SHORT COMMUNICATION

Diffusion of a gas through a membrane

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1. Introduction

Diffusion of a soluble gas through a membrane is an important process that has been studied by using an electrochemical method [1–4]. To analyse such systems and estimate the diffusion coefficient, D, and solubility, c_0, a one-dimensional form of Fick's second law of diffusion is used

$$\frac{\partial c(x, t)}{\partial t} = D\frac{\partial^2 c(x, t)}{\partial x^2} \qquad (1)$$

where $c(x, t)$ represents the concentration of the diffusing species and its diffusion coefficient, D, is assumed to be constant. The initial condition and the boundary conditions are

$$c(x, t) = 0 \text{ for } 0 < x < L \text{ for } t = 0 \qquad (2)$$

$$c(x, t) = 0 \text{ at } x = 0 \text{ for } t \geqslant 0 \qquad (3)$$

$$c(x, t) = c_0 \text{ at } x = L \text{ for } t \geqslant 0 \qquad (4)$$

The reaction current at the membrane surface is defined as

$$i(t) = nFAD\left.\frac{\partial c(x, t)}{\partial x}\right|_{x=0} \qquad (5)$$

and the steady state limiting current is

$$i_\infty = \frac{nFADc_0}{L} \qquad (6)$$

where n is the number of electrons transferred in the reaction occurring at the membrane surface; A is the area of the membrane; L is the thickness of the membrane; and F is the Faraday constant.

2. Existing solution approximations

Several authors have attempted to approximate the solution of Equations 1–4 to evaluate the current ratio, $i(\tau)/i_\infty$ by using Equations 5 and 6. McBreen *et al.* [2] obtained the following expressions using the Laplace transformation and Fourier methods, respectively:

$$\frac{i(\tau)}{i_\infty} = \frac{2}{\sqrt{(\pi\tau)}}\exp\left(\frac{-1}{4\tau}\right)$$

$$\frac{i(\tau)}{i_\infty} = 1 - 2\exp(-\pi^2\tau) \qquad (7)$$

where

$$\tau = Dt/L^2 \qquad (8)$$

Recently Yeh and Shih [4] presented another solution:

$$\frac{i(\tau)}{i_\infty} = 1 - \exp(-6\tau) \qquad (9)$$

These expressions were obtained by truncating after the first term of the infinite series of the analytical solution presented by the authors. All of these equations are approximate formulae for the current ratio; therefore, they are not accurate over the entire range of time as demonstrated by Kimble *et al.* [4]. The infinite series solution presented by McBreen *et al.* [2] is the following:

$$\frac{i(\tau)}{i_\infty} = \frac{2}{\sqrt{(\pi\tau)}}\sum_{n=0}^{\infty}(-1)^n\exp\left[-\frac{(2n+1)^2}{4\tau}\right] \qquad (10)$$

Unfortunately, Equation 10 is not correct as can be seen in Fig. 1 which shows that Equation 10 does not yield the correct current ratio for long times ($\tau > 0.3$) regardless of the number of terms included in the infinite series in Equation 10. The reason for this is that the $(-1)^n$ multiplier in Equation 10 is incorrect, as shown below.

3. Solution procedures

Two different solution procedures are presented here to obtain a solution to the above equations. The first is the Laplace transformation method and the second is the separation of variables.

3.1. *Laplace transformation*

Performing the Laplace transformation on the diffusion equation in Equation 1 and the boundary conditions in Equations 3 and 4 gives

$$\frac{d^2\bar{c}(x, s)}{dx^2} - \frac{s}{D}\bar{c}(x, s) = 0 \qquad (11)$$

$$\bar{c}(0, s) = 0 \qquad (12)$$

$$\bar{c}(L, s) = c_0/s \qquad (13)$$

where $\bar{c}(x, s) = L[c(x, t)]$ is the concentration of the diffusing species in the Laplace domain, s is the Laplace transform parameter. The general solution of Equation 11 is

$$\bar{c}(x, s) = A\sinh[x\sqrt{(s/D)}] + B\cosh[x\sqrt{(s/D)}] \qquad (14)$$

Application of the boundary conditions, Equations 12 and 13, yields

$$A = \frac{c_0}{s\sinh[L\sqrt{(s/D)}]} \quad \text{and} \quad B = 0 \qquad (15)$$

therefore

$$\bar{c}(x, s) = \frac{c_0\sinh[x\sqrt{s/D)}]}{s\sinh[L\sqrt{(s/D)}]} \qquad (16)$$

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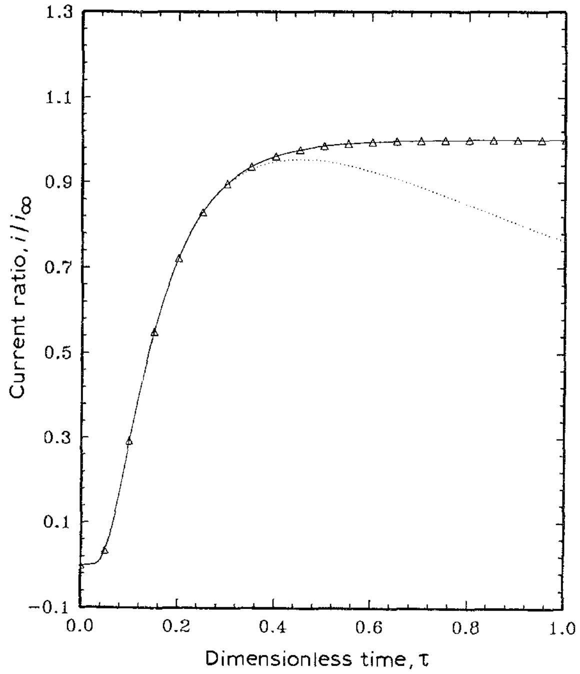

Fig. 1. The $i(\tau)/i_\infty$ ratio using the McBreen *et al.* solution (····) (Equation 10) and analytical approaches by Laplacian transform (——) (Equations 23 and 25) compared with a numerical solution using a three point finite difference method (△).

which can be written as

$$\bar{c}(x, s) = \frac{c_0}{s} \times \frac{\exp[-\sqrt{(s/D)}(L - x)] - \exp[-\sqrt{(s/D)}(L + x)]}{1 - \exp[-2L\sqrt{(s/D)}]} \quad (17)$$

By using a Taylor series

$$\frac{1}{1 - x} = \sum_{n=0}^{\infty} x^n \quad \text{for } |x| < 1 \quad (18)$$

Equation 17 becomes

$$\bar{c}(x, s) = \frac{c_0}{s}\{\exp[-\sqrt{(s/D)}(L - x)] - \exp[-\sqrt{(s/D)}(L + x)]\} \times \sum_{n=0}^{\infty} \exp[-2nL\sqrt{(s/D)}] \quad (19)$$

or

$$\bar{c}(x, s) = \frac{c_0}{s}\sum_{n=0}^{\infty}\{\exp[-\sqrt{(s/D)}((2n + 1)L - x)] - \exp[-\sqrt{(s/D)}((2n + 1)L + x)]\} \quad (20)$$

Performing an inverse Laplace transformation of Equation 20, one obtains

$$c(x, t) = c_0\left\{\sum_{n=0}^{\infty} \operatorname{erf} c\left[\frac{(2n + 1)L - x}{2\sqrt{(Dt)}}\right] - \sum_{n=0}^{\infty} \operatorname{erf} c\left[\frac{(2n + 1)L + x}{2\sqrt{(Dt)}}\right]\right\} \quad (21)$$

and, correspondingly, the derivative of Equation 21 with respect to x is

$$\left.\frac{\partial c}{\partial x}\right|_{x=0} = \frac{2c_0}{\sqrt{(Dt\pi)}}\sum_{n=0}^{\infty}\exp\left[-\frac{(2n + 1)^2L^2}{4Dt}\right] \quad (22)$$

Thus, the current ratio in this case is

$$\frac{i(t)}{i_\infty} = \frac{2}{\sqrt{(\pi\tau)}}\sum_{n=0}^{\infty}\exp\left[-\frac{(2n + 1)^2}{4\tau}\right] \quad (23)$$

Comparison of Equation 23 to Equation 10 shows that the $(-1)^n$ multiplier is not needed in Equation 10.

An alternative method is to perform the inverse Laplace transformation directly from Equation 16 [5]

$$c(x, t) = c_0\left\{\frac{x}{L} + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{n} \times \exp\left[-\frac{n^2\pi^2Dt}{L^2}\right]\sin\left(\frac{n\pi}{L}x\right)\right\} \quad (24)$$

The current ratio obtained by using Equation 24 is

$$\frac{i(\tau)}{i_\infty} = 1 + 2\sum_{n=1}^{\infty}(-1)^n\exp[-n^2\pi^2\tau] \quad (25)$$

It is worth noting that Equation 25 converges more rapidly than Equation 23 for long times. This feature maybe useful for data reduction.

Also, it should be mentioned that Equation 24 can be obtained from Carslaw and Jaeger [6] with $\lambda = 0$, $\phi_1 = 0$, and $\phi_2 = 1$.

3.2. *Separation of variables*

Equation 24 can also be obtained by using the method of separation of variables with the solution being the sum of the non-homogeneous and homogeneous solutions. Let

$$u(x, t) = c(x, t) - \frac{x}{L}c_0 \quad (26)$$

then Equations [1–4] become

$$\frac{\partial u(x, t)}{\partial t} = D\frac{\partial^2 u(x, t)}{\partial x^2} \quad (27)$$

$$u(x, t) = -\frac{x}{L}c_0 \text{ for } 0 < x < L \text{ for } t = 0 \quad (28)$$

$$u(x, t) = 0 \text{ at } x = 0 \text{ for } t \geqslant 0 \quad (29)$$

$$u(x, t) = 0 \text{ at } x = L \text{ for } t \geqslant 0 \quad (30)$$

Assume that

$$u(x, t) = f(t)g(x) \quad (31)$$

Equation 27 becomes

$$\frac{f'(t)}{f(t)} = D\frac{g''(x)}{g(x)} = -\lambda \quad (32)$$

The general solutions to $f(t)$ and $g(x)$ are

$$f(t) = e^{-\lambda t} \quad (33)$$

$$g(x) = A\sin(x\sqrt{(\lambda/D)}) + B\cos(x\sqrt{(\lambda/D)}) \quad (34)$$

Application of boundary conditions in Equations 29 and 30 yields $B = 0$ and

$$A\sin(L\sqrt{(\lambda/D)}) = 0 \quad \text{or} \quad \lambda = \frac{n^2\pi^2D}{L^2} \quad (35)$$

Then the solution to $u(x, t)$ is of the form

$$u(x, t) = \sum_{n=1}^{\infty} A_n \exp\left(-\frac{n^2\pi^2 Dt}{L^2}\right) \sin\left(\frac{n\pi x}{L}\right) \quad (36)$$

where A_n is determined using the initial condition in Equation 28

$$A_n = \frac{2}{L}\int_0^L \left(-\frac{x}{L}c_0\right) \sin\left(\frac{n\pi x}{L}\right) dx \quad (37)$$

$$A_n = \frac{2(-1)^n}{n\pi} c_0 \quad (38)$$

Combining Equations 26, 36, and 38, one can obtain the solution for $c(x, t)$ as given by Equation 24.

4. Results

A comparison of Equations [10], [23], [25], and the solution computed numerically using a three point finite difference method is shown in Fig. 1. As expected, the solutions by the analytical methods (Equations 23 and 25) coincide with the solution computed numerically. However, as mentioned above, Equation 10 deviates from the correct solution for τ greater than about 0.3.

5. Summary

The analysis of current-time data to determine the diffusion coefficient and the solubility of hydrogen diffusing through a membrane should be done using Equation 23 or Equation 25, but not Equation 10. The numerical method used by Kimble *et al.* [4] may be replaced by either Equation 23 or Equation 25 to reduce the computation time needed for data reduction.

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