

# Diffusion/Adsorption Model of Cellulose Dyeing. I. The Diffusion through Never-Dry Cellulose

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## Synopsis

The diffusion coefficients  $D_0$ , of C.I. Direct Yellow 12, Red 2, Blue 1, and Blue 15 in aqueous NaCl solution were measured at 90°C by the diaphragm cell method. The values of  $D_0$  for Yellow 12 and Red 2 showed a salt concentration dependence and those for Blue 1 and Blue 15 were constant over the ionic strength range from 0.01 to 0.10. In the adsorption/diffusion models proposed so far for the direct dye-cellulose system, the Standing-Warwicker-Willis model was shown to be similar in principle to the Weisz-Zollinger model. The adsorption/diffusion behaviors in never-dry cellophane sheet for C.I. Direct Yellow 12 and Blue 15 were examined by the method of cylindrical film roll at 90°C. The concentration dependence of the apparent diffusion coefficient for these dyes showed an incomplete validity of both the models.

## INTRODUCTION

The model of cellulose dyeing system where the diffusion of the dye through an aqueous medium along the pores of cellulose accompanied by the adsorption on cellulose was proposed by Morton.<sup>1</sup> Standing, Warwicker, and Willis formulated this model by the use of Freundlich-type adsorption isotherms.<sup>2</sup> The validity was tested by applying the equations to the experimental data by Neale and Patel.<sup>3</sup> They mentioned in summary that this equation was partially successful in correlating data obtained when the concentration of inorganic electrolyte of the external solution was high and that it failed entirely at the lower electrolyte concentrations. They did not exclude the possibility of surface diffusion of dyes.

Warwicker investigated the edge-wise diffusion of C.I. Direct Yellow 12 into the never-dry cellophane sheet and confirmed the validity of their model from the concentration profiles of the dye in cellulose.<sup>4</sup> He excluded the possibility of surface diffusion.

Weisz and Zollinger<sup>5-8</sup> applied a sorption-diffusion model developed mainly in the chemical engineering to the data by Neale.<sup>9</sup> They seem to have proved the validity of their model.

On the other hand, the theoretical treatments of diffusion of gases in glassy polymers were developed on the basis of the "multiple sorption" models.<sup>10-13</sup>

The concept of the multiple sorption was first introduced by Michaels et al.<sup>14</sup> as the dual-mode sorption model of gases in glassy polymers. In this

model, it was assumed that the diffusion of penetrant was that of dissolved molecules which were in local equilibrium with molecules adsorbed by Langmuir's law whose mobility were regarded to be zero ("total immobilization" model).

Later, Petropoulos modified their treatment and proposed the "partial immobilization" model, since the assumption of total immobilization was physically unrealistic.<sup>15</sup> This model was developed into the "dual-mode partial immobilization" model by Paul and Koros,<sup>16</sup> and was also applied to the sorption and diffusion systems of ions in charged polymer membranes.<sup>17,18</sup> Although the molecular picture of these treatments is different from that proposed for direct dye-cellulose systems, their mathematical treatments are fundamentally identical. Comparison among the dual sorption-diffusion models and that used in the present study is shown in Table I.

In the series of these studies, similarity among the models proposed so far is clarified, a more general model is proposed, and whether to what degree the theories can explain the practical diffusion behavior of direct dyes in cellulose is examined. The authors measured the diffusion coefficients of some direct dyes in the aqueous sodium chloride solution of wide ionic strength ( $I = 0.01-0.10$ ) and found that the values obtained for some dyes had the salt concentration dependence.<sup>19</sup> Therefore, the general validity of the diffusion/adsorption model for the direct dye-cellulose system should be examined by using various kinds of direct dyes and substrates.

In the present paper, the diffusion of C.I. Direct Yellow 12 and Blue 15 in never-dry cellophane sheet is examined and the validity of the treatment by Standing et al.,<sup>2</sup> Warwicker,<sup>4</sup> and Weisz et al.<sup>5-8</sup> is tested.

## THEORETICAL

### Standing-Warwicker-Willis Model<sup>2</sup>

The formulation of diffusion/adsorption behavior of direct dyes in the water-swollen cellulose was first made by Standing et al.<sup>2</sup> According to this model, direct dyes diffuse through the water-filled pores in cellulose, adsorbing simultaneously on the pore wall, cellulose.

The total concentration of the dye,  $C$  (mol/dm<sup>3</sup> swollen cellulose), is given as the sum of mobile dye molecules in the pore solution whose concentration is  $C_m$  (mol/dm<sup>3</sup>) and adsorbed ones whose concentration is  $C_{im}$  (mol/dm<sup>3</sup> swollen cellulose):

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

where  $P$  (dm<sup>3</sup>/dm<sup>3</sup> swollen cellulose) is the porosity defined as a fraction of pore solution in the total volume of swollen cellulose. The dimensions of  $C$  and  $C_{im}$  are converted into those of mol/kg dry cellulose, by multiplying the degree of swelling,  $W$  (dm<sup>3</sup> swollen cellulose/kg dry cellulose).

If the dyes in pore solution and those adsorbed on pore wall diffused

TABLE I  
Examples of Dual Mode Sorption and Diffusion Model

No.	1	2	3	4
Substrate	Water-swollen cellulose	Solution-filled solid (catalysis, carbon black)	Polyamide membrane	Glassy polymers
Penetrant Sorption isotherm Molecular picture	Direct dye Freundlich Mobile species in solution-filled pore Total immobilization	Solute Freundlich Mobile species in solution-filled pore Total and/or partial immobilization	Acid dye Nernst = Langmuir Dual mode sorption Partial immobilization	Gas Nernst = Langmuir Dual mode sorption Total and/or partial immobilization
Model				
References	Present study	23, 24 (chemical engineering)	17, 18	14, 15, 16

independently and the diffusion coefficients of both the species,  $D_m$  and  $D_{im}$  ( $\text{cm}^2 \text{s}^{-1}$ ), were constant, the one-dimensional diffusion equation is

$$\frac{\partial C}{\partial t} = PD_m \frac{\partial^2 C_m}{\partial x^2} + D_{im} \frac{\partial^2 C_{im}}{\partial x^2} \quad (2)$$

where  $t$  is the time (s) and  $x$  is the distance (cm).

As the rhs of eq. (2) may be regarded as the diffusion of "total" species, eq. (2) can be rewritten as follows:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D_c \frac{\partial C}{\partial x} \right) \quad (3)$$

Then, the apparent diffusion coefficient,  $D_c$  ( $\text{cm}^2 \text{s}^{-1}$ , for the "total" concentration is given as follows:

$$D_c = PD_m \frac{\partial C_m}{\partial C} + D_{im} \frac{\partial C_{im}}{\partial C} \quad (4)$$

Equation (4) defines the theoretical differential diffusion coefficients for the constant porosity model. According to the classification by Petropoulos, this model corresponded to the "partial immobilization" model since the two different diffusion coefficients,  $D_m$  and  $D_{im}$ , were considered. Standing et al. further assumed that the adsorption equilibria between the adsorbed species on pore wall and the mobile species in pore solution were equal to those between the sorbed species in cellulose and the species in the external solution.<sup>2</sup> They described the adsorption equilibria by Freundlich-type adsorption isotherms:

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

where  $K$  and  $n$  are constants specific to the system, and  $C_0$  ( $\text{mol dm}^{-3}$ ) denotes the dye concentration in the external solution when equilibrium is achieved.

Inserting the second equation of eq. (5) into eq. (4),  $D_c$  is written:

$$D_c = P(D_m - D_{im})nK^{-n}C^{n-1} + D_{im} \quad (6)$$

Warwicker regarded the  $D_{im}$  to be zero or negligibly small ("total immobilization" model), since no diffusion of dyes occurred at very low salt concentration, and examined the dependence of  $D_c$  on the dye concentration  $C$  and the salt concentration in the dyebath for the system of C.I. Direct Yellow 12 and never-dry viscose sheet.<sup>4</sup> He explained the monotonical decrease of the diffusion coefficients with an increase of salt concentration by the relation between the apparent porosity and the thickness of electrical double layer.

### Weisz-Zollinger Model

Weisz et al.<sup>5-8</sup> proposed a sorption/diffusion model as a general behavior of dyes in all kinds of fibers. They introduced some additional parameters, tortuosity factor  $b_m$  (1.7 for isotropic substrate),  $n$  [a constant dependent on the particular form of the adsorption isotherm which did not vary beyond the range of values of from 1.0 (weak) to 1.6 (strong immobilization)],  $a$  (the equilibrium partition coefficients between the mobile portion of the internal dye concentration and the external dye concentration), and so on.

The basic equation of the apparent diffusion coefficient  $D_{app}$  is

$$D_{app} = n \left( \frac{P}{b_m} \right) \left( \frac{C_0}{C} \right) a D_m \quad (7)$$

They assumed  $a$  to be unity, applied eq. (7) to the data by Neale<sup>9</sup> with  $b_m = 1.7$ ,  $n = 1.6$ , and  $P = 0.25$ , and estimated the values of  $D_m$  for some 40 direct dyes. The porosity was regarded as equal to the fractional volume uptake of water by the fiber system. They regarded the surface diffusion coefficient to be negligible. Therefore, this model also corresponded to the "total immobilization" model.

### Similarity of the Two Models

The similarity of the two models is not clear from their original equations. As  $a = C_m/C_0$ , eq.(7) is rewritten as follows:

$$D_{app} = n \left( \frac{P}{b_m} \right) \left( \frac{C_m}{C} \right) D_m \quad (8)$$

On the other hand, the rearrangement of eq.(6) with the second equation of eq.(5) leads to the following equation, if  $D_{im} = 0$ :

$$D_c = P D_m n \frac{C_m}{C} \quad (9)$$

Although the factors of  $b_m$  and  $n$  are not taken into consideration, eq. (9) agrees with eq. (6), if  $D_m$  is regarded as containing these factors. Thus, the factor  $n$  in the Weisz-Zollinger model describes the constant  $n$  in Freundlich-type adsorption isotherm. As shown in a series of these studies, 1.6 is not the upper limit of the values of  $n$ .

On the other hand, Weisz and Zollinger assumed eq. (10) instead of eq. (5), there may be some differences between the two models when  $C_{im}/C_m$  or  $C/C_m$  is small:

$$C_{im} = K C_m^{1/n} \quad (10)$$

When applied this model to the dyeing system, Weisz et al. showed that the relation between the dye uptake and dyeing time could be described by their equations derived for the substrates of various geometries.<sup>5-8</sup> In the present study, however, the validity of the model is tested by applying the basic equation to the concentration profiles of dyes in substrate or by analyzing the concentration dependence of apparent diffusion coefficients.

## EXPERIMENTAL

### Materials

Never-dry viscose sheet, manufactured by Tokyo Cellophane Sheets Co., for #300 Cellophane, were used as substrate after scouring in boiling distilled water for 3 h. The thickness of a swollen cellophane was 100.0  $\mu\text{m}$  and the degree of swelling was  $4.02 \pm 0.221$  ( $\text{dm}^3$  swollen cellulose/kg dry cellulose). Direct dyes used shown in Table II were purified from a commercial sample by recrystallizing six times with sodium acetate and by extracting thoroughly sodium acetate with absolute ethanol by the use of a Soxhlet's extractor.

### Diffusion

The cylindrical film roll method was used for the diffusion experiments. A never-dry cellophane sheet, cut 5 cm wide and 60 cm long (direction of manufacturing), was wound on a glass tubing ( $\phi = 1.0$  cm). This cylindrical film roll was immersed in the dyebath (500 mL) at 90°C for 2 h. The dye concentration in the dyebath was  $1.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ . The concentration of sodium chloride were 0.01, 0.02, 0.05, and 0.10 mol  $\text{dm}^{-3}$ . After dyeing, the film roll was quickly washed by distilled water, rewound, and dried naturally by putting it between leaves of papers. The optical densities of every layer were measured by a UVIDEC-505 spectrophotometer (Japan Spectroscopic Co., Ltd.), from which the concentration profiles of the dye in substrate were obtained by the use of the calibration curves made from the adsorption experiments.

### Equilibrium Adsorption

Never-dry cellophane sheets of the same size (45 mm wide and 25 mm long, dry weight  $28.65 \pm 1.507$  mg) were dyed in the dyebath (500 mL) at 90°C for 24 h to attain the adsorption equilibria. The salt concentrations

TABLE II  
Dyes Used

C.I. Direct	Commercial name	Manufacturer <sup>a</sup>
Yellow 12	Chrysophenine G	NSK
Red 2	Kayaku Benzopurpurine 4B	KYK
Blue 1	Diacotton Sky Blue 6B	MCI
Blue 15	Nippon Sky Blue 5B	NSK

<sup>a</sup> The same abbreviations of the name of manufacturer as those in *Colour Index*, 3rd ed., were used.

in the dyebath were same as those of the diffusion experiments. The concentration range of dye was  $2 \times 10^{-5}$ – $2 \times 10^{-4}$  mol dm<sup>-3</sup>. After dyeing, the dyed sheets were extracted into 25% pyridine solution and the amounts of adsorption were obtained from the optical densities of the solutions.

### Diffusion in Aqueous Solution

The diffusion coefficients of direct dyes in aqueous solution were measured by the use of diaphragm cell method. The salt concentration ranged from 0.01 to 0.10 mol dm<sup>-3</sup>. The dye concentration in the cell of higher concentration side was  $5.0 \times 10^{-5}$  mol dm<sup>-3</sup>. The dye was allowed to diffuse into a definite volume of the salt solution of the same concentration, sectioned by a horizontal diaphragm glass filter. The solutions of both sides were stirred slowly at a definite speed. The concentration of lower concentration side was optically measured after the diffusion for 30 min at 90°C. The diffusion coefficients were calculated by the method of Holmes and Standing.<sup>19</sup> The cell constant was decided by the use of potassium chloride.

## RESULTS AND DISCUSSION

### Concentration Dependence of $D_c$

The concentration dependence of  $D_c$ , calculated by the Matano's method<sup>20</sup> from the diffusion profiles obtained by the method of cylindrical film roll, is shown in Figures 1 and 2 for C. I. Direct Yellow 12 and Blue 15, respectively. In the present study, the diffusion in the perpendicular direction from the film surface were observed in contrast to the edgewise diffusion by Warwicker.<sup>4</sup> Although no rapid increase of the  $D_c$  with  $C$  was observed in the high concentration region of  $C$  and at the low salt concentration, similar curves for the  $D_c$  vs.  $C$  plots to those of Warwicker were obtained.<sup>4</sup>

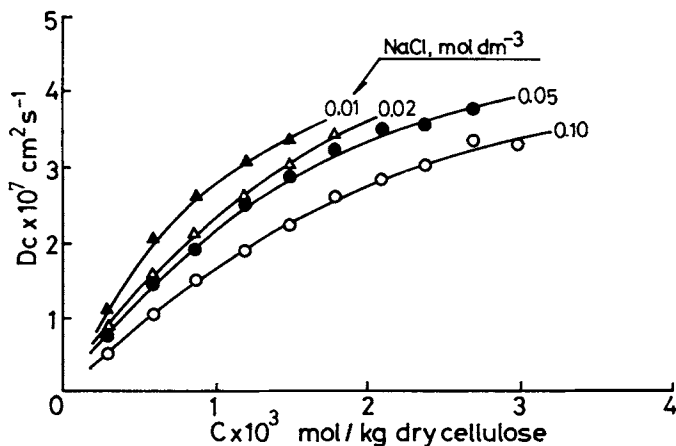


Fig. 1. Concentration dependence of apparent diffusion coefficients,  $D_c$ , for C.I. Direct Yellow 12 in never-dry cellulose sheet at various salt concentrations (90°C).

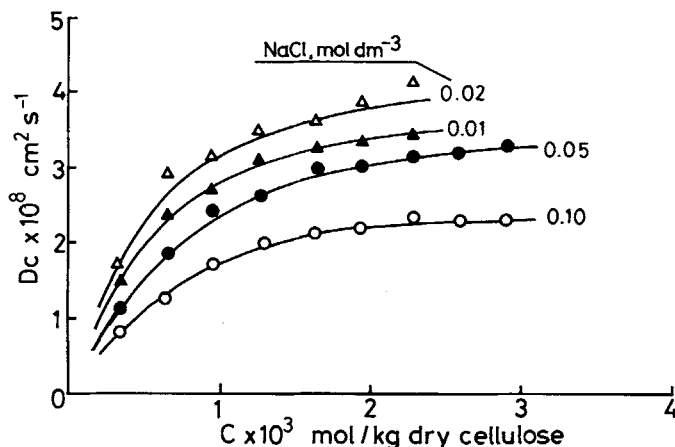


Fig. 2. Concentration dependence of apparent diffusion coefficients,  $D_c$ , for C.I. Direct Blue 15 in never-dry cellulose sheet at various salt concentrations (90°C).

As the  $D_c$  approached zero when  $C \rightarrow 0$  in all the cases, it was concluded that the values of  $D_{im}$  for eq. (6) were negligibly small or zero.

The adsorption isotherms for these systems are shown as the data of equilibrium adsorption by Freundlich constants shown in Table III. The diffusion coefficients of dyes at various salt concentrations are shown in Figure 3 and the values of  $D_0$  under the conditions where the adsorption experiments were carried out are shown in Table III. Holmes and Standing<sup>19</sup> also reported the salt concentration dependence of  $D_0$  for some direct dyes, a decrease of the values of  $D_0$  with an increase in ionic strength.

The values of  $D_0$  recalculated by Weisz and Zollinger<sup>8</sup> were not in consistent accord with the values of diffusion coefficients in aqueous solution for the corresponding dyes, measured in a series of these studies. The values of  $D_0$  interpolated at the same salt concentrations are also shown in Table IV.

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

C. I. Direct	NaCl (mol dm <sup>-3</sup> )	Freundlich constants <sup>a</sup>			$D_0 \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )
		$K$	$n$	$r^b$	
Yellow 12	0.01	0.366	1.746	0.996	1.37
	0.02	0.577	1.773	0.995	1.17
	0.05	0.773	1.801	0.994	0.74
	0.10	0.938	1.823	0.998	0.56
Blue 15	0.01	0.319	2.474	0.999	1.05
	0.02	1.116	2.053	0.996	
	0.05	1.324	2.261	0.971	
	0.10	1.370	2.395	0.981	

<sup>a</sup>  $C = KC_0^{1/n}$ .

<sup>b</sup>  $r$  = correlation coefficients.



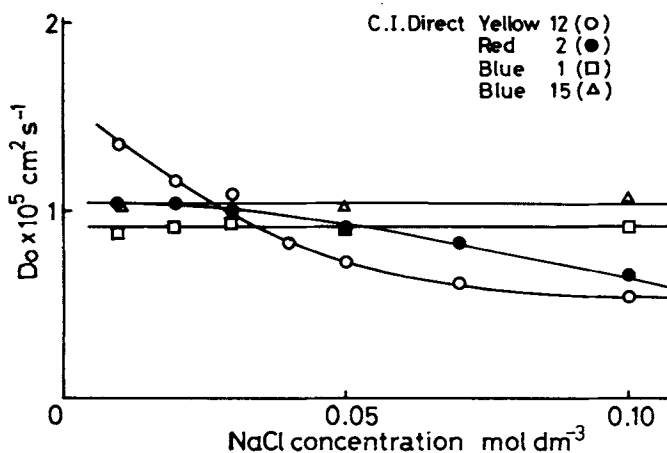


Fig. 3. Salt concentration dependence of diffusion coefficients,  $D_0$ , in aqueous NaCl solution at 90°C; (○) C.I. Direct Yellow 12; (●) Red 2; (□) Blue 1; (△) Blue 15.

### Apparent Porosity of Cellulose

If the values of  $D_m$  in the pore solution were regarded to be equal to the values of  $D_0$ , the values of apparent porosity were obtained by the use of eq. (6) ( $D_{im} = 0$ ) from the data shown in Table II according to the Warwicker's treatment.<sup>4</sup>

Strictly speaking, however, the apparent diffusion coefficients,  $D_c$ , of dyes in cellulose based on the adsorption/diffusion model [eqs.(2) and (4)] should be rewritten by the addition of tortousity factors,  $b_m$  and  $b_{im}$ , for the mobile and the adsorbed species, respectively:

$$D_c = P \frac{D_m}{b_m} \frac{\partial C_m}{\partial C} + \frac{D_{im}}{b_{im}} \frac{\partial C_{im}}{\partial C} \quad (11)$$

If the values of  $D_m$  were estimated from those of diffusion coefficients  $D_0$  in aqueous solution, there would be a relation:

$$D_m = kD_0 \quad (12)$$

TABLE IV  
Comparison of Diffusion Coefficients<sup>a</sup>

C.I. Direct	$D_0 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ (as reported)	$D_0 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ (measured)
Yellow 12	2.5	5.8
Red 2	2.1	7.5
Blue 1	1.1	9.2
Blue 15	1.3	10.5

<sup>a</sup>  $I = 0.086$  (NaCl 50.5 dm<sup>-3</sup>).

<sup>b</sup>  $D_0$ 's estimated by Weisz and Zollinger.<sup>8</sup>

where  $k$  is a constant dependent on the geometry of penetrant and probably independent of that of membrane. The larger the anisotropy of penetrant, the larger may be the values of  $k$ , if the pore in cellulose is larger than the smallest cross section of spheroid of the penetrant and not so much larger of smaller than the largest one.

Since the apparent porosity of anionic penetrant in cellulose membrane containing anionic groups has been shown to decrease with increase in the amount of anionic groups and/or with decrease in the ionic strength,<sup>21,22</sup> the values of  $kP/b_m$  of C. I. Direct Yellow 12 and Blue 15 calculated by the use of eqs. (11) and (12) are plotted against the total amount,  $A$  (meq/kg dry cellulose), of anionic groups fixed in the substrate (Fig. 4):

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

where  $S$  is the carboxyl group content in the cellulose ( $33.2 + 1.80$  meq/kg dry cellulose) and  $z$  is the number of sulfonic acid groups in a dye molecule.

The apparent porosity of C.I. Direct Yellow 12 in never-dry cellophane were constant over the all range of  $C$ , but those of Blue 15 are not constant and may be dependent on the amount of the anionic groups in the substrate.

In the models proposed by Warwicker et al.<sup>3,4</sup> and Weisz et al.,<sup>5-8</sup> they assumed the porosity to be constant and independent on  $C$ .

This is the case for Yellow 12 but not for Blue 15. The values of  $kP/b_m$  for Blue 15 at  $I = 0.01$  and  $0.02$  converged a value,  $0.67$  at  $I = 0.01$  and  $1.48$  at  $I = 0.02$ , with increasing  $A$  or  $C$ , and the values for  $I \geq 0.05$  could not be estimated in the present study.

As the values of  $kP/b_m$  for Yellow 12 were estimated to be  $0.34$  and  $0.83$  at  $I = 0.01$  and  $0.02$ , respectively, the ratio of  $kP/b_m$  for both the dyes was constant,  $1.9 \pm 0.1$  at  $I = 0.01$  and  $0.02$ . This fact may show that the constant porosity model is applicable even to Blue 15 in the regions in

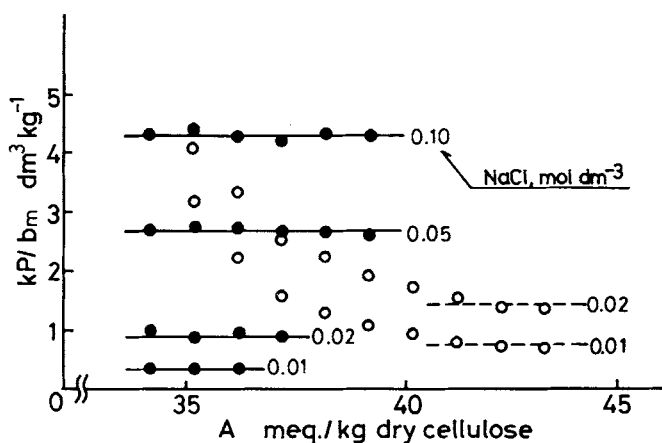


Fig. 4. Relationships between the apparent porosity,  $kP/b_m$ , and the total amount  $A$  of anionic groups fixed in the substrate at various salt concentrations by the use of eqs. (11), (12), and (13); (●) C.I. Direct yellow 12; (○) Blue 15.

which the ionic strength is low and the amount of adsorptions is relatively large.

Furthermore, the values of  $kP/b_m$  for Yellow 12 were dependent on the values of  $D_0$  because of the salt concentration dependence of  $D_0$ . The values of  $kP/b_m$  shown in Figure 4 were estimated by the use of variable  $D_0$  in Table II. As the proportion of water for this swollen substrate is 3.47 dm<sup>3</sup> water in pore/kg dry cellulose and the values of  $k/b_m$  may be inferred to be order of unity from this series of studies, the values of  $kP/b_m$  at the high ionic strength seem to be too large. If the values of  $kP/b_m$  were estimated by the use of constant  $D_0$ , for example,  $1.37 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, they seem to have reasonable values even at higher ionic strengths. This may be the case of Warwicker's treatment.<sup>4</sup>

If the variation of  $D_0$  with ionic strength was due to the aggregation of dyes in solution, this effect cannot be excluded from the adsorption experiments. Thus, Yellow 12 is not a suitable dye to test the general validity of diffusion/adsorption model in cellulose, though this model could be shown to hold for this dye under the conditions of low ionic strengths.

#### Capillary Model by Warwicker<sup>4</sup>

On the other hand, Warwicker used a capillary model of constant diameter to explain the dependence of apparent porosity on the ionic strength and lead the relationship:

$$P^{1/2} = L - QI^{-1/2} \quad (13)$$

where  $L$  and  $Q$  are constants. The relationship of eq. (13) for this study are shown in Figure 5 for the constant  $D_0$  and variable  $D_0$ . In the range of low

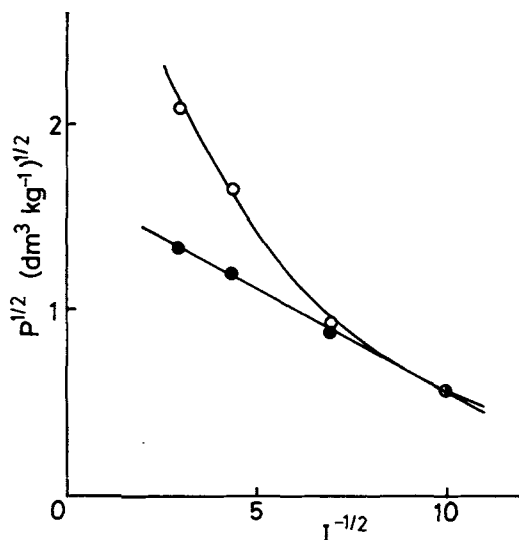


Fig. 5. Relationship between  $P^{1/2}$  and  $I^{-1/2}$  for the constant  $D_0$ ,  $1.37 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> (●) and for the variable  $D_0$ ,  $0.56$ – $1.37 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> (○); C.I. Direct Yellow 12.

ionic strength, both the plots coincide with each other and the plots for variable  $D_0$  deviate upward from the straight line for the constant  $D_0$  at high ionic strengths. Warwicker proved the validity of the capillary model by the linear relationship between  $P^{1/2}$  and  $I^{-1/2}$  for the constant  $D_0$  ( $1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ).

In the present study, only for the Yellow 12 systems, a reasonable value of apparent porosity,  $kP/b_m = 2.76 \text{ dm}^3/\text{kg}$  dry cellulose for  $I \rightarrow \infty$ , and the linear relationship of eq. (13) were obtained if the constant  $D_0$  ( $1.37 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) was used, but no validity of capillary model was shown if the variable  $D_0$ s were taken into consideration. However, such a treatment was not applicable to Blue 15 at all because of the unreasonable values of the apparent porosity obtained. The upward deviation of apparent porosity was observed at high ionic strengths, i.e., in the range where large amount of adsorption occurred. This behavior, therefore, may qualitatively be explained as the deviation from the true adsorption equilibria between the adsorbed and mobile species in cellulose. As the adsorption of Yellow 12 in the present study was larger than those observed by Warwicker, a clear deviation may be observed in this experiment.

A more general diffusion adsorption behavior in cellulose will be investigated in a series of these studies.

### SUMMARY

1. In the diffusion/adsorption behavior of direct dyes in cellulose, the Standing-Warwicker-Willis model was shown to be similar in principle to the Weisz-Zollinger model. Some differences between them were clarified.

2. The diffusion coefficients  $D_0$  of direct dyes in aqueous solution containing various concentrations of sodium chloride were measured at 90°C. The values of  $D_0$  for C. I. Direct Blue 1 and Blue 15 had no salt concentration dependence and those for Red 2 and Yellow 12 has the concentration dependence.

3. Weisz-Zollinger treatment of Neale's data did not lead a consistent relation with the values of  $D_0$  obtained in the present study.

4. The diffusion of C. I. Direct Yellow 12 and Blue 15 in never-dry cellulose did not show the complete validity of the Standing-Warwicker-Willis model.

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