

Diffusion/Adsorption Model of Cellulose Dyeing. II. Ordinary Cellulose-Direct Dye System

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Synopsis

The diffusion and adsorption of C.I. Direct Yellow 12 and Blue 15 in water-swollen ordinary cellophane sheets were examined at various ionic strengths. The concentration dependence of apparent diffusion coefficients, D_c , for these dyes was obtained from the diffusion profiles in the substrate, which were measured by the use of the cylindrical film roll method. The decrease of apparent porosity with an increase in the amounts of adsorption was observed. To explain the diffusion/adsorption behaviors of these systems, a variable porosity model was proposed and was applied to analyze the concentration dependence of D_c 's. The diffusion/adsorption behaviors of these dyes could be quantitatively described by this model at relatively low ionic strengths. At higher ionic strengths and/or lower values of C , i.e., at the large values of C_{im}/C_m , where the C 's are the concentrations of immobilized (suffix *im*) and mobile (suffix *m*) species, it needed to introduce the concept of dynamic equilibria which occurred simultaneously with diffusion but deviated from the true equilibria measured by the adsorption experiments.

INTRODUCTION

In the previous paper,¹ the diffusion of C.I. Direct Yellow 12 and Blue 15 in the never-dry viscose sheet was studied and the applicability of the diffusion/adsorption model proposed so far was tested. The salt concentration dependence of the diffusion coefficients, D_0 , in aqueous solution for C.I. Direct Yellow 12 was a major factor which influenced the validity of the diffusion/adsorption model. No model explained the concentration dependence of apparent diffusion coefficients, D_c , for Blue 15.

The D_c of Yellow 12 decreased monotonically with an increase in salt concentration.^{1,2} In general, however, the D_c at a given concentration of C (C is the total concentration) had a maximum with increasing salt concentration.^{3,4} This behavior has been used to test the validity of diffusion/adsorption model.^{2,5}

Standing et al. could not explain the increase of D_c with an increase in salt concentration below a concentration where the maximum of D_c was observed.⁵ From this point, Warwicker's treatment did not prove the validity of their model, as Yellow 12 was not a proper dye.²

On the other hand, the values of apparent porosity estimated from the diffusion profiles of Yellow 12 in never-dry cellulose were constant in spite of an increase in the adsorption of Yellow 12. Those for Blue 15 gave unreasonable values, a failure of diffusion/adsorption model. Horii et al.⁶ and Tsimboukis and Petropoulos⁷ showed an decrease of apparent porosity

for anionic penetrant with an increase in the amount of fixed anionic site or adsorption of dye. There may be, therefore, contradictions between them.

In the present study, the diffusion and adsorption of some direct dyes in ordinary cellulose are examined, and the concentration dependence of D_c is analyzed to test the validity of diffusion/adsorption model in cellulose. In order to explain the decrease of apparent porosity with an increase in the amount of adsorption, a variable porosity model for the diffusion/adsorption behavior of direct dyes in cellulose is proposed. The validity or limit of this model is tested by experiments.

THEORETICAL

Basic Equations for Variable Porosity Model

In the diffusion/adsorption model of water-swollen cellulose, the direct dyes present as mobile species, whose concentration is denoted by C_m , in the pore solution, and immobilized (adsorbed) species, whose concentration is denoted by C_{im} , on cellulose molecule:

$$C = PC_m + C_{im} \quad (1)$$

where P is the fraction of the solution phase where the dyes can diffuse to the total volume of swollen cellulose. The values of P in the diffusion of anionic penetrant should decrease with a decrease of ionic strength and/or with an increase of fixed anionic groups.^{6,7} The adsorption of direct dyes on cellulose should bring about an increase of fixed anionic groups, i.e., a decrease of apparent porosity.

Since, therefore, $\partial P / \partial C \neq 0$, the one-dimensional diffusion equation based on the diffusion/adsorption model:

$$\frac{\partial C}{\partial t} = \frac{\partial(PC_m)}{\partial t} + \frac{\partial C_{im}}{\partial t} = \frac{\partial}{\partial x} \left(D_c \frac{\partial C}{\partial x} \right) \quad (2)$$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[\frac{D_m}{b_m} \left(P \frac{\partial C_m}{\partial C} + C_m \frac{\partial P}{\partial C} \right) + \frac{D_{im}}{b_{im}} \frac{\partial C_{im}}{\partial C} \right] \frac{\partial C}{\partial x} \quad (3)$$

where D_c is the apparent diffusion coefficient of "total" species, b_m and b_{im} are the tortuosity factors for the diffusion of mobile and immobilized species, respectively.

If the adsorption equilibria described by Freundlich-type isotherms were attained between the mobile and the immobilized species, either assumption has been made in the diffusion/adsorption model as follows:

$$C = KC_0^{1/n} \rightarrow C = KC_m^{1/n} \quad (4)$$

or

$$C = KC_0^{1/n} \rightarrow C_{im} = KC_m^{1/n} \quad (5)$$

where C_0 is the dye concentration in the external solution. The relations between C and C_0 , described by Freundlich constants K and n , are determined by the experiments of equilibrium adsorption.

If the first relation (4) is inserted in eq. (3), the apparent diffusion coefficient D_c , described by the square bracket on the rhs of eq. (3), is given by

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

When $D_{im} = 0$, this equation becomes

$$D_c = \frac{D_m}{b_m} \left(nP + C \frac{\partial P}{\partial C} \right) K^{-n} C^{n-1} \quad (7)$$

When $\partial P / \partial C = 0$, eq. (6) leads a corresponding equation of the Standing-Warwick-Willis model, to which terms of tortuosity factors are added:

$$D_c = P \left(\frac{D_m}{b_m} - \frac{D_{im}}{b_{im}} \right) n K^{-n} C^{n-1} + \frac{D_{im}}{b_{im}} \quad (8)$$

On the other hand, when eq. (5) is used, another equation for D_c is obtained when $\partial P / \partial C = 0$:

$$D_c = \left(P \frac{D_m}{b_m} + K n \frac{D_{im}}{b_{im}} C^{n-1} \right) \left(P + K n C^{n-1} \right) \quad (9)$$

When $PC_m \ll C_{im}$ or C , eq. (9) is equal to eq. (8). In order to analyze the relations between D_c and C , eq. (8) is more suitable than eq. (9).

In these treatments, the values of D_m must be determined from the diffusion coefficient D_0 of the dye in aqueous solution. Since the values of D_0 may not be always equal to those of D_m , there would be a relation

$$D_m = k D_0 \quad (10)$$

The values of k may depend upon the anisotropy of penetrant. If the diffusions through various membrane are examined, they may also depend upon the membrane.

On the analysis of the D_c by eq. (7), factors kP/b_m are estimated as the apparent porosity, since the values of k and b_m cannot be experimentally and independently determined.

EXPERIMENTAL

The same experiments of equilibrium adsorption and diffusion by the use of cylindrical film roll method were carried out by using the same dyes as before.¹ Cellophane sheets (# 300), manufactured and supplied by Tokyo Cellophane Sheets Co., were used as substrates. In order to estimate the

apparent porosity, the permeation of β -Naphthol Violet (pH indicator, reagent grade, Tokyo Kasei Kogyo Co.) was carried out by the method of Hori et al.⁶ In order to increase the amount of fixed anionic sites, the cellophane sheets were evenly dyed and fixed with C.I. Reactive Blue 2. The thickness of a water-swollen cellophane was measured to be 36.28 μm and the degree of swelling, W , was $1.53 \pm 0.017 \text{ dm}^3$ swollen cellulose/kg dry cellulose.

RESULTS AND DISCUSSION

Concentration Dependence of D_c

Results of equilibrium adsorption for C.I. Direct Yellow 12 and Blue 15 are shown as Freundlich constants in Table I. The values of K and n had no consistent relation with those for never-dry cellulose (cf. Table II in Ref. 1). Thus, Freundlich constants K and n would contain a factor of membrane geometry. The authors tried to use the equation of "standard affinity," $\Delta\mu^0$, for Freundlich isotherm:

$$-\Delta\mu^0 = RT \ln C(\text{Na})_f^z / V^{z+1} - RT \ln C_0(\text{Na})_s^z \quad (11)$$

where (Na) is the concentration of sodium ions in fiber (suffix f) and solution (suffix s) phase, V is the volume term (dm^3/kg dry cellulose), and z is the number of anionic groups in a dye molecule. On minimizing the deviation of data from eq. (11), the values of $\Delta\mu^0$ and V depended upon the substrate, ionic strength, and dyes. Thus, the constants in the standard affinity equation contain, besides the original factors of membrane, factors of the dye dependent upon the ionic strength as well. Equation (11) may not be superior to describe the adsorption equilibrium of the diffusion/adsorption behavior in the direct dye-cellulose system. As the Freundlich isotherm is easy to be combined with diffusion/adsorption equation, the isotherm is used in the present study.

Although Weisz and Zollinger determined the limit of n to be 1.6, both dyes had larger values of n than 1.6.⁸

TABLE I
Freundlich Constants and Diffusion Coefficients in Aqueous Salt Solution at 90°C

C.I. Direct	NaCl (mol dm ⁻³)	Freundlich constants ^a			$D_0 \times 10^5$ (cm ² s ⁻¹)
		K	n	r	
Yellow 12	0.01	0.169	2.00	0.994	1.37
	0.02	0.193	2.02	0.998	1.17
	0.05	0.244	2.12	0.995	0.74
	0.10	0.325	2.14	0.989	0.56
Blue 15	0.01	0.390	1.83	0.997	1.05
	0.02	0.676	1.89	0.991	
	0.05	1.536	1.90	0.987	
	0.10	2.896	1.98	0.999	

^a $C = K C_0^{1/n}$; r is the correlation coefficient.

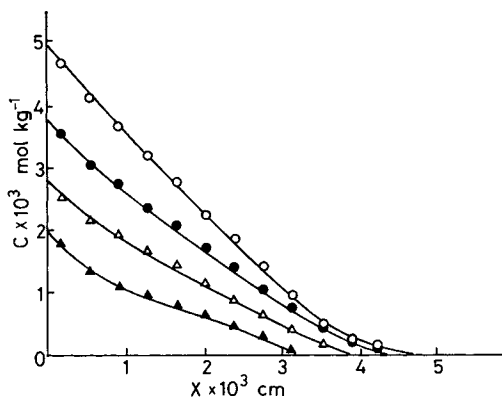


Fig. 1. Concentration profiles at various salt concentrations; C.I. Direct Yellow 12 (90°C). NaCl (mol dm⁻³): (▲) 0.01; (△) 0.02; (●) 0.05; (○) 0.10.

The diffusion profiles for C.I. Direct Yellow 12 in the cellophane sheet are shown in Figure 1 for an example. Similar curves are also obtained for Blue 15. The relationships between D_c and C are obtained by Matano's method from the diffusion profiles (Figs. 2 and 3). There were found no essential differences between the diffusion behaviors in the never-dry and ordinary cellophane sheets.

Apparent Porosity of Cellulose

As in the previous paper,¹ it was concluded that $D_{im} = 0$. Then, theoretical differential diffusion coefficients D_c for the variable porosity model with $D_{im} = 0$ are given:

$$D_c = \frac{kD_0}{b_m} \left(nP + C \frac{\partial P}{\partial C} \right) K^{-n} C^{n-1} \quad (12)$$

By the difference method, the relationship between kP/b_m and C could be obtained by applying eq. (12) to the experimental concentration dependence of D_c shown in Figures 2 and 3. The results obtained were confirmed to

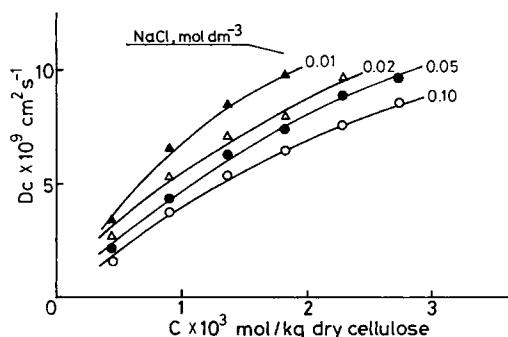


Fig. 2. Concentration dependence of apparent diffusion coefficients, D_c , for C.I. Direct Yellow 12 in ordinary cellulose sheet at various salt concentrations (90°C).

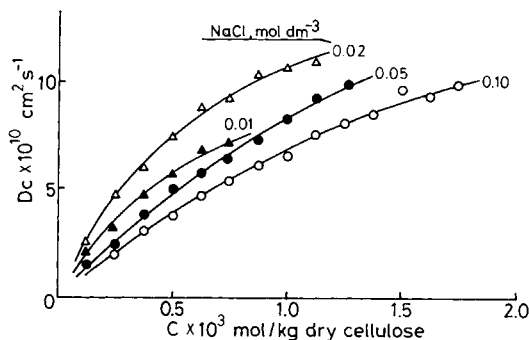


Fig. 3. Concentration dependence of apparent diffusion coefficients, D_c , for C.I. Direct Blue 15 in ordinary cellulose sheet at various salt concentrations (90°C).

satisfy the experimental values of D_c . In Figures 4 and 5, the relationships between P and A for both the dyes when $kD_m/b_m = D_0$ are shown and the values of apparent porosity measured by β -Naphthol Violet when the assumption of $k/b_m = 1$ was made are also shown. Here, A is the total amount of anionic groups fixed in the substrate (meq/kg dry cellulose) and is given as follows:

$$A = S + zC \quad (13)$$

where S is the carboxy group content in cellulose (39.0 meq/kg dry cellulose) and z is the number of sulfonic groups in a dye molecule.

On multiplying P shown in Figures 4 and 5 by a constant factor k/b_m , both the curves of direct dyes and β -Naphthol Violet for various ionic strengths could coincide with or approximate to each other (Fig. 6). In the case of Blue 15, the coincides were observed when $I = 0.01$ and 0.02 and when $I \geq 0.05$, the deviations at smaller C and the approximations at larger C .

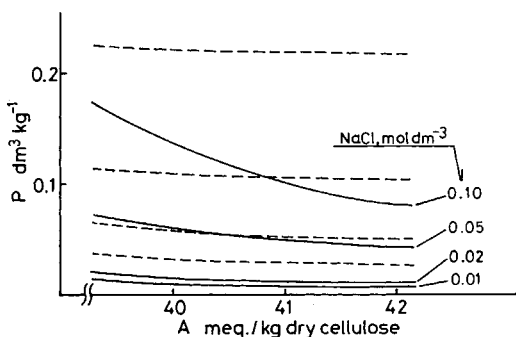


Fig. 4. Relationships between the apparent porosity P and the amount A of anionic groups fixed in the substrate described by eq. (13); C.I. Direct Yellow 12 (—) and β -Naphthol Violet (---); the values of k/b_m were assumed to be unity for β -Naphthol Violet.

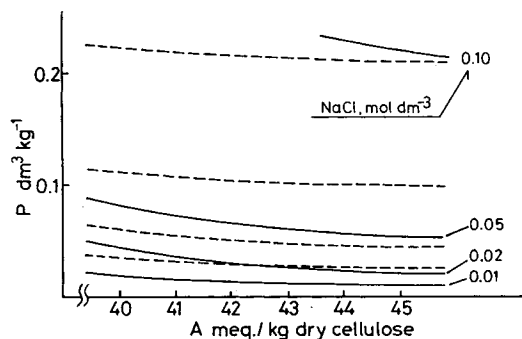


Fig. 5. Relationships between the apparent porosity P and the amount A of anionic groups fixed in the substrate described by eq. (13); C.I. Direct Blue 15 (—) and β -Naphthol Violet (---); the values of k/b_m were assumed to be unity for β -Naphthol Violet.

As reported in previous paper, the values of diffusion coefficients, D_0 , in aqueous solution for Blue 15 were constant and those for Yellow 12 showed a salt concentration dependence. For Yellow 12, the constancy of k/b_m over the applied salt concentration range was obtained when the variable D_0 's were used in these calculations.

In the range of C where the values of porosity estimated by the use of β -Naphthol Violet coinciding with those of kP/b_m obtained by eq. (12) from the D_c of direct dyes, the variable porosity model holds for the system. These situations become clearer if the theoretical D_c described by eq. (12) are compared with the experimental values of D_c shown in Figures 2 and 3.

Limit of Variable Porosity Model

The relationships between P and A in Figures 4 and 5 can be shown as those between D_c and C . In Figure 7(a), the D_c vs. C plots for Blue 15 at $I = 0.02$ are shown as an example. Assuming that $k/b_m = 1$, the theoretical curve of D_c deviated upward from the experimental curve of D_c . Thus, by introducing a factor of k/b_m , the concentration dependence of D_c could be

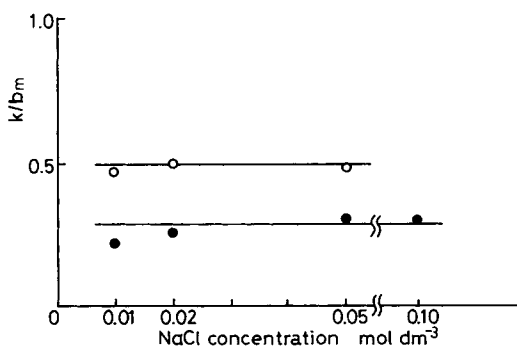


Fig. 6. The values of k/b_m at various salt concentrations for C.I. Direct Yellow 12 (○) and Blue 15 (●).

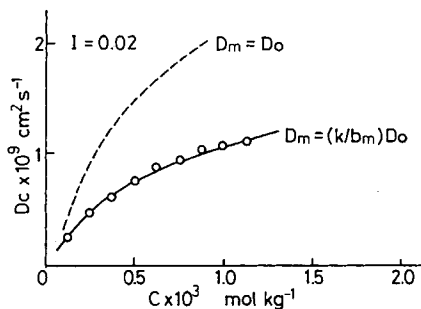


Fig. 7(a). Comparison among the experimental diffusion coefficients (\circ), D_c (Fig. 3), the theoretical curves of D_c when $k/b_m = 1$ and $D_m = D_0$ (---) and when $D_m = (k/b_m)D_0$ (—) for Blue 15 at $I = 0.02$.

described by the variable porosity model at lower ionic strengths. At $I = 0.05$ for Blue 15, the same situation as in the case of $I = 0.02$ was observed, and both the curves approached to each other at large values of C [Fig. 7(b)].

Here, the stronger immobilization effect by adsorption was observed at smaller values of C . In general, the deviation occurred under the conditions of C/C_m larger than about 2×10^2 ($\text{dm}^3 \text{kg}^{-1}$). In the Freundlich isotherm, we consider a discontinuous two-phase model. In the real adsorption system, the concentration profiles of dyes should be continuous in the direction of adsorption interaction. When the slope of profiles was very steep or the values of C/C_m was large, the adsorption equilibria accompanied by diffusion may not be able to follow the equilibria described by the Freundlich isotherm, which was determined from the experiments of equilibrium adsorption. The larger the values of C , the smaller the values of C/C_m become; then the retardation effect may disappear.

The diffusion/adsorption behavior of direct dyes in cellulose can be quantitatively explained by the variable porosity model combined with Freundlich isotherm at relatively low ionic strengths. The deviation from this treatment occurs at higher ionic strengths and lower values of C , which

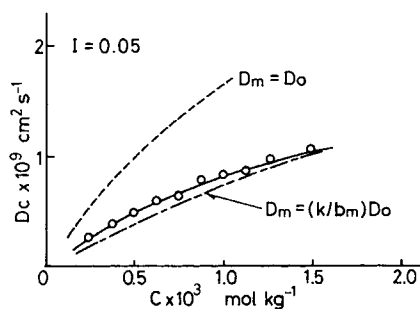


Fig. 7(b). Comparison among the experimental diffusion coefficients (\circ), D_c (Fig. 3), the theoretical curves of D_c when $k/b_m = 1$ and $D_m = D_0$ (---) and when $D_m = (k/b_m)D_0$ (—) for Blue 15 at $I = 0.05$.

can be qualitatively explained by the dynamic equilibria of diffusion/adsorption system.

The salt concentration dependence of D_c can also be explained by these treatments. The increase of D_c at low salt concentrations at a given value of C with an increase in the salt concentration is due to the larger increase of apparent porosity than the immobilization effect by adsorption. The decrease of D_c above a salt concentration where the maximum value of D_c was observed is due to the reverse effect since the increase of apparent porosity with an increase in ionic strength becomes smaller at higher ionic strength.

A quantitative treatment for the relationship among the apparent porosity, ionic strength, and the amount of anionic groups fixed in the substrate is under investigation.

APPENDIX: NOMENCLATURE

A	total amount of anionic groups fixed in the substrate (meq/kg dry cellulose)
b_m, b_{im}	tortuosity factors for the diffusion of mobile and immobilized species
C	total concentration of dye in cellulose (mol/dm ³ swollen cellulose)
C_m	concentration of mobile species in the pore solution (mol dm ⁻³)
C_{im}	concentration of immobilized species on cellulose (mol/dm ³ swollen cellulose)
C_0	concentration of dye in the external solution (mol dm ⁻³)
D_0	diffusion coefficient of dye in aqueous salt solution (cm ² s ⁻¹)
D_c	apparent diffusion coefficient for the total concentration (cm ² s ⁻¹)
D_m, D_{im}	diffusion coefficients of mobile and immobilized species (cm ² s ⁻¹)
k	ratio of D_0/D_m
K, n	Freundlich constants
P	porosity (dm ³ /dm ³ swollen cellulose)
t	time (s)
S	carboxy group content in cellulose (39.0 meq/kg dry cellulose)
W	degree of swelling 1.53 dm ³ swollen cellulose/kg dry cellulose; when C or C_{im} is multiplied by W , the unit of concentration is converted into mol/kg dry cellulose
x	distance (cm)
z	number of sulfonic groups in a dye molecule

References

1. Z. Morita, T. Tanaka, and H. Motomura (part 1), *J. Appl. Polym. Sci.* in press.
2. J. O. Warwicker, *J. Polym. Sci., Part A*, **1**, 3105 (1963).
3. S. M. Neale and A. M. Patel, *Trans. Faraday Soc.*, **30**, 905 (1963).
4. R. McGregor, R. H. Peters, and J. H. Petropoulos, *Trans. Faraday Soc.*, **58**, 1045 (1961).
5. H. A. Standing, J. O. Warwicker, and H. F. Willis, *J. Text. Inst.*, **38**, T335 (1947).
6. T. Hori, R. J. Ott, and P. Rys, *Polym. Eng. Sci.*, **20**, 264 (1980).
7. D. G. Tsimboukis and T. H. Petropoulos, *J. Chem. Soc. Faraday I*, **20**, 705, 717 (1979).
8. P. B. Weisz and H. Zollinger, *Trans. Faraday Soc.*, **64**, 1693 (1968).

Received August 14, 1984

Accepted January 22, 1985