Transport of Direct Dye into Cellulose Membrane

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Synopsis

The dyeing process for a cellulose membrane–direct dye system is analyzed based on a parallel transport mechanism of surface and pore diffusion with Freundlich isotherm. Numerical solutions were obtained in order to clarify how the surface and pore diffusion resistances affect the uptake curve. The numerical solutions were also compared with an analytical solution for surface diffusion control to establish the range where the analytical solution can be considered as an acceptable approximation. The uptake curves in the cellulose membrane-chromophore (C.I. Direct Yellow 12) system in the presence of inorganic electrolyte were measured. The rate of adsorption and the maximum amount of adsorption increased with an increase in the concentration of those electrolytes. The rate of adsorption was approximately controlled by the surface diffusion rather than by pore diffusion. The surface diffusivities of the dye were little affected by either the concentration and or nature of the electrolyte.

INTRODUCTION

In the analysis of kinetics of dyeing of cellulose by a direct dye, attention has been focussed on pore diffusion[1-7] because cellulose materials swell remarkably in aqueous solution of 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 of cellulose or not.

In the present work, a parallel transport mechanism of pore and surface diffusion with Freundlich isotherm is proposed for the cellulose membrane–direct dye system. A theoretical equation is solved numerically, and the effect of the values of equilibrium parameter and pore and surface diffusivities on the uptake curve are discussed. An analytical solution for surface diffusion control is compared with the numerical solution, and the range where it can be considered as an acceptable approximation is shown. Experimental uptake curves and the concentration profile in cellulose membrane–chromophore (C.I. Direct Yellow 12) system are presented and discussed in relation to the theory. An inorganic electrolyte has been used as a stimulator of the dyeing. It has not been established how the electrolyte

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affects the adsorption rate. We used NaCl and CsCl as the stimulators, and their effect on the uptake curve is also shown.

THEORETICAL ANALYSIS

It is assumed that (1) surface and pore diffusions occur in parallel within a cellulose membrane, (2) pore and surface diffusivities are constant during the adsorption process, (3) pore diameter and void fraction of the sheet are constant during the adsorption process, and (4) the concentration of dye in the pore is in local equilibrium with the concentration of the adsorbed dye on the surface of the pore wall. Assumptions (1)–(3) give the following mass balance equation:

$$\varepsilon_p \frac{\partial C}{\partial t} + \frac{\partial q}{\partial t} = \varepsilon_p D_p \frac{\partial^2 C}{\partial z^2} + D_s \frac{\partial^2 q}{\partial z^2} \tag{1}$$

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

$$\tau_p = \frac{D_p t}{l^2}, \quad \rho = \frac{z}{l}, \quad x = \frac{C}{C_0}, \quad y = \frac{q}{q_0}, \quad \alpha = \frac{q_0}{\varepsilon_p C_0}, \quad \beta = \alpha \frac{D_s}{D_p} \tag{2}$$

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

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

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

where $\tau_s = D_s t/l^2$.

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

$$y = x^\gamma \tag{5}$$

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

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

Initial and boundary conditions are given by

$$
\begin{array}{lll}
\text{(I.C.)} & y = 0 & \text{at } \tau_p = 0 \ \text{ or } \ \tau_s = 0 \\[2mm]
\text{(B.C.)} & y = 1 & \text{at } \rho = 0 \\[3mm]
& \dfrac{\partial y}{\partial \rho} = 0 & \text{at } \rho = 2
\end{array}
\right\} \tag{8}
$$

Local concentration of the dye $[D]_L$, mean concentration $[D]$, and fractional attainment of equilibrium F are expressed by eqs. (9)–(11), respectively:

$$
[D]_L = q + \varepsilon_p C \tag{9}
$$

$$
[D] = \int_0^1 (q + \varepsilon_p C)\, dz/l \tag{10}
$$

$$
F = \frac{[D]}{q_0 + \varepsilon_p C_0} = \frac{\alpha \displaystyle\int_0^1 y\, d\rho + \displaystyle\int_0^1 x\, d\rho}{\alpha + 1} \tag{11}
$$

Where $\alpha = \infty$, eq. (4) is reduced to eq. (12) and the solutions are given by eqs. (13) and (14):[8]

$$
\frac{\partial y}{\partial \tau_s} = \frac{\partial^2 y}{\partial \rho^2} \tag{12}
$$

$$
y = 1 - 2 \sum_{n=0}^{\infty} \frac{(-1)^n}{(n + 0.5)\pi}\, e^{-(n + 0.5)^2 \pi^2 \tau_s} \cos(n + 0.5)\pi\rho \tag{13}
$$

$$
F = 1 - 2 \sum_{n=0}^{\infty} \frac{1}{(n + 0.5)^2 \pi^2}\, e^{-(n + 0.5)^2 \pi^2 \tau_s} \tag{14}
$$

These equations are not affected by the concentration of dye in the pore, because when $\alpha = \infty$, the concentration of the dye adsorbed on the surface of the pore wall is much higher than that in the pore. Therefore, when α is large enough, the $F - \tau_s$ curve is unaffected not only by α but also by γ.

Equations (6) and (7) are solved numerically by being transformed to finite difference equations. Figure 1 shows the effect of β on the uptake curve when $\alpha = 100$ and $\gamma = 0.5$. As β increases, the adsorption rate increases. When $\beta \leq 0.1$, the adsorption rate can be approximated by that in pore diffusion control ($\beta = 0$). The dotted lines indicate the analytical solution eq. (14) for large α. The uptake curve in $\beta \geq 10$ can be estimated by the solution. Figure 2 shows the effect of β on the concentration profile at $\tau_p = 2.0$ in this case. It is clear that the larger β is, the faster becomes the adsorption
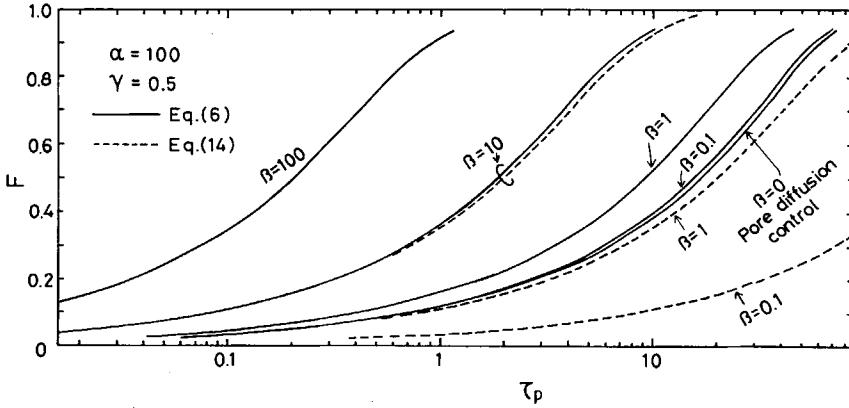
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Fig. 1. Effect of β on uptake curve (both resistances exist). $\alpha = 100$; $\gamma = 0.5$: (—) eq. (6); (----) eq. (14).

rate. The effect of γ on the concentration profile is also presented in the case of $\beta = 1$. The concentration near the membrane surface for $\gamma = 0.1$ is higher than that for $\gamma = 0.5$ and the profile for $\gamma = 0.1$ is steeper than that for $\gamma = 0.5$. This means that the boundary between dyed and undyed parts becomes sharper with a decrease of γ; this is because dye molecules are adsorbed well on the pore surface in the case of small γ, and thus the pore surface is saturated from the membrane surface in turn. Figure 3 represents the effect of α and γ on the uptake curve in the case of pore diffusion control ($\beta = 0$). The adsorption rate is affected by α considerably. The smaller α is, the faster becomes the adsorption rate. This is because when α is smaller, the surface of the pore wall is saturated sooner than when α is larger. The smaller γ is, the faster the adsorption rate becomes. The effect of γ on the adsorption rate is little affected by α. Figure 4 shows uptake curves in the case of surface diffusion control ($\beta = \infty$). The adsorption rate decreases with decreasing values of α and γ. When $\alpha \geq 10$, the effect of α and γ is small.
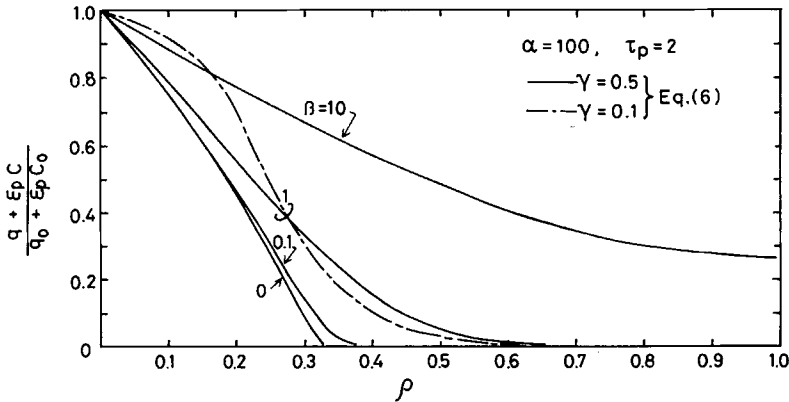

Fig. 2. Effects of β and γ on concentration profile (both resistances exist). $\alpha = 100$; $\tau_p = 2$; γ [eq. (6)]: (—) 0.5; (----) 0.1.
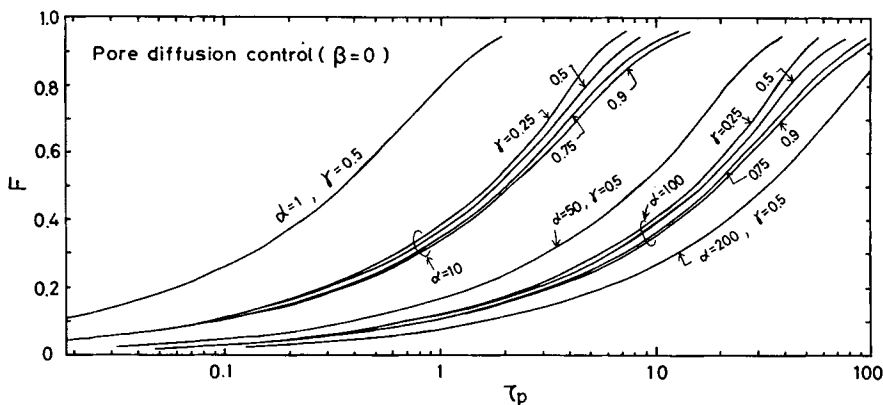
Fig. 3.   Effects of α and β on uptake curve.

The uptake curve for $\alpha \geq 50$ can be approximated by eq. (14) shown by the one-point-dashed line.

EXPERIMENTAL

Materials

Chromophore (C.I. Direct Yellow 12, sodium salt) was obtained from Sumitomo Chemical Co.. The chromophore was purified by the method of Robinson and Mills[9] and converted to the cesium salt with the corresponding hydroxide. The conversion of counterion was above 90% by analysis using a Hitachi 50A atomatic absorption spectrophotometer. The inorganic electrolytes used were sodium chloride and cesium chloride. Cellulose membrane (cellophane film) was a gift from Dr. T. Hori (obtained from Fukui Chemicals, Ltd.). The cellulose membrane was soaked in boiled deionized distilled water for 3 h and then washed with deionized distilled water. The thickness (l) and porosity (ε_p) of the membrane were 40 μm and 0.621, respectively.[10]
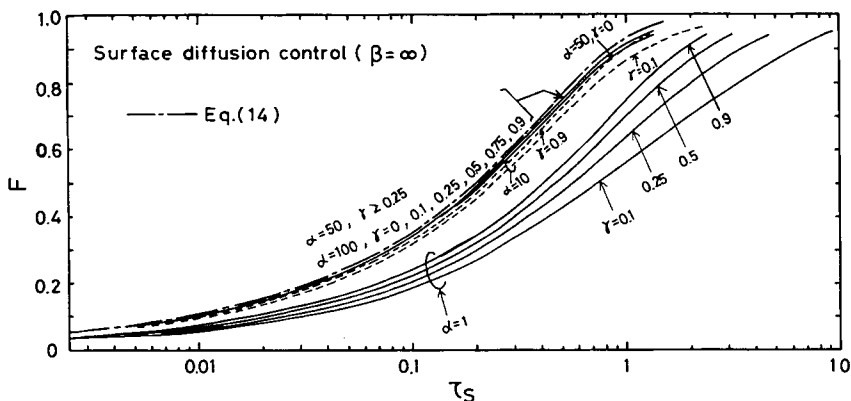

Fig. 4.   Effects of α and γ on uptake curve: (———) eq. (14).

Carboxyl group contents of the membrane determined by iodometry was 62.5×10^{-3} mol/kg.[11] As the cellulose film does not contain a significant concentration of carboxyl groups, the internal volume term will not be affected by surface potential and ionic strength in the theoretical treatment for this text. Vickerstaff indicated that the water content of cellulose membrane was 0.33 m³/kg, which is consistent with the volume of the membrane determined theoretically.[12] To evaluate α in eq. (4), the values of ε_p (0.621) and the volume term (0.33 m³/kg) were used.

EQUILIBRIA AND TRANSPORT OF CHROMOPHORE

Equilibrium uptake of chromophore for cellulose membrane was carried out at a temperature of $25 \pm 0.5°C$ for 48 h as described in the previous articles.[13,14] The concentration of the chromophore in solution ranged from 0.100 to 2.16 mol/m³. Diffusion of the chromophore was measured in an ultrafilltration-type cell as shown in Figure 5. The membrane, swollen by deionized water, (6) was put on the stainless steel fitting (1). Uptake curves (the relation between F–time or [D]–time) were measured by using one sheet of the membrane. The concentration profiles were obtained by superposing 10 sheets of the membrane. The solution was stirred at a high enough rate to prevent hydrodynamic boundary layer effects. Uptaken membranes were extracted with 25% aqueous pyridine. The concentration of the chromophore eluted was determined using a Hitachi 124 type spectrophotometer with 25% pyridine as reference. To prevent complication of chromophore, bisazodye derivative, the chromophore solution was illuminated for about
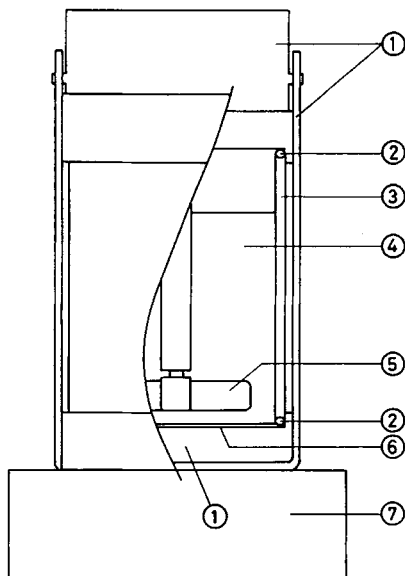

Fig. 5. Experimental apparatus: (1) metal fitting; (2) rubber packing; (3) cylinder cell; (4) aqueous solution of dye and electrolyte; (5) magnet for stir; (6) cellophane membrane; (7) magnetic stirrer.

1 h just before measurement. pH was about 6.5 in the presence of different amount of dye and electrolyte.

RESULTS AND DISCUSSION

The equilibrium isotherms reveal Freundlich-type adsorption as shown in Figure 6. The obtained Freundlich constants γ are summarized in Table I.

The amounts of chromophore (sodium salt) adsorbed by one sheet of cellulose membrane, [D'], are plotted vs time in Figure 7. The concentration of the stimulator NaCl affects the adsorption rate. As the concentration of NaCl in the bulk solution increase, the maximum amount of adsorption, which is in equilibrium with the bulk solution concentration of the dye, becomes larger and the adsorption rate therefore gets faster.

Figure 8 shows the relation between fractional attainment of equilibrium F and time in runs 1–4. The data for each run are nearly independent of α, and they are approximately correlated by the solid line. The values of α are 15.1–164, as shown in Table I. The adsorption rate may therefore be controlled by the surface diffusion, because the comparison of Figures 3 and 4 led to the conclusion that if the uptake curves in $\alpha > 10$ are little affected by α, the adsorption rate is controlled by the surface diffusion. We then tried to match the theoretical equation (7) for surface diffusion control with the uptake data. The solid lines in Figure 7 are the theoretical lines calculated using the values of α, γ, and D_s in Table I. The values of D_s were
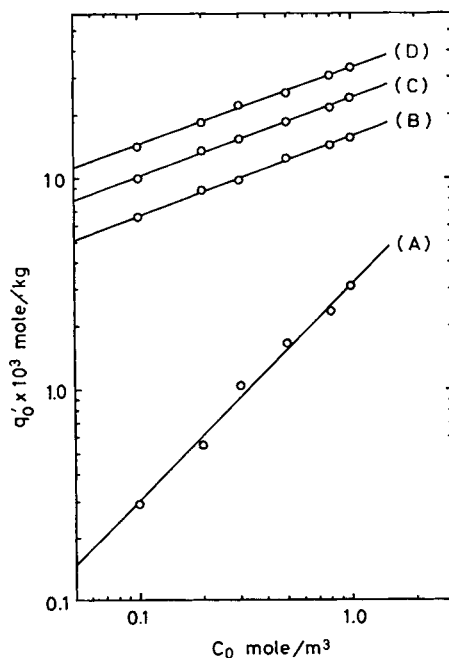

Fig. 6.   Uptake isotherms of C.I. Direct Yellow 12 on cellulose membrane in aqueous sodium chloride solutions: (A) in the absence of sodium chloride, $C_E = 0$ (mol/m³); (B,C, D) in the presence of sodium chloride, $C_E = 10$, 20, and 30, respectively.

TABLE I
Physical Properties in the Cellulose Membrane–Chromophore System

Run no.[a]	C_0 (mol/m^3)	C_E (mol/m^3)	α	γ	$D_s \times 10^{14}$ (m^2/s)
		NaCl			
1(1)	1	0	15.1	1.00	2.69
2(1)	1	10	73.2	0.377	3.50
3(1)	1	20	122	0.372	3.55
4(1)	1	30	164	0.363	3.45
5(10)	1	10	73.2	0.377	3.50
		CsCl			
6(1)	1	0	22.2	0.872	3.29
7(1)	1	10	87.4	0.325	3.56
8(10)	1	10	87.4	0.325	3.56

[a] Runs 1–5: Sodium salt of chromophore was used.

Runs 6–8: Cesium salt of chromophore was used. The number in the parentheses shows the number of sheets of the membrane superposed.

obtained by matching the theoretical values with the data. The agreement between the solid lines and the data is reasonably good. The dotted lines show the analytical solution (14) for surface diffusion control and large α. Not much difference exists between the solid and dotted lines except for run 1 (α = 15.1). From these results, eq. (14) can be approximately used for $\alpha > 50$.

Figure 9 shows the concentration profiles in the membrane. The solid lines represent the theoretical profiles for surface diffusion control calcu-
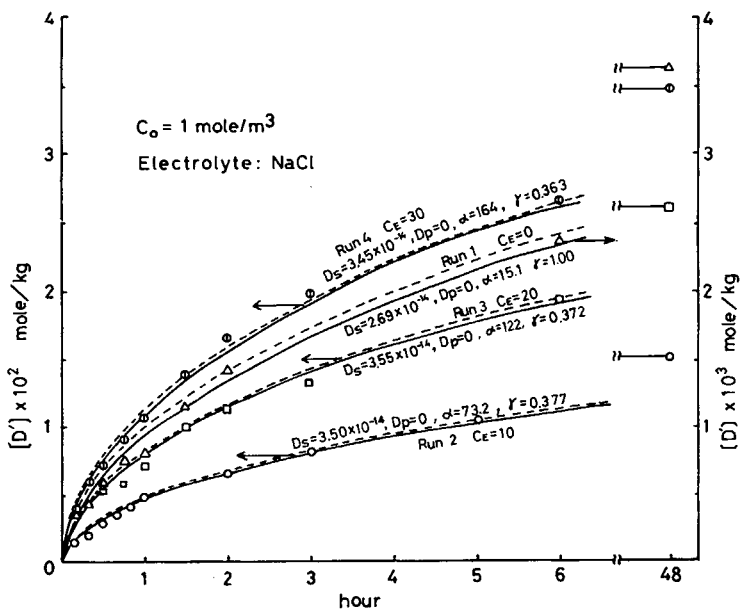

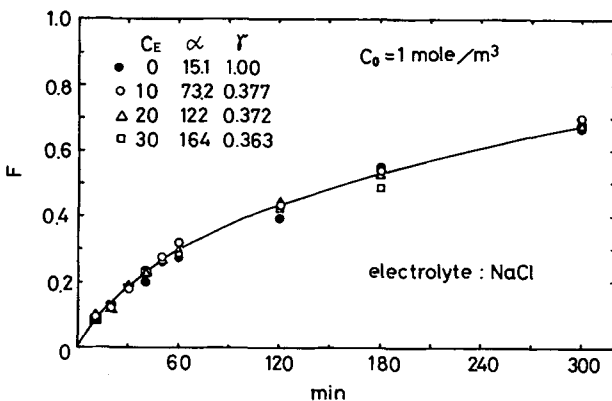Fig. 7.   Effect of C_E on uptake curve

Fig. 8.   Effect of α on F–time curve: $C_{\cdot E}$, α, γ: (●) 0, 15.1, 1.00; (○) 10, 73.2, 0.377; (△) 20, 122, 0.372; (□) 30, 164, 0.363.

lated by using D_s, which was obtained from the uptake curve for one sheet of the membrane, α and γ in Table I. The data in both figures agree reasonably well with the solid lines. In addition, uptake curves and concentration profiles for the cellulose membrane–chromophor (cesium salt) system, runs 6–8, were also represented well by the theoretical lines calculated by eq. (7) ang α, γ, and D_s in Table I. From these results, it can be concluded that the dominant resistance to mass transfer of the dye is surface diffusion rather than pore diffusion.

In Figure 10, the experimental surface diffusivities D_s of the dye are plotted vs. q_0' [mol/kg], which is the equilibrium concentration in the membrane with the bulk solution concentration C_0. D_s is little affected by the electrolytes. It is nearly constant, $3.5 \times 10^{-14}\,\mathrm{m^2/s}$, for $q_0' > 0.01$, decreasing slightly with decrease of q_0' for $q_0' < 0.01$. As the size of the inorganic electrolyte used here is much smaller than that of the dye, the electrolyte diffuses into the pore much faster than the dye. It can therefore be assumed that
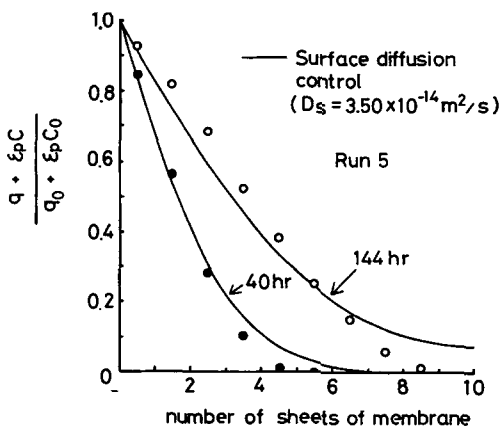

Fig. 9.   Concentration profile in cellophane membrane: (—) surface diffusion control.
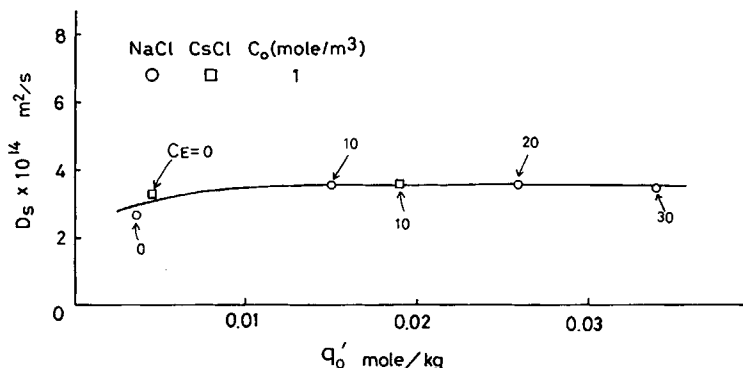
Fig. 10. Relation between surface diffusivity and q_0': (○) NaCl; (□) CsCl.

the concentration of the electrolyte in any position of the pore is the same as that in the bulk solution while the dye diffuses into the membrane. From these points of view, it may be thought that the electrolytes do not affect the diffusion mechanism of the dye, although they considerably influence the equilibrium (α and γ). Pore diffusivity has been presented by assuming pore diffusion control.[1-7] We also calculated D_p by assuming pore diffusion control and the obtained values are shown in Figure 11. D_p depends on q_0' very much. If pore diffusion is the significant resistance, D_p must be independent of q_0'. From these results shown in Figures 10 and 11, one may conclude that surface diffusion is much more significant than pore diffusion.

CONCLUSION

Transport of direct dye through a cellulose membrane was analyzed assuming a parallel transport mechanism of surface and pore diffusions with a Freundlich isotherm. Numerical solutions of the appropriate diffusion
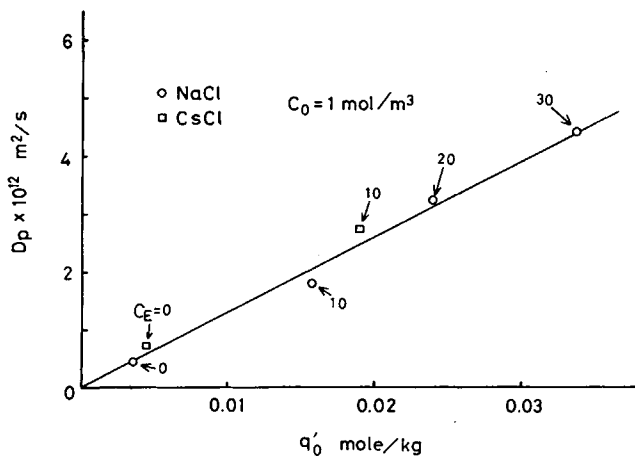

Fig. 11. Relation between pore diffusivity and q_0': (○) NaCl; (□) CsCl.

equation gave the following conclusions: When $0.1 < \beta < 10$, both resistances should be considered. When $\beta \leq 0.1$, the adsorption rate can be approximated by pore diffusion and when $\beta \geq 10$, it approaches surface diffusion control. The adsorption rate is considerably affected by α in the case of pore diffusion control but not so much in surface diffusion control. When $\alpha \geq 50$ in surface diffusion control, eqs. (13) and (14) can be used. Experimental data for the cellulose membrane–chromophore system in the presence of inorganic electrolyte as a stimulator show good agreement with the theory of surface diffusion control rather than that of pore diffusion control. The surface diffusivities are little affected by the concentration of electrolyte and by the different electrolytes.

APPENDIX: NOTATION

C	concentration of dye in pore (mol/m³)
C_E	concentration of electrolyte in bulk solution (mol/m³)
C_0	concentration of dye in bulk solution (mol/m³)
D_p	pore diffusivity (m²/s)
D_s	surface diffusivity (m²/s)
[D]	mean concentration of dye in membrane ($= \int_0^1 [D]_L \, dz/l$) (mol/m³)
$[D]_L$	local concentration of dye in membrane ($= q + \varepsilon_p C$) (mol/m³)
[D']	mean concentration of dye in membrane ($= \int_0^1 [D']_L \, dz/l$) (mol/kg)
$[D']_L$	local concentration of dye in membrane ($= q' + \varepsilon_p C$) (mol/kg)
F	fractional attainment of equilibrium
l	thickness of membrane (m)
q	concentration of dye adsorbed on pore wall (mol/m³)
q_0	adsorbed concentration of dye in equilibrium with C_0 (mol/m³)˙
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)
x	C/C_0
y	q/q_0
z	distance through membrane (m)
α	$q_0/\varepsilon_p C_0$
β	$\alpha D_s/D_p$
γ	coefficient of Freuundlich isotherm
ε_p	void fraction of pore
ρ	z/l
τ_p	$D_p t/l^2$
τ_s	$D_s t/l^2$

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