ANZIAM J. 48(2007), 503–521

EXTENSION OF A SHORT-TIME SOLUTION OF THE DIFFUSION EQUATION WITH APPLICATION TO MICROPORE DIFFUSION IN A FINITE SYSTEM

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(Received 12 October, 2004; revised 18 January, 2007)

Abstract

The diffusion equation is used to model and analyze sorption, a process used in the purification or separation of fluids. For the diffusion inside a spherical porous solid immersed in a limited-volume and well-stirred fluid, Ruthven [5], Crank [3] and, for the analogous flow of heat, Carslaw and Jaeger [2] give an eigenfunction expansion solution to the diffusion equation that provides accurate long-time solutions when only a few terms are used. However, to obtain the same accuracy for short-time solutions the number of eigenfunction terms required increases exponentially. An alternative error function solution of Carman and Haul [1] is accurate for sufficiently short times but not for long times. Although their solution is well quoted ([3],[4] and [6]), Carman and Haul do not provide a derivation in their paper. This paper provides a full derivation of the short-time solution of Carman and Haul that uses only the first term of a negative exponential series in the Laplace domain. It is shown that the accuracy and range of the short-time result is improved by the inclusion of additional terms of the negative exponential series. An analysis of short-time and long-time results is presented, together with recommendations as to their use.

2000 *Mathematics subject classification*: primary 76R50; secondary 35K20, 80A20.
Keywords and phrases: adsorbent, adsorption, diffusion, eigenfunction expansion, error function, finite-volume fluid, fractional uptake, Laplace domain, Laplace transform, long-time solution, series of negative exponentials, short-time solution, sorption.

1. Introduction

In purification or separation of fluids processes involving sorption, the fluid is passed through an insoluble porous solid called a *sorbent*. With theoretical results that do not appear to agree with experimental data using activated carbon sorbents, Phillip Pendleton, from the Centre for Molecular and Materials Sciences, School of Pharmaceutical,

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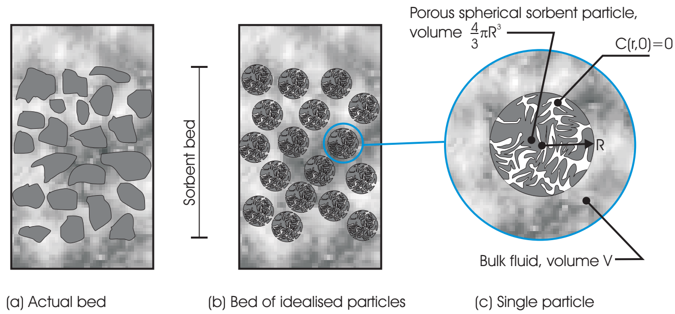

FIGURE 1. Adsorbent bed immersed in bulk fluid and a single particle.

Molecular and Biomedical Sciences, University of South Australia, asked for our help with the mathematics, and recommended several readings including Ruthven [5] and Crank [3]. Ruthven uses the diffusion equation to model the transportation for isothermal single-component sorption within the micropores of a single adsorbent particle, idealized as a uniform sphere of radius R, immersed in bulk fluid — see Figure 1. Ruthven gives both a long-time solution and a short-time solution where the amount of solute transferred from the fluid is negligible, but only provides a long-time solution for a finite volume fluid where the concentration in the fluid varies significantly during the transfer of solute into the sphere. Crank provides a solution suitable for short times that is given, without a derivation, by Carman and Haul [1] in their discussion of the use of sorption from a finite-volume of well-stirred fluid to measure the diffusion coefficients in spherical, cylindrical and parallel-sided slab solids. The short-time solution is more suited for short dimensionless times, $\tau = Dt/R^2 < 0.2$, or for $t < 44$ hours where the diffusivity $D = 5 \times 10^{-20}$ m^2/s and $R = 2 \times 10^{-7}$ m. For notational convenience we express many relations in terms of $\omega = \tau^{1/2}$.

This paper is organized as follows. The mathematical model for diffusion inside a porous solid sphere immersed in a finite-volume and well-stirred liquid is given in Section 2, together with the short-time and long-time solutions. Section 3 provides a derivation of the short-time solution given by Carman and Haul, showing that the solution is a simplified version of a solution with an infinite number of exponential and error function terms. The accuracy of various versions of the short-time solution, with and without additional terms, and the long-time solution are discussed in Section 4. Conclusions and recommendations are given in Section 5.

2. Mathematical model and solutions

2.1. Model for diffusion in a sphere immersed in a finite volume Consider a porous and uniform spherical solid of radius R, immersed in a well-stirred bulk liquid of finite volume V, excluding the volume of the particle. Assume the diffusivity, D, to be constant so that the diffusion equation in spherical coordinates is

$$\frac{\partial C(r,t)}{\partial t} = D\left(\frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C(r,t)}{\partial r}\right), \tag{2.1}$$

where $C(r,t)$ is the concentration of diffusing substance in the sphere. This assumption is acceptable, even if the diffusivity is concentration dependent, $D = D(C)$, provided the uptake of the diffusing substance in the sphere is measured over a small enough change in concentration, $C(r,t)$.

Since the bulk fluid is well stirred, the concentration of solute in the fluid is uniform and depends only on time. The total mass of solute transferring across the surface of the sphere per unit time is given by

$$-4\pi R^2 D \frac{\partial C(r,t)}{\partial r}\bigg|_{r=R},$$

and is equal to the rate at which the total mass of diffusing substance in the sphere increases,

$$V\frac{\partial C(r,t)}{\partial t}\bigg|_{r=R}.$$

Thus, if the initial concentration in the bulk liquid is C_0 and in the sphere is zero, we solve (2.1) in the form

$$\frac{\partial (rC(r,t))}{\partial t} = D\frac{\partial^2 (rC(r,t))}{\partial r^2}, \quad 0 < r < R, \tag{2.2}$$

for the following initial and boundary conditions:

$$C(r,0) = C_0^* = 0, \qquad 0 < r < R, \tag{2.3}$$

$$C(R,0) = C_0, \tag{2.4}$$

$$\frac{V}{4\pi R^2}\frac{\partial C(r,t)}{\partial t}\bigg|_{r=R} = -D\frac{\partial C(r,t)}{\partial r}\bigg|_{r=R}, \quad t > 0, \tag{2.5}$$

$$\frac{\partial C(r,t)}{\partial r}\bigg|_{r=0} = 0, \qquad t > 0. \tag{2.6}$$

Boundary condition (2.6) is obtained by assuming symmetry of radial diffusion about the centre of the sphere.

If the initial equilibrium concentration in the sphere is not zero, $C_0^* \neq 0$, let $U(r,t) = C(r,t) - C_0^*$, so that $U(r,0) = 0$ and boundary condition (2.4) is replaced by $U(R,0) = C_0 - C_0^*$.

2.2. Short-time solution given by Crank The following fractional uptake solution given by Crank [3], where m_t is the total increase in mass of diffusing substance in the sphere during time t, expressed as a fraction of the total increase in mass of diffusing substance in the sphere after infinite time,

$$\frac{m_t}{m_\infty} = (\alpha+1)\left\{1 - \frac{\gamma_1}{\gamma_1+\gamma_2}\; e\,\mathrm{erfc}\left(\frac{3\gamma_1}{\alpha}\sqrt{\frac{Dt}{R^2}}\right) - \frac{\gamma_2}{\gamma_1+\gamma_2}\; e\,\mathrm{erfc}\left(-\frac{3\gamma_2}{\alpha}\sqrt{\frac{Dt}{R^2}}\right)\right\} + \text{higher terms}, \tag{2.7}$$

is obtained from Carman and Haul [1], where in their notation

$$\gamma_1 = \frac{\sqrt{1+4\alpha/3}+1}{2}, \quad \gamma_2 = \gamma_1 - 1, \tag{2.8}$$

and

$$e\,\mathrm{erfc}\,(z) = e^{z^2}\,\mathrm{erfc}\,(z)\,. \tag{2.9}$$

Carman and Haul[1] state that the solution was *'obtained by one of us (P.C.C.) by applying the Laplace transformation ...'*, without providing further details of the derivation.

Although the solution is accurate only for times close to zero, the accuracy and range may be improved by the inclusion of additional terms as shown in Figures 2 and 3. The accuracy and range of the solution with and without additional terms is discussed further in Section 4.

2.3. Long-time solution given by Ruthven. The fractional uptake solution, given as an eigenfunction expansion by Ruthven [5]

$$\frac{m_t}{m_\infty} = \frac{C_t - C_0^*}{C_\infty - C_0^*} = 1 - 6\sum_{n=1}^{\infty} \frac{1}{9\frac{\Lambda}{1-\Lambda} + (1-\Lambda)p_n^2}\, e^{-p_n^2 Dt/R^2}, \tag{2.10}$$

where $\{p_n\}_{n=0,1,2,\ldots}$ are the non-negative non-zero roots of

$$\tan p_n = \frac{3p_n}{3+(1/\Lambda - 1)p_n^2}, \quad \Lambda = \frac{C_0 - C_\infty}{C_0}, \tag{2.11}$$

is obtained from the solution given by Crank [3, Section 6.33] in terms of α, the ratio of the volumes of the bulk fluid and the sphere,

$$\alpha = \frac{V}{\frac{4}{3}\pi R^3} \quad \Rightarrow \quad \tan p_n = \frac{3p_n}{3+\alpha p_n^2}, \quad \Lambda = \frac{C_0 - \frac{\alpha C_0}{\alpha+1}}{C_0} = \frac{1}{\alpha+1} \in [0,1]. \tag{2.12}$$

[1]Carman and Haul present both long-time and short-time solutions to the equations for diffusion in a parallel-sided slab, infinite circular cylinder and a sphere, and illustrate their application for the measurement of diffusion coefficients for diffusion into a (porous) solid from a gas or liquid.

The solution converges rapidly for long times, but for short times (t close to zero) the number of terms required to calculate the fractional uptake accurately increases rapidly — see Section 4, Figure 4.

3. Derivation of short-time solution

Applying the Laplace transformation to (2.2) an exponential function is derived that will give the long-time solution if the Laplace inversion theorem is applied.

To derive the short-time solution, the exponential function is expressed as a series of negative exponentials before applying the Laplace inversion theorem.

In the following derivation, the terms associated with $n = 0$ and $n = 1$ of the series in the Laplace domain are arranged into a form for which the inverse Laplace transformations are known for each part of each term.

After deriving the short-time solution associated with the $n = 0$ term only, Crank's solution (2.7) is derived by omitting parts of the solution that tend to zero as t tends to zero.

The inverse transforms of each part of the terms of the series associated with $n = 1$ are then included to give a solution associated with the $n = 0$ and $n = 1$ terms of the series in the Laplace domain.

3.1. Laplace transform Taking the Laplace transform of (2.2) and writing $\hat{C}(r, s) = \mathscr{L}[C(r, t)]$, we obtain

$$\frac{\partial^2}{\partial r^2}(r\hat{C}) - p^2(r\hat{C}) = 0, \quad 0 < r < R, \quad p^2 = \frac{s}{D}, \tag{3.1}$$

subject to the boundary conditions

$$\frac{V}{4\pi R^2}(s\hat{C} - C_0) + D\frac{\partial}{\partial r}\hat{C} = 0, \qquad r = R, \tag{3.2}$$

$$\frac{\partial \hat{C}}{\partial r} = 0, \qquad r = 0. \tag{3.3}$$

The general solution to (3.1) is

$$r\hat{C} = Ae^{pr} + Be^{-pr}, \quad p = +\sqrt{\frac{s}{D}}. \tag{3.4}$$

At $r = 0$, condition (3.3) implies that $\hat{C}$ is finite, and from (3.4) we have $r\hat{C} = 0 = A + B$. Therefore $A = -B$ and

$$r\hat{C} = A(e^{pr} - e^{-pr}). \tag{3.5}$$

Differentiating both sides,

$$\hat{C} + r\frac{\partial \hat{C}}{\partial r} = pA(e^{pr} + e^{-pr}) \quad \Rightarrow \quad r\frac{\partial \hat{C}}{\partial r} = A\left[p(e^{pr} + e^{-pr}) - \frac{1}{r}(e^{pr} - e^{-pr})\right].$$

Therefore, multiplying (3.2) throughout by R/D, it can be shown that to satisfy the boundary condition at $r = R$,

$$A = \frac{\alpha C_0}{D}\frac{R^3}{3pR(e^{pR} + e^{-pR}) + (\alpha p^2R^2 - 3)(e^{pR} - e^{-pR})}, \quad \alpha = \frac{3V}{4\pi R^3}.$$

Thus (3.5) gives

$$r\hat{C} = \frac{\alpha C_0 R^3}{D}\frac{e^{pr} - e^{-pr}}{3pR(e^{pR} + e^{-pR}) + (\alpha p^2R^2 - 3)(e^{pR} - e^{-pR})}. \tag{3.6}$$

Applying the Laplace inversion theorem and using (3.12) to give the average concentration inside the sphere, the long-time solution (2.10) can be obtained.

3.2. Inverse transform of the first two terms of a series of negative exponentials in the Laplace domain To derive the short-time solution, the geometric series $1/(1-x) = \sum_{n=0}^{\infty} x^n$, $|x| < 1$ is used to express Equation (3.6) as a series of negative exponentials,

$$\begin{aligned}
\frac{r\hat{C}}{C_0} &= \frac{\alpha R^3}{D}\frac{e^{pr} - e^{-pr}}{(\alpha p^2R^2 - 3)(e^{pR} - e^{-pR}) + 3pR(e^{pR} + e^{-pR})} \\
&= \frac{R}{D}\frac{e^{-p(R-r)} - e^{-p(R+r)}}{g(1 - e^{-2pR}) + h(1 + e^{-2pR})} = \frac{R}{D}\frac{e^{-p(R-r)} - e^{-p(R+r)}}{(g+h)}\frac{1}{1 - \frac{g-h}{g+h}e^{-2pR}} \\
&= \frac{R}{D}\sum_{n=0}^{\infty}\frac{(g-h)^n}{(g+h)^{n+1}}(e^{-p((2n+1)R-r)} - e^{-p((2n+1)R+r)})
\end{aligned} \tag{3.7}$$

where

$$g = p^2 - \frac{3}{\alpha R^2} \quad \text{and} \quad h = \frac{3p}{\alpha R}.$$

The series converges since

$$\left|\frac{g-h}{g+h}\right| = \left|\frac{\alpha R^2p^2 - 3 - 3pR}{\alpha R^2p^2 - 3 + 3pR}\right| < 1 \quad \Rightarrow \quad \left|\left(\frac{g-h}{g+h}\right)e^{-2Rp}\right| < 1.$$

Thus, rearranging (3.7) and using only the first two terms for $n = 0, 1$ of the series,

$$\begin{aligned}
\frac{r\hat{C}}{C_0} &= \frac{R}{D}\sum_{n=0}^{\infty}\frac{\left[\left(p - \frac{3}{\alpha R}\gamma_1\right)\left(p + \frac{3}{\alpha R}\gamma_2\right)\right]^n}{\left[\left(p + \frac{3}{\alpha R}\gamma_1\right)\left(p - \frac{3}{\alpha R}\gamma_2\right)\right]^{n+1}}(e^{-p((2n+1)R-r)} - e^{-p((2n+1)R+r)}) \\
&= \frac{R}{D}(e^{-p(R-r)} - e^{-p(R+r)})\frac{1}{(p+h_1)(p-h_2)} + \frac{R}{D}(e^{-p(3R-r)} - e^{-p(3R+r)}) \\
&\quad \times \left\{\frac{1}{(p+h_1)(p-h_2)} - 2(h_1 - h_2)\frac{p}{(p+h_1)^2(p-h_2)^2}\right\} + \mathrm{O}(e^{-5Rp})
\end{aligned}$$

where

$$\gamma_i = \frac{\sqrt{1+\frac{4}{3}\alpha} - (-1)^i}{2}, \quad h_i = \frac{3}{\alpha R}\gamma_i, \quad i = 1, 2. \tag{3.8}$$

Thus, noting

$$\frac{1}{(x+a)(x-b)} = \frac{1}{a+b}\left[\frac{1}{x-b} - \frac{1}{x+a}\right] \quad \text{and}$$

$$\frac{x}{(x+a)^2(x-b)^2} = \frac{(a-b)}{(a+b)^3}\left[\frac{1}{x-b} - \frac{1}{x+a}\right] + \frac{1}{(a+b)^2}\left[\frac{b}{(x-b)^2} - \frac{a}{(x+a)^2}\right],$$

we have

$$\frac{Dr\hat{C}}{RC_0} = \sum_{i=1,2}\sum_{j=-1,1}(-1)^i j\left\{H_1\frac{e^{-p(R-jr)}}{p+(-1)^{i+1}h_i} - H_2\frac{e^{-p(3R-jr)}}{p+(-1)^{i+1}h_i}\right.$$
$$\left. - H_3 h_i\frac{e^{-p(3R-jr)}}{(p+(-1)^{i+1}h_i)^2}\right\} + \mathrm{O}(e^{-5Rp}), \tag{3.9}$$
$$H_1 = \frac{1}{h_1+h_2}, \quad H_2 = \frac{h_1^2+h_2^2-6h_1h_2}{(h_1+h_2)^3} \quad \text{and} \quad H_3 = \frac{2(h_1-h_2)}{(h_1+h_2)^2}.$$

The inverse Laplace transform for e^{-xp}, $p = \sqrt{S/D}$, is given as $x/\bigl(2\sqrt{\pi Dt^3}\bigr)e^{-x^2/4Dt}$ by Carslaw and Jaeger [2, Appendix V(6)]. Hence, omitting the higher terms, $n = 2, 3, 4, \ldots$, gives an error of the order e^{-5Rp} in the Laplace domain and an error of the order

$$\frac{5}{2t\omega\sqrt{\pi}}\,e^{-25/4\omega^2}$$

in the time domain. If the $n = 1$ term is also omitted, the order of the error increases to e^{-3Rp} in the Laplace domain and increases to

$$\frac{3}{2t\omega\sqrt{\pi}}\,e^{-9/4\omega^2}$$

in the time domain. Since the error is small for short times, the error associated with the omitted higher terms for n is denoted by HT in the time domain.

Using the inverse of the transforms

$$\mathscr{L}\left[\sqrt{\frac{D}{\pi t}}e^{-\frac{x^2}{4Dt}} - hDe^{hx+Dth^2}\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + h\sqrt{Dt}\right)\right] = \frac{e^{-px}}{p+h} \quad \text{and}$$

$$\mathscr{L}\left[-2h\sqrt{\frac{D^3t}{\pi}}e^{-\frac{x^2}{4Dt}} + D(1+hx+2h^2Dt)e^{hx+Dth^2}\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + h\sqrt{Dt}\right)\right]$$
$$= \frac{e^{-px}}{(p+h)^2}$$

given by Carslaw and Jaeger [2], Appendices V(12) and V(17) respectively, we have, after dividing both sides by D,

$$\frac{rC}{RC_0} = \sum_{i=1,2}\sum_{j=-1,1}\left\{H_1 f_{i,j}(R) - H_2 f_{i,j}(3R) - H_3\left[1-(-1)^i h_i(3R-jr)+2\varepsilon_i^2\right](-1)^i f_{i,j}(3R)\right\} - H_4(\varepsilon_1-\varepsilon_2)\left[e^{-\frac{(3R-r)^2}{4Dt}} - e^{-\frac{(3R+r)^2}{4Dt}}\right] + \text{HT}, \tag{3.10}$$

where, letting $m = 2n+1$,

$$f_{i,j}(mR) = \left\{ j h_i e^{(-1)^{i+1}h_i(mR-jr)+\varepsilon_i^2} \operatorname{erfc}\left(\frac{mR-jr}{2\sqrt{Dt}} + (-1)^{i+1}\varepsilon_i\right)\right\},$$
$$H_4 = \frac{4(h_1^2+h_2^2)}{\sqrt{\pi}(h_1+h_2)^2} \quad \text{and} \quad \varepsilon_i = \frac{3\gamma_i}{\alpha}\tau = h_i\sqrt{Dt}. \tag{3.11}$$

3.3. Short-time solution associated with the $n = 0$ term only. Considering only the terms of the series in the Laplace domain associated with $n = 0$ in (3.7) and ignoring the higher terms for n, the corresponding $f_{i,j}(R)$ terms of (3.10) in the time domain gives

$$\frac{rC}{RC_0} = H_1 \sum_{i=1,2} h_i e^{(-1)^{i+1}h_i R+\varepsilon_i^2} \sum_{j=-1,1} j e^{(-1)^i j h_i r} \operatorname{erfc}\left(\frac{R-jr}{2\sqrt{Dt}} + (-1)^{i+1}\varepsilon_i\right).$$

For the fractional approach to equilibrium, the average concentration in the sphere is calculated using the integral

$$C_t = \frac{\int_0^R dm}{\int_0^R dV} = \frac{3}{R^3}\int_0^R C(r,t)r^2\,dr, \tag{3.12}$$

and note that as $t \to \infty$ the asymptotic average concentration of diffusing substance in the sphere is given by the ratio of initial quantity of solute in the bulk solution, C_0V, and the combined volume of the bulk solution and the sphere,

$$C_\infty = \frac{C_0 V}{V + \frac{4}{3}\pi R^3} = \frac{\alpha}{\alpha+1}C_0. \tag{3.13}$$

Thus, the fractional uptake is given by

$$\begin{aligned}\frac{m_t}{m_\infty} = \frac{C_t}{C_\infty} &= \frac{3(\alpha+1)}{\alpha R^2}\int_0^R r\frac{rC}{RC_0}\,dr \\ &= \frac{3(\alpha+1)}{\alpha R^2} H_1 \sum_{i=1,2} h_i e^{(-1)^{i+1}h_i R+\varepsilon_i^2}\int_{-R}^R r e^{(-1)^i h_i r}\operatorname{erfc}(\xi_i)\,dr \\ &= \frac{6(\alpha+1)\omega}{\alpha} H_1 \sum_{i=1,2} h_i e^{-\varepsilon_i^2}\left[2\omega I_{2,i} - I_{1,i}\right]\end{aligned}$$

where $\xi_i = (R-r)/\left(2\sqrt{Dt}\right) + (-1)^{i+1}\varepsilon_i$,

$$I_{1,i} = \int_{\omega^{-1}+(-1)^{i+1}\varepsilon_i}^{(-1)^{i+1}\varepsilon_i} e^{(-1)^{i+1}2\varepsilon_i\xi_i} \operatorname{erfc}(\xi_i)\, d\xi_i \quad \text{and}$$

$$I_{2,i} = \int_{\omega^{-1}+(-1)^{i+1}\varepsilon_i}^{(-1)^{i+1}\varepsilon_i} \left(\xi_i - (-1)^{i+1}\varepsilon_i\right) e^{(-1)^{i+1}2\varepsilon_i\xi_i} \operatorname{erfc}(\xi_i)\, d\xi_i.$$

Using the relationships

$$\int_0^x e^{a\xi} \operatorname{erfc}(\xi)\, d\xi = \frac{e^{a^2/4}}{a}\left[\operatorname{erf}\left(\frac{a}{2}\right) + \operatorname{erf}\left(x - \frac{a}{2}\right)\right] + \frac{e^{ax}\operatorname{erfc}(x) - 1}{a},$$

$$\int_0^x (\xi-\varepsilon)e^{a\xi} \operatorname{erfc}(\xi)\, d\xi = \frac{a\varepsilon+1}{a^2} + \frac{1-e^{-x^2+ax}}{a\sqrt{\pi}} + \frac{a(x-\varepsilon)-1}{a^2} e^{ax}\operatorname{erfc}(x) + \frac{a^2-2a\varepsilon-2}{2a^2} e^{a^2/4}\left[\operatorname{erf}\left(\frac{a}{2}\right) + \operatorname{erf}\left(x-\frac{a}{2}\right)\right],$$

then

$$I_{1,i} = -\frac{(-1)^i e^{2\varepsilon_i^2}\operatorname{erfc}\left((-1)^{i+1}\varepsilon_i\right)}{2\varepsilon_i} + \frac{(-1)^i e^{\varepsilon_i^2}}{2\varepsilon_i}\operatorname{erf}\left(\omega^{-1}\right) + \frac{(-1)^i e^{(-1)^{i+1}2\varepsilon_i\left(\omega^{-1}-(-1)^i\varepsilon_i\right)}}{2\varepsilon_i}\operatorname{erfc}\left(\omega^{-1}-(-1)^i\varepsilon_i\right) \quad \text{and}$$

$$I_{2,i} = -\frac{(-1)^i e^{\varepsilon_i^2}\left(e^{-\omega^{-2}}-1\right)}{2\varepsilon_i\sqrt{\pi}} - \frac{1}{4\varepsilon_i^2}e^{2\varepsilon_i^2}\operatorname{erfc}\left((-1)^{i+1}\varepsilon_i\right) + \frac{1}{4\varepsilon_i^2}e^{\varepsilon_i^2}\operatorname{erf}\left(\omega^{-1}\right) + \frac{1+(-1)^i 2\omega^{-1}\varepsilon_i}{4\varepsilon_i^2} e^{(-1)^{i+1}2\omega^{-1}\varepsilon_i+2\varepsilon_i^2}\operatorname{erfc}\left(\omega^{-1}-(-1)^i\varepsilon_i\right).$$

Thus, noting that $h_i/\varepsilon_i = 1/\sqrt{Dt}$ and $(h_1+h_2) = (\gamma_1+\gamma_2) * 3/(\alpha R)$,

$$\frac{m_t}{m_\infty} = \frac{\alpha+1}{\gamma_1+\gamma_2}\sum_{i=1,2}\left\{\frac{\omega}{\varepsilon_2}\left[-e^{\varepsilon_i^2}\operatorname{erfc}\left((-1)^{i+1}\varepsilon_i\right) + \operatorname{erf}\left(\omega^{-1}\right) + \left(1+(-1)^i 2\omega^{-1}\varepsilon_i\right)e^{(-1)^{i+1}2\omega^{-1}\varepsilon_i+\varepsilon_i^2}\operatorname{erfc}\left(\omega^{-1}-(-1)^i\varepsilon_i\right)\right] + (-1)^i e^{\varepsilon_i^2}\operatorname{erfc}\left((-1)^{i+1}\varepsilon_i\right) - (-1)^i e^{(-1)^{i+1}2\omega^{-1}\varepsilon_i+\varepsilon_i^2}\operatorname{erfc}\left(\omega^{-1}-(-1)^i\varepsilon_i\right)\right\}.$$

Thus, using (3.11),

$$\frac{m_t}{m_\infty} = \frac{\alpha+1}{\gamma_1+\gamma_2}\sum_{i=1,2}\left\{-\left(\frac{\alpha}{3\gamma_i} - (-1)^i\right)e^{\varepsilon_i^2}\operatorname{erfc}\left((-1)^{i+1}\varepsilon_i\right) + \frac{\alpha}{3\gamma_i}\operatorname{erf}\left(\omega^{-1}\right) + \left(\frac{\alpha}{3\gamma_i} + (-1)^i\right)e^{(-1)^{i+1}\frac{6}{\alpha}\gamma_i+\varepsilon_i^2}\operatorname{erfc}\left(\omega^{-1}-(-1)^i\varepsilon_i\right)\right\}.$$

Define $\bar{i} = i - (-1)^i$ and using $\operatorname{erf}(x) = 1 - \operatorname{erfc}(x)$, $\gamma_1\gamma_2 = \alpha/3$,

$$\frac{\alpha}{3\gamma_i} - (-1)^i = \gamma_{\bar{i}} - (-1)^i = \gamma_i \quad \text{and} \quad \frac{\alpha}{3\gamma_i} + (-1)^i = \gamma_{\bar{i}} + (-1)^i, \tag{3.14}$$

we have

$$\frac{m_t}{m_\infty} = \alpha + 1 - \frac{\alpha+1}{\gamma_1+\gamma_2} \sum_{i=1,2} \Big\{ \gamma_i e^{\varepsilon_i^2} \operatorname{erfc}\left((-1)^{i+1}\varepsilon_i\right) + \gamma_i \operatorname{erfc}\left(\omega^{-1}\right)$$
$$- \left(\gamma_{\bar{i}} + (-1)^i\right) e^{(-1)^{i+1}\frac{6}{\alpha}\gamma_i + \varepsilon_i^2} \operatorname{erfc}\left(\omega^{-1} - (-1)^i \varepsilon_i\right) \Big\} + \mathrm{HT}. \tag{3.15}$$

Since $\operatorname{erfc}(z) \to 0$ as $z \to \infty$, dropping the last two terms that tend to zero as $t \to 0$, and substituting (3.11), we obtain Crank's short-time solution (2.7).

REMARK 1. At $t = 0$, $\varepsilon_1 = \varepsilon_2 = 0$ and

$$\frac{m_0}{m_\infty} = (\alpha+1)\left\{1 - \frac{\gamma_1}{\gamma_1+\gamma_2} - \frac{\gamma_2}{\gamma_1+\gamma_2}\right\} = 0,$$

which is consistent with the initial condition that the concentration of solute in the sphere is zero, that is, $m_0 = 0$.

3.3.1. Carman and Haul short-time solution. For the same problem, except that the diffusing substance is a pure gas or vapour, where C is measured by the pressure p, p_1 is the initial pressure ($t < 0$), p_2 is the pressure at $t = 0$, and p_∞ is the equilibrium pressure as $t \to \infty$, Carman and Haul [1] give

$$1 - \frac{W}{W_\infty} = \frac{p - p_\infty}{p_2 - p_\infty}, \quad \text{and} \quad \lambda = \frac{p_\infty - p_1}{p_2 - p_\infty}, \tag{3.16}$$

and give the solution as

$$\frac{p - p_1}{p_2 - p_1} = \left[\frac{\gamma_1}{\gamma_1+\gamma_2}\; e \operatorname{erfc}\left(\frac{3\gamma_1}{\lambda}\sqrt{\tau}\right) + \frac{\gamma_2}{\gamma_1+\gamma_2}\; e \operatorname{erfc}\left(-\frac{3\gamma_2}{\lambda}\sqrt{\tau}\right)\right]$$
$$+ \text{higher terms}, \tag{3.17}$$

where

$$\tau = \frac{Dt}{a^2}, \quad \lambda = \frac{3V_g}{4\pi a^3}, \quad \gamma_1 = \frac{1}{2}\left(\sqrt{1 + \frac{4}{3}\lambda} + 1\right), \quad \gamma_2 = \gamma_1 - 1. \tag{3.18}$$

Crank's solution (2.7) is for the concentration of a diffusing fluid inside a sphere where C_0^* is the initial concentration in the sphere, and C_0 is the concentration of solute in the bulk fluid at $t = 0$. Thus, by the conservation of mass,

$$(C_0 - C_\infty)V = (C_\infty - C_0^*)\frac{4}{3}\pi R^3 \quad \Rightarrow \quad \alpha = \frac{3V}{4\pi R^3} = \frac{C_\infty - C_0^*}{C_0 - C_\infty},$$

which is consistent with relationships given for λ in (3.16) and (3.18) for $a \equiv R$, $\lambda \equiv \alpha$, $V_g \equiv V$, $p \equiv C$, $p_1 \equiv C_0^*$, $p_2 \equiv C_0$ and $p_\infty \equiv C_\infty$. From (3.16) we have

$$\frac{W}{W_\infty} = 1 - \frac{p - p_\infty}{p_2 - p_\infty} = \frac{p_2 - p}{p_2 - p_\infty},$$

where $W/W_\infty \equiv m_t/m_\infty$. Thus, subtracting both sides of Carman and Haul (3.17) from unity, then multiplying both sides by $(\lambda + 1)$, the RHS is the same as the RHS of Crank's solution (2.7), and

$$\begin{aligned} LHS = (\lambda + 1)\left(1 - \frac{p - p_1}{p_2 - p_1}\right) &= \left(\frac{p_\infty - p_1}{p_2 - p_\infty} + 1\right)\left(1 - \frac{p - p_1}{p_2 - p_1}\right) \\ &= \frac{(p_2 - p_\infty) + (p_\infty - p_1)}{p_2 - p_\infty} \cdot \frac{(p_2 - p_1) - (p - p_1)}{p_2 - p_1} \\ &= \frac{p_2 - p_1}{p_2 - p_\infty} \cdot \frac{p_2 - p}{p_2 - p_1} = \frac{p_2 - p}{p_2 - p_\infty} = \frac{W}{W_\infty} \equiv \frac{m_t}{m_\infty}, \end{aligned}$$

establishing that Crank's solution (2.7) is equivalent to the Carman and Haul solution.

3.4. Extending the solution to include the $n = 1$ term. Result (3.15) pertains only to the terms of the series in the Laplace domain associated with $n = 0$ in (3.7). To obtain a more accurate solution, additional terms associated with $n = 1$ are included by applying the fractional approach to equilibrium to the other terms of (3.10) in the time domain. That is,

$$\begin{aligned} \frac{m_t}{m_\infty} = M_0 + \frac{3(\alpha + 1)}{\alpha R^2} \int_0^R r \Bigg\{ &-H_2 \sum_{i=1,2} h_i e^{(-1)^{i+1} h_i 3R + \varepsilon_i^2} \sum_{j=-1,1} j e^{(-1)^i j h_i r} \Theta_{i,j} \\ &- H_3 \sum_{i=1,2} \left[1 - (-1)^i h_i 3R + 2\varepsilon_i^2\right] (-1)^i h_i e^{(-1)^{i+1} h_i 3R + \varepsilon_i^2} \sum_{j=-1,1} j e^{(-1)^i j h_i r} \Theta_{i,j} \\ &- H_3 \sum_{i=1,2} r h_i^2 e^{(-1)^{i+1} h_i 3R + \varepsilon_i^2} \sum_{j=-1,1} e^{(-1)^i j h_i r} \Theta_{i,j} \\ &- H_4(\varepsilon_1 - \varepsilon_2)\left[e^{-\frac{(3R - r)^2}{4Dt}} - e^{-\frac{(3R + r)^2}{4Dt}}\right] \Bigg\} \, dr + \text{HT}, \end{aligned}$$

where $\Theta_{i,j} = \operatorname{erfc}\left(\frac{3R - jR}{2\sqrt{Dt}} - (-1)^i \varepsilon_i\right)$ and $M_0 = m_t/m_\infty$ given by (3.15) for $n = 0$.

Hence

$$\frac{m_t}{m_\infty} = M_0 + \frac{3(\alpha+1)}{\alpha R^2}\frac{1}{(h_1+h_2)^3}\Big\{g_3 I_3 - g_4 I_4 - \sum_{i=1,2} g_{1,i}\,\varepsilon_i e^{-\varepsilon_i^2}\left\{\left[2\omega^2 R h_i - (-1)^i 3\right] I_{0,i} + (-1)^i 2\omega I_{1,i}\right\} R + \sum_{i=1,2} g_2 \varepsilon_i^2 e^{-\varepsilon_i^2} R \left\{\left[4\omega\varepsilon_i^2 - (-1)^i 12\varepsilon_i + 9\omega^{-1}\right] I_{0,i} + \left[(-1)^i 8\omega\varepsilon_i - 12\right] I_{1,i} + 4\omega I_{2,i}\right\}\Big\} + \text{HT}, \tag{3.19}$$

where

$$\xi_i = \frac{3R-r}{2\sqrt{Dt}} - (-1)^i\varepsilon_i, \qquad \chi = \frac{3R-r}{2\sqrt{Dt}},$$

$$g_{1,i} = 2\left\{(-1)^i\left[h_1^2+h_2^2-6h_1h_2\right] + 2(h_1^2-h_2^2)\left[1-(-1)^i 3Rh_i + 2Dth_i^2\right]\right\}$$

$$g_2 = 4(h_1^2-h_2^2), \qquad g_3 = 24(h_1^2+h_2^2)(h_1^2-h_2^2)\frac{RDt}{\sqrt{\pi}},$$

$$g_4 = 16(h_1^2+h_2^2)(h_1^2-h_2^2)\frac{Dt\sqrt{Dt}}{\sqrt{\pi}},$$

$$I_{k,i} = \int_{2\omega^{-1}-(-1)^i\varepsilon_i}^{\omega^{-1}-(-1)^i\varepsilon_i} \xi_i^k e^{(-1)^{i+1}2\varepsilon_i\xi_i}\,\mathrm{erfc}\,(\xi_i)\;d\xi_i, \quad k=0,1,2,$$

$$\xi_i^0 \equiv 1, \quad i = 1,2,$$

$$I_3 = \int_{2\omega^{-1}}^{\omega^{-1}} e^{-\chi^2}\,d\chi = \frac{\sqrt{\pi}}{2}\left[\mathrm{erf}\left(\omega^{-1}\right) - \mathrm{erf}\left(2\omega^{-1}\right)\right] \quad \text{and}$$

$$I_4 = \int_{2\omega^{-1}}^{\omega^{-1}} \chi e^{-\chi^2}\,d\chi = -\frac{1}{2}\left[e^{-\omega^{-2}} - e^{-4\omega^{-2}}\right].$$

Using the identities

$$\int_0^x e^{a\xi}\,\mathrm{erfc}\,(\xi)\;d\xi = \frac{e^{a^2/4}}{a}\left[\mathrm{erf}\left(\frac{a}{2}\right) + \mathrm{erf}\left(x-\frac{a}{2}\right)\right] + \frac{e^{ax}\,\mathrm{erfc}\,(x) - 1}{a},$$

$$\int_0^x \xi e^{a\xi}\,\mathrm{erfc}\,(\xi)\;d\xi = \frac{1}{a^2} + \frac{1-e^{-x^2+ax}}{a\sqrt{\pi}} + \frac{ax-1}{a^2}\,e^{ax}\,\mathrm{erfc}\,(x) + \left(\frac{1}{2}-\frac{1}{a^2}\right)e^{a^2/4}\left[\mathrm{erf}\left(\frac{a}{2}\right) + \mathrm{erf}\left(x-\frac{a}{2}\right)\right] \quad \text{and}$$

$$\int_0^x \xi^2 e^{a\xi}\,\mathrm{erfc}\,(\xi)\;d\xi = \frac{a^3-4a-4\sqrt{\pi}}{2\sqrt{\pi}a^3} - \frac{a^2+2ax-4}{2\sqrt{\pi}a^2}e^{-x^2+ax} + \frac{a^2x^2-2ax+2}{a^3}\,e^{ax}\,\mathrm{erfc}\,(x) + \frac{a^4-2a^2+8}{4a^3}\,e^{a^2/4}\left[\mathrm{erf}\left(\frac{a}{2}\right) + \mathrm{erf}\left(x-\frac{a}{2}\right)\right],$$

we have

$$\varepsilon_i e^{-\varepsilon_i^2} \left\{ \left[2\omega^2 R h_i - (-1)^i 3 \right] I_{0,i} + (-1)^i 2\omega I_{1,i} \right\} R$$
$$= \frac{Rh_i - (-1)^i}{2h_i} e^{(-1)^{i+1} 2Rh_i + \varepsilon_i^2} \operatorname{erfc}\left(\omega^{-1} - (-1)^i \varepsilon_i\right)$$
$$+ \frac{Rh_i + (-1)^i}{2h_i} e^{(-1)^{i+1} 4Rh_i + \varepsilon_i^2} \operatorname{erfc}\left(2\omega^{-1} - (-1)^i \varepsilon_i\right)$$
$$+ \frac{3Rh_i - (-1)^i}{2h_i} \left\{ \operatorname{erf}\left(\omega^{-1}\right) - \operatorname{erf}\left(2\omega^{-1}\right) \right\} + \sqrt{\frac{Dt}{\pi}} \left\{ e^{-\omega^{-2}} - e^{-4\omega^{-2}} \right\} \quad \text{and}$$

$$\varepsilon_i^2 e^{-\varepsilon_i^2} R \left\{ \left[4\omega\varepsilon_i^2 - (-1)^i 12\varepsilon_i + 9\omega^{-1} \right] I_{0,i} + \left[(-1)^i 8\omega\varepsilon_i - 12 \right] I_{1,i} + 4\omega I_{2,i} \right\}$$
$$= -\left(\frac{(-1)^i}{2} R^2 h_i - R + \frac{(-1)^i}{h_i} \right) e^{(-1)^{i+1} 2Rh_i + \varepsilon_i^2} \operatorname{erfc}\left(\omega^{-1} - (-1)^i \varepsilon_i\right)$$
$$+ \left(\frac{(-1)^i}{2} R^2 h_i + R + \frac{(-1)^i}{h_i} \right) e^{(-1)^{i+1} 4Rh_i + \varepsilon_i^2} \operatorname{erfc}\left(2\omega^{-1} - (-1)^i \varepsilon_i\right)$$
$$+ \left((-1)^{i+1} \frac{9}{2} R^2 h_i - (-1)^i Dt h_i + 3R - \frac{(-1)^i}{h_i} \right) \left[\operatorname{erf}\left(\omega^{-1}\right) - \operatorname{erf}\left(2\omega^{-1}\right) \right]$$
$$+ 2\sqrt{\frac{Dt}{\pi}} \left(1 - (-1)^i 2Rh_i\right) e^{-\omega^{-2}} - 2\sqrt{\frac{Dt}{\pi}} \left(1 - (-1)^i Rh_i\right) e^{-4\omega^{-2}}.$$

Hence, collecting terms and using (3.8) and (3.11), (3.19) becomes

$$\frac{m_t}{m_\infty} = M_0 + \frac{3(\alpha+1)}{\alpha R^2 (h_1+h_2)^3} \left\{ \sum_{i=1,2} g_{5,i}\, e^{(-1)^{i+1} 2Rh_i + \varepsilon_i^2} \operatorname{erfc}\left(\omega^{-1} - (-1)^i \varepsilon_i\right) \right.$$
$$+ \sum_{i=1,2} g_{6,i}\, e^{(-1)^{i+1} 4Rh_i + \varepsilon_i^2} \operatorname{erfc}\left(2\omega^{-1} - (-1)^i \varepsilon_i\right)$$
$$- (h_1+h_2) \left[2 + \frac{h_1^2 + h_2^2}{h_1 h_2} \right] \left(\operatorname{erf}\left(\omega^{-1}\right) - \operatorname{erf}\left(2\omega^{-1}\right) \right)$$
$$+ 4(h_1^2 - h_2^2)\left[1 + Rh_1 + (1 - Rh_2)\right] \sqrt{\frac{Dt}{\pi}} e^{-\omega^{-2}}$$
$$\left. - 4(h_1^2 - h_2^2)\left[1 - Rh_1 + (1 + Rh_2)\right] \sqrt{\frac{Dt}{\pi}} e^{-4\omega^{-2}} \right\} + \mathrm{HT},$$

$$\text{where } g_{5,i} = 3h_i \left[1 + (-1)^i Rh_i\right] - 6h_{\bar{i}} \left[1 - (-1)^i Rh_i\right] - (-1)^i 5Rh_{\bar{i}}^2 - \frac{h_{\bar{i}}^2}{h_i}$$
$$+ (-1)^i 4(R^2 + Dt) h_i (h_1^2 - h_2^2) - 4RDt h_i^2 (h_1^2 - h_2^2)$$
$$\text{and } g_{6,i} = -h_i - 2h_i \left[1 + (-1)^i Rh_i\right] + 6h_{\bar{i}} \left[1 + (-1)^i Rh_i\right] + 7R(h_1^2 - h_2^2)$$
$$+ (-1)^i 4(2R^2 - Dt) h_i (h_1^2 - h_2^2) - 4RDt h_i^2 (h_1^2 - h_2^2) + \frac{h_{\bar{i}}^2}{h_i}.$$

Using the relationships given by (3.14), together with

$$1-(-1)^i Rh_i = \frac{3\gamma_i}{\alpha}\left(\frac{\alpha-(-1)^i 3\gamma_2}{3\gamma_i}\right) = \frac{3\gamma_i^2}{\alpha}, \quad 1+(-1)^i Rh_i = 1+\frac{3\gamma_i}{\alpha},$$

$$h_1 - h_2 = \frac{3}{\alpha R}(\gamma_1-\gamma_2) = \frac{3}{\alpha R},$$

$$h_1 h_2 = \gamma_1\gamma_2\left(\frac{3}{\alpha R}\right)^2 = \frac{\alpha}{3}\left(\frac{3}{\alpha R}\right)^2 = \frac{3}{\alpha R^2},$$

and

$$\gamma_i^2 = \gamma_i(\gamma_{\bar{i}} - (-1)^i) = \frac{\alpha}{3} - (-1)^i\gamma_i$$
$$\Rightarrow \gamma_i^3 = \frac{\alpha}{3}\gamma_i - (-1)^i\frac{\alpha}{3} + \gamma_i = \frac{\alpha}{3}\gamma_{\bar{i}} - (-1)^i 2\frac{\alpha}{3} + \gamma_{\bar{i}} - (-1)^i,$$

the result reduces to

$$\frac{m_t}{m_\infty} = M_0 + \frac{\alpha+1}{3(\alpha R)^2(\gamma_1+\gamma_2)^3}\sum_{i=1,2}\Bigg\{ g_{7,i}\, e^{(-1)^{i+1}\frac{6\gamma_i}{\alpha}+\varepsilon_i^2}\operatorname{erfc}\left(\omega^{-1}-(-1)^i\varepsilon_i\right)$$
$$+ g_{8,i}\, e^{(-1)^{i+1}\frac{12\gamma_i}{\alpha}+\varepsilon_i^2}\operatorname{erfc}\left(2\omega^{-1}-(-1)^i\varepsilon_i\right)$$
$$- \gamma_i(\alpha R)^2(4\alpha+3)\left[\operatorname{erf}\left(\omega^{-1}\right)-\operatorname{erf}\left(2\omega^{-1}\right)\right]$$
$$+12\gamma_i\alpha R\sqrt{\frac{Dt}{\pi}}\left[(2\alpha+3)e^{-\omega^{-2}}-(2\alpha-3)e^{-4\omega^{-2}}\right]\Bigg\} + \mathrm{HT},$$

$$g_{7,i} = -9\left[3\alpha^2+4\alpha+12(\alpha+1)\omega^2\right]\gamma_i R^2 - 4\alpha(\alpha R)^2\gamma_{\bar{i}}$$
$$+ (-1)^i 6\left[\alpha^2+2\alpha\,(2\alpha+3)\,\omega^2\right]R^2 \quad \text{and}$$
$$g_{8,i} = \left[-72\alpha+51\alpha^2+4\alpha^3-36\,(\alpha+3)\,\omega^2\right]\gamma_i R^2$$
$$(-1)^i 12\left[6\alpha^2+\alpha^3-\alpha(2\alpha-3)\omega^2\right]R^2.$$

Hence, expanding M_0 and noting $(\gamma_1+\gamma_2)^2 = (4\alpha+3)/3$ and

$$\operatorname{erfc}\left(\omega^{-1}\right)+\operatorname{erf}\left(\omega^{-1}\right)-\operatorname{erf}\left(2\omega^{-1}\right) = 1-\operatorname{erf}\left(2\omega^{-1}\right) = \operatorname{erfc}\left(2\omega^{-1}\right),$$

the solution is

$$\frac{m_t}{m_\infty} = (\alpha+1)\Bigg\{1-\operatorname{erfc}\left(2\omega^{-1}\right)+A\left[(2\alpha+3)e^{-\omega^{-2}}-(2\alpha-3)e^{-4\omega^{-2}}\right]$$
$$+\frac{1}{\gamma_1+\gamma_2}\sum_{i=1,2}\Big\{-\gamma_i e^{\varepsilon_i^2}\operatorname{erfc}\left((-1)^{i+1}\varepsilon_i\right)$$
$$+B_i e^{(-1)^{i+1}\frac{6\gamma_i}{\alpha}+\varepsilon_i^2}\operatorname{erfc}\left(\omega^{-1}-(-1)^i\varepsilon_i\right)$$
$$+C_i e^{(-1)^{i+1}\frac{12\gamma_i}{\alpha}+\varepsilon_i^2}\operatorname{erfc}\left(2\omega^{-1}-(-1)^i\varepsilon_i\right)\Big\}\Bigg\}+\mathrm{HT}, \qquad (3.20)$$

where

$$A = \frac{12\omega}{(3+4\alpha)\alpha}\frac{1}{\sqrt{\pi}},$$

$$B_i = \frac{-12\left[2\alpha^2+3\alpha+9(\alpha+1)\omega^2\right]\gamma_i + (-1)^i 4\left[\alpha^3+3\alpha^2+3\alpha(2\alpha+3)\omega^2\right]}{(3+4\alpha)\alpha^2}$$

and

$$C_i = \frac{\left[4\alpha^3+51\alpha^2-72\alpha-36(\alpha+3)\omega^2\right]\gamma_i + (-1)^i 12\alpha\left[6\alpha+\alpha^2-(2\alpha-3)\omega^2\right]}{(3+4\alpha)\alpha^2}, \tag{3.21}$$

which reduces to (2.7) for t sufficiently close to zero.

4. Discussion

The accuracy of Crank's short-time solution (2.7) and short-time solutions (3.15) incorporating the $n = 0$ terms and (3.20) incorporating the $n = 0, 1$ terms were compared against Ruthven's long-time solution (2.10). An error of less than 2%, the level of accuracy used by Ruthven [5], was used to determine when to use each of the four solutions.

Plots of the long-time solution (2.10) using only the first 1,000 terms and the three short-time solutions (2.7), (3.15) and (3.20) versus dimensionless time $\tau = Dt/R^2$ for $\Lambda = 0.1$, 0.3, 0.6 and 0.9 are given in Figure 2. The plots show that all three short-time solutions give similar results for t close to zero ($\tau < 0.2$). However, for $\tau > 0.2$, Crank's solution (2.7) diverges from the correct solution rapidly, particularly for smaller Λ. The additional terms in (3.15) reduce the divergence for $\tau > 0.2$ and small Λ, but increase the error for large Λ. Generally, for $0.2 < \tau < 1.0$, solution (3.20) provides more accurate solutions than the other two short-time solutions. Ruthven's long-time solution (2.10) should be used for $\tau > 1.0$.

Figure 3 shows the relative errors of the three short-time solutions compared with the first 1,000 terms of the long-time solution (2.10). The plots show that (2.7), (3.15) and (3.20) have less than 1% error for $\tau < 0.25$, $\tau < 0.3$ and $\tau < 0.9$ respectively. However, the short-time period over which (3.20) has less than 1% error becomes smaller as Λ increases above 0.9.

To achieve a specified accuracy, the number of terms required in the long-time solution increases as τ becomes smaller, whereas the number of terms required in the short-time solutions increases as τ becomes larger. Further, for large Λ, it is necessary to use the following substitutions to evaluate (3.20) at longer times:

$$e^{(-1)^{i+1}\frac{6\gamma_i}{\alpha}+\varepsilon_i^2}\,\mathrm{erfc}\left(\tau^{-1}-(-1)^i\varepsilon_i\right) = e^{(-1)^{i+1}2a_i}e^{\varepsilon_i^2}\,\mathrm{erfc}\left(\left|\frac{a_i}{\varepsilon_i}\right|+\varepsilon_i\right) \quad \text{and}$$

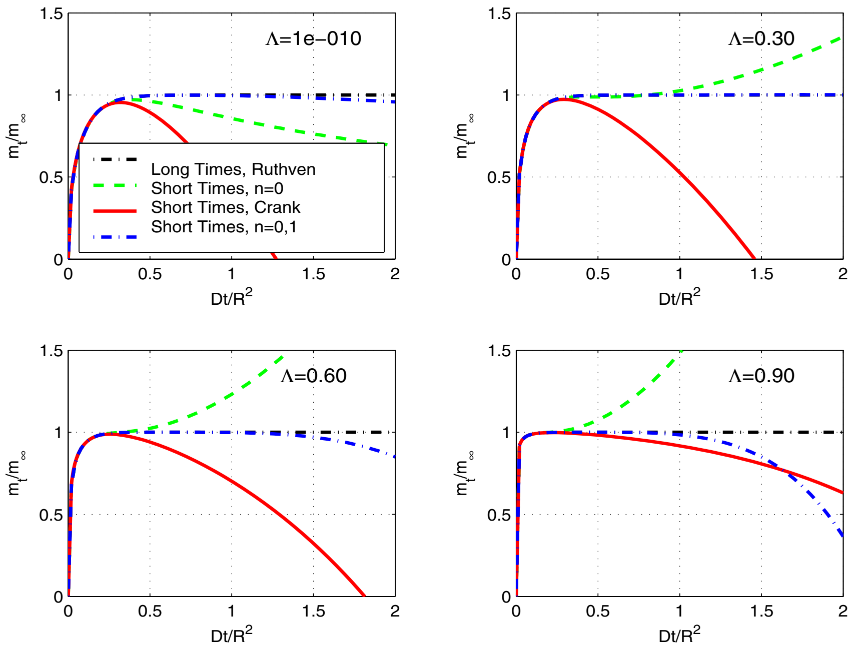

FIGURE 2. Long-time and short-time solutions for various Λ.

$$e^{(-1)^{i+1}\frac{12\gamma_i}{\alpha}+\varepsilon_i^2}\operatorname{erfc}\left(2\tau^{-1}-(-1)^i\varepsilon_i\right)=e^{(-1)^{i+1}4a_i}e^{\varepsilon_i^2}\operatorname{erfc}\left(2\left|\frac{a_i}{\varepsilon_i}\right|+\varepsilon_i\right),$$

where $a_i = 3\gamma_i/\alpha$, $i = 1, 2$.

To determine when to use the long-time solution, the number of terms, N, required in (2.10) to give a relative error of less than 2%, the acceptable level of error suggested by Ruthven [5], is used.

For $\alpha \to \infty$, corresponding to an infinite-volume system, $\Lambda \to 0$, $p_n \to n\pi$, and Crank's long-time solution (2.10) becomes

$$\frac{m_t}{m_\infty} = 1 - 6\sum_{n=1}^{\infty}\frac{1}{n^2\pi^2}e^{-\frac{n^2\pi^2 D}{R^2}t}, \tag{4.1}$$

the long-time solution given by Ruthven [5] for an infinite-volume system. The plot of the relative error and the minimum number of terms required in (4.1) for less than a 2% error against the fractional uptake is similar to the plot of (2.10) for $\alpha = 10$ (or $\Lambda \approx 0.09$) shown in Figure 4 (left).

However, with further reduction of α, the number of terms required increases significantly, as shown in Figure 4 (right) where $\alpha = 0.1$ (or $\Lambda \approx 0.91$).

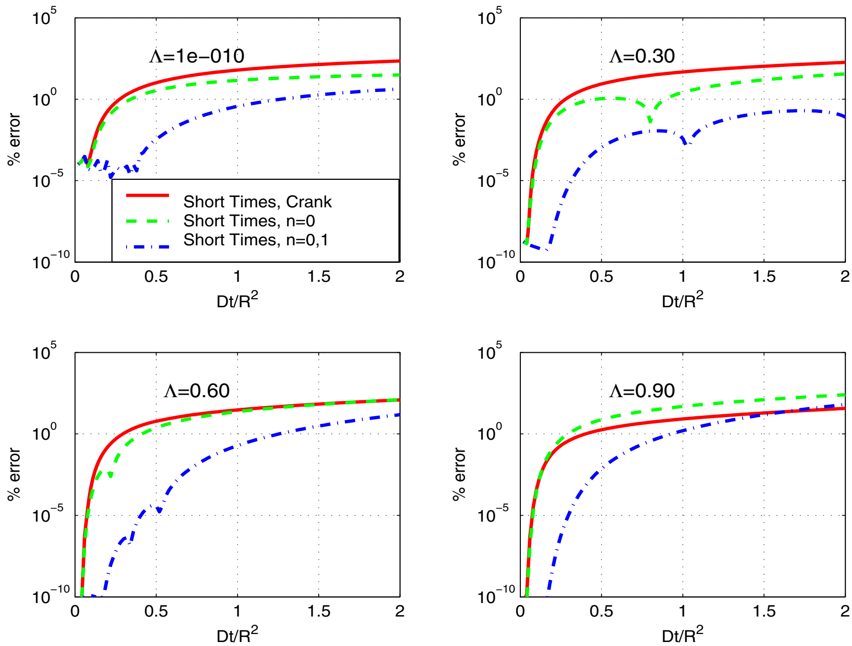

FIGURE 3. Relative error using short-time solutions for various Λ.

Thus, the first $N = 10$ terms of (2.10) shall give a 2% accuracy for fractional uptakes $m_t/m_\infty > 0.12$ for $\alpha > 10$, and $m_t/m_\infty > 0.6$ for $0.1 < \alpha < 10$, where the first 10 roots of (2.11) given for various α in Table 1 are found using Newton's method. Therefore, referring to the plot of the fractional uptakes for various Λ given in Figure 5, for 2% accuracy, use Ruthven's long-time solution (2.10) with the first $N = 10$ terms for $\tau > 0.05$ and use Crank's short-time solution (2.7) for $\tau < 0.2$ — both options provide a 2% accuracy for $0.05 < \tau < 0.2$.

5. Conclusion

A derivation, using the first $n = 0$ term of a negative exponential series in Laplace space, has been given for Crank's short-time solution (2.7) for the diffusion in a sphere immersed in a well-stirred liquid of limited volume. For an accuracy of 2%, (2.7) is suitable only for dimensionless times $\tau < 0.2$. Including the $n = 1$ term of the series in the derivation, the domain can be extended to $\tau < 1.0$ with less than 1% error in most cases. However, using (2.7) for $\tau < 0.2$ and Ruthven's long-time solution (2.10) with the first $N = 10$ terms for $\tau > 0.05$ gives a 2% accuracy with both options providing a 2% accuracy for $0.05 < \tau < 0.2$.

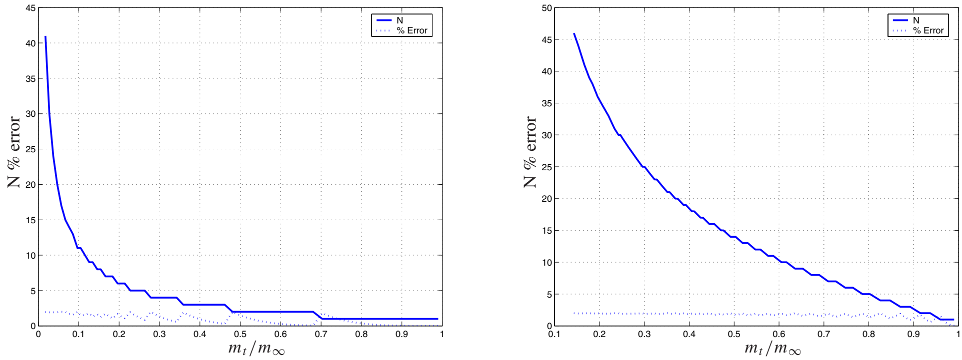

FIGURE 4. Minimum number of summation terms, N, required in (2.10) for 2% accuracy, for $\alpha = 10$ (left) and $\alpha = 0.1$ (right).

TABLE 1. Roots of $\tan p_n = 3p_n/(3 + \alpha p_n^2)$.

	$\alpha = 0$	$\alpha = 1$	$\alpha = 10$	$\alpha = 100$	$\alpha = \infty$
p_1	4.4934095	3.7263847	3.2315901	3.1510842	3.1415927
p_2	7.7252518	6.6814349	6.3301904	6.2879527	6.2831853
p_3	10.9041217	9.7155661	9.4563860	9.4279589	9.4247780
p_4	14.0661939	12.7927116	12.5901493	12.5687570	12.5663706
p_5	17.2207553	15.8923968	15.7270133	15.7098727	15.7079633
p_6	20.3713030	19.0048495	18.8654433	18.8511472	18.8495559
p_7	23.5194525	22.1251081	22.0047727	21.9925126	21.9911486
p_8	26.6660543	25.2504480	25.1446660	25.1339348	25.1327412
p_9	29.8115988	28.3792657	28.2849359	28.2753948	28.2743339
p_{10}	32.9563890	31.5105624	31.4254697	31.4168814	31.4159265

Acknowledgements

We thank Phillip Pendleton for bringing the problem to our attention, and Phil Howlett, Basil Benjamin, John Hewitt, Aileen Haynes and the referees for their useful comments. Also Charles Pearce and Jason Whyte are acknowledged for their help with making the paper more readable.

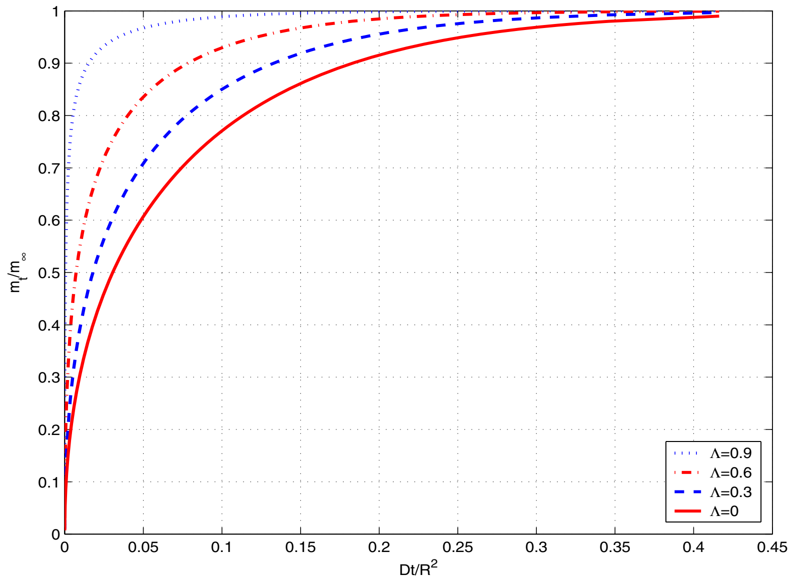

FIGURE 5. Theoretical uptake curves calculated by Equation (2.10) .

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