

Green's functions for a system with a thin membrane

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A procedure to determine concentration profiles of solute in a system with a thin membrane is presented. We assume that the permeability of the membrane is described by a set of general coefficients without the need to investigate its internal structure. This procedure is based on the Smoluchowski equation, but the boundary condition on the membrane is given in a new form. The membrane permeability coefficients are given separately with respect to the diffusion, convection, and migration phenomena. The procedure, relative to existing procedures, considerably reduces the calculations necessary to determine concentration profiles. [S1063-651X(96)02209-X]

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I. INTRODUCTION

One of the most important biophysics processes is the membrane transport process. The theoretical problem is to determine the solution concentration profile in the membrane system when either outside forces acts effectively on diffusing particles of the solute (the migration effect of particles) or these particles are floated by the solvent (the particle convection effect of the solute). The concentration profile on the border between the membrane and the solution has a great effect on the solute and solvent fluxes flowing through the membrane. Indeed, it determines the course of many physiological processes [1–5].

In many previous papers ([6–8] and others) theoretical calculations of concentration profiles in membrane systems are based on the assumption that the concentration within the membrane is described by the Smoluchowski (or Fick) equation (where the coefficient of diffusion is constant). This assumption is not always true because the internal structure of a real membrane is not homogeneous and is, in fact, very complicated. Furthermore, in practice, we only have experimental data that determine the properties of permeability in relation to the whole membrane without taking into consideration its internal structure.

The aim of this paper is to present a procedure that allows the determination of the concentration profile of the solute in a membrane system. We assume that the permeability of the membrane is described by a set of general coefficients without the need to investigate its internal structure. This procedure is based on the well-known Smoluchowski equation, but the boundary condition on the membrane surface is given in a new form. The procedure makes full use of Green's function in Eq. (1). We also assume that the membrane is very thin relative to the size of the system, which allows us to treat it as "a partially permeable wall." In this paper each Green's function depends explicitly on the convection and migration velocities. For diffusion, convection, and migration the membrane permeability is specified with separate coefficients. It is noted that the Green's function, which is sometimes interpreted as a probability density $G(x, t; z, t')$ for finding a particle at location x at time t after departure

from location z at an earlier time t' , is often used to solve diffusion problems in different systems [8–16].

II. MODEL

We assume that the problem is one dimensional. We start with the Smoluchowski equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} - v C \right), \quad (1)$$

where D is the diffusion coefficient, $v = v_C + v_M$, v_C is the convection velocity (equal to the velocity of solvent), and v_M is the migration velocity of solute particles (caused by an external field).

The concentration profile function $C(x, t)$ can be written in the form of the integral formula [8]:

$$C(x, t) = \int_{-\infty}^{\infty} G(x, t; z, 0) C(z, 0) dz, \quad (2)$$

where G is the Green's function for the membrane system and $C(z, 0)$ is the initial concentration profile.

The following have been assumed: (a) there are no "collective" effects for movement of the solute particles in the system, i.e., the movement of any solute particle does not depend on the positions of the other particles; in particular we make the assumptions that (a1) the interactions among the solute particles are negligibly small, (a2) the diffusion coefficient D and the migration velocity v_M do not depend on the concentration value, time, and position, (a3) the parameters of the membrane permeability are constant in time and they do not depend on the value of the solute flux flowing through the membrane, (a4) the convection velocity is constant in time and its changes, determined by the difference in osmotic pressure on the membrane, are negligibly small; (b) the whole flux of the solute J flowing through the membrane is an algebraical sum of fluxes that are generated by the diffusion (J_D), convection (J_C), and migration (J_M) effects.

Let us consider two diffusive systems: one which does not contain a membrane and one with a membrane (placed at $x = x_0$). We assume that the parameters D and v are equal and that the systems be free from solute at time $t < 0$. At time $t = 0$ in the plane at point z the amount of solute (equal in both systems) is produced instantaneously. We denote by J_D^0 , J_C^0 , J_M^0 the fluxes (diffusion, convection, and migration)

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in the first system (without a membrane) generated by this solute and by J_D , J_C , and J_M analogous fluxes in the second one.

Let us define the permeability coefficients of the membrane by the following equations:

$$J_D(x_0, t) = (1 - \delta)J_D^0(x_0, t), \tag{3a}$$

$$J_C(x_0, t) = (1 - \sigma)J_C^0(x_0, t), \tag{3b}$$

$$J_M(x_0, t) = (1 - \mu)J_M^0(x_0, t). \tag{3c}$$

We call the coefficients $(1 - \delta)$, $(1 - \sigma)$, and $(1 - \mu)$ the coefficients of permeability of the membrane with respect to the diffusion, convection, and migration phenomena, respectively. Consistently, the coefficients δ , σ , and μ are understood as the coefficients of reflection of the membrane with respect to the above-mentioned phenomena.

From the microscopic point of view the $(1 - \delta)$ coefficient can be interpreted as a conditional probability of getting the solute particle through the membrane on condition that after removing the membrane the particle can go through the volume that was occupied earlier by the membrane (making the assumption that the particle displacement is caused only by its diffusion movement). We can interpret the $(1 - \sigma)$, and $(1 - \mu)$ coefficients analogously. For the typical membrane system the δ , σ , and μ coefficients should take values in the interval $(0, 1)$.

From the macroscopic point of view the Green's function can be interpreted as the abstract concentration profile that is determined only by one particle, which is located at z at the initial moment. Thus, we can write

$$J_D^0 = -D \frac{\partial G_0}{\partial x}, \quad J_C^0 = v_C G_0, \quad J_M^0 = v_M G_0,$$

where G_0 denotes the Green's function for the system without a membrane:

$$G_0(x, t; z, 0) = \frac{1}{2\sqrt{\pi Dt}} e^{-(x-z-vt)^2/4Dt}. \tag{4}$$

Let the membrane be at $x = x_0$. Taking into account the above equations and the following expression for the full flux of solute in a membrane system,

$$J = -D \frac{\partial G}{\partial x} + vG,$$

we can give the boundary condition on the membrane as follows:

$$\begin{aligned} -D \frac{\partial G}{\partial x} + vG \Big|_{x=x_0} &= \left[\frac{(1 - \delta)(x_0 - z - vt)}{4t\sqrt{\pi Dt}} \right. \\ &\quad \left. + \frac{(1 - \sigma)v_C + (1 - \mu)v_M}{2\sqrt{\pi Dt}} \right] \\ &\quad \times e^{-(x_0 - z - vt)^2/4Dt}. \end{aligned} \tag{5}$$

For the Green's function the initial condition is given by the equation

$$G(x, t; z, 0) \Big|_{t=0} = \delta(x - z).$$

Using Laplace transform techniques [17] the solution of this problem is given by

$$\begin{aligned} G_{--}(x, t; z, 0) &= \frac{1}{2\sqrt{\pi Dt}} e^{-(x-z-vt)^2/4Dt} \\ &\quad + \frac{\delta}{2\sqrt{\pi Dt}} e^{-(2x_0 - x - z - vt)^2/4Dt - v(x_0 - x)/D} \\ &\quad + \frac{\sigma v_C + \mu v_M}{2D} e^{-v(x_0 - x)/D} \\ &\quad \times \operatorname{erfc} \left\{ \frac{2x_0 - x - z - vt}{2\sqrt{Dt}} \right\}, \end{aligned} \tag{6a}$$

$x < x_0, \quad z < x_0,$

$$\begin{aligned} G_{-+}(x, t; z, 0) &= \frac{(1 - \delta)}{2\sqrt{\pi Dt}} e^{-(x-z-vt)^2/4Dt} \\ &\quad - \frac{(\delta - \sigma)v_C + (\delta - \mu)v_M}{2D} e^{-v(z-x)/D} \\ &\quad \times \operatorname{erfc} \left\{ \frac{z - x - vt}{2\sqrt{Dt}} \right\}, \end{aligned} \tag{6b}$$

$x < x_0, \quad z > x_0,$

$$\begin{aligned} G_{+-}(x, t; z, 0) &= \frac{(1 - \delta)}{2\sqrt{\pi Dt}} e^{-(x-z-vt)^2/4Dt} \\ &\quad + \frac{(\delta - \sigma)v_C + (\delta - \mu)v_M}{2D} e^{-v(z-x)/D} \\ &\quad \times \operatorname{erfc} \left\{ \frac{x - z + vt}{2\sqrt{Dt}} \right\}, \end{aligned} \tag{6c}$$

$x > x_0, \quad z < x_0,$

$$\begin{aligned} G_{++}(x, t; z, 0) &= \frac{1}{2\sqrt{\pi Dt}} e^{-(x-z-vt)^2/4Dt} \\ &\quad + \frac{\delta}{2\sqrt{\pi Dt}} e^{-(x+z-2x_0-vt)^2/4Dt - v(z-x_0)/D} \\ &\quad - \frac{\sigma v_C + \mu v_M}{2D} e^{v(x-x_0)/D} \\ &\quad \times \operatorname{erfc} \left\{ \frac{x + z - 2x_0 + vt}{2\sqrt{Dt}} \right\}, \end{aligned} \tag{6d}$$

$x > x_0, \quad z > x_0,$

where erfc is the complementary error function.

In order to fix the δ , σ , and μ coefficients, we must make use of a particular theory. For example, in the Kedem-Katchalsky theory [18] to obtain these coefficients we must take into consideration the following: The diffusive flux, which flows through the membrane, is given by

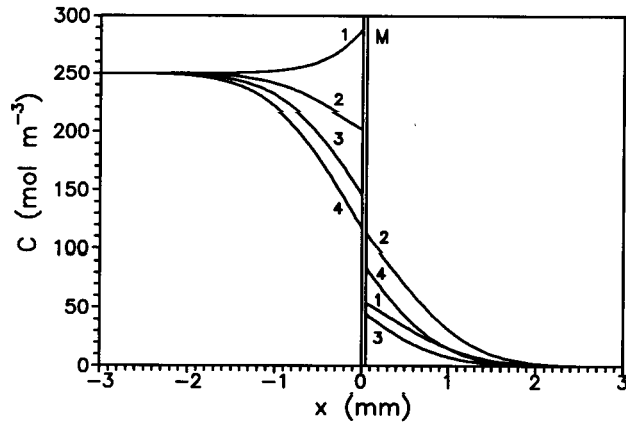


FIG. 1. The concentration profiles for different parameters: $\mu=0.6$, $\delta=0.7$, and $v_M=7.5\times 10^{-7}$ m s $^{-1}$ (plot 1), $\mu=0.3$, $\delta=0.4$, and $v_M=7.5\times 10^{-7}$ m s $^{-1}$ (plot 2), $\mu=0.6$, $\delta=0.7$, and $v_M=-7.5\times 10^{-7}$ m s $^{-1}$ (plot 3), $\mu=0.3$, $\delta=0.4$, and $v_M=-7.5\times 10^{-7}$ m s $^{-1}$ (plot 4). For all cases: $t=240$ s, $D=1.28\times 10^{-9}$ m 2 s $^{-1}$, and $v_C=0$ (M is the membrane).

$$J_D = -\omega RT\Delta c,$$

where ω is the permeability coefficient, R is the gas constant, T is the temperature, and Δc is the solute concentration difference occurring on the membrane. After removing the thin membrane (without any changes of the external conditions) the diffusive flux is (approximately) given by

$$J_D^0 = -D\Delta c/d,$$

where d is the membrane thickness. From the above equations and Eq. (3) we obtain the formula

$$\delta = 1 - (\omega RTd/D).$$

The two other coefficients can be described as follows: σ is the reflection coefficient which appears in Kedem-Katchalsky theory and μ is the additional coefficient that characterizes the effect of the migration transport through the membrane.

III. NUMERICAL CALCULATIONS

The figures illustrate the practical application of Green's functions to calculate the concentration profile in the following model system. Calculations were performed numerically by using Green's functions (6a)–(6d) and the integral formula (2). The initial concentration is described by the equation

$$C(z,0) = \begin{cases} 250 \text{ mol m}^{-3}, & z < 0 \\ 0, & z > 0, \end{cases} \quad (7)$$

the membrane is located at $x_0=0$, the diffusion constant $D=1.28\times 10^{-9}$ m 2 s $^{-1}$. In Fig. 1 the examples of plots of the theoretical dependence $C=C(x,t)$ at time $t=240$ s for different values of the δ , σ , and μ coefficients are shown. In Fig. 2 the theoretical and experimental curves (experimental ones representing the concentration profile of ethanol aqueous solution [7]) are compared for different times. Based on

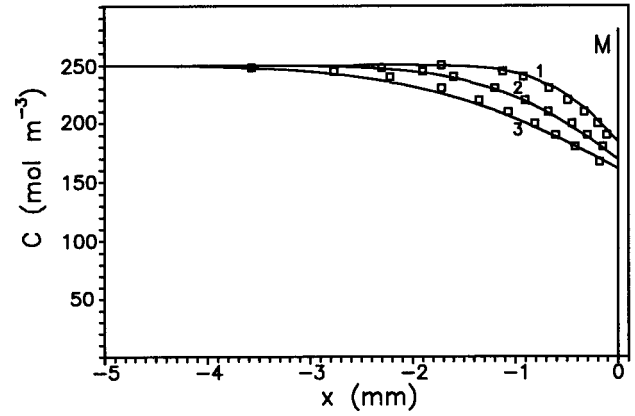


FIG. 2. The concentration profiles for different times (theoretical results, continuous lines): $t=240$ s (plot 1), $t=600$ s (plot 2), and $t=1200$ s (plot 3); the experimental data (squares in the plot) are taken from [7], an additional description is in the text.

the parameter values taken from Dworecki [7], $D=1.28\times 10^{-9}$ m 2 s $^{-1}$, $v_C=0$, and the initial concentration is given by Eq. (7). The migration velocity v_M and the coefficients δ and μ were treated as parameters. The values $v_M=-0.9\times 10^{-7}$ m s $^{-1}$, $\delta=0.18$, and $\mu=0.26$ resulted in the closest conformity of theoretical results with experimental ones.

IV. CONCLUDING REMARKS

The results shown in this paper are in accordance with the results that have been obtained until now and so prove internally consistent. Consider the following special cases.

(i) Substituting $\delta=\sigma=\mu=0$ (full permeable membrane) for the functions (6a)–(6d) we obtain the “free” Green's functions (4).

(ii) Substituting $\delta=\sigma=\mu=1$ (full reflecting membrane) and $v_C=0$, $v_M=0$ for the functions G_{--} and G_{++} we obtain the Green's function for the case of the full reflecting wall (identical with the function given in [8,11]).

(iii) Substituting $\delta=\sigma=\mu=1$ and $v_C=0$ for G_{--} we obtain the function that determines the concentration profile of sedimentating particles in the system with an impenetrable base [11].

Finally, we make the following remarks.

(a) Assumptions (a2), (a3), and (a4) from Sec. II may not be necessary if the calculations are performed numerically; we could then divide the time domain into intervals small enough that these assumptions are approximately valid inside each one of them.

(b) Being familiar with Green's functions for this system allows us to use them for constructing Green's functions in the multimembrane systems. In this case the following procedure can be used: let us assume that for the system containing $(n-1)$ membranes Green's functions are known. Let us add to that system a new (n th) membrane. Using the above-mentioned procedure we obtain Green's functions for the n -membrane system, but in Eq. (5) δ , σ , and μ refer to the new (n th) membrane and G_0 is an adequate Green's function for the $(n-1)$ membrane system. In this way if we

know Green's functions for a one-membrane system we can find Green's functions for a two-membrane system and so on.

(c) The above-mentioned considerations refer to the thin membrane; this is justified because the thickness of real membranes (10^{-8} – 10^{-9} m) is small in comparison with the size of a typical system. However, it is possible to take into account the internal structure of a membrane by treating it as a system of many partially permeable walls. The permeabil-

ity coefficients of these walls may be connected with, for example, the shape of the potential inside the membrane or with chemical reactions taking place inside the membrane [19,20].

It is worth noting that by giving the boundary condition in the manner presented in this paper [Eq. (5)], the calculations necessary to determine the concentration profile in a membrane system are considerably reduced (it can be especially useful in multimembrane systems).

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