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ESTIMATION OF THE THICKNESS OF DIFFUSIONAL BOUNDARY LAYER FROM KINETIC DATA OF FILM DYEING

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ABSTRACT

The values of diffusion coefficient of non-ionic dyes in nylon 6 and polyester film (D_f) were evaluated by analyzing the concentration profiles of the dyes in the films and the kinetic data of the film dyeing (or desorption from the film). For many cases, the values of D_f evaluated by the both method agreed well each other. However, when the dye having high affinity on nylon 6 film was desorbed under an insufficient agitation, the values of D_f from the kinetic data sometimes appreciably smaller than the corresponding D_f from the profiles.

The values of boundary layer parameter (L) in the film dyeing were estimated by the curve fitting to the kinetic data of the dyeing by use of a relevant Newman's equation coupled with D_f determined from the profile.

The thickness of the diffusional boundary layer (δ_D), estimated from the value of L , decreased rapidly as the rate of agitation of the specimens in the bath was increased; i. e., the values of δ_D estimated at 40–90°C under the reciprocation (30mm) of the specimen of 0, 30, 80 and 146 strokes/min ranged 20–80, 5.9–18.5, 14–15 and $0.2-0.7 \times 10^{-3}$ cm, respectively.

It was found that when the film dyeing carried out under the vigorous agitation, such as at the flow rate of 14.6cm/sec near the film surface, the resistance to the dye transport across the diffusional boundary layer gives little effect on the rate of the dyeing, in contrast to the dyeing of fabrics or yarns.

1. INTRODUCTION

In practical dyeing of fiber assemblies, such as yarn packages or fabrics, the flow rate of dye liquor through the spaces between the individual fibers in yarns is usually low¹⁾; the thickness of the diffusional boundary layer (δ_D) adjacent to the outer surface of the fibers is fairly large. In such dyeing system, the rate of dyeing is controlled by both the diffusion of dye across the stagnant solution layer and that into the fiber itself.²⁾ Therefore, the estimation of the values of δ_D for various dyeing system is of interest to understand the problems concerning the rate of practical dyeing.

We have estimated the numerical values of δ_D in the dyeing of nylon and polyester yarns with non-ionic dyes by analyzing the kinetic data of dyeing³⁾, where the estimation was based on the assumption that the individual fibers are uniformly accessible to the liquor flow. However, the local velocity of liquor flow close to the

surface of the individual fibers vary at different point of the fiber assemblies, therefore, the values of δ_D thus estimated may be taken as the average thickness for the equivalent diffusional boundary layer around individual fibers⁴⁾; the values seems to indicate that the sorption delay corresponding to the resistance to the dye transport across the diffusional boundary layer of thickness of δ_D will occur in those dyeing systems. It seems that the value of δ_D close to actual one can be obtained by analyzing the kinetic data of dye sorption by films or mono filament fibers if we consider the uniformity of fluid flow near the surface of these substrates.

In the present paper, the values of δ_D in the dyeing of nylon and polyester films with non-ionic dyes will be estimated from the kinetic data of the sorption (or desorption) of the dyes by the films and the diffusion coefficients of the dyes in the films (D_f) determined from the concentration profiles of the dyes in the films, and the effects of agitation of the film specimens in dye bath

on δ_D will also be discussed.

2. THEORY

Rate of sorption of a non-ionic dye by a homogeneous film surrounded with diffusional boundary layer of thickness δ_D from an infinite dye bath is expressed by eq. 1.^{5,6)}

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp - X}{B_n^2 (B_n^2 + L^2 + L)}, \quad X = \frac{D_t}{l^2} t \quad (1)$$

where M_t and M_∞ are the amount of dye taken up by the film at time t and at equilibrium, respectively, D_t is concentration independent diffusion coefficient of the dye in the film, l is the half-thickness of the film, B_n 's are positive non-zero roots of the equation $B_n \times \tan(B_n) - L = 0$ and L is boundary layer parameter given by eq. 2.²⁾

$$L = \frac{D_s l}{D_t K \delta_D} \quad (2)$$

where D_s is the diffusion coefficient of the dye in the boundary layer or in the bulk solution, K is the partition coefficient of the dye between the solution and the film. The smaller value of L indicates the larger sorption delay due to the resistance to the dye transport across the diffusional boundary layer.

Non-ionic dye system in which D_t , D_s and K vary very little with dye concentration. Hence, the values of L and

Fig. 1 Rates of desorption of Dye 1 from nylon 6 film into water at 40°C.

Experimental points, ○ and ● were measured without agitation and under the agitation of 80 strokes/min, respectively.

The curves passing through the experimental points ○ and ● were calculated by eq. 1 using $L=3.06$, $D_t=4.86 \times 10^{-9} \text{ cm}^2/\text{min}$ and $L=19.9$, $D_t=4.70 \times 10^{-9} \text{ cm}^2/\text{min}$, respectively. The dotted line, ·····, was calculated similarly using $L=\infty$ and $D_t=4.97 \times 10^{-9} \text{ cm}^2/\text{min}$.

D_t in a film dyeing can be estimated from the kinetic data of sorption (or desorption) of a non-ionic dye by the film by means of a curve fitting technique using eq. 1 as shown in Fig. 1. In general, the most reliable value of D_t in a film is obtained from the concentration profile of dyes in the film; the profile can be determined exactly by means of the film roll methods developed by Sekido et al.⁷⁾ Therefore, by comparing the value of D_t estimated from the kinetic data of sorption with that from the profile, one can verify the validity of the values of L and D_t obtained from the kinetic data by the curve fitting. The value of K for a certain dyeing system is measurable experimentally and D_s can be estimated from the van der Waals volume of the dye (V_w) by eq. 3.⁸⁾

$$\log\left(\frac{T}{\eta D_s}\right) = 0.65787 \log V_w + 6.37439 \quad (3)$$

where T and η are the absolute temperature and viscosity of solution, respectively.

Hence the value of δ_D can be estimated from experimental K , D_t and the kinetic data of film dyeing with non-ionic dyes from an infinite bath.

3. EXPERIMENTAL

3.1 Materials

The film used were nylon 6 (thickness=ca. 0.0027cm, prepared by Unitika Ltd.) and poly-ethylene terephthalate (thickness=0.0012cm, prepared by Toray Ltd.; here after abbreviated as polyester film). They were treated in water at 95°C for 25 h prior to dyeing.

The dyes used were the same as used in previous paper.³⁾ The structure of the dyes and van der Waals volume are shown in Table 1.

Table 1 Structure and van der Waals volume of dyes used.

No.	Dye Structure	M. W.	$V_w^a)$ (ml/mol)
1		285.3	160.1
2		299.4	171.2
3		238.2	123.9

^{a)} van der Waals volume estimated by means of Bondi's method.^{8,9)}

3.2 Measurements of rate of desorption and sorption

Nylon 6 film was evenly dyed with Dye 1 and 2, then cut into small pieces (2.0×2.5 cm). Each film was held between the stainless steel plates with rectangular window of $1 \text{ cm} \times 2 \text{ cm}$ as shown in Fig. 2 A, then pretreated in water at $0-5^\circ\text{C}$ for 5 min. After that, the specimen was desorped in 1000 ml of water at required temperature ($0 \pm 0.1^\circ\text{C}$) for relevant time using the apparatus shown in Fig. 2B; the rate of agitation of the specimen was controlled by changing the frequency of reciprocation of the holder up-to downward. To maintain the zero dye concentration in the bath, 0.5 g of active carbon fiber (prepared by Osaka Gas Ltd.) was added in the bath.

Polyester film was pretreated in water for 10 min at the same temperature of the dyeing, just after that, the film was dyed in 1000 ml of an aqueous fine dispersion of Dye 3 containing 0.5 g of pure dye³⁾ by the similar manner as in the desorption described above.

The relative amount of dye on the films, M_t/M_∞ , was estimated from the difference in the optical density of film at a relevant wavelength before and after the dyeing (or desorption); a good linear relation between the amount of dye on the film and the optical density of the dyed film was observed for each dye used.

Dye 1 and 2 on nylon 6 film are sensitive to light, cis-trans isomerization of the dyes will occur even on standing the dyed films near a window for a few minutes. The isomerization is accompanied by a spectral change with

isosbestic points. Therefore, the optical density of these films was determined at the wavelength of an isosbestic point (Dye 1: 383 nm and Dye 2: 379.5 nm). The optical density of the polyester film dyed with Dye 3 was measured at 556 nm which was an absorption maximum of the dye on the film in visible region.

The optical measurements were made on a Simadzu UV-150-02 spectrophotometer and calculations were made on an NEC-PC-VX-0 personal computer.

4. RESULTS AND DISCUSSION

Fig. 3 shows the concentration profile of Dye 1 in the nylon 6 film; the curve passing through the experimental points was calculated by eq. 4 using D_f ($4.84 \times 10^{-9} \text{ cm}^2/\text{min}$) obtained by the curve fitting to the experimental profile using eq. 4. The agreement between the experimental points and the calculated curve is fairly well.

$$\frac{C}{C_0} = \text{erfc} \frac{x}{2(D_f t)^{1/2}} \quad (4)$$

, where C and C_0 are the concentration of the dye at a distance x from the surface of the substrate and at the surface, respectively, t is the time of diffusion.

Similar profiles were also obtained for Dye 2 and 3 in nylon 6 film and in polyester film, respectively. Hence, the standard values of D_f of each dye at various temperatures were determined from the profiles having C_0 close

Fig. 2 Apparatus used for the dyeing and desorption of films

Fig. 3 Diffusion of Dye 1 in nylon 6 film at 40°C for 25920 min, a concentration profile measured by means of the film roll method.

● : experimental point, — : calculated by eq. 4 using $D_f = 4.84 \times 10^{-9} \text{ cm}^2/\text{min}$.

The concentration of the dye on the film at the sorption equilibrium was taken as the dye concentration at the film surface.

Table 2 Comparison of Diffusion coefficient of the non-ionic dyes in films determined from the concentration profile with those calculated from the kinetic data of dyeing.

Dye	Temp (°C)	Stirring (strokes/min)	(A) ^{c)}		L
			$D_f \times 10^9$ (cm ² /min)	(B) ^{d)} $D_f \times 10^9$ (cm ² /min)	
1 ^{a)}	40.0	0		4.86	3.06
		30	4.84	4.72	13.9
		80		4.70	19.9
2 ^{a)}	40.0	30		3.08	21.4
		80	4.07	3.35	17.1
		146		4.16	92.9
	50.0	30	10.0	8.39	18.2
	60.0	30	24.9	19.4	13.5
	70.0	30		45.3	11.8
		146	55.0	57.5	62.5
	80.0	30		9.91	9.49
3 ^{b)}	95.0	0	0.374	0.373 ₉	282

^{a)} Desorption from nylon 6 film into an aqueous bath maintained at zero dye concentration.

^{b)} Sorption by polyester film from an infinite bath.

^{c)} Determined from the concentration profiles measured by the film roll method.

^{d)} Calculated from the kinetic data of the sorption or the desorption.

Fig. 4 Rates of desorption of Dye 2 from nylon 6 film into water at 40°C.

Experimental point, ○ and ● were measured under the agitation of 30 and 146 strokes/min, respectively.

Curves passing through the experimental points ○ and ● were calculated by eq. 1 using $L=21.4$, $D_f=3.08 \times 10^{-9}$ cm²/min and $L=92.9$, $D_f=4.16 \times 10^{-9}$ cm²/min, respectively.

Dotted line, ·····, was calculated by eq. 1 using $L=\infty$ and $D_f=4.07 \times 10^{-9}$ cm²/min.

to M_∞ in the corresponding sorption or desorption experiments. The values of D_f thus determined are given in the column (A) in Table 2.

Figs. 1 and 4 show the effect of agitation of the specimen on the rate of desorption of Dye 1 and 2 from nylon 6 film, respectively. Each curve passing through the experimental points (○, ●) was calculated by eq. 1 using L and D_f obtained by the curve fitting to the corresponding kinetic data. The deviation of the experimental points from the theoretical curve was very small for each dyeing system. The desorption delay at the initial stage decreased rapidly as the rate of the agitation was increased. These findings indicate that the desorption delay is ascribed to the resistance to the dye transport across the diffusional boundary layer. The film used seemed to have no surface barrier layers for the dye diffusion, since the diffusion behavior of the dye in the film approached to that of normal Fickian (Fig. 4, ·····) as the rate of the agitation of the specimen was increased up to 146 strokes/min (Fig. 4, ●).

Hence the values of L and D_f were estimated from the kinetic data of the dye desorption (or sorption) by the curve fitting using eq. 1 as given in the column (B) of Table 2. The values of D_f of Dye 1 and 3 obtained from the kinetic data agreed with the corresponding D_f 's from the profile, given in the column (A), within ca. 3 % deviation, indicating that the values of L for Dye 1 and 3 given in the column (B) are almost valid. The value of D_f should be independent of the rate of the agitation, however, for Dye 2, the values of D_f from the kinetic data decreased as the rate of agitation was decreased. The values of D_f of Dye 2 from the kinetic data measured under the agitation of 146 strokes/min were only slightly larger than the corresponding D_f values from the profile. On the other hand, the values of D_f from the kinetic data measured under the agitation below 80 strokes/min were appreciably smaller than the corresponding D_f values from the profile. The reason for the discrepancy in the value of D_f has not been clarified yet, however, this indicates that in some cases, the reasonable value of L can not be estimated only from the kinetic data of sorption or desorption. It seems that the curve fitting to the kinetic data of the desorption by using eq. 1 coupled with D_f from the profile gives a more reasonable value of L , since the most reliable value of D_f is usually obtained from the profile.

Fig. 5 Estimation of boundary layer parameter L by the curve fitting to the rate of desorption data of Dye 2 from nylon 6 film at 40°C .

Experimental points, ○ and ● were measured under the agitation of 30 and 146 strokes/min, respectively.

The curves passing through the experimental points ○ and ● were obtained by the curve fitting to each set of the kinetic data using eq. 1 and $D_f = 4.07 \times 10^{-9} \text{ cm}^2/\text{min}$ which is the value of diffusion coefficient of the dye in the film determined from the concentration profile of the dye in the film.

Fig. 5 shows the curve fitting thus made to the same data as given in Fig. 4, the deviation of each experimental point from the curve calculated by using eq. 1 and D_f from profile ($4.07 \times 10^{-9} \text{ cm}^2/\text{min}$) was somewhat larger than that in Fig. 4, however considering the high reliability of D_f from the profile, the value of L for each dyeing system was estimated from the kinetic data given in Tables 3, 4 and D_f from the profile. The values of L thus determined are given in the Table 5 from which the value of δ_D for each dyeing system was calculated as given in the last column in the same Table.

When a plate is placed in a laminar flow of velocity V_0 , the average thickness of the diffusional boundary layer (δ_D) adjacent to the surface of the plate is expressed by eq. 5.¹⁾

$$\delta_D = 1.47 \left(\frac{D_s}{\nu} \right)^{1/3} \left(\frac{\nu \lambda}{V_0} \right)^{1/2} \quad (5)$$

where ν is kinematic viscosity, $\nu = \mu/\rho$, μ is viscosity of fluid, ρ is density of the fluid and λ is the length of the plate. When $V_0 = 0$, δ_D is not ∞ but a limiting value δ_D^* .

For the present study, if we let $\lambda = 2 \text{ cm}$, the length of the rectangular window of the film folder, and V_0 is the average velocity of the reciprocation of the specimen, we

Table 3 Effect of agitation of specimen on the rate of desorption of Dye 1 and 2 from nylon 6 film at 40°C .

Dye	1			2		
Agitation (strokes/min)	0	30	80	30	80	146
Kinetic Data	Time M_t/M_∞ (min)	Time M_t/M_∞ (min)	Time M_t/M_∞ (min)	Time M_t/M_∞ (min)	Time M_t/M_∞ (min)	Time M_t/M_∞ (min)
	10 0.071 ₆	3 0.066	3 0.073 ₇	3 0.058 ₂	3 0.062 ₁	1 0.048 ₅
	25 0.133	10 0.152	7 0.108	10 0.104	7 0.093 ₄	5 0.114
	50 0.212	20 0.218	10 0.150	20 0.168	10 0.108	10 0.163
	80 0.275	35 0.293	20 0.200	35 0.241	20 0.171	20 0.236
	87 0.319	40 0.307	35 0.295	40 0.274	35 0.236	30 0.303
	120 0.380	60 0.400	40 0.325	50 0.296	40 0.259	40 0.330
	170 0.491	80 0.472	60 0.401	60 0.342	60 0.321	50 0.393
	240 0.626	110 0.548	70 0.430	80 0.410	70 0.344	60 0.409
	330 0.728	145 0.650	80 0.479	110 0.462	80 0.394	80 0.473
	430 0.800	185 0.741	110 0.561	120 0.501	110 0.472	100 0.548
	600 0.891	230 0.786	145 0.637	145 0.542	145 0.551	120 0.588
		280 0.853	185 0.730	185 0.600	185 0.615	150 0.652
		330 0.905	230 0.783	230 0.665	230 0.685	180 0.717
		390 0.940	280 0.831	280 0.744	280 0.738	240 0.808
		450 0.954	330 0.871	330 0.784	390 0.836	300 0.860
			390 0.915	390 0.834	500 0.886	380 0.901
				450 0.880	600 0.930	
				570 0.923	720 0.955	
M_∞ (mol/kg)	8.00×10^{-3}	5.73×10^{-3}	4.41×10^{-3}	1.65×10^{-2}	1.65×10^{-2}	5.90×10^{-3}

Table 4 Kinetic data of the desorption of Dye 2 from nylon 6 film and the sorption of Dye 3 by polyester film.

Dye and film	Dye 2 from nylon 6 film								Dye 3 on polyester film					
Temp. (°C)	50		60		70		80		95					
agitation (strokes/min)	30		30		30		146		30		146		0	
Kinetic data	Time (min)	M _t /M _∞	Time (min)	M _t /M _∞	Time (min)	M _t /M _∞	Time (min)	M _t /M _∞	Time (min)	M _t /M _∞	Time (min)	M _t /M _∞	Time (min)	M _t /M _∞
	3	0.077 ₈	3	0.145	1	0.117	1	0.176	1	0.181	0.5	0.186	15	0.140
	5	0.119	5	0.208	2	0.175	2	0.280	1.5	0.202	1	0.275	30	0.192
	10	0.189	7	0.226	3	0.235	3	0.350	2	0.279	1.5	0.349	60	0.276
	15	0.227	10	0.318	5	0.310	4.5	0.432	3	0.366	2	0.398	120	0.393
	20	0.298	15	0.382	7	0.401	6	0.489	4	0.425	2.5	0.452	210	0.528
	30	0.354	20	0.448	10	0.475	8	0.575	5	0.462	3.5	0.526	330	0.659
	35	0.406	25	0.516	15	0.578	10	0.634	7	0.572	5	0.664	480	0.760
	40	0.406	30	0.580	20	0.671	13	0.715	10	0.706	6	0.711	660	0.843
	50	0.495	35	0.620	25	0.750	15	0.763	15	0.806	9	0.808	720	0.862
	60	0.516	40	0.652	30	0.810	20	0.838	20	0.889	10	0.826		
	80	0.610	50	0.719	35	0.862	30	0.903	25	0.914	15	0.910		
	110	0.703	60	0.784	40	0.898	40	0.942	30	0.960	20	0.931		
	145	0.775	80	0.863	50	0.927			35	0.977				
	185	0.856	90	0.893	60	0.949								
230	0.899	110	0.925											
280	0.959													
M _∞ (mol/kg)	1.65 × 10 ⁻²		1.65 × 10 ⁻²		1.65 × 10 ⁻²		5.90 × 10 ⁻³		1.65 × 10 ⁻²		5.90 × 10 ⁻³			

Table 5 Estimation of the thickness of diffusional boundary layer (δ_D) for each film dyeing system.

Dye	Temp (°C)	Stirring (strokes/min)	$D_t \times 10^9$ ^{c)} (cm ² /min)	L	K	$D_s \times 10^4$ ^{d)} (cm ² /min)	$l \times 10^3$ (cm)	$\delta_D \times 10^3$ (cm)
1 ^{a)}	40.0	0		3.08			1.37 ₈	80.2
		30	4.84	12.4	494	4.29	1.27 ₅	18.5
		80		17.1			1.33 ₅	14.0
2 ^{a)}	40.0	30		7.03			1.28 ₆	16.5
		80	4.07	8.13	1120	4.11	1.32 ₀	14.6
		146		167			1.31 ₅	0.71
	50.0	30	10.0	9.00	724	5.07	1.39 ₀	10.8
	60.0	30	24.9	5.80	565	6.13	1.34 ₃	10.1
	70.0	30		6.25			1.37 ₉	7.51
		146	55.0	222	390	7.30	1.30 ₅	0.20
	80.0	30		5.00			1.39 ₅	5.94
3 ^{b)}	95.0	146	125	142	322	8.57	1.37 ₈	0.21
		0	0.374	280	367	13.2	0.600	20.6

^{a)} Desorption from the nylon 6 film into aqueous bath at zero dye concentration.

^{b)} Sorption from an infinite dye bath by the polyester film.

^{c)} Determined from the concentration profile of dye in the film.

^{d)} Estimated from van der Waals volume of dye.^{8,9)}

can estimate the value of δ_D for each film dyeing system on assumption that the flow near the film is laminar one. The values of δ_D estimated by eq. 5, however, may be taken as an indication of the thickness of diffusional boundary layer for the film dyeing since the prerequisites required to apply eq. 5 to the film dyeing system have not been verified yet. Table 6 shows the comparison of the values of δ_D estimated in present study for

the film dyeing with those estimated from kinetic data of yarn dyeing³⁾ and with the values of δ_D calculated by eq. 5.

McGregor et al.¹⁾ predicted theoretically that for dyeing from unstirred dye bath, the sorption behavior corresponds to $2 < L < 10$, and that from good stirring corresponds to $\delta_D = \text{ca. } 3 \times 10^{-3} \text{ cm}$. The experimental values of δ_D obtained in this study are discussed briefly

Table 6 Comparison of the values of δ_D estimated from kinetic data of film dyeing with those estimated from kinetic data of yarn dyeing and the values of δ_D calculated by eq. 5.

Temp. (°C)	Dye	Agitation ^{a)} (strokes/min)	Estimated from kinetic data of dyeing			Calculated ^{b)} by eq. 5
			film		yarn ³⁾	film
			L	$\delta_D \times 10^3$ (cm)	$\delta_D \times 10^3$ (cm)	
40.0	1	0	3.08	80.2	181	
		30	12.4	18.5	37.0	10.0
		50			27.8	7.75
		80	17.1	14.0	2.0	6.13
		146			2.7	4.54
	2	30	7.03	16.5		9.87
		50			25.8	7.64
		80	8.13	14.6		6.04
		146	167	0.71		4.47
50.0	1	50			10.1	8.08
	2	30	9.00	10.8		10.3
60.0	1	50			5.8	8.39
	2	30	5.80	10.1		10.7
70.0	2	30	6.25	7.51		11.1
		146	222	0.20		5.01
80.0	2	30	5.00	5.94		11.4
		146	142	0.21		5.18
95.0	3	0	280	20.6	592	

^{a)} Agitation of 30, 50, 80 and 146 strokes/min correspond to the average velocity of the reciprocation of the specimen of 3.0, 5.0, 8.0, and 14.6 cm/sec, respectively. ^{b)} Calculated by eq. 5 using $\lambda = 2.0$ cm

from the view point of the theoretical prediction described above. The experimental values of L estimated for unstirred systems were 3.08 (the desorption of Dye 1 from nylon 6) and 280 (sorption of Dye 3 by polyester film), respectively. The former agrees well with the predicted value, whereas the latter is much larger than that predicted. However, the deviation of the latter from the predicted value may be attributable to the very small value of D_f since the value of δ_D 20.6×10^{-3} cm, calculated using $L = 280$ seems to be reasonable. The values of δ_D in the film dyeing systems decreased as the rate of agitation of the specimen was increased, particularly up to 146 strokes/min (14.6 cm/sec) at which the δ_D values decreased to $2.0 - 7.1 \times 10^{-4}$ cm; these values are much smaller than the predicted value but close to the values of δ_D at the surface of cellulose membrane, $3.8 - 5.9 \times 10^{-4}$ cm,³⁾ which were estimated by measuring the permeability of Dye 2 through the multilayer of the membrane under vigorous stirring at 30°C. The predicted value, $\delta_D = \text{ca. } 3 \times 10^{-3}$ cm for dyeing from well stirred solution, may be referred to the dyeing of fiber assemblies, in which the rate of fluid flow at the surface of the individual fiber is much lower than that of the bulk flow. The small values of δ_D estimated for the film dyeing

under the agitation of 146 strokes/min indicate that in the dyeing of films from well stirred solution, the resistance to the dye transport across the diffusional boundary layer gives little effect on the rate of dyeing, in contrast to the dyeing of packed yarns of fabrics.

McGregor et al. have also estimated the values of δ_D in a film dyeing with acid dyes from the kinetic data of dye sorption by the film; $17.2 - 4.1 \times 10^{-3}$ cm at the bulk flow of 4.2 - 10.0 cm/sec, 67°C.¹⁰⁾ The values of δ_D obtained in this study (the fifth column of Table 6) are comparable with those estimated by McGregor et al.

The comparison of the values of δ_D estimated for the film dyeing with those for the yarn dyeing with the same dyes³⁾ (the sixth column of Table 6) indicates that the value of δ_D in the film dyeing is, as a whole, smaller than that of yarn dyeing³⁾ under the same stirring conditions, particularly under the vigorous agitation, though in some cases the values of δ_D in the film dyeing are larger than those of corresponding yarn dyeing. This is a result of the fact that the flow rate of dye liquor in the yarn is lower than that at the film surface. However, the difference in δ_D between the film dyeing and the yarn dyeing seems to be rather smaller than that predicted intuitively except for the values of δ_D estimated under the agitation

of 146 strokes/min. This is ascribed to the fact that in the previous work,³⁾ only a thread of the yarn hanged loosely on a holder was dyed in an infinite bath, the dye liquor can permeate more easily under such conditions than in the practical yarn dyeing, in which yarns are packed tightly to some extent; the permeation of the fluid in the packed yarn is more difficult.

The values of δ_D obtained in the present study under the agitation of 30–80 strokes/min are also comparable with those calculated by eq. 5, although the values of δ_D obtained under the agitation of 146 strokes/min are much smaller than those calculated. However, if we consider that the values of δ_D calculated by eq. 5 may be taken as an indication of the thickness of diffusional boundary layer as described before, the agreement between them seems to be satisfactory.

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フィルムの染色速度データからの 拡散の境界層の厚さの見積り

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非イオン染料のナイロン6フィルムからの水中への脱着速度と無限浴からポリエチレンテレフタレートフィルムの染色速度を測定した。得られた染色速度データに対して Newman 式を用いた曲線のあてはめを行ない、フィルム中の染料の拡散係数 (D_f) 並びに境界層パラメータ (L) を求めた。同じ染料-フィルム系についてフィルム巻層法で D_f を求めた。両法で求めた D_f の値は多くの場合は一致したが、ナイロン6フィルムに高い親和力を持つ染料が攪拌が不十分な染浴中で脱着される時は、脱着速度データから得られた D_f の値はフィルム巻層法からのそれよりかなり小さな値となった。

一般に、濃度分布曲線から得られる D_f の値は染色速度データからのそれよりも信頼性が高い。この点を考慮して、測定された染色速度 (脱着速度) データに対し、Newman 式にフィルム巻層法で得られた D_f を入れて曲線のあてはめを行なって、 L の値を求め、これより

各フィルム染色系の拡散の境界層の厚さ (δ_D) を見積もった。得られた値は試料の浴中の攪拌速度 (上下方向 30mm の往復運動) が 0, 30, 80 及び 146 strokes/min の時、 $\delta_D = 20-80, 5.9-18.5, 14-15$ 及び $0.2-0.7 \times 10^{-3}$ cm 程度であった。これらの値を同じ染料でナイロン6, ポリエステル紡績糸を染色した時に見積もられている δ_D の値と比較した。繊維の集合体である糸や布の染色では攪拌が十分であっても、拡散の境界層中に染料が透過する速度が染色速度に影響を与えるが、フィルム染色系では基質の近傍の染液流速が 14.6 cm/sec 程度まで増加すると、境界層中の拡散抵抗は染色速度に殆ど影響を与えないことが分かった。

この報告で見積もられた δ_D の値は、酸性染料によるメトキシメチルナイロン66フィルムの染色速度の解析や流体力学に基づく Levich の式で計算した結果とほぼ一致した。