Sorption of Diffusants by Polymeric Cylinders Under Isothermal, Finite Bath Conditions: Advances in Mathematical Modeling

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ABSTRACT: Diffusion-controlled, isothermal sorption (or desorption) of diffusants by cylindrical polymeric materials can be modeled for finite bath conditions by the use of the conventional diffusion equation solutions of Wilson or Crank when certain limiting assumptions apply. Iterative determination of diffusion coefficients by the use of these advanced equations, however, requires accurate "seed roots" for efficient solution. An empirical seed root generating function has been found that is so very accurate that it can be used in place of the conventional diffusion equation solutions for all but the most extreme levels of definitude. The parameters of the empirical equation as functions of equilibrium bath exhaustion are given, and values of fractional equilibrium uptake, M_t/M_∞, as a function of dimensionless time, Dt/r^2, found by the use of both the diffusion equation solutions and the empirical equation are compared. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1237–1242, 1997

INTRODUCTION

Many diffusion-controlled sorption or desorption processes involving polymeric materials occur under "finite bath" conditions, i.e., as sorption or desorption proceeds, the concentration of diffusant at the surface of the polymeric material continually changes to maintain equilibrium with the external medium. For those systems in which the diffusion and distribution coefficients are constant, concentration-independent quantities and no diffusional boundary layer or polymeric inhomogeneity exists at the solid surface, diffusant sorption (or desorption) can be described by use of the conventional diffusion equation solutions. In the case of a cylinder—the geometrical shape that most closely resembles a polymeric fiber—the diffusion equation solutions provided by Wilson[1] and by Crank[2] may be used.

The purpose of the present article is to explore the use of a "seed root" generating function. Use of the function can facilitate iterative calculations made with the equations of Wilson and Crank and may, in fact, be used as an accurate analytical substitute for the conventional diffusion equation solutions. It is hoped that use of the new function will make analyses of diffusant sorption or desorption systems more accessible.

WILSON'S AND CRANK'S FINITE BATH EQUATIONS

Boundary Conditions

For sorption processes the primary initial boundary condition is that the concentration of diffusant within the cylinder is zero, i.e., the fractional uptake of diffusant at time t and equilibrium, M_t/M_∞, is equal to zero when the dimensionless time parameter also is equal to zero. Dimensionless time can be expressed as Dt/r^2, where D is the diffusion coefficient (cm^2/s), t is time (s), and r is the radius of an "endless" cylinder (cm). In the case of desorption processes, the primary boundary condition is that the initial concentration of diffusant is uniformly distributed within the cylindrical cross-section at zero time. For use in the diffusion equation solutions of Wilson or Crank for desorption processes, the term, M_t/M_∞, is replaced, therefore, by the term, $1 - M_t/M_o$, where M_o is the initial, uniformly distributed concentration of diffusant in the cylinder. Although both diffusion-controlled sorption and desorption processes can be described by the use of the diffusion equation solutions of Wilson and Crank, the present discussion will be limited to that of diffusant sorption by homogeneous, morphologically stable, "endless" cylinders.

Wilson's Equation

The well-known 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_∞ and Dt/r^2 are defined previously, and 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 cylinder 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_ns 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.

As noted in previous discussions of diffusion equation solutions,[3,4] 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 roundoff error. For this reason, the error function equation of Crank is much more reliable when bath exhaustion is high and Dt/r^2 is low.

Crank's Equation

Crank's error function based equation is

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

where $erfc$ is the error function complement, and X is

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

EMPIRICAL APPROXIMATION

Over 15 years ago the present author discovered that the functional relationship between M_t/M_∞ and Dt/r^2 for various values of E_∞ could be expressed roughly by a three parameter exponential equation of the following form[5]:

$$\frac{M_t}{M_\infty} = [1 - \exp(-a(Dt/r^2)^b)]^c \quad (8)$$

where the parameters, a, b, and c are functions of equilibrium exhaustion, E_∞; however, the previously found functional relationships between the parameters of eq. (8) and fractional equilibrium exhaustion were not particularly accurate.[5] Equation (8) also has been shown recently to be an effective analytical approximation for infinite bath systems, and can be used to express the functional relationship between M_t/M_∞ and Dt/r^2 for various values of the dimensionless boundary layer parameter, L.[3]

Data generated by use of Wilson's or Crank's

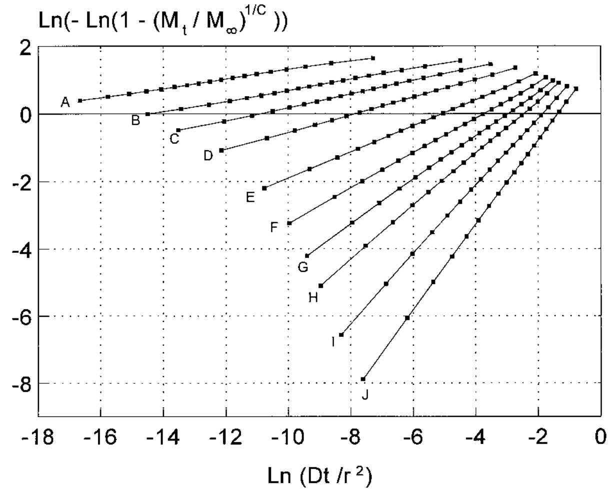

Figure 1 Linear relationship between M_t/M_∞ and Dt/r^2 for various values of equilibrium Exhaustion. (A) $E_\infty = 0.995$; (B) $E_\infty = 0.975$; (C) $E_\infty = 0.95$; (D) $E_\infty = 0.90$; (E) $E_\infty = 0.80$; (F) $E_\infty = 0.70$; (G) $E_\infty = 0.60$; (H) $E_\infty = 0.50$; (I) $E_\infty = 0.30$; (J) $E_\infty = 0.00$.

equation may be plotted in linear fashion according to the following form of eq. (8):

$$\ln\left[-\ln\left(1 - \left(\frac{M_t}{M_\infty}\right)^{1/c}\right)\right] \text{ vs. } \ln\left(\frac{Dt}{r^2}\right) \quad (9)$$

A typical plot is illustrated in Figure 1 for a range of equilibrium exhaustion values. The line slopes in Figure 1 define the parameter value b in eq. (8), and the line intercept I (at $Dt/r^2 = 1$) gives the parameter a from the following relationship:

$$a = \exp(I). \quad (10)$$

The strength of the linear relationship between M_t/M_∞ and Dt/r^2 shown in Figure 1 also holds for all other values of E_∞. For example, eq. (8) has been fitted to data obtained by the use of formal solutions to Wilson's or Crank'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 E_∞ ranging from 0.995 to zero. The "goodness of fit" is expressed as adjusted R-square, 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 E_∞, adjusted for the degrees of freedom or number of data points. The closer the value of adjusted R-square is to 1.0, the better is the fit of the given equation to the data points. The adjusted R-square found for the regression analysis of M_t/M_∞ vs. Dt/r^2 and the three corresponding parameter values of eq. (8) are given in Table I. Because all R-square values are greater than 0.999, eq. (8) is nearly as accurate as the results of the formal equation solutions of Wilson or Crank and can be used with confidence.

Parameter Values as Function of E_∞

For eq. (8) to have empirical utility for all values of E_∞ values, it is necessary to express the parameters, a, b, and c of the equation as a function of E_∞. It was shown in the previous boundary layer study involving eq. (8) that the parameters of the equation can be expressed as functions of the dimensionless parameter L by the use of rational polynomials.[3] Additional rational polynomial equations now have been found that express the parameter values very accurately as a function of E_∞. For a range of E_∞ values from 0 to 0.995, the relationship in the case of parameter a is given by

$$a = \frac{q_0 + q_1E_\infty + q_2E_\infty^2 + q_3E_\infty^3 + q_4E_\infty^4}{1 + q_5E_\infty + q_6E_\infty^2 + q_7E_\infty^3 + q_8E_\infty^4} \quad (11)$$

and in the case of parameters, b and c, a somewhat simpler rational polynomial expresses the functionality:

$$b \text{ or } c = \frac{q_0 + q_1E_\infty + q_2E_\infty^2 + q_3E_\infty^3}{1 + q_4E_\infty + q_5E_\infty^2 + q_6E_\infty^3} \quad (12)$$

The relationships between the parameters a, b, and c and fractional equilibrium exhaustion, E_∞, are shown in Figures 2, 3, and 4.

In addition, the coefficients of eq. (8) for the various parameters are given in Table II.

ESTIMATING APPARENT DIFFUSION COEFFICIENTS

When the necessary conditions for the applicability of Wilson's or Crank's equation are present, the equations may be solved iteratively to determine diffusion coefficients from a knowledge of equilibrium bath exhaustion, diffusant uptake at a given time, and radius of the polymeric cylinder. A useful iterative method is that of the Newton–

Table I Results of Curve Fitting with Eq. (8) (M_t/M_∞ vs. Dt/r^2)

E_∞	a	b	c	Adj R-Square
0.995	15.3427	0.1419	8.9444	.9995
0.990	12.9494	0.1478	8.0497	.9995
0.975	10.4551	0.1656	6.0975	.9997
0.950	9.0425	0.2020	3.8835	.9998
0.925	8.2904	0.2313	2.9907	.9999
0.900	7.8280	0.2610	2.4125	.9999
0.875	7.5135	0.2911	2.0128	.9999
0.850	7.2877	0.3214	1.7226	.9999
0.825	7.1202	0.3521	1.5037	.9999
0.800	6.9936	0.3830	1.3335	.9999
0.750	6.8217	0.4456	1.0879	.9999
0.700	6.7184	0.5089	0.9205	.9999
0.650	6.6540	0.5725	0.8003	.9999
0.600	6.6107	0.6360	0.7105	.9998
0.550	6.5764	0.6991	0.6414	.9998
0.500	6.5418	0.7611	0.5871	.9998
0.450	6.5008	0.8217	0.5437	.9998
0.400	6.4487	0.8803	0.5087	.9999
0.350	6.3825	0.9366	0.4801	.9999
0.300	6.3013	0.9903	0.4566	.9999
0.250	6.2040	1.0409	0.4372	.9999
0.200	6.0918	1.0885	0.4212	.9999
0.150	5.9658	1.1327	0.4080	.9999
0.100	5.8295	1.1743	0.3968	.9999
0.050	5.6823	1.2121	0.3878	.9999
0.000	5.5306	1.2479	0.3798	.9999

Raphson technique, incorporating Newton's forward difference approximation to the first derivative of the function being iterated.[6] However, such iterative techniques require a good initial estimate of the value of the diffusion coefficient. Equation (8) may be rearranged to a form that

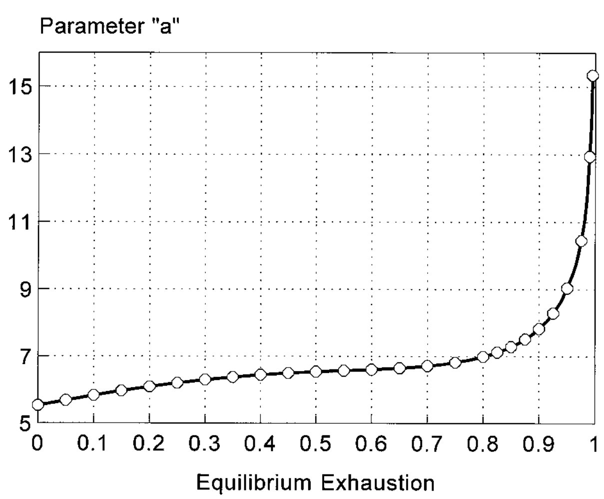

Figure 2 Parameter a of eq. (8) as a function of fractional equilibrium exhaustion, E_∞. Adjusted R-square = 0.99999.

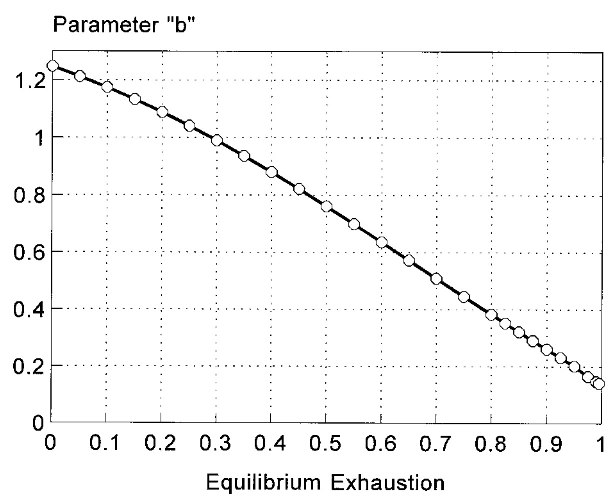

Figure 3 Parameter b of eq. (8) as a function of fractional equilibrium exhaustion, E_∞. Adjusted R-square = 0.99999.

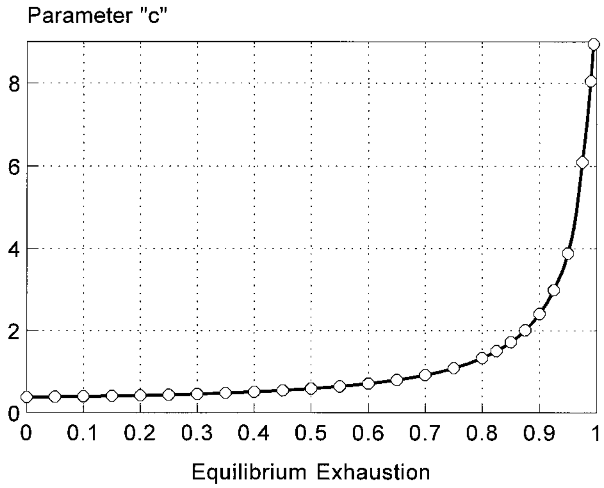

Figure 4 Parameter c of eq. (8) as a function of fractional equilibrium exhaustion, E_∞. Adjusted R-square = 0.9998.

permits the apparent diffusion coefficient, D, to be estimated with a high level of accuracy:

$$D = \frac{r^2}{t}\left[\frac{-\mathrm{Ln}\left(1 - \left(\frac{M_t}{M_\infty}\right)^{1/c}\right)}{a}\right]^{1/b} \quad (13)$$

In fact, as will be shown, eq. (13) is so very accurate that the researcher may choose to use the results obtained with the equation in place of the results found by iteration of the classic equations of Wilson or Crank.

Practical Example

Consider the sorption of 1-amino-4-hydroxyanthraquinone (red disperse dye) by cellulose acetate fiber under finite bath conditions. Twenty grams of coarse, cellulose acetate staple fiber, having a mean radius of 1.581×10^{-5} cm, is immersed with constant agitation into a 1 liter aqueous solution of purified 1-amino-4-hydroxyanthraquinone. The initial concentration of the diffusant is 0.01 g/L, but after treatment for 4 h at 80°C, the equilibrium bath concentration is found to be about 0.0005 g/L. By use of eq. (3), the fractional bath exhaustion, E_∞, at the 50/1 liquor to fiber ratio is found to be about 0.95. The fractional uptake, M_t/M_∞, of the diffusant by the fiber is followed over time and is given in Table III, along with the diffusion coefficients calculated by use of both Wilson's equation and eq. (13). Wilcoxon's Signed Rank Test[7] of the differences between diffusion coefficient values found by the two methods reveals a p-value of 0.6835 in a test of the hypothesis that the mean difference is equal to zero. Be-

Table III Calculated Diffusion Coefficients (cm^2/s)

Time (s)	M_t/M_∞	Wilson's Equation	Equation (13)
60	0.297	3.069×10^{-10}	2.977×10^{-10}
240	0.535	4.632×10^{-10}	4.668×10^{-10}
540	0.583	2.878×10^{-10}	2.926×10^{-10}
960	0.677	3.195×10^{-10}	3.282×10^{-10}
1500	0.770	4.364×10^{-10}	4.448×10^{-10}
2160	0.814	4.609×10^{-10}	4.624×10^{-10}
2940	0.810	3.252×10^{-10}	3.268×10^{-10}
3840	0.861	4.384×10^{-10}	4.265×10^{-10}
4860	0.850	3.034×10^{-10}	2.978×10^{-10}
6000	0.720	3.226×10^{-10}	3.108×10^{-10}
Mean		3.66×10^{-10}	3.65×10^{-10}
%CV		19.91	20.40

Table II Coefficients of Eqs. (11) and (12)

q_ns	Parameters a	b	c
q_0	5.530475549	1.247766371	0.379913098
q_1	−11.7102568	−2.81371363	−0.71372045
q_2	10.31735955	2.069815047	0.517942273
q_3	−6.44379035	−0.49689926	−0.19134098
q_4	2.314599961	−1.71335546	−2.24629036
q_5	−2.67609803	1.200048298	1.493029352
q_6	3.488739837	−0.43393909	−0.24742936
q_7	−2.83554036	—	—
q_8	1.023237931	—	—

cause the hypothesis cannot be rejected at usual levels of significance, it is clear that there is no significant difference between the value of the diffusion coefficients that are determined by use of the two methods.

CONCLUDING REMARKS

Equation (8) can be used as an efficient analytical approximation to the classic diffusion equation solutions of Wilson or Crank. Under the quite specific assumptions given in the introduction to the present article, the equation can be used to predict diffusant concentration in cylindrical polymeric substrates during both isothermal sorption or desorption processes when the diffusion coefficient and fractional equilibrium exhaustion are known. In addition, when the same assumptions are fulfilled, the rearranged form of the equation, eq. (13), can be used to determine the diffusant diffusion coefficient directly without the need for iterative calculations.

It is well known that not all sorption systems are well described by the use of the diffusion equation solutions of Wilson or Crank. In fact, eq. (8) can be used to reveal deviations of real systems from Fick's law due to fiber microstructural heterogeneity or other reasons. It is believed that use of the new analytical approximation can make investigations into diffusion processes more accessible to many researchers by alleviating the mathematical complexity associated with use of conventional diffusion equation solutions.

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