

Diffusion Mechanism of Direct Dyes into a Cellulose Membrane: The Structural Effect of Direct Dyes on the Adsorption Rate

MASAKO MAEKAWA,* MASAKO UDAKA, MIKA SASAKI, and YASUKO TUJII, *Department of Clothing Science, Nara Women's University Nara 630, Japan*, HIROYUKI YOSHIDA and TAKESHI KATAOKA, *Department of Chemical Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan*, and MAMORU NANGO, *Department of Applied Chemistry, University of Osaka Prefecture, Sakai, Osaka 591, Japan*

Synopsis

The transport of three typical direct dyes, C.I. Direct Yellow 12, C.I. Direct Red 2, and C.I. Direct Blue 15, into a cellulose membrane has been studied at 55°C. Sodium chloride was used as a stimulator for dyeing. The effects of the concentration of the stimulator on the adsorption isotherms, the adsorption rate, and the concentration profiles in the membrane were tested. The experimental adsorption rates of three dyes were quite different. The diffusion mechanism of the dyes into a cellulose membrane was analyzed on the basis of the parallel transport equation of surface and pore diffusion as developed in our previous paper. The experimental uptake curves showed good agreement with the theoretical curves for surface diffusion control. Experimental concentration profiles also agreed reasonably well with the theoretical lines for surface diffusion control rather than pore diffusion control. The surface diffusivities of three dyes were quite different and nearly independent of the adsorbed phase concentration of the dye.

INTRODUCTION

The diffusion of direct dyes into a cellulose fiber has mainly been described by pore model, which was assumed that the dye molecule diffuses through the pore and are simultaneously adsorbed on the pore wall. In the analysis of kinetics of dyeing of a cellulose by a direct dye, attention has been focused on pore diffusion because cellulose materials swell remarkably in aqueous solution of the dye and a network of interconnecting pores containing water is formed. A "pore model" has therefore been developed, assuming that the dye molecules diffuse through the pore and are simultaneously adsorbed on the pore wall. It has not been clarified whether the assumption can be applied to the actual dyeing system of the cellulose or not.¹⁻⁸

In our previous paper,⁹ the parallel transport mechanism of pore and surface diffusion with Freundlich isotherm was proposed for the cellulose membrane-direct dye system. The contribution of both diffusion has been discussed theoretically. The experimental uptake curves and concentration profiles of C.I. Direct Yellow 12 at 25°C showed better agreement with the

*To whom all correspondence should be addressed.

theoretical curves for surface diffusion control rather than pore diffusion control. Observed surface diffusivities depend little on the adsorbed phase concentration of the dye.

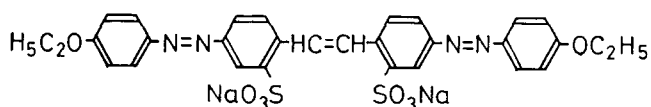
In the present work, the diffusion mechanism of the two typical direct dyes, C.I. Direct Red 2 and C.I. Direct Blue 15, are examined as well as C.I. Direct Yellow 12 (Scheme 1):

The way in which the molecular structure of the dyes affects the adsorption rate is discussed. The effects of the concentration of the stimulator, sodium chloride on the adsorption rate, and the diffusivity are discussed. The experimental results of uptake curves and the concentration profiles are compared with the theoretical values and are discussed in relation to the theory. All experiments were conducted at 55°C because practical dyeing is performed at relatively high temperature.

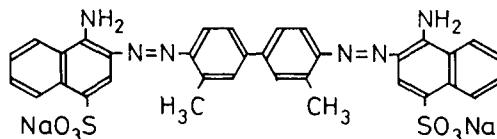
EXPERIMENTAL

Materials

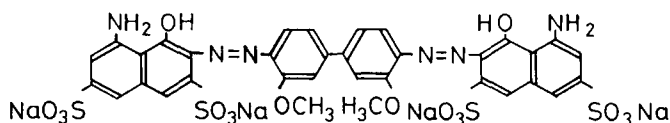
Sulfonated direct dyes, C.I. Direct Yellow 12 (MW = 680.7), C.I. Direct Red 2 (MW = 724.7) and C.I. Direct Blue 15 (MW = 992.8) were obtained from Tokyo Kasei Co. and were purified as described elsewhere.¹⁰ The molecular structures are shown in Scheme 1. The cellulose membrane (cellophane film) was soaked in boiled deionized distilled water for 3 h (30 min × 6 times) and



C.I. Direct Yellow 12



C.I. Direct Red 2



C.I. Direct Blue 15

Scheme 1. The dyes used.

washed with deionized distilled water. Carboxyl group content in the cellulose membrane which was determined by iodometry¹¹ was 6.25×10^{-2} eq/kg. The thickness of the cellulose membrane in water (l) was 40 μm . The volume of the membrane swollen with water per unit dry cellulose was 1.55 dm^3/kg . The porosity of the cellulose membrane in water (ϵ_p) was assumed to be 0.621, though it has not been measured. An assumed porosity model has been adopted as a convenient, albeit arbitrary, means for interpreting the experimental data.

Adsorption Isotherms and Transport of the Dye

Adsorption isotherms of the dyes were measured at 55°C by dyeing the cellulose membrane for 8 h (C.I. Direct Yellow 12), 72 h (C.I. Direct Red 2), and 48 h (C.I. Direct Blue 15), which were long enough period to achieve the equilibrium. The concentration of the dye in solutions ranged from 0.1 to 1.0 mol/m^3 . Sodium chloride was used as a stimulator for dyeing and the concentration ranged from 10 to 100 mol/m^3 . The dye bath ratio was 1 : 2000, and, under this condition, the decrease of the dye concentration by adsorption is negligible.

Transport of the dye into a membrane was measured with a Sartorius ultrafiltration type cell with water jacket. Uptake curves (the relation between the amount of the adsorbed dyes, $[D^*]$ and time) were measured for periods ranging from 10 min to 6 h using one sheet of the cellulose membrane in the cell. The concentration profiles after periods from 1 to 144 h were obtained by superposing 10 sheets of the membrane in the cell. The concentration of the dye in the cell was 1.0 mol/m^3 . The concentration of sodium chloride was the same as those in the case of the adsorption isotherms. The solutions in the cell were stirred using magnetic stirrer in order to prevent hydrodynamic boundary layer effects.

Accurately weighed uptake samples were extracted with 25% aqueous pyridine. The concentration of the dye extracted was determined using a Hitachi U-3200 spectrophotometer with 25% aqueous pyridine as a reference. To prevent complication arising from cis-trans isomerization of C.I. Direct Yellow 12 at room temperature, the dye solutions were illuminated for 30 min just before measurement.

THEORETICAL

It is assumed that (1) surface and pore diffusion occur in parallel within a cellulose membrane, (2) pore and surface diffusivities are constant during the adsorption process, (3) pore diameter and the porosity of the membrane are constant during the adsorption process, and (4) the concentration of dye in the pores is in local equilibrium with the concentration of the adsorbed dye on the surface of the pore wall.

Assumptions (1), (2), and (3) give the following mass balance equation:

$$\epsilon_p \frac{\partial C}{\partial t} + \frac{\partial q}{\partial t} = \epsilon_p D_p \frac{\partial^2 C}{\partial z^2} + D_s \frac{\partial^2 q}{\partial z^2} \quad (1)$$

where C and q are the concentrations of the dye in the pores and on the surface of the pore wall, respectively. ϵ_p is the void fraction of the pores. D_p and D_s represent the pore and surface diffusivities, respectively. Using dimensionless variables given by eq. (2), eq. (1) is transformed to eq. (3):

$$\left. \begin{aligned} \tau_p &= \frac{D_p t}{l^2}, \quad \rho = \frac{z}{l}, \quad x = \frac{C}{C_0}, \quad y = \frac{q}{q_0} \\ \alpha &= \frac{q_0}{\epsilon_p C_0}, \quad \beta = \alpha \frac{D_s}{D_p} \end{aligned} \right\} \quad (2)$$

$$\frac{\partial x}{\partial \tau_p} + \alpha \frac{\partial y}{\partial \tau_p} = \frac{\partial^2 x}{\partial \rho^2} + \beta \frac{\partial^2 y}{\partial \rho^2} \quad (3)$$

There are two limiting cases: $\beta = 0$ (pore diffusion control) and $\beta = \infty$ (surface diffusion control). As eq. (3) cannot be solved in the case of $\beta = \infty$, eq. (1) is also transformed to

$$\frac{\partial x}{\partial \tau_s} + \alpha \frac{\partial y}{\partial \tau_s} = \alpha \frac{\partial^2 y}{\partial \rho^2} \quad (\text{surface diffusion control}) \quad (4)$$

where $\tau_s = D_s t / l^2$. Surface diffusion control means the surface diffusion is much faster than the pore diffusion, but it does not mean there is no dye in the pores, that is, the first term must exist in eq. (4). The relation between x and y is calculated according to the equilibrium isotherm (fourth assumption).

Applying the Freundlich isotherm defined by eq. (5), eqs. (3) and (4) become eqs. (6) and (7), respectively:

$$y = x^\gamma \quad (5)$$

$$\left(\alpha + \frac{1}{\gamma} y^{(1-\gamma)/\gamma} \right) \frac{\partial y}{\partial \tau_p} = \frac{1}{\gamma} \frac{\partial}{\partial \rho} \left(y^{(1-\gamma)/\gamma} \frac{\partial y}{\partial \rho} \right) + \beta \frac{\partial^2 y}{\partial \rho^2} \quad (6)$$

$$\left(\alpha + \frac{1}{\gamma} y^{(1-\gamma)/\gamma} \right) \frac{\partial y}{\partial \tau_s} = \alpha \frac{\partial^2 y}{\partial \rho^2} \quad (\text{surface diffusion control}) \quad (7)$$

The initial and boundary conditions are given by

$$\text{(I.C.)} \quad y = 0 \quad \text{at} \quad \tau_p = 0 \quad \text{or} \quad \tau_s = 0$$

$$\text{(B.C.)} \quad y = 1 \quad \text{at} \quad \rho = 0 \quad (8)$$

$$\partial y / \partial \rho = 0 \quad \text{at} \quad \rho = 1$$

Local concentration of the dye $[D]_L$, mean concentration $[D]$, and fractional

attainment of equilibrium, F , are expressed, respectively, by

$$[D]_L = q + \epsilon_p C \quad (9)$$

$$[D] = \int_0^l (q + \epsilon_p C) dz/l \quad (10)$$

$$F = \frac{[D]}{q_0 + \epsilon_p C_0} = \frac{\alpha \int_0^1 y d\rho + \int_0^1 x d\rho}{\alpha + 1} \quad (11)$$

Equations (6) and (7) can be solved numerically after transformation to finite difference equations.

RESULTS AND DISCUSSION

Figure 1 shows the experimental adsorption isotherms of (a) C.I. Direct Yellow 12, (b) C.I. Direct Red 2, and (c) C.I. Direct Blue 15 on to the cellulose membrane in the presence of various concentration of sodium chloride at 55°C. The adsorption isotherms for three dyes reveal Freundlich-type adsorption. The Freundlich constant γ , which is obtained from the slope of each line in Figure 1, and the value of $\alpha (= q_0/\epsilon_p C_0)$ at $C_0 = 1.0 \text{ mol/m}^3$ are summarized in Tables I–III. Although the addition of sodium chloride is accompanied by the decrease in the value of γ , the values of γ for three dyes are affected little by the concentration of sodium chloride. The value of γ of C.I.

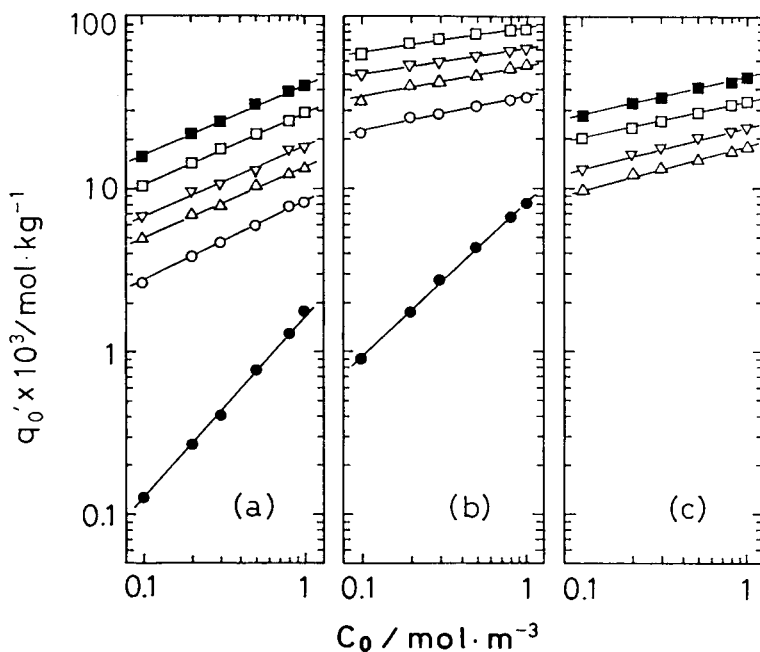


Fig. 1. Adsorption isotherms of (a) C.I. Direct Yellow 12, (b) C.I. Direct Red 2, and (c) C.I. Direct Blue 15 onto a cellulose membrane in the presence of sodium chloride: (●) 0, (○) 10 mol/m³, (△) 20 mol/m³, (▽) 30 mol/m³, (□) 50 mol/m³, and (■) 100 mol/m³ at 55°C.

TABLE I
Physical Properties in the Cellulose Membrane-C.I. Direct Yellow 12 System at 55°C

Run no. ^a	C_E (mol/m ³)	α	γ	$D_s \times 10^{14}$ (m ² /s)	$D_p \times 10^{14}$ (m ² /s)
1 (1)	0	1.92	1.00	29.5	56.8
2 (1)	10	9.73	0.468	29.0	192
3 (1)	20	14.5	0.436	27.9	305
4 (1, 10)	30	22.1	0.424	27.5	410
5 (1)	50	30.5	0.441	26.0	628
6 (1)	100	43.9	0.430	22.0	800

^aThe number in the parentheses shows the number of sheets of the membrane superposed.

TABLE II
Physical Properties in the Cellulose Membrane-C.I. Direct Red 2 System at 55°C

Run no. ^a	C_E (mol/m ³)	α	γ	$D_s \times 10^{14}$ (m ² /s)	$D_p \times 10^{14}$ (m ² /s)
1 (1)	0	9.25	0.947	0.358	2.92
2 (1, 10)	10	36.9	0.207	0.404	11.4
3 (1)	20	59.2	0.175	0.401	17.1
4 (1)	30	72.7	0.152	0.378	24.1
5 (1)	50	95.3	0.144	0.318	29.9

^aThe number in the parentheses shows the number of sheets of the membrane superposed.

TABLE III
Physical Properties in the Cellulose Membrane-C.I. Direct Blue 15 System at 55°C

Run no. ^a	C_E (mol/m ³)	α	γ	$D_s \times 10^{14}$ (m ² /s)	$D_p \times 10^{14}$ (m ² /s)
1 (1)	20	20.8	0.277	1.54	20.9
2 (1, 10)	30	27.1	0.248	1.98	35.8
3 (1)	50	36.8	0.220	2.23	52.0
4 (1)	100	54.2	0.230	1.93	73.5

^aThe number in the parentheses shows the number of sheets of the membrane superposed.

Direct Red 2 is the smallest and that of C.I. Direct Yellow 12 is the largest. The values of α of three dyes increase with increasing the concentration of sodium chloride. The value of α for C.I. Direct Red 2 is the largest among three dyes. The values of α for C.I. Direct Blue 15 are a little larger than that of C.I. Direct Yellow 12. These results reveal that the selectivity of C.I. Direct Red 2 is the highest, and the selectivity of C.I. Direct Yellow 12 is the lowest among three dyes. C.I. Direct Red 2 has the highest affinity for the cellulose because it aggregates most among three dyes in aqueous solution. C.I. Direct Yellow 12 has the lowest affinity because of low aggregation due to the steric hindrance between the sulfonic acid group situated ortho to the ethylene group. C.I. Direct Blue 15 has the highest molecular weight among three dyes,

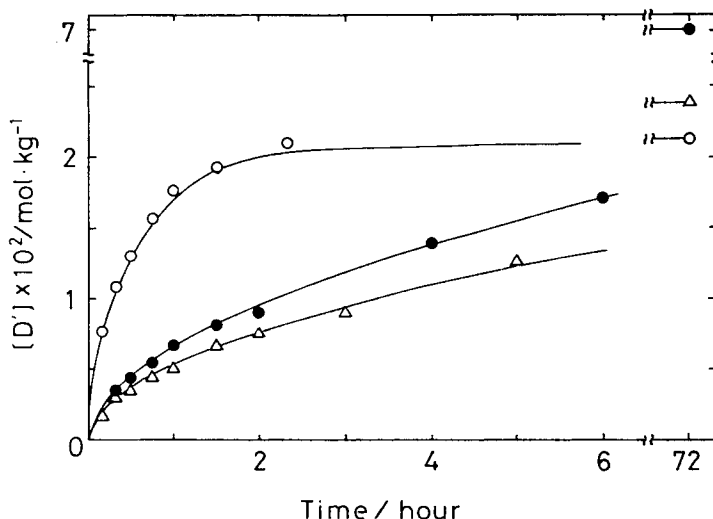


Fig. 2. Uptake curves of (○) C.I. Direct Yellow 12, (●) C.I. Direct Red 2, and (△) C.I. Direct Blue 15 in the presence of sodium chloride 30 mol/m³ at 55°C. The solid lines are the theoretical lines for surface diffusion control.

but the adsorption force for cellulose is less than that of C.I. Direct Red 2 because of the high solubility due to the presence of four sulfonic acid groups.

Figure 2 shows the relationship between the amount of the dye adsorbed onto one sheet of cellulose membrane $[D']$, and time. The adsorption rate of three dyes into the cellulose membrane are fairly different. The rate of the diffusion follows the order, C.I. Direct Yellow 12 > C.I. Direct Red 2 > C.I. Direct Blue 15. On the other hand, the amount of equilibrium adsorption of dyes follows the order, C.I. Direct Red 2 > C.I. Direct Blue 15 > C.I. Direct Yellow 12.

Figure 3 shows the relation between the fractional attainment of equilibrium, F , calculated from eq. (11) and time for (a) C.I. Direct Yellow 12, (b) C.I. Direct Red 2, and (c) C.I. Direct Blue 15. The data for each run [(a) runs 2–6 in Table I, $\alpha = 9.73$ –43.9, $C_E \geq 10$ mol/m³; (b) runs 1–5 in Table II, $\alpha = 9.25$ –95.3, and (c) runs 1–4 in Table III, $\alpha = 20.8$ –54.2, $C_E \geq 20$ mol/m³] are nearly independent of α and are approximately correlated by the solid line. In addition in Figure 3(a), the adsorption rate for the system without electrolyte (run 1 in Table I, $\alpha = 1.92$) is slower than the other systems.

According to the theoretical analysis based on a parallel transport mechanism of surface and pore diffusion when $\alpha \geq 10$ and the surface diffusion is the rate controlling step is little affected by α .⁹ In contrast, when pore diffusion control is assumed, the dependence of α on the uptake curve is very large over every range of α and the adsorption rate becomes slow with the increase of α . From the comparison between the theoretical trend and the experimental data in Figure 3, we understood that the contribution of surface diffusion on the rate of diffusion is appreciably larger than that of pore diffusion.

We then tried to match the theoretical equation [eq. (7)] for surface diffusion control with the uptake data in Figure 2. The lines in Figure 2 are the theoretical lines calculated according to eq. (7) and the values of α , γ , and

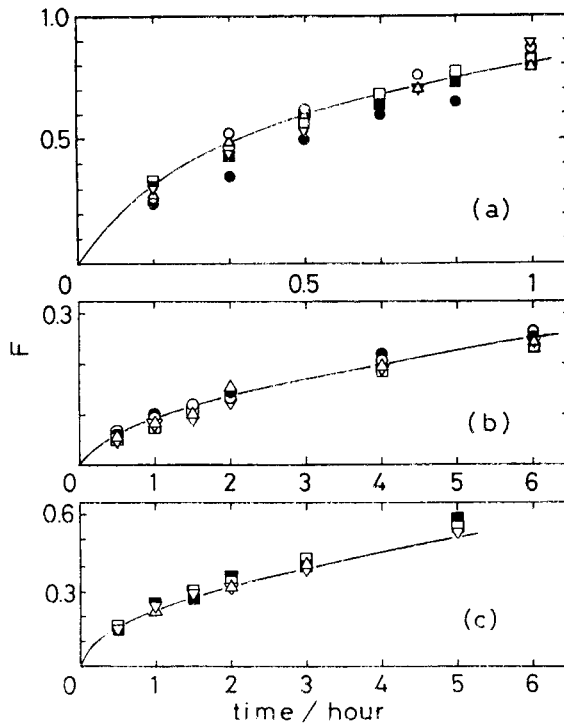


Fig. 3. The relation between diffusion time and the fractional attainment of equilibrium, F , for (a) C.I. Direct Yellow 12, (b) C.I. Direct Red 2, and (c) C.I. Direct Blue 15 in the presence of sodium chloride: (●) 0, (○) 10 mol/m³, (△) 20 mol/m³, (▽) 30 mol/m³, (□) 50 mol/m³, and (■) 100 mol/m³ at 55°C.

D_s in Tables I–III. We can find good agreement between the theoretical lines and the uptake data. Surface diffusivities D_s were obtained by matching the data with the theoretical values. The values of D_s obtained here are summarized in Tables I–III. For reference, pore diffusivities D_p were obtained from eq. (6) by substituting $\beta = 0$ and using α and γ in Tables I–III, and are also listed in the tables. D_p is affected by α considerably.

Figure 4 shows the concentration profiles of C.I. Direct Yellow 12 for different diffusion times: 1, 4, 8, and 48 h (run 4 in Table I). Figure 5 shows the concentration profiles of (a) C.I. Direct Red 2 (run 2 in Table II) and (b) C.I. Direct Blue 15 (run 2 in Table III) for 144 h of diffusion time. The solid lines in the figures represent the theoretical profiles for surface diffusion control calculated using D_s which was obtained from the uptake curve for one sheet of the membrane, α and γ in Tables I–III. The dashed lines show the theoretical profiles for pore diffusion control calculated using D_p , which was also obtained from uptake curve for one sheet of the membrane, α and γ in Tables I–III.

Figures 4 and 5 show that the experimental concentration profiles agree reasonably well with the theoretical lines for surface diffusion control. These results may suggest that the diffusion of direct dyes is controlled by surface diffusion rather than pore diffusion. The difference between the theoretical lines for surface and pore diffusion control in Figure 5 is clearer than that in

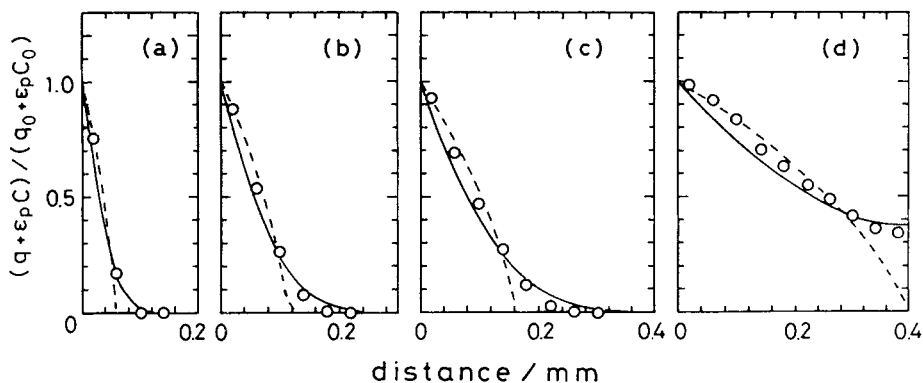


Fig. 4. Concentration profiles of C.I. Direct Yellow 12 in the cellulose membrane after various periods of diffusion time in the presence of sodium chloride 30 mol/m^3 at 55°C : (a) 1 h; (b) 4 h; (c) 8 h; (d) 48 h. The solid lines are calculated on the assumption of surface diffusion control ($D_s = 2.75 \times 10^{-13} \text{ m}^2/\text{s}$) and the dashed lines are calculated assuming pore diffusion control ($D_p = 4.10 \times 10^{-12} \text{ m}^2/\text{s}$).

Figure 4. The theoretical lines for pore diffusion control in Figure 5 show a steeper slope than those in Figure 4. This is because the values of coefficient of Freundlich isotherm γ for C.I. Direct Red 2 and C.I. Direct Blue 15 are smaller than that of C.I. Direct Yellow 12 as shown in Tables I–III. In the previous paper,⁹ we showed that the smaller the value of γ is, the steeper the concentration profile for pore diffusion control is, and the boundary between dyed and undyed part becomes sharper with decreasing the value of γ .

In Figure 6, the experimental surface diffusivities are plotted versus q'_0 which denotes the equilibrium dye concentration in the membrane with the bulk solution $C_0 (= 1.0 \text{ mol/m}^3)$. The surface diffusivities of the three dyes

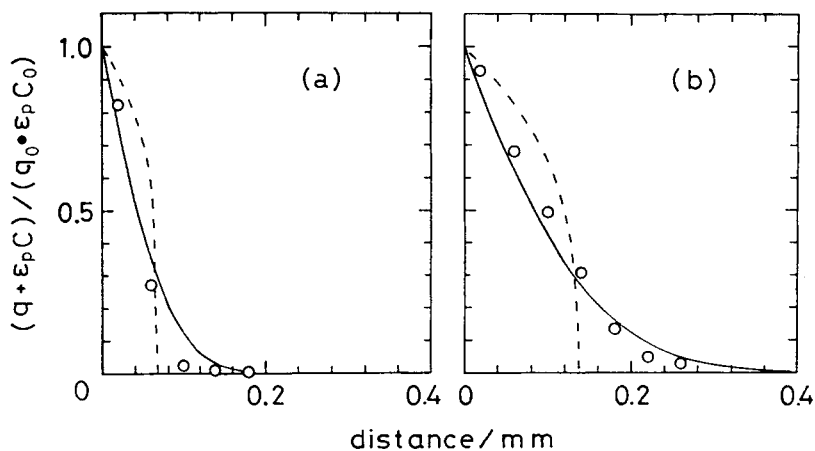


Fig. 5. Concentration profiles of (a) C.I. Direct Red 2 (run 2 in Table II, $C_E = 10 \text{ mol/m}^3$) and (b) C.I. Direct Blue 15 (run 2 in Table III, $C_E = 30 \text{ mol/m}^3$) in the cellulose membrane after period of 144 h at 55°C : The solid lines are theoretical lines calculated assuming surface diffusion control [(a) $D_s = 4.04 \times 10^{-15} \text{ m}^2/\text{s}$; (b) $D_s = 1.98 \times 10^{-14} \text{ m}^2/\text{s}$], and the dashed lines are also theoretical lines calculated assuming pore diffusion control [(a) $D_p = 1.14 \times 10^{-13} \text{ m}^2/\text{s}$; (b) $D_p = 3.58 \times 10^{-13} \text{ m}^2/\text{s}$].

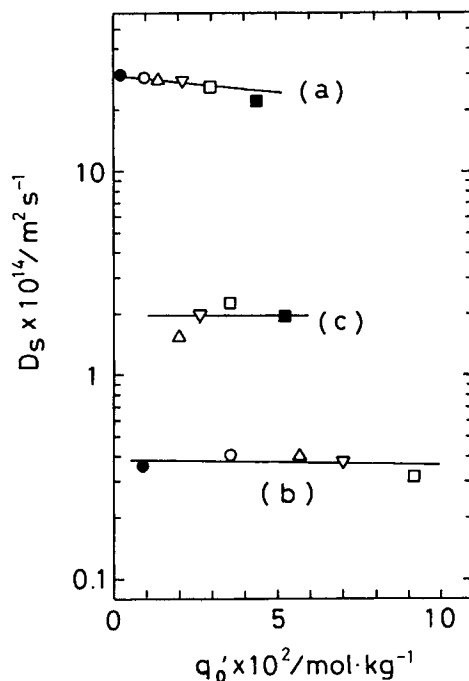


Fig. 6. The relation between the surface diffusivity D_s and the equilibrium dye concentration in the membrane, q_0' for (a) C.I. Direct Yellow 12, (b) C.I. Direct Red 2, and (c) C.I. Direct Blue 15 at 55°C in the presence of sodium chloride: (●) 0; (○) 10 mol/m³; (△) 20 mol/m³; (▽) 30 mol/m³; (□) 50 mol/m³; (■) 100 mol/m³.

are quite different and follows the order, C.I. Direct Yellow 12 > C.I. Direct Blue 15 > C.I. Direct Red 2. The reason why the values of the surface diffusivities of three dyes follow the above order may be due to the affinity between the dye molecule and the surface of the pore wall. C.I. Direct Yellow 12 showed the smallest affinity due to the smallest molecular weight and low aggregation because of the steric hindrance between the sulfonic acid group situated ortho to the ethylene group (see Scheme 1 and Fig. 1). On the other hand, as the molecules of C.I. Direct Red 2 aggregate and become bigger molecules than the other two dyes, the value of the surface diffusivity of C.I. Direct Red 2 may show the smallest. The values of D_s of three direct dyes show nearly constant at the various concentration of dye adsorbed.

Warwicker¹² and Weisz and Zollinger⁵ presented a pore diffusion model in which the presence of surface diffusion was denied. Morita et al.^{8,9} tested their model for cellulose-direct dye systems. Morita et al.'s experimental diffusivities depended on the concentration of the dye. In order to keep the pore diffusivity constant, Morita et al. concluded that the porosity of the cellulose changed with the ionic strength of the solution. Contrary to their conclusion, our experimental concentration profiles showed better agreement with the theory for surface diffusion control rather than the pore diffusion control as shown in Figures 4 and 5, although our theory assumed that the porosity is constant during the adsorption process as described in the third assumption of the theory.

CONCLUSIONS

The diffusion of C.I. Direct Red 2 and C.I. Direct Blue 15 as well as C.I. Direct Yellow 12 in the cellulose membrane was examined by means of parallel transport mechanism of surface and pore diffusion. The distinction in the theoretical concentration profile between surface diffusion and pore diffusion was clear when the value of γ is small like that of C.I. Direct Red 2 and C.I. Direct Blue 15. The experimental concentration profiles of the three dyes in the membrane agreed reasonably well with the theoretical line for surface diffusion control calculated by using the surface diffusivity obtained from the uptake curve for one sheet of the membrane. The surface diffusivities of three dyes were quite different and followed the order, C.I. Direct Yellow 12 > C.I. Direct Blue 15 > C.I. Direct Red 2. They were independent of the amount of dye adsorbed. The stronger the affinity between the dye molecule and the surface of the pore wall was, the smaller the value of the surface diffusivity was.

APPENDIX: NOMENCLATURE

C	concentration of dye in the pores (mol/m ³)
C_E	concentration of electrolyte in the bulk solution (mol/m ³)
C_0	concentration of dye in the bulk solution (mol/m ³)
D_p	pore diffusivity (m ² /s)
D_s	surface diffusivity (m ² /s)
$[D]$	mean concentration of dye in membrane ($= \int_0^l [D]_L dz/l$) (mol/m ³)
$[D]_L$	mean concentration of dye in membrane ($= q + \epsilon_p C$) (mol/m ³)
$[D']$	mean concentration of dye in membrane ($= \int_0^l [D']_L dz/l$) (mol/kg)
$[D']_L$	local concentration of dye in membrane ($q' + \epsilon_p C$) (mol/kg)
F	fractional attainment of equilibrium
l	thickness of membrane (m)
q	concentration of dye adsorbed on pore wall (mol/m ³)
q_0	adsorbed concentration of dye in equilibrium with C_0 (mol/m ³)
q'	concentration of dye adsorbed on pore wall (mol/kg)
q'_0	adsorbed concentration of dye in equilibrium with C_0 (mol/kg)
t	time (s)
V	volume of membrane swollen with water per unit dry cellulose
x	C/C_0
y	q/q_0
z	distance that dye diffused in membrane (m)
α	$q_0/\epsilon_p C_0$
β	$\alpha D_s/D_p$
γ	coefficient of the Freundlich isotherm
ϵ_p	porosity of cellulose membrane
ρ	z/l
τ_p	$D_p t/l^2$
τ_s	$D_s t/l^2$

References

1. T. H. Morton, *Trans. Faraday Soc.*, **31**, 262 (1935).
2. S. M. Neale, *Trans. Faraday Soc.*, **31**, 282 (1935).
3. E. Valko, *Trans. Faraday Soc.*, **31**, 278 (1935).
4. H. T. Morton, *J. Soc. Dyers Colour.*, **62**, 272 (1946).

5. P. B. Weisz and H. Zollinger, *Trans. Faraday Soc.*, **63**, 1815 (1967).
6. T. Hori, M. Mizuro, and T. Simizu, *Colloid Polym. Sci.*, **258**, 1070 (1980).
7. Z. Morita, T. Tanaka, and H. Motomura, *J. Appl. Polym. Sci.*, **31**, 777 (1986).
8. Z. Morita, T. Tanaka, and H. Motomura, *J. Appl. Polym. Sci.*, **30**, 3697 (1985).
9. H. Yoshida, T. Kataoka, M. Nango, S. Ohta, N. Kuroki, and M. Maekawa, *J. Appl. Polym. Sci.*, **32**, 4185 (1986).
10. C. Robinson and H. Mills, *Proc. Roy. Soc. Lond. Ser. A*, **131**, 576 (1931).
11. G. M. Nabar, F. A. Sc and C. V. Padmanbhan, *Proc. Indian Acad. Sci.*, **31A**, 371 (1950).
12. J. O. Warwicker, *J. Polym. Sci., Part A*, **1**, 3105 (1963).

Received June 16, 1987

Accepted April 4, 1988