A Method of Estimating the Diffusion Coefficient of Disperse Dyes into Hydrophobic Fibers from the Initial Sorption Data of Dyeing by Means of the Polynomial Least-squares Method[1)]

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For the initial and the medium stage of diffusion, Hill's equation was approximated by the simple polynomial in the form of $M_t/M_\infty \approx P_1(Dt/r^2)^{1/2} - P_2(Dt/r^2)$, where P_1 and P_2 are constants depending on the interval in which the approximation is used, while the other symbols have a usual meanings. On the other hand, several experimental M_t's were plotted against square root of t, and an experimental formula describing the regression curve passing through a discrete set of experimental points, $M_t = A_0 + A_1t^{1/2} - A_2t$, was obtained by means of curve fitting with a polynomial of degree 2. From the polynomial approximation and the experimental formula, the following equations which are capable of calculating the approximate value of M_∞ and D were obtained.

$$(D/r^2)^{1/2} \approx (A_2P_1)/(A_1P_2), \quad M_\infty \approx (A_1^2P_2)/(A_2P_1^2)$$

Then the method for obtaining more probable values of D and M_∞ was described, in this method the approximations to inverse function of Hill's equation and the curve fitting with polynomial of degree 2 were used.

The diffusion coefficient of a dye into a fiber is frequently calculated from the kinetic data of dyeing obtained in an infinite bath using Eq. 1 (Hill's equation)[2)] or its approximations.[3)]

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{q_n^2} \exp\left(-q_n^2 \frac{Dt}{r^2}\right) \qquad (1)$$

where M_t and M_∞ are the quantities of dye taken up by a fiber of radius r at time t and equilibrium respectively, D is concentration independent diffusion coefficient and q_n's are positive roots of the Bessel function of the first kind of order zero, $J_0(q_n) = 0$.

However, it is often difficult to determine a reasonable value of M_∞ experimentally, since the decomposition of dye and the degradation of polymer substrate are apt to occur during a long period of the dyeing. Therefore, several studies have been made regarding the method of estimating D without using M_∞.[4—7)]

In this paper, we propose a polynomial least-squares method which is capable of estimating the probable value of D and M_∞ from several values of M_t determined at the early stage of dyeing.

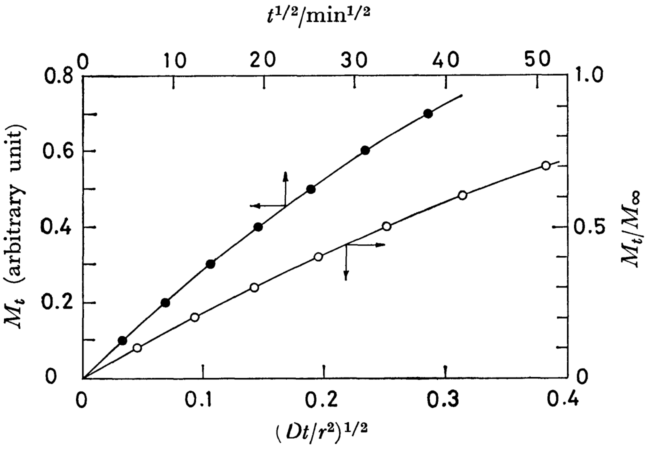

Fig. 1. Curve fitting by least squares with a polynomial of degree 2.
—●—: $M_t = A_0 + A_1t^{1/2} - A_2t$, —○—: $M_t/M_\infty = Q_0 + Q_1(Dt/r^2)^{1/2} - Q_2(Dt/r^2)$.

Theoretical

For the small and medium values of Dt/r^2, Eq. 1 can be approximated by simple polynomials in the form of Eq. 2.

$$\frac{M_t}{M_\infty} \approx P_1\left(\frac{Dt}{r^2}\right)^{1/2} - P_2\left(\frac{Dt}{r^2}\right) \qquad (2)$$

P_1 and P_2, the coefficients of the polynomial, depend on the interval in which Eq. 2 is used as an approximation to Eq. 1. The values of the coefficients were determined by the minimum maximum error techniques as follows:

Interval	P_1	P_2	$\Delta\left(\frac{M_t}{M_\infty}\right)$
$0 < \frac{M_t}{M_\infty} < 0.6$	2.271	1.122	±0.0005
$0 < \frac{M_t}{M_\infty} < 0.7$	2.277	1.150	±0.001
$0 < \frac{M_t}{M_\infty} < 0.8$	2.297	1.222	±0.002
$0 < \frac{M_t}{M_\infty} < 0.9$	2.331	1.352	±0.005

where $\Delta(M_t/M_\infty)$ is the maximum deviation of Eq. 2 from Eq. 1 in M_t/M_∞ in the interval.

On the other hand, if the plot of the experimental M_t value *vs.* $t^{1/2}$ is made as is shown by the solid circles in Fig. 1, we can obtain Eq. 3 as an experimental formula expressing the rate of diffusion by the curve-fitting technique:

$$M_t \approx A_0 + A_1t^{1/2} - A_2t \qquad (3)$$

empirical constants, A_0, A_1, and A_2, are determined in order to minimize S:

$$S = \sum_{i=0}^{n} \{M_{ti} - (A_0 + A_1t_i^{1/2} - A_2t_i)\}^2 \qquad (4)$$

where, the data at origin ($t=0$, $M_t/M_\infty=0$) are weighted by a factor of ten. This weighting makes A_0 negligible and reduces the effect of the experimental error in the M_t determined at the early stage of dyeing

Table 1. Examination of the accuracy of the diffusion coefficient estimated by polynomial least-squares method

Time of dyeing min	$t^{1/2}$ $\mathrm{min}^{1/2}$	M_t a) Arbitrary unit	$\frac{M_t}{M_\infty}$ b)	$\left(\frac{Dt}{r^2}\right)^{1/2}$ c)
0	0	0	0	0
20.45	4.523	0.1000	0.10025	0.04533
85.53	9.248	0.2000	0.20049	0.09272
202.07	14.215	0.3000	0.30074	0.14254
379.35	19.477	0.4000	0.40099	0.19532
630.58	25.111	0.5000	0.50123	0.25184
976.31	31.246	0.6000	0.60148	0.31340
1453.42	38.124	0.7000	0.70173	0.38252
		$A_0=0.000095$	$Q_0=-0.000094$	
		$A_1=0.022785$	$Q_1=2.2786$	
		$A_2=0.00011544$	$Q_2=1.1549$	
		$M_\infty=0.9975_4$ d)	$M_\infty=1.0003$	
		$(D/r^2)^{1/2}=0.01003_1$ $\mathrm{min}^{-1/2}$ d)	$(D/r^2)^{1/2}=0.009996$ $\mathrm{min}^{-1/2}$	

a) Calculated by Eq. 1 using $M_\infty=1.0000$ and $(D/r^2)^{1/2}=0.01\ \mathrm{min}^{-1/2}$. b) Calculated by using $M_\infty=0.9975_4$. c) Calculated using the M_t/M_∞ given in the fourth column by Eq. 7. d) Calculated by Eq. 6 using $P_1=2.277$ and $P_2=1.150$.

on the value of D estimated by this method.

A comparison of Eqs. 2 and 3 gives:

$$\left(\frac{D}{r^2}\right)^{1/2} \approx \frac{A_2P_1}{A_1P_2} \tag{5}$$

$$M_\infty \approx \frac{A_1^2P_2}{A_2P_1^2}. \tag{6}$$

Equation 5 enables us to estimate an approximate value of D without using M_∞. The appropriate P_1 and P_2 values in Eq. 5 are selected as follows. The rate of dyeing data given in the columns from the first to the third of Table 1 were calculated by Eq. 1 using $(D/r^2)^{1/2}=0.01000\ \mathrm{min}^{-1/2}$ and $M_\infty=1.000$ (arbitrary unit) in order to examine the accuracy of D, estimated by this method. From the data given in the second and the third columns of Table 1, $A_0=0.000095$, $A_1=0.022785$, and $A_2=0.00011544$ are obtained as the empirical constants in Eq. 3 by means of curve fitting with a polynomial of degree 2. For this case, if we use $P_1=2.271$ and $P_2=1.122$(suitable for $M_t/M_\infty=0$—0.6), we get $M_\infty=0.9784$ by Eq. 6. By dividing the values of M_t by the M_∞ value obtained above, we can estimate that the M_t's range about $M_t/M_\infty=0$—0.715 and that the appropriate P_1 and P_2 values are that for $M_t/M_\infty=0$—0.7. Similarly, if $P_1=2.297$ and $P_2=1.222$(suitable for $M_t/M_\infty=0$—0.8) are used at first, we get $M_\infty\approx1.0416$ and find that P_1 and P_2 for $M_t/M_\infty=0$—0.7 are suitable for this case. The appropriate P_1 and P_2 values are thus determined. By using $P_1=2.277$ and $P_2=1.150$ which are suitable for $M_t/M_\infty=0$—0.7, approximate values, $(D/r^2)^{1/2}=0.01003\ \mathrm{min}^{-1/2}$ and $M_\infty=0.9975$, are obtained by the use of Eqs. 5 and 6 respectively. This result shows that the use of appropriate P_1 and P_2 values gives an accurate value of D in Eq. 5. However, we can not always use values of P_1 and P_2 as appropriate as in the case of simulation described above, so that, in most cases, further calculations are required to get a more probable value of D, as will be described below.

An accurate value of $(Dt/r^2)^{1/2}$ yielding a given value of M_t/M_∞ in Eq. 1 can be obtained by the use of Eq. 7 or 8, which were derived by means of the method described by Hastings[8] as the approximations to the inverse function of Eq. 1.

For $M_t/M_\infty<0.855$,

$$\left(\frac{Dt}{r^2}\right)^{1/2} \approx \frac{0.44292M-0.480014M^2+0.069127M^3}{1-1.282686M+0.31912M^2}. \tag{7}$$

For $0.855<M_t/M_\infty<0.998$,

$$\left(\frac{Dt}{r^2}\right)^{1/2} \approx \left\{-\frac{0.36839+\ln(1-M)}{5.7836}\right\}^{1/2} \tag{8}$$

where $M\equiv M_t/M_\infty$; the maximum deviation of Eqs. 7 and 8 from the inverse function of Eq. 1 in $(Dt/r^2)^{1/2}$ are within ±0.000015 at the each interval.

By dividing the experimental M_t values by the M_∞ estimated by Eq. 6, we can get the series of M_t/M_∞ values given in the fourth column of Table 1. The value of $(Dt/r^2)^{1/2}$ yielding each M_t/M_∞ in Eq. 1 is obtained by the use of Eq. 7 or 8 as is shown in the fifth column of Table 1. The set of data: $\{(Dt_i/r^2),\ M_{t_i}/M_\infty,\ i=0,1,2,\cdots n\}$ is thus obtained. If the data are plotted as is shown by the empty circles in Fig. 1, we can get Eq. 9 as a regression equation passing through these points by means of the curve-fitting with polynomial of degree 2, where the data at origin, $\{(Dt/r^2)^{1/2}=0,\ M_t/M_\infty=0\}$, are also weighted by a factor of ten.

$$\frac{M_t}{M_\infty} = Q_0 + Q_1\left(\frac{Dt}{r^2}\right)^{1/2} - Q_2\left(\frac{Dt}{r^2}\right) \tag{9}$$

Q_1, Q_2, and Q_0 are the regression coefficients and constant respectively.

A comparison of Eqs. 3 and 9 gives:

$$\left(\frac{D}{r^2}\right)^{1/2} \approx \frac{A_2Q_1}{A_1Q_2} \tag{10}$$

and:

$$M_\infty \approx \frac{A_1^2Q_2}{A_2Q_1^2}. \tag{11}$$

More probable values of D and M_∞ are obtained by the use of Eqs. 10 and 11 respectively. For example, from the data given in the fourth and fifth columns of Table 1, the regression coefficients, $Q_1=2.2786$ and $Q_2=1.1549$, are obtained by means of the curve-fitting with polynomial of degree 2. By inserting this values into Eqs. 10 and 11, we get $(D/r^2)^{1/2}=0.009996\ \mathrm{min}^{-1/2}$ and $M_\infty=1.0003$ respectively.

If we repeat the calculations described above using the M_∞ value obtained by means of Eq. 11 and the experimental M_t's, we can get a far more probable value of D, *e.g.*, in the case of the M_t's given the third column of Table 1, $Q_1=2.2784$, $Q_2=1.1540$ and $(D/r^2)^{1/2}=0.010003$ and $M_\infty=0.99979$. However, taking into account the precision with which the experimental M_t's can be obtained, repeated calculations are not required in most cases if the appropriate P_1 and P_2

Table 2. Estimation of the diffusion coefficient of C.I. disperse violet 1 into poly(ethylene terephthalate) fiber at 95 °C from the initial sorption data of dyeing

Time of dyeing h	$t^{1/2}$ $\mathrm{min}^{1/2}$	M_t $(\mathrm{mol/kg})\times 10^{-2}$	$\frac{M_t}{M_\infty}$ a)	$\left(\frac{Dt}{r^2}\right)^{1/2}$ b)	$\frac{M_t}{M_\infty}$ c)	D d) $(\mathrm{cm^2 \cdot min^{-1}})\times 10^{-11}$
0	0	0	0	0		
1	7.75	0.40	0.0904	0.04077	0.091	1.30
2	10.95	0.53	0.1197	0.05434	0.121	1.16
5	17.32	0.81	0.1830	0.08427	0.185	1.12
12	26.83	1.25	0.2824	0.13320	0.285	1.16
25	38.73	1.78	0.4021	0.19591	0.406	1.21
45	51.96	2.26	0.5105	0.25729	0.516	1.16
70	64.81	2.73	0.6167	0.32330	0.623	1.18
285		4.11			0.938	1.12
409		4.38				Average = 1.18

a) Calculated by using $M_\infty=4.427\times 10^{-2}$ mol/kg. b) Calculated using the M_t/M_∞ given in the fourth column by Eq. 7. c) Calculated using $M_\infty=4.38\times 10^{-2}$ mol/kg. d) Calculated using the M_t/M_∞ given in the sixth column by Eq. 7 or 8.

values are used in Eq. 6.

The results of simulations using M_t's including experimental error show that the value of D estimated by this method is insensitive to the error in M_t at the early stage of diffusion, but relatively sensitive to that at the later stage. Therefore, by increasing the accuracy of the M_t determined at the last two or three points of measurement, we can get an accurate value of D without using M_∞.

Experimental

Materials. The dye used was purified C.I. Disperse Violet 1 (1,4-diaminoanthraquinone, mp: 271—272 °C, Found: N, 11.9%, Calcd for: N, 11.8%). The crystal of the dye was grounded in a ball mill with a dispersing agent for 48 h and then dispersed in water. The dispersing agent was thus removed from the dispersion by the use of a membrane filter (average pore size: 0.65 μm). The dispersion containing 0.5 g/l pure dye was used for dyeing. The fiber used poly(ethylene terephthalate) spun yarn (40 s, pretreated in boiling water for 2 h, $r=6.79\times 10^{-4}$ cm).

Determination of Rate of Dyeing. About 10 mg of the fiber was dyed in the dye dispersion of one liter for a certain period at 95 °C using an apparatus similar to that used by Peters *et al.*[9] The dyed fiber was rinsed with cold acetone to remove the surface dye. Then the dye on the fiber was extracted with hot chlorobenzene, and the amount of dye in the fiber was determined colorimetrically using a Hitachi 101 spectrophotometer.

All the calculations were made using a Canon SX 110 programmable calculator.

Results and Discussion

The kinetic data of the dyeing were determined to be as given in the first three columns of Table 2. From the set of data given in the second and third columns of the table, the values of the empirical constants in Eq. 3 were calculated to be $A_1=0.050109$ and $A_2=0.0001234$ respectively by means of the polynomial least-squares method. Consequently, approximate values of $(D/r^2)^{1/2}\approx 0.00498_4\ \mathrm{min}^{-1/2}$, and $M_\infty\approx 4.42_7\times 10^{-2}$ mol/kg were obtained by the use of Eqs. 5 and 6, where $P_1=2.271$ and $P_2=1.122$ were used. If we use $P_1=2.297$ and $P_2=1.222$, which are suitable for $M_t/M_\infty=0$—0.8, we get $M_\infty\approx 4.71_3\times 10^{-2}$ mol/kg from Eq. 6. However, by dividing the experimental M_t's by the M_∞ obtained above, we find that the values of M_t/M_∞ range about 0—0.58 and that the appropriate P_1 and P_2 values for this case are 2.271 and 1.122 respectively.

Therefore, the values of M_t/M_∞ were calculated using $M_\infty=4.42_7\times 10^{-2}$ mol/kg and the experimental M_t values given in the fourth column of Table 2. The values of $(Dt/r^2)^{1/2}$ yielding these M_t/M_∞ in Eq. 1 were calculated by the use of Eqs. 7 or 8, as listed in the fifth column. The application of the polynomial least-squares method to the set of data listed in the fourth and fifth columns of Table 2 gave these regression coefficients: $Q_1=2.2697$ and $Q_2=1.116_4$. The substitution of these values into Eqs. 10 and 11 gave $(D/r^2)^{1/2}\approx 0.00500_7\ \mathrm{min}^{-1/2}$, $D=1.15_4\times 10^{-11}\ \mathrm{cm^2\cdot min^{-1}}$ and $M_\infty\approx 4.41_0\times 10^{-2}$ mol/kg respectively.

If we use the M_t obtained at $t=409$ h as M_∞, we get the values of D given in the last column of Table 2 by means of the standard method, which gives an average value of $D=1.18\times 10^{-11}\ \mathrm{cm^2\cdot min^{-1}}$. This value agrees well with the value of D estimated by the polynomial least-squares method proposed in this paper.

Conclusions

Since the numerical calculations of Eqs. 7 and 8 and the curve-fitting with a polynomial of degree 2 can easily be carried out using one of the programmable pocket calculator commercially available today, the method of estimating D and M_∞ from the initial sorption data by the polynomial least squares-method is relatively simple. The values of D and M_∞ estimated by this method are accurate enough when the several experimental M_t's fall in the range wider than $M_t/M_\infty=0$—0.6 and each M_t's are equally spaced within the range.

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