

Isothermal Sorption from Finite Baths: Effect of the Boundary Layer on Sorption of Diffusants by Solids of Various Geometrical Shapes

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SYNOPSIS

The literature reveals no equation that expresses the influence of the diffusional boundary layer on diffusion-controlled sorption of dyes or other material by polymeric substrates from *finite* baths. In view of this mathematical void, a technique is proposed that approximates dimensionless sorption time as a function of fractional equilibrium uptake of diffusant by polymer, dimensionless dye bath exhaustion, and dimensionless boundary layer. The computational technique is based on relationships found in transitional kinetics and is shown to be applicable for sorption systems involving polymeric material of different geometrical shapes. To illustrate the technique, dimensionless half-times of sorption are computed for the case of diffusant uptake by a cylinder.

INTRODUCTION

Diffusion-controlled sorption of dyes or other diffusants by polymeric material of various geometrical shapes can occur under both infinite and finite bath conditions. In the case of infinite baths, the concentration of diffusant at the polymer surface does not change during sorption. However, in the case of finite baths, the concentration of diffusant at the polymer surface continuously decreases during the sorption process until an equilibrium between the concentration of diffusant in polymer and in the bath is achieved.

Finite Bath Systems

When a finite bath sorption medium is "well stirred," i.e., when no diffusional boundary layer exists at the solid polymer surface, diffusant uptake by morphologically stable, homogeneous polymeric material can be expressed by the following functional relationship:

$$\frac{M_t}{M_\infty} = f_\infty = f\left(\frac{Dt}{a^2}, \alpha\right) \quad (1)$$

where $(M_t/M_\infty = f_\infty)$ is the ratio of the amount of diffusant in the polymer at time t and at equilibrium, respectively; D is the constant, concentration-independent diffusion coefficient of the diffusant in the polymer; and a is the half-thickness in the case of a polymer film or the radius in the case of a polymeric sphere or cylinder. The dimensionless alpha term is given by

$$\alpha = \frac{R}{K} \quad (2)$$

where R is the ratio of bath to polymer volumes, V_b/V_p , and K is the constant ratio of concentrations of diffusant between the polymer and the bath at equilibrium, C_p/C_b . Alpha also may be expressed by $(1 - E_\infty)/E_\infty$, where E_∞ is the fractional exhaustion of the bath at equilibrium. The computational forms of Eq. (1) for the case of the plane sheet, the sphere, and the cylinder are given in what follows.

Plane Sheet

Wilson¹ has provided the following equation for the case of sorption of diffusant by a plane sheet (film) under finite bath conditions:

$$\frac{M_t}{M_\infty} = f_\infty = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)\exp[-q_n^2(Dt/a^2)]}{1+\alpha+\alpha^2q_n^2} \quad (3)$$

where the q_n 's are the nonzero positive roots of

$$\tan(q_n) = -\alpha q_n \quad (4)$$

Sphere

The corresponding equation for the sphere, as determined by Crank, is²

$$\frac{M_t}{M_\infty} = f_\infty = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(1+\alpha)\exp[-q_n^2(Dt/a^2)]}{9+9\alpha+\alpha^2q_n^2} \quad (5)$$

where the q_n 's are the nonzero roots of

$$\tan(q_n) = \frac{3q_n}{3+\alpha q_n^2} \quad (6)$$

Cylinder

Wilson also has provided an equation for diffusant sorption by a cylinder under finite bath conditions¹:

$$\frac{M_t}{M_\infty} = f_\infty = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(1+\alpha)\exp[-q_n^2(Dt/a^2)]}{4+4\alpha+\alpha^2q_n^2} \quad (7)$$

where the q_n 's are the positive, nonzero roots of

$$\alpha q_n J_0(q_n) + 2J_1(q_n) = 0 \quad (8)$$

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

Infinite Bath Systems

In the case of infinite bath systems, the effect of the diffusional boundary layer on the rate of sorption or desorption of diffusants by polymeric materials is provided by the equations of Newman.³ These equations have been expressed in a notationally more convenient form by Crank.² In functional form the relationship is given by

$$\frac{M_t}{M_\infty} = f_{\text{sat}} = f\left(\frac{Dt}{a^2}, L\right) \quad (9)$$

where ($M_t/M_\infty = f_{\text{sat}}$) is the ratio of the saturation uptake by the polymer at a given time t and at equilibrium, Dt/a^2 is as previously given, and the dimensionless parameter L is given by⁴

$$L = \frac{D_b}{D_p K} \frac{a}{\delta_D} \quad (10)$$

where D_b and $D_p = D$ are the diffusion coefficients of the diffusant in the bath and polymer, respectively; K is the distribution coefficient of the diffusant between the bath and the polymer surface; a is the half-thickness in the case of a film or the radius in the case of a sphere or cylinder; and δ_D is the diffusional boundary layer. For isothermal conditions, the only parameter in Eq. (10) that is a variable quantity is δ_D , the diffusional boundary layer. This imaginary layer is in reality nothing more than a gradient that exists between the concentration of diffusant in the bath and the concentration of diffusant at the surface of the polymer. The layer tends to be inversely proportional to the velocity of flow of the bath by the polymer surface.⁵ With decreasing flow of the bath, the boundary layer becomes "thicker," and the dimensionless parameter L becomes smaller. Equations (11), (13), and (15) reveal that sorption (and desorption) processes become slower as L decreases.

Plane Sheet

Crank's equation for diffusant sorption by a plane sheet (film) under the influence of a diffusional boundary layer can be written as

$$\frac{M_t}{M_\infty} = f_{\text{sat}} = 1 - \sum_{n=1}^{\infty} \frac{2 \exp[-\beta_n^2(Dt/a^2)]}{\beta_n^2(1+1/L+\beta_n^2/L^2)} \quad (11)$$

where the β_n 's are the positive roots of

$$\beta_n \tan(\beta_n) = L \quad (12)$$

Sphere

Crank's corresponding equation for the sphere is

$$\frac{M_t}{M_\infty} = f_{\text{sat}} = 1 - \sum_{n=1}^{\infty} \frac{6 \exp[-\beta_n^2(Dt/a^2)]}{\beta_n^2(1-1/L+\beta_n^2/L^2)} \quad (13)$$

where the β_n 's are the roots of

$$\beta_n \cot(\beta_n) + L - 1 = 0 \quad (14)$$

Cylinder

For the case of diffusant sorption by a cylinder under the influence of a boundary layer, Crank's equation may be written as

$$\frac{M_t}{M_\infty} = f_{\text{sat}} = 1 - \sum_{n=1}^{\infty} \frac{4 \exp[-\beta_n^2(Dt/a^2)]}{\beta_n^2(1 + \beta_n^2/L^2)} \quad (15)$$

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

$$\beta_n J_1(\beta_n) - L J_0(\beta_n) = 0 \quad (16)$$

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

When no diffusional boundary layer exists, i.e., when $L = \infty$, the terms $1/L$ and β_n^2/L^2 are equal to zero and consequently drop out of the infinite bath equations (11), (13), and (15). The corresponding transcendental equations (12), (14), and (16) must be suitably modified to account for an L value of infinity.

It is unfortunate that no ready-made solution to the diffusion equation exists for computing dye uptake from finite baths for various values of L . Many real sorption systems consist of finite baths in which the velocities of flow are insufficient to eliminate any boundary layer that may be present. No computational solution exists for the functional relationship given by

$$\frac{M_t}{M_\infty} = f(Dt/a^2, \alpha, L) \quad (17)$$

Crank has suggested that finite difference or finite element techniques can be used to obtain numerical values to satisfy the relationship given in the preceding.⁶ However, the literature does not appear to be replete with examples of solutions obtained by use of Crank's suggested technique.

The purpose of the present work is to provide a new, nonrigorous approximation technique that enables one to determine by iteration a dimensionless time for a given value of M_t/M_∞ under finite bath, boundary layer conditions. The technique is applicable to sorption of diffusants by polymeric solids of various geometrical shapes and is based on the physicochemical relationship between f_∞ and f_{sat} for

continuously transitional systems, as revealed by an examination of transitional kinetics.

TRANSITIONAL KINETICS

Transitional kinetics is a form of kinetics that occurs when a sorption process abruptly changes from infinite bath to finite bath kinetics. Such a phenomenon can occur, for example, in dyeing acrylic fibers with basic dyes or in dyeing hydrophobic fibers with disperse dyes. McGregor and Etters⁷ were the first to explore transitional kinetics in dyeing of polyester fiber with disperse dye. These authors point out that disperse dyeing systems will exhibit infinite, finite, or transitional kinetic behavior, depending on the value of certain system parameters.⁷ Infinite bath kinetics will occur if

$$C_0 \geq C_{\text{sat}}[1 + (1/\alpha)] \quad (18)$$

where C_0 is the initial concentration of particulate and dissolved dye in the dye bath, C_{sat} is the saturation solubility of the dye in the bath, and α is as previously defined. Finite kinetics will occur if

$$C_0 \leq C_{\text{sat}} \quad (19)$$

and transitional kinetics will occur if

$$C_{\text{sat}} < C_0 < C_{\text{sat}}[1 + (1/\alpha)] \quad (20)$$

The unique behavior of transitional systems offers a possible solution to the problem of tying together finite bath and infinite bath equations to achieve the desired goal of the present work. Dye uptake in the case of transitional systems may be described in terms of both fractional saturation uptake, f_{sat} , and fractional equilibrium uptake, f_∞ . At the point of transition from an infinite bath to a finite bath, fractional saturation uptake is defined by

$$f_{\text{sat}} = \alpha[(C_0/C_s) - 1] \quad (21)$$

and fractional equilibrium uptake is defined by

$$f_\infty = [1 - (C_s/C_0)](\alpha + 1) \quad (22)$$

Substitution of Eq. (22) into Eq. (21) results in the cancellation of the dye concentration ratios, resulting in the more general equation

$$f_{\text{sat}} = \frac{\alpha f_\infty}{1 + \alpha - f_\infty} \quad (23)$$

For the condition $0 < \alpha < \infty$, Eq. (23) relates f_{sat} to f_{∞} for all fractional uptake values at transition. Equation (23) is the link that permits the tying together of infinite bath and finite bath diffusion equation solutions. Although the equation has been derived for a transitional disperse dyeing system, the equation can be used in attempts to determine the effect of the diffusional boundary layer on finite bath kinetics. The use of the equation in this area is made possible by adopting the convention that a *continuously transitional system*, i.e., a system for which transition occurs for all values of M_t/M_{∞} , is really equivalent to a finite bath system. Such a mathematical protocol appears to hold after the equivalency of f_{sat} and f_{∞} at transition has been established and the corresponding values of Dt/a^2 for the finite bath system have been adjusted for the boundary layer effect.

COMPUTATIONAL TECHNIQUE

The following example will illustrate the proposed computational technique. Our goal is to determine the dimensionless time Dt/a^2 associated with a fractional equilibrium value, f_{∞} , at an α value of x and an L value of y . Such a dimensionless value of time can be represented as

$$([Dt/a^2]_{(f_{\infty}, \alpha=x, L=y)}) = \chi_0 \quad (24)$$

in which the subscripted chi term is used to represent the left-hand portion of the equation for notational convenience later.

Step 1

The use of Eqs. (3), (5), or (7) iteratively determines the value of dimensionless time corresponding

to f_{∞} for α equal to x and L equal to infinity. The dimensionless parameter can be designated as

$$([Dt/a^2]_{(f_{\infty}, \alpha=x, L=\infty)}) = \chi_1 \quad (25)$$

Step 2

The use of Eq. (23) determines the value of f_{sat} that corresponds to f_{∞} .

Step 3

Equations (11), (13), or (15) iteratively determines the dimensionless time for f_{sat} using an α value of infinity and an L value of y . The parameter can be designated as

$$([Dt/a^2]_{(f_{\text{sat}}, \alpha=\infty, L=y)}) = \chi_2 \quad (26)$$

Step 4

Equations (11), (13), or (15) iteratively determines the dimensionless time for f_{sat} using a α value of infinity and an L value of infinity. The parameter can be designated as

$$([Dt/a^2]_{(f_{\text{sat}}, \alpha=\infty, L=\infty)}) = \chi_3 \quad (27)$$

Step 5

Using the subscripted values of chi given in Eqs. (24)–(27) for notational convenience, the value of dimensionless time corresponding to f_{∞} for an α value equal to x and an L value equal to y is given by

$$\chi_0 = \chi_1 + (\chi_2 - \chi_3) \quad (28)$$

The preceding technique can be used to compute Dt/a^2 for all values of M_t/M_{∞} for given values of

Table I Dimensionless Half-Time for Diffusant Uptake by a Cylinder as a Function of α and $1/L$

α	$1/L = 0$	$1/L = 0.01$	$1/L = 0.04$	$1/L = 0.16$
0.0050251	3.6745×10^{-6}	3.5530×10^{-5}	1.1940×10^{-4}	4.3679×10^{-4}
0.0101010	1.4609×10^{-5}	8.1532×10^{-5}	2.5559×10^{-4}	9.0256×10^{-4}
0.0204081	5.7742×10^{-5}	1.9720×10^{-4}	5.6040×10^{-4}	1.8841×10^{-3}
0.0416666	2.2557×10^{-4}	5.1083×10^{-4}	1.2673×10^{-3}	3.9778×10^{-3}
0.0869565	8.6183×10^{-4}	1.4283×10^{-3}	2.9769×10^{-3}	8.4862×10^{-3}
0.1904761	3.1596×10^{-3}	4.2369×10^{-3}	7.2841×10^{-3}	1.8209×10^{-2}
0.4705882	1.0789×10^{-2}	1.2724×10^{-2}	1.8329×10^{-2}	3.8874×10^{-2}
1.7777778	3.3029×10^{-2}	3.6227×10^{-2}	4.5637×10^{-2}	8.1078×10^{-2}
∞	6.3058×10^{-2}	6.7249×10^{-2}	7.9672×10^{-2}	1.2726×10^{-1}

α and L . Values of Dt/a^2 corresponding to $M_t/M_\infty = 0.5$ are given in Table I for the case of the cylinder. Such dimensionless times often are referred to as half-times. For very low values of dimensionless time, the exponential summation equations tend to be tedious to use. In such cases other equations based on Laplace transforms can be used. Urbanik has made significant contributions to the modern mathematics of diffusion in this area.⁸

CONCLUDING REMARKS

The purpose of the present work has not been to present a new theory of diffusion-controlled sorption. Rather, the purpose has been to suggest a new technique by which the uptake of diffusants by polymeric materials under quite specific, finite bath, boundary layer conditions may be approximated. It is believed that the new technique may offer a means by which sorption systems can be modeled more fully than they have been in the past. Criticisms and improvements to the proposed method no doubt will appear and will be warmly welcomed.

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