

Diffusion-Controlled Sorption of Dye by Cylindrical Fibers: Matching Empirical and Theoretical Models

J. NOLAN ETTERS

The University of Georgia, Dawson Hall, Athens, Georgia 30602

SYNOPSIS

Under quite specific, limiting assumptions, sorption of molecular probes by cylindrical fibers can be described by use of the conventional diffusion equation solutions of Hill, Newman, Wilson, Crank, Carman-Haul, or Urbanik. In addition, sorption also may be described by use of relatively simple empirical equations. Statistical analysis reveals which one of three empirical, exponential equations best fits theoretical data generated by use of formal solutions to the diffusion equation, and the selected equation is then applied to real data. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Monitoring sorption of molecular probes (dyes) by cylindrical fibers can provide useful information with regard to a fiber's morphological characteristics. Both equilibrium sorption and kinetics of dye uptake can help to differentiate important properties between fibers that have been subjected to various processing conditions. When equilibrium sorption is known, kinetics of dye uptake can be estimated by use of the classical diffusion equation solutions. However certain limiting assumptions must exist for these mathematical solutions to be valid. These assumptions are

1. The diffusion coefficient is a constant, concentration independent quantity.
2. The equilibrium distribution coefficient of dye between fiber and the external medium is linear for a wide range of concentrations.
3. The fibers are morphologically stable, homogeneous, and uniformly accessible endless cylinders.
4. No surface barrier exists at the cylindrical surface that impedes mass transfer of diffusive from the external medium to the sorbent, i.e., no diffusional boundary layer exists

in the external phase and no "skin-core" effect exists in the fiber.

When the assumptions listed above are found to hold, dye uptake can be estimated by the diffusion equation solutions of Wilson,¹ Crank,² Carman-Haul,³ and Urbanik⁴ for finite bath conditions, i.e., conditions of decreasing concentration of dye in the external medium and at the fiber surface during the course of dye uptake. On the other hand, if sorption occurs under infinite bath conditions, i.e., under conditions of constant concentration of dye in the external medium and at the fiber surface during the course of dye uptake, the equations of Hill⁵ or Newman⁶ are used. The advantage of Newman's equation is that assumption 4 listed above is not necessary.

FINITE BATH EQUATIONS

Wilson's Equation

The classical diffusion equation solution of Wilson is

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(1 + \alpha) \exp(-q_n^2(Dt/r^2))}{4 + 4\alpha + \alpha^2 q_n^2} \quad (1)$$

where M_t/M_∞ is the fractional equilibrium uptake of diffusant by the cylinder, i.e., diffusant uptake at a given time, M_t , and at equilibrium, M_∞ . The dimensionless parameter, Dt/r^2 , consists of the diffusion coefficient, D , (cm^2/s), the uptake time, t (s), and the radius of the cylinder, r (cm). The alpha term is a measure of equilibrium bath exhaustion

$$\alpha = \frac{1 - E_\infty}{E_\infty} \quad (2)$$

where equilibrium exhaustion, E_∞ , is

$$E_\infty = \frac{C_o - C_\infty}{C_o} \quad (3)$$

where C_o and C_∞ are, respectively, the initial and equilibrium concentration of diffusant in the external medium. Alpha also is expressed by

$$\alpha = \frac{R}{K} \quad (4)$$

where R is the ratio of external medium to fiber volumes, V_m/V_f , and K is the constant ratio of concentrations of diffusant between fiber and bath at equilibrium, C_f/C_b . In eq. (1), the q_n s are the positive, nonzero roots of

$$\alpha q_n J_0(q_n) + 2J_1(q_n) = 0 \quad (5)$$

in which J_0 and J_1 are zero- and first-order Bessel functions.

When bath exhaustion is very high, convergence of Wilson's equation requires an exceedingly high number of summation terms for small values of Dt/r^2 , and can result in a significant decrease in accuracy due to round-off error. For this reason, the error function equations of Crank, Carman-Haul, and Urbanik are much more reliable when bath exhaustion is high and Dt/r^2 is low.

Crank's Equation

Crank's equation, which was published at the same time as was Wilson's equation, is

$$\frac{M_t}{M_\infty} = \frac{4(1 + \alpha)(1 - \exp(X^2)\text{erfc}(X))}{4 + \alpha} \quad (6)$$

where erfc is the error function complement, and X is

$$X = 2 \left(1 + \frac{\alpha}{4} \right) \frac{\sqrt{Dt/r^2}}{\alpha} \quad (7)$$

Carman and Haul's Equation

The equation of Carman and Haul is a slight improvement over that of Crank for small values of Dt/r^2 :

$$\frac{M_t}{M_\infty} = \frac{\gamma_3}{\gamma_3 + \gamma_4} \exp(X^2)\text{erfc}(X) + \frac{\gamma_4}{\gamma_3 + \gamma_4} \exp(Y^2)\text{erfc}(Y) \quad (8)$$

where

$$\gamma_3 = \frac{\sqrt{1 + \alpha} + 1}{2} \quad (9)$$

and

$$\gamma_4 = \gamma_3 - 1 \quad (10)$$

The X and Y terms of the equation of Carman and Haul are

$$X = \frac{2\gamma_3}{\alpha} \sqrt{\frac{Dt}{r^2}} \quad (11)$$

$$Y = -\frac{2\gamma_4}{\alpha} \sqrt{\frac{Dt}{r^2}} \quad (12)$$

Urbanik's Equation

Urbanik's equation, although somewhat more complex, is an improvement over the equations of Crank and Carman-Haul. Urbanik's equation may be written as

$$\begin{aligned} \frac{M_t}{M_\infty} = & 1 + \frac{2(1 + \alpha) \exp(-BT)}{\alpha(X - Y)} \\ & \times \left[\frac{\exp(Y^2T) \text{erfc}\sqrt{Y^2T}}{1 - B/Y^2} \right. \\ & - \frac{\exp(X^2T) \text{erfc}\sqrt{X^2T}}{1 - B/X^2} \\ & + \sqrt{B} \left(\frac{X}{X^2 - B} - \frac{Y}{Y^2 - B} \right) \\ & \left. \times \exp(B^2T) \text{erfc}\sqrt{B^2T} \right] \quad (13) \end{aligned}$$

where the constant B is an empirical parameter, having a value of 8.42, and the parameter T is Dt/r^2 . In addition, the parameters X and Y are

$$X = \frac{4 + \alpha - \sqrt{(4 + \alpha)^2 + 16\alpha^2(B - 1.5\sqrt{B})}}{4\alpha} \quad (14)$$

$$Y = \frac{4 + \alpha + \sqrt{(4 + \alpha)^2 + 16\alpha^2(B - 1.5\sqrt{B})}}{4\alpha} \quad (15)$$

As pointed out elsewhere,⁷ Urbanik's equation is quite valuable because it can be used for essentially all values of bath exhaustion and dimensionless time—a limitation of the equations of Crank and Carman-Haul.

Many real dyeing systems occur under finite bath conditions; however, for such systems, dye uptake can be approximated only roughly by the finite dye-bath diffusion equation solutions given above. The inaccuracies in application of the mathematical solutions are traceable to the nonexistence of the necessary assumptions for the appropriate use of such equations. It must be recognized that only rarely are the assumptions necessary for the use of the finite dye-bath equations present in the case of real dyeing systems.

If it is one's purpose to analyze morphological characteristics of fibers by use of molecular probes, it is wiser to conduct sorption experiments under infinite bath conditions. Sorption of dye from a constant surface concentration is a much simpler system—from an experimental and analytical point of view.

INFINITE BATH EQUATIONS

Hill's Equation

In the absence of surface barrier effects, the equation of Hill may be used:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{\beta_n^2} \exp(-\beta_n^2 (Dt/r^2)) \quad (16)$$

where the β_n s are the positive transcendental Bessel roots given by

$$J_0\beta_n = 0 \quad (17)$$

An unfortunate limitation of Hill's infinite bath equation is that all of the four assumptions previ-

ously listed must be present. This fact can be particularly distressing if one is using probe sorption as an analytical tool.

Newman's Equation

An equation that is superior to Hill's for analytical use is that of Newman. In the case of Newman's equation, the presence of assumption four—the absence of surface barrier effects—is not necessary. The equation of Newman can be written more concisely as

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4 \exp(-\beta_n^2 (Dt/r^2))}{\beta_n^2 (1 + \beta_n^2/L^2)} \quad (18)$$

where the β_n 's are the roots of the transcendental equation

$$\beta_n J_1(\beta_n) - L J_0(\beta_n) = 0 \quad (19)$$

in which J_0 and J_1 again are zero- and first-order Bessel functions, and the dimensionless parameter, L , is defined by⁸

$$L = \frac{D_m r}{DK\delta_D} \quad (20)$$

where D_m and D are the diffusion coefficients of the diffusant in the external medium and polymer, respectively; K is the equilibrium distribution coefficient of the diffusant between the external medium and the polymer; r is the radius of the cylinder, and δ_D is the thickness of the diffusional boundary layer—a quantity that impedes sorption or desorption and is inversely proportional to the rate of flow of the external medium past the surface of the polymeric cylinder. When the rate of flow of the external medium is very high, the thickness of the diffusional boundary layer approaches zero and the value of L approaches infinity. As the value of L approaches infinity, the term β_n^2/L^2 drops out and eq. (18) becomes equivalent to Hill's equation.

Newman's equation is particularly useful for diagnostic or analytical work. Purified, molecularly simple, nonionic probes (disperse dyes) can be used on hydrophobic fibers such as nylon, for example, to characterize fiber morphology as a function of some physico-chemical fiber processing condition. The disappearance of the mean apparent^{9,10} diffusional boundary layer at the fiber surface as a function of increasing bath flow rate through the fiber

bundle can be followed by the use of Newman's equation. In fact, the equation may be useful in detecting the presence of fiber skin-core effects when no diffusional boundary layer is present in the external medium.^{11,12}

EMPIRICAL APPROXIMATIONS

Although Newman's equation is to be preferred for analytical investigations of fiber properties and is easily handled by those possessing mathematical skill on modern, high-speed personal computers, the equation is not easily accessible to many researchers who are not comfortable with Bessel functions, transcendental roots, or iterative computations. Empirical approximations often are offered in many scientific disciplines in an attempt to circumvent the need for a high level of mathematical skill. In the present discussion, three exponential equations are compared for their efficacy in simulating the functional relationship between M_t/M_∞ , Dt/r^2 , and L that is found by formal use of Newman's equation. The equations that will be examined are one-, two-, and three-parameter exponential equations.

One Parameter Equation

The one-parameter equation was first suggested as an empirical approximation by Vickerstaff¹³ and is written as

$$\frac{M_t}{M_\infty} = 1 - \exp(-a(Dt/r^2)) \quad (21)$$

Two-Parameter Equation

The two-parameter equation has been used by others to characterize many different kinds of dynamic processes.¹⁴⁻¹⁶ Urbanik was among the first to use eq. (22) to describe dye uptake.¹⁷ The equation can be expressed as

$$\frac{M_t}{M_\infty} = 1 - \exp(-a(Dt/r^2)^b) \quad (22)$$

Three-Parameter Equation

The three-parameter equation is believed to be an original exponential equation and was first used by the author¹⁸ to express the functional relationship

between M_t/M_∞ and Dt/r^2 for various values of fractional equilibrium exhaustion for finite bath systems. The new equation is

$$\frac{M_t}{M_\infty} = [1 - \exp(-a(Dt/r^2)^b)]^c \quad (23)$$

The empirical parameter, a , is common to all three equations; the exponent, b , is common to eqs. (22) and (23), and the exponent, c , is a parameter for eq. (23) only.

Each of the three equations has been fitted to data obtained by the use of formal solutions to Newman's equation for an M_t/M_∞ range of 0.05 to 0.95 at 0.05 intervals and associated values of Dt/r^2 for values of L ranging from infinity to 1.0. The "goodness of fit" is expressed as adjusted R^2 , i.e., the fraction of the total variability of M_t/M_∞ that is "associated with or explained by" the variability of Dt/r^2 for given values of L , adjusted for the degrees of freedom or number of data points. The closer the value of adjusted R^2 is to 1.0, the better is the fit of the given equation to the data points. Results of the curve fitting process are given in Table I.

As revealed in Table I, eq. (23) provides the best fit of the three empirical exponential equations to the data generated by the formal use of Newman's equation for a very wide range of L values. Only for the very low L values does eq. (22) provide a fit nearly as good as that of eq. (23). Equation 21 generally is inferior to the higher parameter equations for all values of L .

Table I Curve Fitting Results (M_t/M_∞ vs. Dt/r^2)

L-Value	Adjusted R^2		
	Eq. (21)	Eq. (22)	Eq. (23)
∞	0.9135	0.9965	0.9999
10,000	0.9136	0.9966	0.9999
2,000	0.9142	0.9966	0.9999
1,000	0.9148	0.9967	0.9999
200	0.9201	0.9972	0.9999
100	0.9260	0.9976	0.9999
80	0.9288	0.9978	0.9999
50	0.9362	0.9982	0.9998
40	0.9405	0.9984	0.9998
30	0.9470	0.9987	0.9998
20	0.9572	0.9990	0.9998
10	0.9755	0.9995	0.9999
5	0.9898	0.9997	0.9999
2	0.9983	0.9999	0.9999
1	0.9997	0.9999	0.9999

Parameter Values as Function of L

For eq. (23) to have empirical utility for a wide range of L values, it is necessary to express the parameters, a , b , and c of the equation as a function of L . A rational polynomial equation has been found that expresses the parameter values (PV) very accurately as a function of L . For a range of L values from infinity to 20, the relationship is given by:

$$PV = \frac{q_0 + \frac{q_1}{L} + \frac{q_2}{L^2}}{1 + \frac{q_3}{L} + \frac{q_4}{L^2}} \quad (24)$$

where PV is the a , b , or c parameter of eq. (23), and q_0 to q_4 are the coefficients of eq. (24). In the case of parameter a the coefficient values q_0 to q_4 , respectively are: 5.530554, 160.58898, -1750.616, 37.494042, and -374.48753. For parameter b the coefficients are: 1.2479036, 27.400938, 88.43848, 33.90477, and 52.505626. Parameter c coefficients are: 0.37985136, 12.004462, -6.8204581, 11.003091, and 5.3552691.

For the range of L values from 20 to 1, the following three equations accurately express the parameter values, a , b , and c of eq. (23) as a function of L .

$$a = q_0 + \frac{q_1}{L} \text{Ln}\left(\frac{1}{L}\right) + q_2 \sqrt{\frac{1}{L}} \text{Ln}\left(\frac{1}{L}\right) + q_3 \sqrt{\frac{1}{L}} \quad (25)$$

where the coefficients q_0 , q_1 , q_2 , and q_3 , respectively, are: 4.098044891, 3.024653177, -2.49630292, and -2.59232464.

$$b = q_0 + \frac{q_1}{L} + q_2 \text{Ln}\left(\frac{1}{L}\right) + \frac{q_3}{\frac{1}{L} \sqrt{\frac{1}{L}}} \quad (26)$$

where the q_0 to q_3 coefficients are: 1.179748591, -0.14496394, 0.094386506, and 0.001282442.

$$c = q_0 + \frac{q_1}{L^2} + \frac{q_2}{L^2} \sqrt{\frac{1}{L}} + \frac{q_3}{\sqrt{\frac{1}{L}}} \quad (27)$$

where the q_0 to q_3 coefficients are: 0.916905399, 0.146475883, -0.08873859, and -0.06737345.

Linear Form of Eq. (23)

Data generated by use of Newman's equation may be plotted in linear fashion according to the following form of eq. (23):

$$\text{Ln}\left[-\text{Ln}\left(1 - \left(\frac{M_t}{M_\infty}\right)^{1/c}\right)\right] \text{ vs. } \text{Ln}\left(\frac{Dt}{r^2}\right) \quad (28)$$

A typical plot is illustrated in Figure 1 for an L values of 2000. The line slope in Figure 1 defines the parameter value b in eq. (23), and the line intercept I (at $Dt/r^2 = 1$) gives the parameter a from the following relationship:

$$a = \exp(I) \quad (29)$$

The strength of the linear relationship between M_t/M_∞ and Dt/r^2 shown in Figures 1 also holds for all other values of L . Equation 23, therefore, is nearly as accurate as the formal equation of Newman and can be used with confidence as an analytical tool in investigations of fiber morphology.

ESTIMATING APPARENT DIFFUSION COEFFICIENTS

Equation 23 may be rearranged to a form that permits the apparent diffusion coefficient, D , to be estimated:

$$D = \frac{r^2}{t} \left[\frac{-\text{Ln}\left(1 - \left(\frac{M_t}{M_\infty}\right)^{1/c}\right)}{a} \right]^{1/b} \quad (30)$$

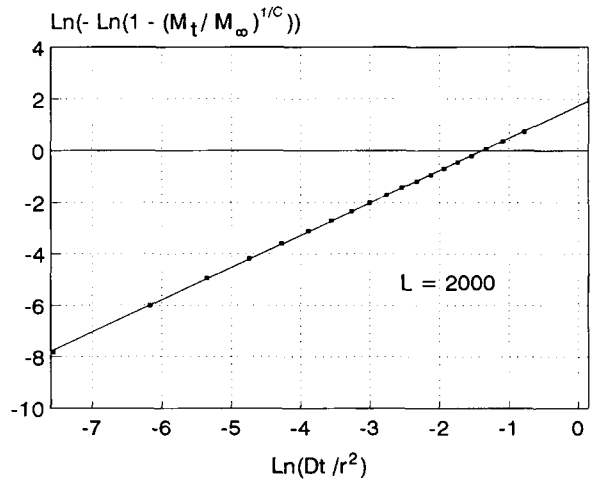


Figure 1 Strength of the relationship between M_t/M_∞ and Dt/r^2 as depicted by the linear form of eq. (23).

Table II Summary of Desorption Data

Time (min)	Dye Content (g/100 g)		
	15 opm	30 opm	90 opm
0.50	1.039	0.815	0.806
1.00	1.001	0.718	0.714
2.00	0.898	0.626	0.543
3.00	0.856	0.511	0.466
4.00	0.866	0.393	0.393
5.00	0.678	0.351	0.308
10.00	0.456	0.148	0.153
15.00	0.297	0.053	0.074

In the present investigation, eq. (30) has been used to approximate the apparent diffusion coefficient of Disperse Red 11 in stabilized, 40 denier, 13 filament nylon 66 tricot from desorption experiments, under conditions of extreme differences in dyebath agitation rate. White has shown that Disperse Red 11 is a useful molecular probe for characterizing the morphology of polyester fiber that has been subjected to various heat-setting temperatures.¹⁹ Part of the utility of Disperse Red 11 as a probe dye is found in the dye's chemical stability, molecular simplicity, lack of ionic activity, and relatively high-water solubility for a disperse dye. Experimental technique that was used in securing data for the present analysis is given in the sections to follow.

Experimental Technique

Nylon tricot fabric was stabilized by boiling for 2 h in distilled water. One hundred grams of the fabric then was dyed for 2 h at 90°C in 2 liters of distilled water, containing enough (7.5 g/L) of a commercial dispersion of Disperse Red 11 to reach saturation uptake. The fabric was then rinsed in a bath consisting of 80/20 DMF/water at room temperature until all unfixed surface dye was removed from the nylon fibers, as indicated by a rinse bath that was free of color. The fabric then was rinsed in distilled water to remove any trace of DMF from the fabric. The dye content of the fabric was found by warm extraction (95°C) of triplicate fabric samples with DMF and was determined to be 1.094 ± 0.001 g of dye per 100 g of fabric (g/100 g), expressed as commercial dye.

Five hundred milliliters aqueous baths were prepared, containing 10 g of activated charcoal, and heated to 90°C in a Gaston County skein dyeing

machine. Activated charcoal was used in an attempt to create "infinite sink, infinite bath" conditions that would assure that the concentration of dye in the bath and at the fiber surface would remain constant (zero) during subsequent desorption experiments. One gram samples of dyed fabric were attached to very thin wire stainless steel sample holders; the holders were attached to the oscillating mechanism of the dyeing machine, and the samples were entered into the desorption bath and treated for different times, removed from the desorption baths and placed into an ice-water bath to interrupt the desorption process. Three different oscillation rates were used: 15, 30, and 90 oscillations per minute (opm). After being treated in the ice-water bath, the samples were cleaned of any adhering charcoal and extracted with warm (95°C) DMF to determine the dye content as a function of desorption time and oscillation rate. The resulting data are summarized in Table II. However, in order for eq. (30) to be used in analysis of the desorption data, the expression, $1 - M_t/M_o$, (where M_o is the initial concentration of dye in the fabric before desorption), is substituted for M_t/M_∞ in the equation. Desorption values that are calculated by use of the expression are given in Table III.

When the data of Table III are substituted into eq. (30), along with the value of the fiber radius squared ($r^2 = 9.4\text{E-}7$ cm²), the apparent diffusion coefficient (cm²/s) can be estimated for each value of time and oscillation rate. However, there is an unfortunate amount of experimental variation in the desorption data, leading to uncertainty in the computation of not only the diffusion coefficient, but also the L value associated with each oscillation rate. The "best estimate" of the diffusion coefficient and corresponding L values can be made by use of a technique proposed elsewhere.^{7,20}

Table III Summary of Desorption Data

Time (min)	$1 - M_t/M_o$		
	15 opm	30 opm	90 opm
0.50	0.050	0.255	0.263
1.00	0.085	0.344	0.347
2.00	0.179	0.428	0.504
3.00	0.218	0.533	0.574
4.00	0.208	0.641	0.641
5.00	0.380	0.679	0.719
10.00	0.583	0.865	0.860
15.00	0.729	0.952	0.932

The proposed method consists of calculating the diffusion coefficient for each value of time, using eq. (30) for different values of L and determining the resulting coefficient of variation of the diffusion coefficient. When an L value is found that results in the minimum coefficient of variation (% CV), that L value and the mean diffusion coefficient are accepted as the "best estimates." Although the technique is tedious, the method is satisfactory for the analysis of uncertain data that often result from either sorption or desorption experiments. Results of the use of the technique are given in Table IV.

The approximate L values and apparent diffusion coefficients that were determined for each desorption bath oscillation rate by use of the % CV minimization technique are shown in Table IV. It is noteworthy that the % CV value decreases as bath oscillation rate increases. In view of the wide scatter of data points and the uncertainty with regard to the uniformity of accessibility of the fiber surfaces in the yarn bundles of the tricot fabric, it is quite significant that the mean apparent diffusion coefficients are statistically equal for the range of oscillation rates and resulting apparent L values.

The experimental data are plotted according to Newman's equation in Figure 2, using the mean value of the diffusion coefficient for each value of L . As revealed in the plot, when $1 - M_t/M_0$ is plotted vs. the square root of time, an intercept on the root time axis is detected for the lowest value of L . This behavior is typical for systems in which a surface barrier exists in either the bath or the fiber.

It is important to note that since an L value of infinity is found for the highest oscillation rate, no skin-core effect is detected for the nylon fiber at

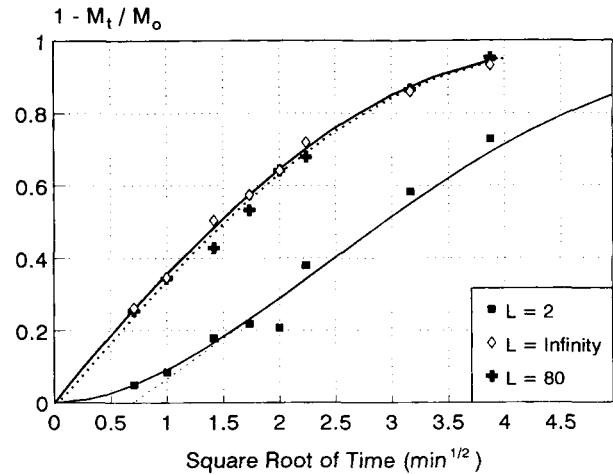


Figure 2 Desorption of Disperse Red 11 into an infinite sink, when plotted according to Newman's equation. The dotted line represents the theoretical line for desorption for an L value of 80 and is nearly superimposed on the theoretical line for an L value of infinity. When the linear portion of the theoretical line for desorption for an L value of 2 is extrapolated to zero desorption, an intercept on the root time axis occurs.

hand. If the value of L had not increased very much as the oscillation rate of the bath increased, an argument could be made that the effect was caused by a barrier that existed in the fiber surface—rather than in the bath itself.

CONCLUDING REMARKS

In view of the tremendous power and speed of modern personal computers, it is ironic that these instruments are not utilized more often in solving complex problems of molecular probe sorption and desorption by the use conventional diffusion equation solutions or by finite difference approximations. Perhaps the answer is to be found through new, specialized computer programs that address diffusion problems in detail. However, until such programs become available, it is believed that analysis of fiber morphology by use of molecular probes can be made more convenient for the researcher by substitution of mathematically simple empirical equations for the more complex, formal diffusion equations.

REFERENCES

1. A. H. Wilson, *Philosophical Magazine*, **39**, 48 (1948).
2. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Clarendon Press, Oxford, 1975, pp. 44-103.

Table IV Estimated Diffusion Coefficients

Time (min)	cm ² /s × 10 ⁻¹⁰		
	15 opm ($L = 2$)	30 opm ($L = 80$)	90 opm ($L = \infty$)
0.50	4.72	5.38	4.81
1.00	4.17	4.89	4.38
2.00	5.06	3.84	5.03
3.00	4.29	4.11	4.56
4.00	3.04	4.75	4.50
5.00	5.31	4.39	4.89
10.00	5.06	4.63	4.34
15.00	<u>5.14</u>	<u>5.08</u>	<u>4.20</u>
Mean	4.60	4.63	4.59
% CV	16.33	10.94	6.38

3. P. C. Carman and R. A. W. Haul, *Proc. R. Soc.*, **222A**, 109 (1954).
4. A. Urbanik, *Text. Chem. Colorist*, **21**(6), 33 (1989).
5. A. V. Hill, *Proc. R. Soc.*, **104**(Ser. B), 39 (1928).
6. A. B. Newman, *Trans. Am. Instit. Chem. Eng.*, **27**, 203 (1931).
7. J. N. Eppers, *J. Appl. Polym. Sci.*, **49**, 1205 (1993).
8. R. McGregor, *Diffusion and Sorption in Fibers and Films*, Vol. 1, Academic Press, New York, 1974, pp. 172-192.
9. H. Sasaki, H. Morikawa, T. Miyaguchi, and H. Araki, *Text. Res. J.*, **62**, 657 (1992).
10. H. Sasaki, E. Yanai, and H. Araki, *Text. Res. J.*, **63**, 614 (1993).
11. J. A. Medley and M. W. Andrews, *Text. Res. J.*, **29**, 398 (1959).
12. J. A. Medley and M. W. Andrews, *Text. Res. J.*, **30**, 855 (1960).
13. T. Vickerstaff, *The Physical Chemistry of Dyeing*, Interscience Publishers Inc., New York, 1954, p. 149.
14. M. Avrami, *J. Chem. Phys.*, **8**, 212 (1940).
15. W. Weibull, *J. Appl. Mech.*, **18**, 293 (1951).
16. A. Sippel and E. Heim, *Angewandte Chem.*, **74**, 580 (1962).
17. A. Urbanik, *J. Soc. Dyers Colorists*, **92**, 377 (1976).
18. J. N. Eppers, *Text. Chem. Colorist*, **12**, 140/37 (1980).
19. M. White, Ph.D. Dissertation, Clemson University, 1975.
20. J. N. Eppers, *J. Soc. Dyers Colorists*, **97**, 170 (1981).

Received June 2, 1995

Accepted July 27, 1995