

# Dye Leveling in PET Fibers.

## II. Mathematical Model

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### Synopsis

A mathematical model is developed for the dye leveling process. Good agreement between experimental and theoretical data supports the validity of the proposed model. Also, the applicability of the proposed model is shown through its effectiveness in predicting leveling times, when the working temperature is above the  $T_g$  of the fibers. The results demonstrate that chain mobility is a prerequisite for rapid leveling, and that morphological changes in the fiber during the migration process are important and must be considered.

### INTRODUCTION

During the dyeing of textile fibers regions of different dye concentration, and therefore different color, sometimes occur. Reasons may be as simple as blockage of some fibers by being near or in contact with others, or by mass transfer problems in the solution or at the fiber-solution boundary layer. It is well known that, by retaining the fibers in the bath for a longer time under good agitation and fiber separation, the dye tends to desorb into the solution from fiber regions of higher dye concentration, and to adsorb from the solution onto regions of lower concentration. This process is called "leveling," and results in more uniform color of the dyed material. It may be done in the presence of polymer-plasticizing agents known as "carriers," which have the effect of increasing the diffusivity of the dye within the fibers by making the polymeric chains more mobile. In the preceding paper we discuss in detail some of the effects of polymer physical structure and carrier upon the leveling process. In this paper we develop a mathematical model and compare it with experimental leveling data. We are not aware of any previous model for the process.

The leveling experiment modeled involves placing a bundle (0.1–0.3 g) of fibers, dyed to equilibrium, in a 100-mL bottle, in which they are separated from a similar weight of undyed fibers by a fine screen. A fixed amount of a blank liquid medium, initially containing no dye, is added. The liquid is agitated by horizontal shaking, and is maintained at 100°C in an oil bath. Dye desorbs from the initially dyed fibers into the solution, and some of this adsorbs onto and diffuses within the undyed fibers. Experiments are run for various times, after which both sets of fibers are analyzed for dye content. The entire process is described in greater detail in Paper I.

In terms of a model, we have the unsteady state diffusion of a solute

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within and from a cylinder, into an agitated bath, and simultaneously into and within a cylinder of overall lower solute concentration. For the overall leveling process the desorption and adsorption processes must be considered simultaneously; the concentrations within both sets of fibers and within the bath are changing as a function of time.

### DEVELOPMENT OF THE MODEL FOR DYE LEVELING

To develop a model, the leveling process will be considered in two parts: (a) diffusion in the dyed fibers and desorption and (b) adsorption and diffusion within the undyed fibers. The equations for the two parts will then be combined and solved simultaneously.

The dye desorption into a well-stirred solution of limited volume, initially free from solute, from a cylinder (fiber) in which the dye concentration is initially uniform and equal to  $C_0$ , represents the opposite case from that of diffusion from a finite dyebath. Solutions for such a problem can be found in the literature.<sup>1,2</sup> For convenience, the solutions are shown in the equations below:

$$\frac{\bar{M}_t}{\bar{M}_\infty} = \frac{2}{\alpha} (1 + \alpha) \left[ \frac{2}{\pi^{1/2}} \left( \frac{Dt}{a^2} \right)^{1/2} - \left( \frac{1}{2} + \frac{2}{\alpha} \right) \frac{Dt}{a^2} - \frac{4}{3\pi^{1/2}} \left( \frac{1}{8} - \frac{2}{\alpha} - \frac{4}{\alpha^2} \right) \left( \frac{Dt}{a^2} \right)^{3/2} + \dots \right] \quad (1)$$

where  $\alpha = A/\pi a^2$  is the ratio of the volumes of solution and cylinder of radius  $a$ . If there is a partition factor  $K$  between solute in equilibrium inside the cylinder, and in the solution,  $\alpha = A/(\pi a^2 K)$ .  $\bar{M}_\infty$  = amount of solute in the solution after infinite time, and  $\bar{M}_t$  the corresponding amount after time  $t$ .  $D$  is the diffusion coefficient. In the migration experiment,  $\alpha$  is large; eq. (2) presents a satisfactory solution for the desorption process. Also, the relationship between  $\alpha$  and the final fraction uptake of solute by solution is given by

$$\frac{\bar{M}_\infty}{\pi a^2 C_0} = \frac{1}{1 + 1/\alpha} \quad (2)$$

Carman and Haul<sup>2</sup> have derived an alternative equation which is less easy to use, but which is accurate up to considerably higher values of  $\bar{M}_t/\bar{M}_\infty$ :

$$1 - \frac{\bar{M}_t}{\bar{M}_\infty} = (1 + \alpha) \left\{ \frac{\gamma_3}{\gamma_3 + \gamma_4} e \operatorname{erfc} \left[ \frac{2\gamma_3 (Dt)^{1/2}}{\alpha (a^2)^{1/2}} \right] + \frac{4}{\gamma_3 + \gamma_4} e \operatorname{erfc} \left[ - \frac{2\gamma_4 (Dt)^{1/2}}{\alpha (a^2)^{1/2}} \right] \right\} \quad (3)$$

where

$$\gamma_3 = \frac{1}{2} [(1 + \alpha)^{1/2} + 1], \quad \gamma_4 = (\gamma_3 - 1), \quad (4)$$

$e = \exp x^2$  and  $x$  corresponds to the expression inside the brackets of  $\operatorname{erfc}$  (complementary error function). Values of  $\exp x^2 \operatorname{erfc} x$  as a function of  $x$  are found in the literature.<sup>1</sup>

A comparison between eqs. (2) and (3) demonstrates that differences occur only at high values of  $\overline{M}_t/\overline{M}_\infty$  or of time (Figs. 1 and 2). This difference can be corrected by increasing the number of terms of the series in eq. (2).

The following discussion is concerned with the derivation of an equation to describe the absorption case in the migration experiment. The solute, which is being released from another fiber, diffuses into the solution and finally into the blank fiber. The concentration of the solute in the originally dyed fiber is initially homogeneous and equal to  $C_0$ .

Since we are treating the case of a well-stirred solution (shaking bath), it is reasonable to neglect the diffusion of the solute in the solution. Therefore, we neglect the time elapsed from the solute release from the dyed fiber to the solute absorption by the blank fiber. Let us denote the dyed fiber by  $F_1$ . It is known<sup>1</sup> that the total amount of solute  $\overline{M}_t$  in the solution after time  $t$  can be expressed by the equation below:

$$\overline{M}_t = \overline{M}_\infty \left[ 1 - \sum_{n=1}^{\infty} \frac{4\alpha(\alpha + 1)}{4 + 4\alpha + \alpha^2 q_m^2} \exp\left(\frac{-D_1^2 q_m^2 t}{a^2}\right) \right] \tag{5}$$

where  $\overline{M}_\infty$ , as already defined, is the amount of solute in the solution after infinite time (equilibrium state), and the  $q_m$ s are the positive, nonzero roots of (1). Equation (5) is a general form: Eqs. (1) and (2) are simplified solutions

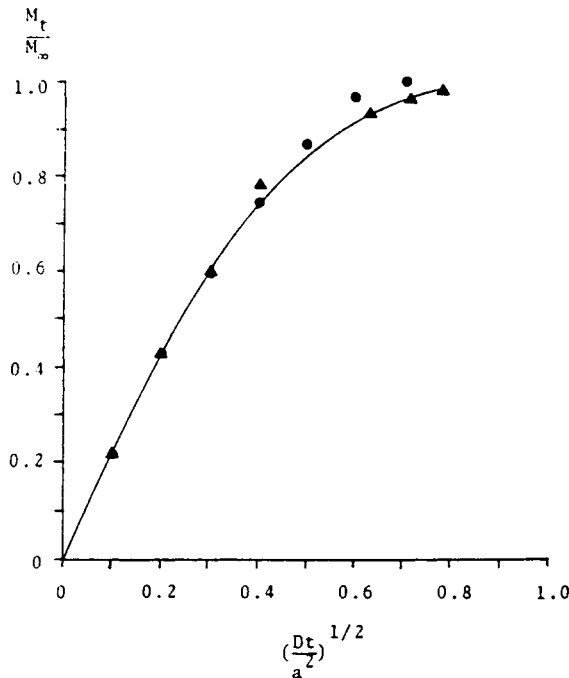


Fig. 1. Dye desorption by a cylinder into a stirred solution of limited volume and initially free of solute:  $\alpha = 26$ ; (●) model; (▲) Carman and Haul.

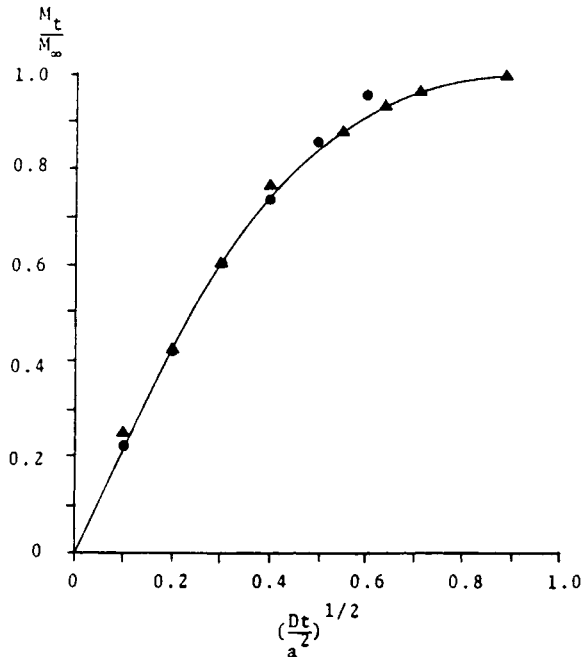


Fig. 2. Dye desorption by a cylinder into a stirred solution of limited volume and initially free of solute:  $\alpha = 34$ ; (●) model; (▲) Carman and Haul.

of it. The general form is needed for the absorption case:

$$\alpha q_m J_0(q_m) + 2J_1(q_m) = 0 \quad (6)$$

$\alpha$  is defined by eq. (3) and  $D_1$  = the  $F_1$  fiber's diffusion coefficient.

At this point we assume that the concentration of solute just within the surface of  $F_2$ , which hereafter denotes the blank fiber, is the same as that in the solution and also that, after time  $t$ , the amount of solute taken up by  $F_2$  is negligible compared to the amount of the solute left in the solution.

This approximation, backed by the experimental results (Figs. 1–3 of Paper I of this series) must be made in order to obtain an explicit mathematical solution.

By virtue of the above assumptions, the surface concentration  $C_0(t)$  of  $F_2$  can be defined as

$$C_0(t) = \frac{M_t}{V} \quad (7)$$

where  $V$  is the volume of solution in the bath.

If the initial concentration in  $F_2$  is zero and that at the surface is  $C_0(t)$ , the concentration in  $F_2$  is given by<sup>1</sup>

$$C(r,t) = \frac{2D_2}{a} \sum_{n=1}^{\infty} e^{-D_2\alpha_n^2 t} \frac{\alpha_n J_0(r\alpha_n)}{J_1(a\alpha_n)} \int_0^t \exp(D_2\alpha_n^2 s) C_0(s) ds \quad (8)$$

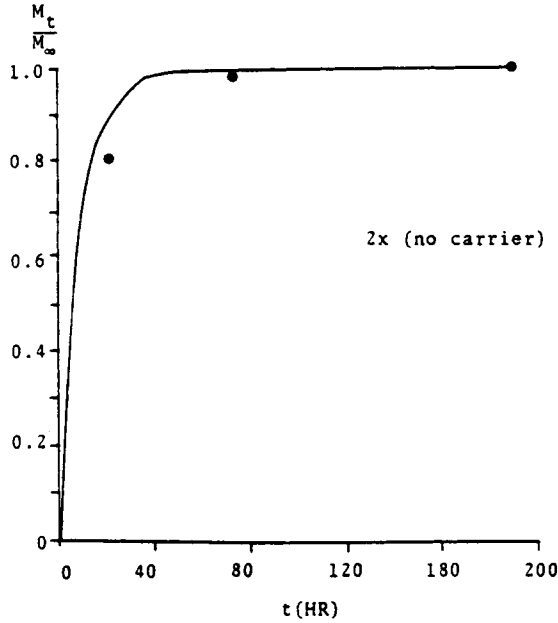


Fig. 3. Dye absorption vs. time for the 2x fiber from a stirred solution of limited volume in absence of benzoic acid: (●) experimental; (—) model.

where  $D_2$  is  $F_2$ 's diffusion coefficient,  $a =$  radius of  $F_2$  fiber, the  $\alpha_n$ 's are the roots of  $J_0(a\alpha_n) = 0$ , and  $J_0$  and  $J_1$  are Bessel functions of the first kind of order 0 and 1, respectively. The  $\alpha_n$ 's values can be found in the literature.<sup>1</sup>

By replacing  $C_0(t)$  in eqs. (8) and (7) and using the following integral,

$$\int_0^t e^{D_2\alpha_n^2 s} ds = \frac{1}{D_2\alpha_n^2} e^{D_2\alpha_n^2 t} - \frac{1}{D_2\alpha_n^2} = \frac{1}{D_2\alpha_n^2} [\exp(D_2\alpha_n^2 t) - 1],$$

we obtain the following expression:

$$\begin{aligned} C(t,r) &= \frac{2D_2}{a} \sum_{n=1}^{\infty} \exp(-D_2\alpha_n^2 t) \frac{\alpha_n J_0(r\alpha_n)}{J_1(a\alpha_n)} \left\{ \int_0^t \frac{\bar{M}_\infty}{V} \exp(D_2\alpha_n^2 s) ds \right. \\ &\quad \left. - \sum_{m=1}^{\infty} \frac{4\alpha(\alpha+1)}{4+4\alpha+\alpha^2 q_m^2} \cdot \frac{\bar{M}_\infty}{V} \int_0^t \exp\left[ \left( D_2\alpha_n^2 - \frac{D_1 q_m^2}{a^2} \right) s \right] ds \right\} \\ &= \frac{2D_2 \bar{M}_\infty}{a D_2 V} \sum_{n=1}^{\infty} \frac{\alpha_n J_0(r\alpha_n)}{\alpha_n^2 J_1(a\alpha_n)} [1 - \exp(-D_2\alpha_n^2 t)] \\ &\quad - \frac{2D_2 \bar{M}_\infty}{a V} \sum_{n=1}^{\infty} \exp(-D_2\alpha_n^2 t) \frac{\alpha_n J_0(r\alpha_n)}{J_1(a\alpha_n)} \left\{ \sum_{m=1}^{\infty} \frac{4\alpha(\alpha+1)}{4+4\alpha+\alpha^2 q_m^2} \right. \\ &\quad \left. \cdot \frac{\exp[t(D_2\alpha_n^2 - D_1 q_m^2/a^2)] - 1}{D_2\alpha_n^2 - D_1 q_m^2/a^2} \right\} \end{aligned} \tag{9}$$

The expression (9) yields the concentration in  $F_2$  at time  $t$ .

Therefore, to obtain the amount of solute  $M_t$  in  $F_2$  after time  $t$ , we multiply the expression (9) by  $r$  and integrate over  $0 \leq r \leq a$ ,  $0 \leq \theta \leq 2\pi$ , where  $\theta$  corresponds to the cylindrical coordinates:

$$M_t = \int_0^{2\pi} \int_0^a rC(r,t) dr d\theta = \int_0^{2\pi} \left\{ \frac{2M_\infty}{aV} \sum_{n=1}^\infty \frac{a}{\alpha_n^2} [1 - \exp(-D_2\alpha_n^2 t)] + \frac{2D_2M_\infty a}{aV} \sum_{n=1}^\infty \sum_{m=1}^\infty \frac{4\alpha(\alpha+1)}{4+4\alpha+\alpha^2q_m^2} \cdot \frac{\exp(-D_2\alpha_n^2 t) - \exp(D_1q_m^2 t/a^2)}{D_2\alpha_n^2 \left(\frac{D_1q_m^2}{a^2}\right)} \right\} d\theta$$

By resorting to the series (1)  $\sum_{n=1}^\infty (1/\alpha_n^2) = a^2/4$  we can finally obtain

$$M_t = \pi a^2 \frac{\overline{M_\infty}}{V} - 4\pi \frac{\overline{M_\infty}}{V} \sum_{n=1}^\infty \frac{e^{-D_2\alpha_n^2 t}}{\alpha_n^2} + 4\pi D_2 \frac{\overline{M_\infty}}{V} \sum_{n=1}^\infty \sum_{m=1}^\infty \frac{4\alpha(\alpha+1)}{4+4\alpha+\alpha^2q_m^2} \cdot \frac{e^{-D_2\alpha_n^2 t} - e^{-D_1q_m^2 t/a^2}}{D_2\alpha_n^2 - D_1q_m^2/a^2} \tag{10}$$

The first term on the right-hand side is obtained as follows:

$$2\pi \frac{2\overline{M_\infty}}{V} \sum_{n=1}^\infty \frac{1}{\alpha_n^2} = 4\pi \frac{\overline{M_\infty}}{V} \frac{a^2}{4} = \pi a^2 \frac{\overline{M_\infty}}{V} \tag{11}$$

Now, by denoting the final  $F_2$  amount of solute  $\pi a^2 \overline{M_\infty} / V$  by  $M_\infty$ , the absorption time curve is given by

$$\frac{M_t}{M_\infty} = 1 - \frac{4}{a^2} \sum_{n=1}^\infty \frac{e^{-D_2\alpha_n^2 t}}{\alpha_n^2} + \frac{4D_2}{a^2} \sum_{n=1}^\infty \sum_{m=1}^\infty \frac{4\alpha(\alpha+1)}{4+4\alpha+\alpha^2q_m^2} \cdot \frac{e^{-D_2\alpha_n^2 t} - e^{-D_1q_m^2 t/a^2}}{D_2\alpha_n^2 - D_1q_m^2/a^2} \tag{12}$$

Looking at expression (12), one can make an interesting comparison between our system and the case of absorption of a solute by a cylindrical fiber whose initial concentration is zero and whose surface concentration is kept constant and equal to  $C_0$ . Obviously, in our case, the  $F_2$  surface concentration depends on  $t$ .

Since the expression

$$1 - \sum_{n=1}^\infty \frac{4}{a^2} \frac{e^{-D_2\alpha_n^2 t}}{\alpha_n^2}$$

in (12) gives the amount of solute taken up by a cylindrical fiber with

boundary and initial conditions referred to the case italicized above and the last term on the right-hand side of (12) (double series) is always negative, we immediately conclude that the absorption process in  $F_2$  is *slower* than the one in which the surface concentration is kept constant. By slower, we mean that a smaller amount of solute is absorbed after time  $t$ .

### COMPARISON OF THE MODEL WITH EXPERIMENTAL RESULTS

In order to examine the validity of the proposed mathematical model described above, the experimental data were compared with calculated data from the proposed equations.

First of all, the proposed model that describes the dye absorption by the blank fiber with changing surface concentration in a system of finite volume is discussed [eq. (12)].

Then, the general model is tested by comparing the experimental and calculated amount of dye left in the medium (water) during the entire migration process. Finally we show that this proposed model can be used to predict leveling times when the working temperature is above the  $T_g$  of the fibers.

It is interesting to note that the proposed model has no adjustable parameters—absolute calculation methods are used, including only measured values of  $D$  from separate infinite dye bath experiments.

#### The Absorption Case

Since the fibers involved in the particular migration experiment have been subjected to the same kinds of treatments (heat setting, use or not of carrier) and they have the same draw ratios we can expect to obtain  $D_1 = D_2$ , where  $D_1$  is the diffusion coefficient of the fiber that released dye to the medium and  $D_2$  is the diffusion coefficient of the fiber which is absorbing dye.

Also, it was considered the diffusion coefficients obtained through Hill's equation,<sup>3</sup> which describes an infinite dyebath system, where applicable for  $D_1$  and consequently  $D_2$ . The use of diffusivities from an infinite dyebath condition was necessary in order to make the mathematical model more general and easy to use. It assumes that the diffusivities are not dependent upon the dye concentration.

Table I shows the diffusivities calculated from infinite dyebath data; these were also used in evaluation of eq. (12). Figures 3–6 show the results ob-

TABLE I  
Diffusivities Calculated from Hill's Equation (9) Using Infinite Dyebath Data

Sample draw ratio	$D_1 = D_2$ (cm <sup>2</sup> /min)	
	No carrier	Carrier
2x	$3.23 \times 10^{-9}$	$3.14 \times 10^{-8}$
4x		$4.50 \times 10^{-9}$
6x		$1.09 \times 10^{-9}$

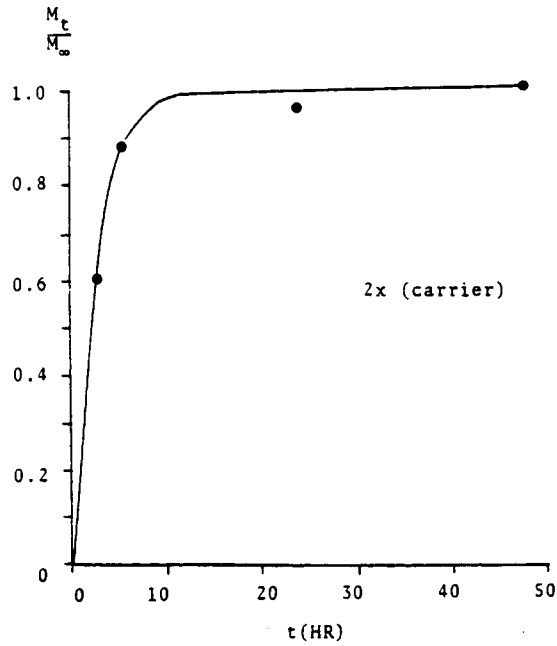


Fig. 4. Dye absorption versus time for the 2x fiber from a stirred solution of limited volume in presence of benzoic acid (concn 13 g/L): (●) experimental; (—) model.

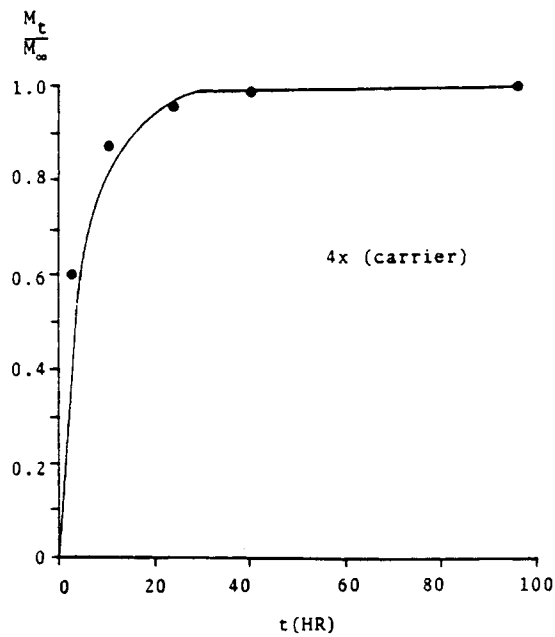


Fig. 5. Dye absorption vs. time for the 4x fiber from a stirred solution of limited volume in presence of benzoic acid (concn 13 g/L): (●) experimental; (—) model.



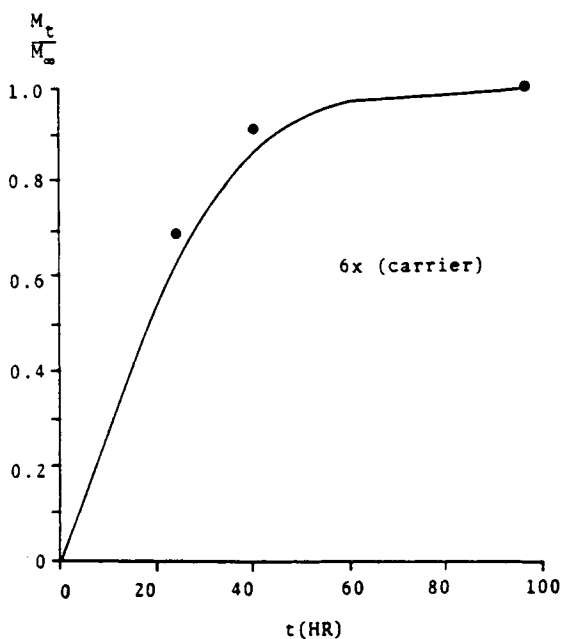


Fig. 6. Dye absorption vs. time for the 6x fiber from a stirred solution of limited volume in presence of benzoic acid (concn 13 g/L): (●) experimental; (—) model.

tained. Agreement between calculated and experimental finite bath dye uptake data can be observed.

### The General Model

As explained before, there is a considerable amount of dye left in the water during the migration experiment. There will be a steady increase of the amount of dye in the water with time, during the entire migration process.

Therefore, the increased amount of dye in the water with time is expected to be predicted by the mathematical models involved, i.e., eqs. (2) and (12). The comparison between calculated and experimental data was made in the following way:

From eq. (2), a master curve or a table of  $\bar{M}_t/\bar{M}_\infty$  vs.  $(Dt/a^2)^{1/2}$  can be constructed. Then, the values of  $\bar{M}_t$ , i.e., the amount of dye in the water at time  $t$ , can be calculated since  $\bar{M}_\infty$  or amount of dye in water at infinite time is known experimentally. The values of diffusion coefficients used were those from Table I. As already explained, the use of diffusion coefficients determined from an independent experiment is required, in order to avoid doubts concerning the validity of the comparison.

Next, the values of  $M_t/M_\infty$  can be determined from eq. (12). Then,  $M_t$  or the amount of dye taken up by the originally undyed fiber at time  $t$  can be calculated, since  $M_\infty$ , the corresponding amount at infinite time, is known experimentally.  $\bar{M}_\infty$  and  $M_\infty$  are given by the following expressions:

$$\bar{M}_\infty = M_0 - M'_\infty \quad (13)$$

$$M_\infty = M_0 - \bar{M}_\infty \quad (14)$$

where  $M_0$  = the initial amount of dye in the originally dyed fiber. This value was obtained from the infinite dyebath experiment at equilibrium.  $M'_\infty$  = the amount of dye in the originally dyed fiber after infinite time for diffusion into the bath. Finally, by subtracting  $M_t$  from  $\bar{M}_t$ , the calculated values of  $(\bar{M}_t^*)_{\text{calc}}$ , the amount of dye in the water at a given time is obtained.

Now, the experimental values of  $(\bar{M}_t^*)_{\text{exp}}$  are calculated for the corresponding times from the experimental curves. For more precision, a large scale plot of the experimental curves (Figs. 1-3 of Paper I from this series) were constructed.

$$(\bar{M}_t^*)_{\text{exp}} \text{ is given by} \quad (15)$$

$$(\bar{M}_t^*)_{\text{exp}} = M_0 - (M'_t)_{\text{exp}} - (M_t)_{\text{exp}}$$

Where  $(M'_t)_{\text{exp}}$  = amount of dye in the originally dyed fiber at time  $t$  and  $(M_t)_{\text{exp}}$  = amount of dye in the originally undyed fiber at time  $t$ .

Figures 7-9 show the results. The values for high times, i.e., close to equilibrium, are not shown in the figures. The lack of precision for high values of time is due to the need for more terms in the series of the eq. (2). In order to show a better agreement between calculated and experimental data close to equilibrium, a few more points were calculated using the Carman and Haul master curve (Figs. 1 and 2). The final result is shown in Figure 10.

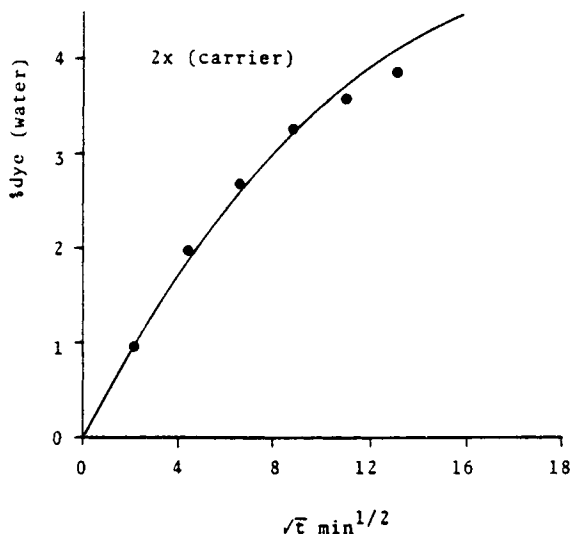


Fig. 7. Percent of dye in the water vs. (time)<sup>1/2</sup> for migration experiment in absence of benzoic acid (concn 13 g/L): (●) experimental; (—) model.

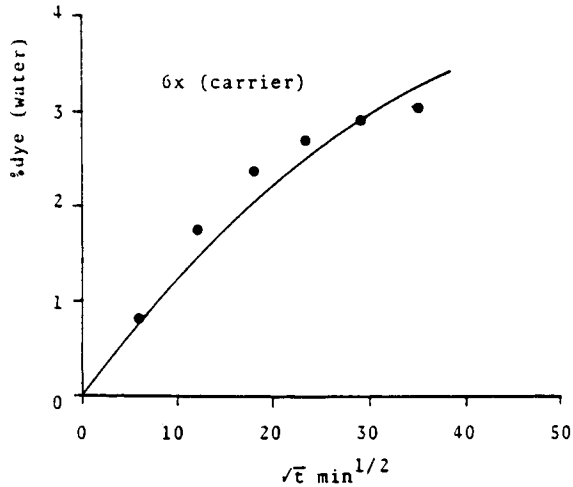


Fig. 8. Percent of dye in the water vs. (time)<sup>1/2</sup> for migration experiment in presence of benzoic acid (concn 13 g/L): (●) experimental; (—) model.

### The Leveling Time Prediction

It was shown in the previous section that eqs. (2) and (12) can accurately describe the migration experiments. The next step is to use the proposed mathematical models to predict leveling times, which is of value for both practical and scientific purposes.

The migration factor  $m$  was defined in the experimental section.  $m$  can vary from 0 to 1. When  $m = 1$ , the leveling time has been reached, i.e., the amount of dye in the originally dyed fiber equals the amount of dye in the originally undyed one.

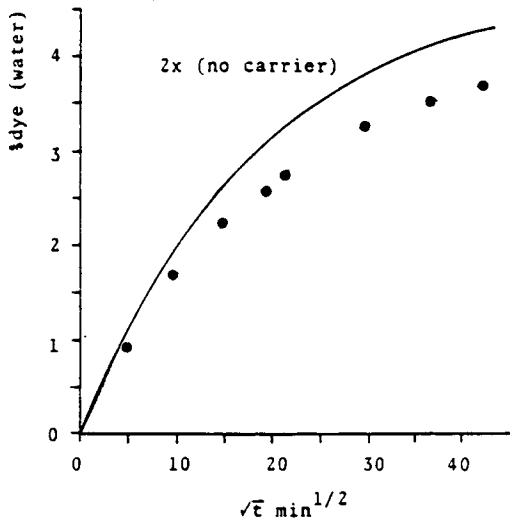


Fig. 9. Percent of dye in the water vs. (time)<sup>1/2</sup> for migration experiment in presence of benzoic acid: (●) experimental; (—) model.

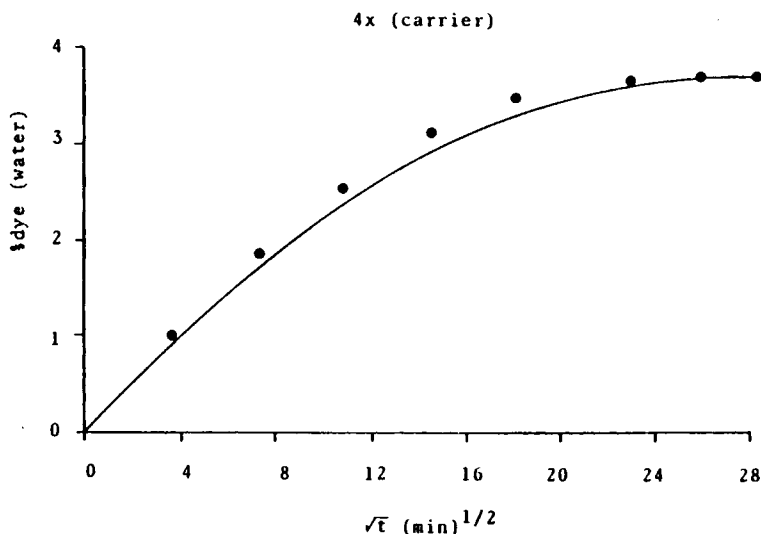


Fig. 10. Percent of dye in the water vs.  $(\text{time})^{1/2}$  for migration experiment in presence of benzoic acid: (●) experimental; (—) model.

In order to use the mathematical model, only two experiments are necessary. First, the sample must be dyed to the equilibrium state using an infinite dye bath system. This experiment will give the diffusion coefficient and  $M_0$ , the amount of dye in the originally dyed fiber. The second experiment measures the dye desorption of this sample. The desorption experiment must be done to high values of time, approaching equilibrium. This second experiment will give the  $\bar{M}_\infty$  value, the amount of dye in the water at infinite time. Then, eq. (14) will give the  $M_\infty$  value, the amount of dye in the originally undyed fiber at infinite time.

As for the determination of the amount of dye in the water, a table of  $\bar{M}_t/\bar{M}_\infty$  against  $(Dt/a^2)^{1/2}$  can be constructed. Then, the  $(M_t)_1$  values, or the amount of dye in the originally dyed fiber, can be determined from the following expression:

$$(M_t)_1 = M_0 - \bar{M}_t \quad (16)$$

Next, after determination of the  $(M_t)_2$  values, the amount of dye at time  $t$  in the originally undyed fiber from eq. (12), the migration factor for different times can be determined.

Figures 11–14 compare the calculated and experimental values for the migration experiments in the presence and absence of benzoic acid. Before discussing these figures, let us review the model–data correlations we have established earlier.

As was observed in Figures 3–6 the mathematical model [eq. (12)] represents the absorption mechanism in the migration experiments very well. This equation predicts the amount of dye being absorbed by a blank fiber in a finite system where the source of dye is another fiber.

The general mathematical model represented the migration experiment nicely as well. This was proven by predicting the amount of dye left in the

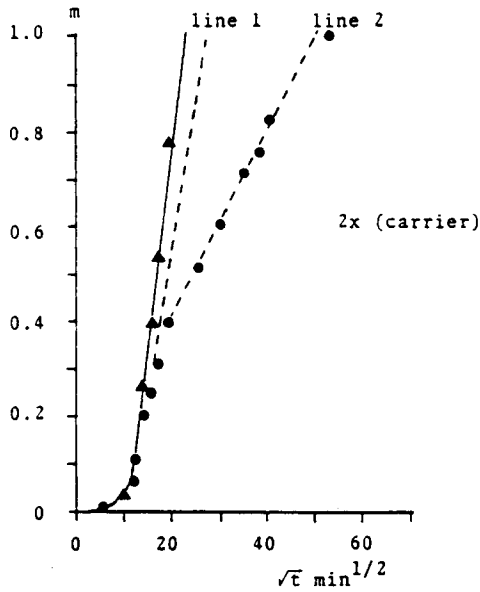


Fig. 11. Migration factor vs. (time)<sup>1/2</sup> for the fiber drawn 2x: (●) experimental; (▲) model.

bath (water) with time. The agreement between experimental and calculated data was shown in Figures 7-10.

Figure 9 gives the percent of dye in water as a function of square root of time for the sample of lower draw ratio. This migration experiment was carried out in absence of carrier and this fact means the working temperature was below the  $T_g$  of the fiber. If it is assumed no structural modifications of this fiber during the time of the experiment occur, it can be said

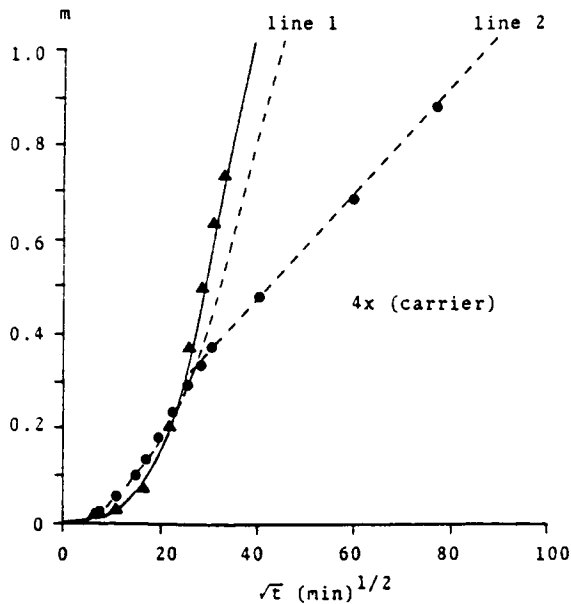


Fig. 12. Migration factor vs. (time)<sup>1/2</sup> for the fiber drawn 4x: (●) experimental; (▲) model.

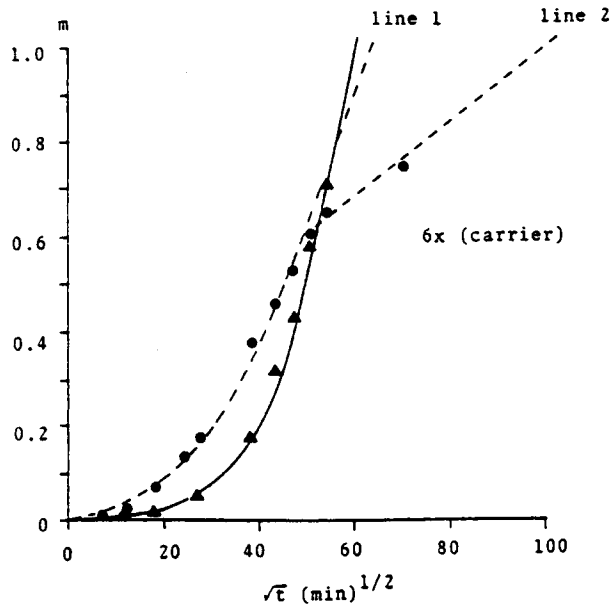


Fig. 13. Migration factor vs. (time)<sup>1/2</sup> for the fiber drawn 6x: (●) experimental; (▲) model.

that the discrepancy between theoretical and experimental data observed is due to the incorrect supposition of Fickian diffusion for this sample. The general diffusion below  $T_g$  is usually non-Fickian.<sup>4</sup> The model is predicting a higher amount of dye in the water than is found. Such an amount would be expected if chain flexibility was controlling the process, as occurs above  $T_g$ .

An evaluation of Figures 11-14 indicates again that the mathematical model can predict leveling times only for the cases where the working

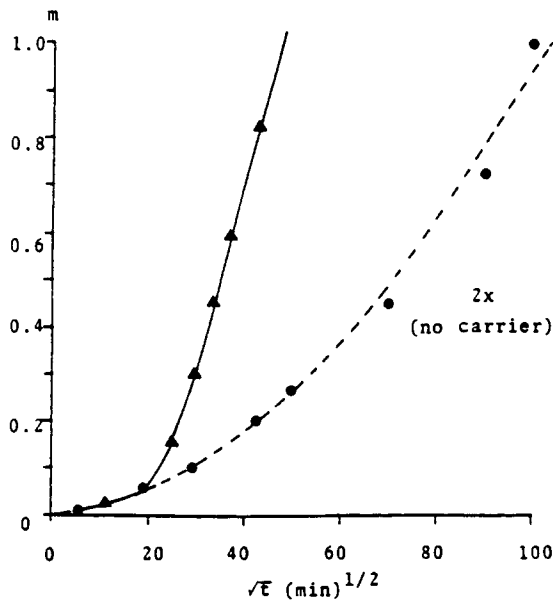


Fig. 14. Migration factor vs. (time)<sup>1/2</sup> for the fiber drawn 2x: (●) experimental; (▲) model.

TABLE II

Sample draw ratio	Leveling times (h)				
	No carrier		Carrier		
	Model	Expt	Model	Expt (a)	Expt (b)
2x	39	167	9	11	41
4x	—	—	22	26	126
6x	—	—	64	66	163

<sup>a</sup> Taken from line 1.

<sup>b</sup> Taken from line 2.

temperature was above or very close to the  $T_g$  of the samples. Also, these figures demonstrate that the model cannot predict the effects of structural changes associated with a long heating time for the fibers.

Figures 11 and 12 indicate that, for times up to 7 h and 15 h for the samples of draw ratio 2x and 4x, respectively, a good agreement between experimental and calculated data is obtained. After these times a steep deviation from an extrapolation line (line 1) of the experimental data occurs. This break point produces another continuing line (line 2) resulting in longer leveling times than predicted by the model. The linearity of this second line is indicative of progressive structural modifications associated with the plasticizing effect of benzoic acid in these fibers under long heating times. Leveling can be more easily reached when chain mobility is increased, but structural stability of the fiber is also an important factor and must be considered. The degree of structural stability has been shown to be higher in the sample of higher draw ratio (6x). Figure 13 shows that the deviation from line 1 occurred only after 50 hours under constant heat for this sample.

In all three cases, if no structural modifications had occurred, the experimental data would be expected to follow the dashed lines indicated as line 1. At  $m = 1$ , line 1 gives the experimental leveling time if structural change had not occurred. These experimental values are shown in Table II, and are very close to the calculated values.

Finally, Figure 14 demonstrates that when the working temperature is below the  $T_g$  of the fiber, the model cannot predict leveling times. Since there is no indication of structural modifications due to long heating times, this result suggests once more that the Fickian diffusion used in this proposed mathematical model is normally observed in the case of penetrants in polymers above  $T_g$ .

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### References

1. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Oxford Univ. Press, London, 1975.
2. P. C. Carman and R. A. W. Haul, *Proc. R. Soc. London*, **A222**, 109 (1954).
3. A. V. Hill, *Proc. R. Soc. London*, **37**, 1043 (1928).
4. H. Jameel, J. Waldman, and L. Rebenfeld, *J. Appl. Polym. Sci.*, **26**, 1795 (1981).

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