relationship between D_c and C under the conditions mentioned earlier (Table 1). The values of K were estimated by use of these n values under the same limited conditions from the relationships between C and C_s calculated from the value of $-\Delta\mu^0$

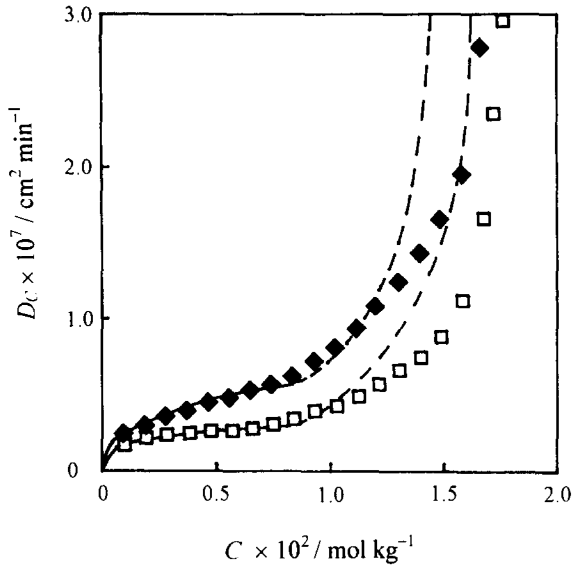


Fig. 6. Comparison between the theoretical and experimental diffusion coefficients (see Fig. 1 and Fig. 3) for CI Reactive Red 120 in swollen cellulose at 80°C, pH 6.8 and at 0.333 (◆) and 0.533 (□) mol dm^{-3} of Na_2SO_4. The theoretical curves of D_c described by eqn 10, the values of parameters of which are listed in Table 1, are represented by solid lines, and those calculated from eqn 7, where an assumption of eqn 9 is made, are represented by broken lines.

TABLE 3

Relationships between the Dye Concentrations in the Dyebath and the Surface Concentrations on Cellulose for CI Reactive Red 120 at Various Salt Concentrations at 80°C

Concn of Na_2SO_4 (*mol dm^{-3}*)	*Dye concn in dyebath* (*mol dm^{-3}*)	*Equilibrium adsorption on cellulose*[a] (*mol kg^{-1}*)	*Surface concn, C_0, estimated by the film roll method* (*mol kg^{-1}*)	*Dye concn on cellulose calculated from the corresponding value of $-\Delta\mu^{0a}$* (*mol kg^{-1}*)
0.0167	8.80×10^{-4}	9.22×10^{-3}	6.5×10^{-3}	1.77×10^{-3}
0.0333	8.80×10^{-4}	1.86×10^{-2}	1.10×10^{-2}	5.82×10^{-3}
0.133	4.33×10^{-5}	8.83×10^{-3}	8.3×10^{-3}	8.80×10^{-3}
0.200	4.33×10^{-5}	1.08×10^{-2}	1.00×10^{-2}	1.00×10^{-2}
0.267	4.33×10^{-5}	1.82×10^{-2}	1.30×10^{-2}	1.30×10^{-2}
0.333	2.20×10^{-4}	1.85×10^{-2}	1.80×10^{-2}	1.80×10^{-2}
0.533	2.20×10^{-4}	1.82×10^{-2}	1.80×10^{-2}	1.80×10^{-2}

[a] See ref. [11].

determined previously at higher ionic strengths [11]. Then, the values of PD_m/b_m were estimated so that the fit between the theoretical and experimental values of D_c might be reasonable, as shown in Table 1. Whether or not the values of PD_m/b_m give reasonable results may be examined by the magnitude of their average values and their scattering. However, the concentration range of C to which the Freundlich equation and, as a result, the pore model could apply became narrower than that used in determining the values of n (see Table 1), although this may be an essential but inevitable feature of the equation itself. Thus, by extrapolating the use of the $-\Delta\mu^0$ values to lower ionic strengths, the application of the diffusion/adsorption model may be extended, approximately, to the system at very low salt concentrations.

3.4. Validity of the pore model for the diffusion of reactive dyes in cellulose

The validity of the application of the pore model to the reactive dye diffusion process in cellulose may be discussed in the following terms:

1. Agreement between the experimental diffusion coefficients and the theoretical ones given by eqn 10.
2. Validity of the PD_m/b_m values including the validity of each value of three parameters.
3. Applicability limit of the present model.
4. Non-applicability to the exceptional cases.

3.4.1. General pattern in the concentration dependence of $\mathrm{D_c}$ *of anionic dyes in cellulose*

The patterns of the D_c vs C plots for CI Reactive Red 120 and Red E had a close resemblance to those for direct dyes, although the experimental values of D_c may inevitably contain some experimental errors. Thus, the agreement between the experimental and theoretical diffusion coefficients should be discussed as a general rule for anionic dye diffusion in cellulose.

It was confirmed that the diffusion behaviour or the concentration dependence in the diffusion coefficients for anionic dyes in cellulose could be described by the pore model, although there may be some limitations in the dye and salt concentrations. Standing et al. [1] introduced the Freundlich equation into the diffusion equation of direct dyes in cellulose in order to express the instantaneous adsorption equilibrium of the dyes between the inner surface of cellulose and the inner solution. The adsorption behaviour can be introduced into the diffusion equation by the two constants n and K, however, strict analysis confirmed that the Freundlich equation did not perfectly express the Donnan equilibrium of anionic dyes on cellulose.

Fortunately, the Freundlich equation can describe the equilibrium of low concentration range, although the values of the Freundlich constant depend upon the range. Moreover, depending upon the concentration range of C, the Freundlich equation has small deviations from the Donnan equilibrium but these may be regarded as being negligible in the present treatment. Beyond the application limit, the large deviation from the Freundlich equation commences rapidly, as shown in Fig. 5. Therefore, in the present paper the applicability of pore model was discussed by eqn 10 in the limited narrow range of low dye concentrations.

Considering the functional relation between D_c and C in eqn 10, it is apparent that the curvature or the pattern of theoretical values of D_c is dependent upon the value of n or the shape of the adsorption isotherm. In the case of the Nernst isotherm, $n = 1$. In general, the values of n for reactive dyes may be $1 \lesssim n \lesssim 2$ in the dye concentration range where the values of $-\Delta\mu^0$ are constant and at high salt concentrations. At concentrations where the values decrease with concentration, the values of n may become larger than 2 (see section 3.4.3 — Non-applicability of simple model at high concentration). The value of n may be a function of salt concentration and of the number of sulphonic acid groups in the dye molecule. When the dye has one or two sulphonic acid groups, the value of n may approach unity at high salt concentrations. Thus, such reactive dyes may have a value of n a little larger than unity (H. Motomura and Z. Morita, unpublished data) and show practically constant diffusion coefficients as reported previously [8–10]. Rys et al. [6,7] introduced an approximation of $n = 1$ in the diffusion model of reactive dyes but since the number of the second digit may be important in the vicinity of unity from the viewpoint of concentration dependence of diffusion coefficients, this approximation may be too approximate.

3.4.2. Validity of the values of $\mathrm{PD_m/b}_m$ *including the validity of each value of three parameters*

Although Figs 3 and 4, as well as Tables 1 and 2, seem to prove the good correlation between the experimental and theoretical diffusion coefficients in many cases, the values of parameters P, D_m, and b_m may contain some problems which need to be addressed.

The mean values for the parameter PD_m/b_m listed in Tables 1 and 2 showed a small scatter within the concentration range in question, implying a good applicability of the pore model to the present system. They have a value of 10^{-5} cm^2 min^{-1}, show a small increase with an increase in salt concentration, and become smaller at low salt concentrations. The magnitude of their values may be mainly determined by the order of diffusion coefficients of dyes in water [3,15]. Since the diffusion coefficients of anionic dye may exist in this order of magnitude, i.e. 10^{-4} cm^2 min^{-1} at 80°C [3–5,15] and the values of P/b_m may be a order of 0.1 (–) under the present conditions [3–5,15], the estimated values of PD_m/b_m may have reasonable values of order. However, since the values of D_m and b_m may be considered to be constant with changing ionic strength [5,15], the values of P may increase with an increase in the ionic strength. The order of variation in the values of PD_m/b_m and the increasing tendency with an increase in ionic strengths may be reasonable. Therefore, although whether an increase in the values of P with an increase in the ionic strength is reasonable or not may decide the validity of the present model, the fact that the values of PD_m/b_m showed an increase with an increase in the ionic strengths, as well as a small one at low ionic strength, may show the validity of this treatment.

In the variable porosity model [15] it is assumed that the value of P may be a function of the Debye length, which is proportional to the inverse square root of the ionic strength. The fact that the values of P are a constant function of the values of the lengths listed in Table 1 may also imply the validity of this model.

These facts may indicate that the present model holds at the low dye concentrations over a wide range of ionic strengths.

3.4.3. Non-applicability of simple model at high concentration

As shown in Fig. 5, the Freundlich equation described by the values of K and n in Table 1 deviated upwards from the experimental values above the application limit of the equation. If the assumptions introduced in the present treatment hold beyond this limit besides the Freundlich equation, the theoretical curve of D_c should deviate downwards from the experimental curve. At dye concentrations a little larger than the application limit, the assumptions may not immediately become invalidated with an increase in the dye concentration.

At sodium sulphate concentrations ≥ 0.333 mol dm^{-3} for CI Reactive Red 120, however, upward deviations of the experimental values of D_c are observed with an increase in the dye concentration, as shown in Fig. 3. Since this dye [11] has a constant value of $-\Delta\mu^0$ and the Freundlich equation exhibits the adsorption isotherm to some extent up to the concentration of 0.017 mol kg^{-1}, the upward deviation of experimental values of D_c may not be explained by the simple application of the present model.

Attempts were made to analyse the diffusion profiles for CI Reactive Red 120 at 0.333 and 0.533 mol dm^{-3} of sodium sulphate (Fig. 6). The correlation between the experimental and theoretical profiles at $C < 0.01$ mol kg^{-1} is a transcription from Fig. 6. Above this concentration limit (see Table 1) since the Freundlich isotherm deviates upwards from the experimental adsorption isotherm, the theoretical values of D_c should deviate downwards from the experimental ones, a reverse tendency. This may be modified by taking the contribution of the term $\partial C_m/\partial C$ in eqn 7 into consideration. By the graphical differentiation of the experimental isotherm of the corresponding conditions, and by neglecting the second term of $\partial P/\partial C$, an increasing curve could be drawn from the result (Fig. 6). Since the second term is neglected, the good correlation may not strictly be correct. The contribution of the second term may increase with an increase in the concentration but the increasing tendency of the experimental diffusion coefficients could be qualitatively explained by the apparent decrease in the substantivity at the corresponding concentration.

On the other hand, a decrease in porosity resulting from an increase in the amount of anionic groups in cellulose by the adsorption of anionic dyes has previously been reported [5,15]. If the repulsive interaction between adsorbed species hinder the instantaneous attainment of adsorption equilibrium between C and C_m, this deviation may be explained by the effects. The retardation of instantaneous equilibration, and of the decrease in porosity with an increase in C, may exist over the whole range of salt concentrations and from the lower dye concentrations, since a cancellation effect of both phenomena may result in the same behaviour.

4. SUMMARY

Diffusion of reactive dyes in cellulose can be described by diffusion/adsorption theory based on a pore model. Up to a certain dye concentration the experimental diffusion coefficients of the dyes could be explained by the diffusion/adsorption theory combined with the Freundlich adsorption equation on the assumption that porosity is dependent only upon the ionic strengths in the dyebath, although no explanation could be made below very low ionic strengths. At and above a certain high ionic strength, where the saturated adsorption appeared, the experimental diffusion coefficients increased abruptly, with an increase in the dye concentration from a concentration smaller than that at which the saturated adsorption occurred. This increase in the coefficients could be qualitatively explained by the same model. Constant diffusion coefficients observed experimentally could be derived from this model at very high ionic strengths. General features of anionic dyes in water-swollen cellulose were also discussed.

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APPENDIX

Notation

b_m, b_{im}	Tortuosity factors for the diffusion of mobile and immobilized species (–)
C	Total concentration of dye in cellulose (mol kg^{-1})
C_0	Surface concentration of dye on cellulose estimated by the cylindrical film roll method (mol kg^{-1})
C_f	Concentration of dyes adsorbed on cellulose (mol kg^{-1})
C_{im}	Concentration of immobilized species on cellulose (mol kg^{-1})
C_m	Concentration of mobile species in the pore solution (mol dm^{-3})
C_s	Concentration of dye in the dyebath (mol dm^{-3})

D_c	Apparent diffusion coefficient for the total concentration ($cm^2\ min^{-1}$)
D_m	Diffusion coefficient of mobilized species ($cm^2\ min^{-1}$)
D_{im}	Diffusion coefficient of immobilized species ($cm^2\ min^{-1}$)
K, n	Freundlich constants (see eqn 5)
P	Fraction of the solution phase where the dyes can diffuse to the total volume of swollen cellulose (see text)
t	Time of diffusion (min)
x	Distance of diffusion (cm)