Transient Response of a Reactive Membrane Bounded by Two Finite Reservoirs

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(Received 10 December 1981; in final form 5 July 1982)

Abstract

The transient response of a reactive membrane bounded by two finite reservoirs is investigated theoretically in this paper using a generalized Sturm–Liouville integral transform of which a generalized orthogonality relationship must be defined. In the limit of thin membranes or large reservoirs, which occur in most practical cases, a combination of the two-timing technique and an ordinary Sturm–Liouville integral transform is employed to obtain useful asymptotic solutions. Solutions of this problem may be used to estimate the effective diffusivity and the reaction rate constant of the membrane.

INTRODUCTION

Membranes enjoy a wide application in many fields of science, such as biology, biochemistry, chemical engineering, chemistry and physics. When using membranes in a specific isothermal system, one is required to determine inherent properties of the membrane — the effective diffusivity and also the reaction rate constant for reactive membranes. Usually, these inherent properties are determined experimentally by placing the membrane between two finite reservoirs of different known concentrations. The experimentally observable steady state material flux across the membrane is then used to determine the desired properties. This type of experimental set-up has been used in the biological field to measure the effective diffusivities of microbial floc or mould particles [1].

Bunow [2] and DeSimone and Caplan [3] solved the governing reaction diffusion equation by assuming that the concentrations in the reservoirs were constant. This, however, is not true for finite reservoirs. Recognizing this fact, Frisch [4] and Versluijs and Smit [5] have analyzed the unsteady diffusion reaction equations by using the Laplace transform method.

As an alternative to previous treatments, the transient behaviour of a reactive membrane bounded by two finite reservoirs is analyzed in this paper using a *generalized* Sturm–Liouville integral transform. Further, in the limit of thin membranes or large reservoirs, which occur in most practical cases, a combination of a two-timing technique and an *ordinary* Sturm–Liouville integral transform is employed to obtain useful asymptotic solutions. Estimation of the parameters is also discussed in this paper.

THEORY

Consider a homogeneous reactive membrane bounded by two finite reservoirs. It is assumed that the contents in these two reservoirs are well mixed and a first-order isothermal chemical reaction occurs uniformly inside the membrane.

The nondimensional governing equations inside the membrane are:

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - \phi^2 u \tag{1a}$$

$$t = 0; \quad u = 0 \tag{1b}$$

$$x = 0; \quad \partial u/\partial x = M_0(u - a) \tag{1c}$$

$$x = 1; \quad \partial u/\partial x = M_1(b - u) \tag{1d}$$

where u is the nondimensional reactant concentration inside the membrane, a and b are bulk concentrations of the two reservoirs at $x = 0$ and $x = 1$, respectively. It is noted here that the nondimensional time has been scaled with respect to the diffusion time inside the membrane.

The nondimensional governing equations for the bulk concentrations in the two reservoirs are:

$$\frac{da}{dt} = N_0 M_0 [u(0,t) - a] = N_0 \frac{\partial u(0,t)}{\partial x} \qquad (2a)$$

$$\frac{db}{dt} = N_1 M_1 [u(1,t) - b] = -N_1 \frac{\partial u(1,t)}{\partial x} \qquad (2b)$$

$$t = 0; \quad a = \alpha, \quad b = \beta \qquad (2c)$$

Definitions of the nondimensional parameters are given in the Nomenclature.

To solve the coupled partial differential equations (1) and (2), we apply finite integral transform techniques to transform them to coupled ordinary differential equations with respect to time in transform space, where the resulting ordinary differential equations can be solved quite readily. The desired solutions are then obtained by inverting their corresponding transforms in transform space.

We define an integral transform as follows:

$$u_n^* = \int_0^1 u(x,t) K_n(x;\xi_n) \, dx \qquad (3)$$

where the integral transform kernel $K_n(x;\xi_n)$ will be determined during the course of analysis.

Applying this transform to eqn. (1a) and integrating by parts twice the first term in the right-hand side of the resulting transform, we obtain

$$\frac{du_n^*}{dt} = \frac{\partial u(1,t)}{\partial x} K_n(1;\xi_n) - u(1,t) \frac{dK_n(1;\xi_n)}{dx} +$$
$$- \frac{\partial u(0,t)}{\partial x} K_n(0;\xi_n) + u(0,t) \frac{dK_n(0;\xi_n)}{dx} +$$
$$- (\xi_n^2 + \phi^2) u_n^* \qquad (4)$$

provided that K_n satisfies

$$d^2 K_n(x;\xi_n)/dx^2 + \xi_n^2 K_n(x;\xi_n) = 0 \qquad (5)$$

Using eqns. (1c), (1d), (2a) and (2b) to eliminate the unwelcome terms $u(0,t)$, $u(1,t)$,

$u_x(0,t)$ and $u_x(1,t)$ in eqn. (4), we obtain

$$\frac{du_n^*}{dt} + (\xi_n^2 + \phi^2) u_n^* = -\frac{K_n'(1;\xi_n) + M_1 K_n(1;\xi_n)}{N_1 M_1} \times$$
$$\times \left[\frac{db}{dt} + \frac{N_1 M_1 K_n'(1;\xi_n) b}{K_n'(1;\xi_n) + M_1 K_n(1;\xi_n)} \right] +$$
$$+ \frac{K_n'(0;\xi_n) - M_0 K_n(0;\xi_n)}{N_0 M_0} \times$$
$$\times \left[\frac{da}{dt} + \frac{N_0 M_0 K_n'(0;\xi_n) a}{K_n'(0;\xi_n) - M_0 K_n(0;\xi_n)} \right] \qquad (6)$$

It is noted that the boundary conditions for eqn. (5) are not yet specified. However, we have reached a stage at which the boundary conditions for $K_n(x;\xi_n)$ at $x = 0$ and $x = 1$ can be defined in such a way that eqn. (6) can be solved explicitly. We observe that the homogeneous solution of the left-hand side of eqn. (6) is

$$\exp[-(\xi_n^2 + \phi^2)t] \qquad (7)$$

Therefore, if we define

$$\frac{N_1 M_1 K_n'(1;\xi_n)}{K_n'(1;\xi_n) + M_1 K_n(1;\xi_n)} = \frac{N_0 M_0 K_n'(0;\xi_n)}{K_n'(0;\xi_n) - M_0 K_n(0;\xi_n)}$$
$$= \xi_n^2 + \phi^2 \qquad (8)$$

then eqn. (6) becomes

$$\frac{du_n^*}{dt} + (\xi_n^2 + \phi^2) u_n^* = -\frac{K_n'(1;\xi_n)}{\xi_n^2 + \phi^2} \left[\frac{db}{dt} + (\xi_n^2 + \right.$$
$$\left. + \phi^2) b \right] + \frac{K_n'(0;\xi_n)}{\xi_n^2 + \phi^2} \left[\frac{da}{dt} + (\xi_n^2 + \phi^2) a \right] \qquad (9)$$

Multiplying both sides of eqn. (9) by the integrating factor $\exp[(\xi_n^2 + \phi^2)t]$ and integrating the result with respect to time from 0 to t, we obtain

$$u_n^* = -\frac{K_n'(1;\xi_n)}{\xi_n^2 + \phi^2} \{ b - \beta \exp[-(\xi_n^2 + \phi^2)t] \} +$$
$$+ \frac{K_n'(0;\xi_n)}{\xi_n^2 + \phi^2} \{ a - \alpha \exp[-(\xi_n^2 + \phi^2)t] \} \qquad (10)$$

in which we have used the initial condition (2c).

Equation (6) is the relationship between the transform u_n^* and the reservoir concentrations a, b at any instant of time t.

For later use in inverting the transform (10), we define differentially an auxiliary function $f(x, t)$ as follows:

$$\partial^2 f/\partial x^2 = 0 \qquad (11a)$$

$$x = 0; \qquad \partial f/\partial x = M_0(f - a) \qquad (11b)$$

$$x = 1; \qquad \partial f/\partial x = M_1(b - f) \qquad (11c)$$

from which the solution is

$$f(x, t) = \frac{(b-a)x}{1 + 1/M_0 + 1/M_1} + \frac{a(1 + M_1) + M_1 b/M_0}{1 + M_1 + M_1/M_0} \qquad (12)$$

In physical terms, this auxiliary function $f(x, t)$ is the instantaneous steady state concentration inside an unreactive membrane if the reservoir concentrations at $x = 0$ and $x = 1$

are maintained at values of a and b, respectively.

Following the result of Do and Bailey [6], the inverse of eqn. (10) can be written as follows:

$$u(x, t) = f(x, t) + \sum_{n=0}^{\infty} c_n K_n(x; \xi_n) \qquad (13)$$

where $f(x, t)$ is regarded as the boundary term of $u(x, t)$ [6]. To obtain the coefficient, one needs to know the orthogonality condition of the kernel $K_n(x; \xi_n)$. Since the eigenvalue ξ_n appears explicitly in the boundary conditions (8), the eigenproblem (5), (8) is called a modified (or generalized) Sturm–Liouville problem. For this type of eigenproblem, a generalized orthogonality condition must be defined. It is

$$\langle K_n, K_m \rangle = \int_0^1 K_n(x; \xi_n) K_m(x; \xi_m) \, dx + \frac{1}{N_1}\left[K_n(1; \xi_n) + \frac{1}{M_1} K_n'(1; \xi_n) \right] \times$$

$$\times \left[K_m(1; \xi_m) + \frac{1}{M_1} K_m'(1; \xi_m) \right] + \frac{1}{N_0}\left[\frac{1}{M_0} K_n'(0; \xi_n) - K_n(0; \xi_n) \right] \times$$

$$\times \left[\frac{1}{M_0} K_m'(0; \xi_m) - K_m(0; \xi_m) \right] = 0 \qquad (14)$$

for $n \neq m$.

Applying this generalized orthogonality condition (14), the coefficient c_n can be found as:

$$c_n = (u_n^* - f_n^*)/\langle K_n, K_n \rangle \qquad (15)$$

where f_n^* is the transform of $f(x, t)$. It is not difficult to prove that

$$f_n^* = -\frac{bK_n'(1; \xi_n)}{\xi_n^2} + \frac{aK_n'(0; \xi_n)}{\xi_n^2} + \frac{(b-a)[N_1 K_n'(1; \xi_n) + N_0 K_n'(0; \xi_n)]}{(1 + 1/M_0 + 1/M_1)(\xi_n^2 + \phi_n^2)\xi_n^2} \qquad (16)$$

Substituting eqns. (15) and (16) into eqn. (13), we have:

$$u(x, t) = f(x, t) + \phi^2 b(t) \sum_{n=0}^{\infty} \frac{K_n'(1; \xi_n) K_n(x; \xi_n)}{\xi_n^2(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} - \phi^2 a(t) \sum_{n=0}^{\infty} \frac{K_n'(0; \xi_n) K_n(x; \xi_n)}{\xi_n^2(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} +$$

$$- \frac{b-a}{1 + 1/M_0 + 1/M_1} \sum_{n=0}^{\infty} \frac{[N_1 K_n'(1; \xi_n) + N_0 K_n'(1; \xi_n)] K_n(x; \xi_n)}{\xi_n^2(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} +$$

$$+ \beta \sum_{n=0}^{\infty} \frac{K_n'(1; \xi_n) K_n(x; \xi_n) \exp[-(\xi_n^2 + \phi^2)t]}{(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} - \alpha \sum_{n=0}^{\infty} \frac{K_n'(0; \xi_n) K_n(x; \xi_n) \exp[-(\xi_n^2 + \phi^2)t]}{(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} \qquad (17)$$

where $f(x, t)$ is given in eqn. (12).

Substituting eqn. (17) into eqns. (2), we obtain the following ordinary differential equations for a and b:

$$\frac{da}{dt} = F_1 a + G_1 b + H_1(t) \tag{18a}$$

$$\frac{db}{dt} = F_2 a + G_2 b + H_2(t) \tag{18b}$$

where

$$F_1 = -N_0 \left\{ \frac{1}{1 + 1/M_0 + 1/M_1} + \phi^2 \sum_{n=0}^{\infty} \frac{[K_n'(0;\xi_n)]^2}{\xi_n^2(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} + \right.$$
$$\left. - \frac{1}{1 + 1/M_0 + 1/M_1} \sum_{n=0}^{\infty} \frac{[N_1 K_n'(1;\xi_n) + N_0 K_n'(0;\xi_n)] K_n'(0;\xi_n)}{\xi_n^2(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} \right\} \tag{19a}$$

$$G_1 = N_0 \left\{ \frac{1}{1 + 1/M_0 + 1/M_1} + \phi^2 \sum_{n=0}^{\infty} \frac{K_n'(1;\xi_n) K_n'(0;\xi_n)}{\xi_n^2(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} + \right.$$
$$\left. - \frac{1}{1 + 1/M_0 + 1/M_1} \sum_{n=0}^{\infty} \frac{[N_1 K_n'(1;\xi_n) + N_0 K_n'(0;\xi_n)] K_n'(0;\xi_n)}{\xi_n^2(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} \right\} \tag{19b}$$

$$H_1(t) = N_0 \sum_{n=0}^{\infty} \frac{[\beta K_n'(1;\xi_n) - \alpha K_n'(0;\xi_n)] K_n'(0;\xi_n) \exp[-(\xi_n^2 + \phi^2)t]}{(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} \tag{19c}$$

$$F_2 = N_1 \left\{ \frac{1}{1 + 1/M_0 + 1/M_1} + \phi^2 \sum_{n=0}^{\infty} \frac{K_n'(1;\xi_n) K_n'(0;\xi_n)}{\xi_n^2(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} + \right.$$
$$\left. - \frac{1}{1 + 1/M_0 + 1/M_1} \sum_{n=0}^{\infty} \frac{[N_1 K_n'(1;\xi_n) + N_0 K_n'(0;\xi_n)] K_n'(1;\xi_n)}{\xi_n^2(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} \right\} \tag{19d}$$

$$G_2 = -N_1 \left\{ \frac{1}{1 + 1/M_0 + 1/M_1} + \phi^2 \sum_{n=0}^{\infty} \frac{[K_n'(1;\xi_n)]^2}{\xi_n^2(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} + \right.$$
$$\left. - \frac{1}{1 + 1/M_0 + 1/M_1} \sum_{n=0}^{\infty} \frac{[N_1 K_n'(1;\xi_n) + N_0 K_n'(0;\xi_n)] K_n'(1;\xi_n)}{\xi_n^2(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} \right\} \tag{19e}$$

$$H_2(t) = N_1 \sum_{n=0}^{\infty} \frac{[\alpha K_n'(0;\xi_n) - \beta K_n'(1;\xi_n)] K_n'(1;\xi_n) \exp[-(\xi_n^2 + \phi^2)t]}{(\xi_n^2 + \phi^2)\langle K_n, K_n \rangle} \tag{19f}$$

Equations (18) are coupled linear ordinary differential equations with respect to time and their solutions are

$$\begin{bmatrix} a(t) \\ b(t) \end{bmatrix} = e^{At} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} + \int_0^t e^{A(t-s)} \begin{bmatrix} H_1(s) \\ H_2(s) \end{bmatrix} ds \tag{20}$$

where

$$A = \begin{bmatrix} F_1 & G_1 \\ F_2 & G_2 \end{bmatrix} \tag{21}$$

Equation (20) is the solution of the bulk reservoir concentrations. The solution for the intra-membrane concentration is then given in eqn. (17).

PERTURBATION SOLUTIONS: $N_0, N_1 \ll 1$

The parameters N_0 and N_1 are the ratios of the membrane volume to that of the two reservoirs, respectively. In most practical cases, these parameters are very small. Therefore, we shall make use of their smallness to obtain the asymptotic solutions by using the so-called two-timing technique.

For the two-timing technique to be applied, the physical system must inherently possess two time scales that are different in order of magnitude. With the assumption of N_0, $N_1 \ll 1$, this system, indeed, has two distinct time scales. One time scale, called the fast time scale, measures the fast change of intra-membrane concentration and the other, called the slow time scale, measures the slow change of concentration in the reservoirs. In quantitative terms, the fast time is t and the slow time is $\tilde{t} = N_0 t$.

Under the transformation of variables $(x, t) \rightarrow (x, t, \tilde{t})$, eqns. (1) and (2) become a new set of equations which are one order of magnitude higher than the order of the original equations. Then, by assuming that the dependent variables have asymptotic expansions in N_0 and substituting them into the new set of equations, we obtain a hierarchy of subproblems, the first two of which are:

$O(1)$:

$$\frac{\partial u_0}{\partial t} = \frac{\partial^2 u_0}{\partial x^2} - \phi^2 u_0 \tag{22a}$$

$$\frac{\partial a_0}{\partial t} = \frac{\partial b_0}{\partial t} = 0 \tag{22b}$$

$$u_0(x, 0, 0) = 0; \quad a_0(0, 0) = \alpha, \quad b_0(0, 0) = \beta \tag{22c}$$

$$\partial u_0(0, t, \tilde{t})/\partial x = M_0(u_0 - a_0) \tag{22d}$$

$$\partial u_0(1, t, \tilde{t})/\partial x = M_1(b_0 - u_0) \tag{22e}$$

$O(N_0)$:

$$\frac{\partial u_1}{\partial t} + \frac{\partial u_0}{\partial \tilde{t}} = \frac{\partial^2 u_1}{\partial x^2} - \phi^2 u_1 \tag{23a}$$

$$\frac{\partial a_1}{\partial t} + \frac{\partial a_0}{\partial \tilde{t}} = \frac{\partial u_0(0, t, \tilde{t})}{\partial x} \tag{23b}$$

$$\frac{\partial b_1}{\partial t} + \frac{\partial b_0}{\partial \tilde{t}} = -\frac{N_1}{N_0} \frac{\partial u_0(1, t, \tilde{t})}{\partial x} \tag{23c}$$

$$u_1(x, 0, 0) = a_1(0, 0) = b_1(0, 0) = 0 \tag{23d}$$

$$\partial u_1(0, t, \tilde{t})/\partial x = M_0(u_1 - a_1) \tag{23e}$$

$$\partial u_1(1, t, \tilde{t})/\partial x = M_1(b_1 - u_1) \tag{23f}$$

Solutions to eqn. (22b) are

$$a_0(t, \tilde{t}) = \tilde{a}_0(\tilde{t}) \tag{24a}$$

$$b_0(t, \tilde{t}) = \tilde{b}_0(\tilde{t}) \tag{24b}$$

This implies that the variations of a_0 and b_0 are only measured in the slow time scale $\tilde{t}$. In other words, the fast time scale, t, is too fast to observe any change in the bulk concentrations.

Substituting eqns. (24) into the boundary conditions (22d) and (22c), we have

$$\partial u_0(0, t, \tilde{t})/\partial x = M_0[u_0(0, t, \tilde{t}) - \tilde{a}_0(\tilde{t})] \tag{25a}$$

$$\partial u_0(1, t, \tilde{t})/\partial x = M_1[\tilde{b}_0(\tilde{t}) - u_0(1, t, \tilde{t})] \tag{25b}$$

Since eqn. (22a) does not involve $\partial/\partial \tilde{t}$, $\tilde{a}_0(\tilde{t})$ and $\tilde{b}_0(\tilde{t})$ in eqns. (25) are regarded as constants. For such a case, we define the following ordinary finite integral transform:

$$u_{0n}^+ = \int_0^1 u_0(x, t, \tilde{t}) T_n(x; \zeta_n) \, dx \tag{26}$$

where the transform kernel $T_n(x; \zeta_n)$ is defined as

$$T_n(x; \zeta_n) = \cos(\zeta_n x) + \frac{M_0}{\zeta_n} \sin(\zeta_n x) \tag{27}$$

and the eigenvalues ζ_n are determined from the following transcendental equation:

$$\tan \zeta_n = \frac{(M_0 + M_1)\zeta_n}{\zeta_n^2 - M_0 M_1} \tag{28}$$

The first 20 roots of eqn. (28) are given in Table 1 for various combinations of parameters M_0 and M_1. It is noted that the transform kernel $T_n(x; \zeta_n)$ belongs to ordinary (or conventional) Sturm–Liouville eigenproblems which are distinguished from the general Sturm–Liouville eigenproblem defined in eqns. (5) and (8).

Applying transform (26) to eqn. (22a), and integrating by parts twice where necessary, we obtain an ordinary differential equation for

TABLE 1

The first 20 eigenvalues of the transcendental equation (28)

n	ζ_n	
	$M_0 = M_1 = 100$	$M_0 = M_1 = 200$
1	3.080012	3.110490
2	6.160138	6.220995
3	9.240491	9.331530
4	12.321183	12.442110
5	15.402319	15.552748
6	18.484002	18.663460
7	21.566328	21.774260
8	24.649389	24.885162
9	27.733267	27.996179
10	30.818037	31.107326
11	33.903768	34.218615
12	36.990519	37.330058
13	40.078341	40.441668
14	43.167279	43.553458
15	46.257368	46.665438
16	49.348636	49.777619
17	52.441105	52.890012
18	55.534788	56.002626
19	58.629695	59.115472
20	61.725827	62.228557

u_0^+ in transform space where the solution for u_0^+ can be obtained as

$$u_{0n}^+(\zeta_n; t, \tilde{t}) = -\tilde{b}_0(\tilde{t}) \frac{T_n'(1; \zeta_n)}{\zeta_n^2 + \phi^2} +$$

$$+ \tilde{a}_0(\tilde{t}) \frac{T_n'(0; \zeta_n)}{\zeta_n^2 + \phi^2} + F_0(\tilde{t}) \exp[-(\zeta_n^2 + \phi^2)t] \tag{29}$$

where $F_0(t)$ is an unknown function of long time.

The inverse of eqn. (29) follows immediately:

$$u_0(x, t, \tilde{t}) = \frac{(\tilde{b}_0 - \tilde{a}_0)x}{1 + 1/M_0 + 1/M_1} +$$

$$+ \frac{\tilde{a}_0(1 + M_1) + \tilde{b}_0 M_1/M_0}{1 + M_1 + M_1/M_0} +$$

$$+ \phi^2 \sum_{n=0}^{\infty} \frac{\tilde{b}_0 T_n'(1; \zeta_n) - \tilde{a}_0 T_n'(0; \zeta_n) T_n(x; \zeta_n)}{\zeta_n^2(\zeta_n^2 + \phi^2)(T_n, T_n)} +$$

$$+ \sum_{n=0}^{\infty} \frac{F_0(\tilde{t}) T_n(x; \zeta_n) \exp[-(\zeta_n^2 + \phi^2)t]}{(T_n, T_n)} \tag{30}$$

where

$$(T_n, T_n) = \int_0^1 T_n^2(s; \zeta_n) \, dx \tag{31a}$$

or

$$(T_n, T_n) = \frac{1}{2} \left[1 + \left(\frac{M_0}{\zeta_n}\right)^2 \right] +$$

$$+ \frac{1}{4\zeta_n} \left[1 - \left(\frac{M_0}{\zeta_n}\right)^2 \right] \sin(2\zeta_n) +$$

$$+ \frac{M}{2\zeta_n^2} [1 - \cos(2\zeta_n)] \tag{31b}$$

Substituting eqn. (30) into eqns. (23b) and (23c) and eliminating the secular terms, which are unbounded for large time t, we obtain

$$\frac{d\tilde{a}_0}{dt} = -(\theta + W)\tilde{a}_0 + (\theta + Y)\tilde{b}_0 \tag{32a}$$

$$\frac{N_0}{N_1} \frac{d\tilde{b}_0}{dt} = (\theta + Y)\tilde{a}_0 - (\theta + Z)\tilde{b}_0 \tag{32b}$$

with

$$\tilde{t} = 0; \quad \tilde{a}_0 = \alpha, \quad \tilde{b}_0 = \beta \tag{32c}$$

where

$$\theta = (1 + 1/M_0 + 1/M_1)^{-1} \tag{33a}$$

$$W = \phi^2 \sum_{n=0}^{\infty} \frac{[T_n'(0; \zeta_n)]^2}{\zeta_n^2(\zeta_n^2 + \phi^2)(T_n, T_n)} \tag{33b}$$

$$Z = \phi^2 \sum_{n=0}^{\infty} \frac{[T_n'(1; \zeta_n)]^2}{\zeta_n^2(\zeta_n^2 + \phi^2)(T_n, T_n)} \tag{33c}$$

$$Y = \phi^2 \sum_{n=0}^{\infty} \frac{T_n'(0; \zeta_n) T_n'(1; \zeta_n)}{\zeta_n^2(\zeta_n^2 + \phi^2)(T_n, T_n)} \tag{33d}$$

Solutions to eqns. (32) are:

$$\tilde{a}_0 = C_1 \exp(r_1 \tilde{t}) + C_2 \exp(r_2 \tilde{t}) \tag{34a}$$

and

$$\tilde{b}_0 = [d\tilde{a}_0/d\tilde{t} + (\theta + W)\tilde{a}_0](\theta + Y)^{-1} \tag{34b}$$

where

$$C_2 = [\alpha r_1 + \alpha(\theta + W) - \beta(\theta + Y)] \Delta^{-1/2} \tag{35a}$$

$$C_1 = [-\alpha r_2 - \alpha(\theta + W) + \beta(\theta + Y)] \Delta^{-1/2} \tag{35b}$$

$$r_{1,2} = \{-[\theta + W + (N_1/N_0)(\theta + Z)] \pm \sqrt{\Delta}\}/2 \tag{35c}$$

$$\Delta = [\theta + W - (N_1/N_0)(\theta + Z)]^2 +$$

$$+ 4(N_1/N_0)(\theta + Y)^2 \tag{35d}$$

Equations (34) are the solutions of the bulk concentrations in the two reservoirs. They can be used to estimate either the effective diffusivities or the chemical reaction rate constant inside the membrane. For the purpose of parameter estimation, an experiment can be designed in which the reservoir at $x = 1$ is infinite ($N_1 = 0$) and its concentration is zero ($\beta = 0$). In such a case, eqn. (34) becomes

$$\tilde{a}_0 = \alpha \exp[-(\theta + W)\tilde{t}] \qquad (36)$$

Therefore, a plot of $\ln(\tilde{a}_0/\alpha)$ versus slow time $\tilde{t}$ will give a straight line of which the slope is $-(\theta + W)$. Knowing the degree of mixing in the two reservoirs (i.e., M_0, M_1 are known), the kernel $T_n(x;\xi_n)$ and its eigenvalues ξ_n are determined. Therefore ϕ^2 can be readily calculated from eqn. (33b). Alternatively, ϕ can be determined graphically in Fig. 1 with W obtained from the slope of $\ln(\tilde{a}_0/\alpha)$ versus time $\tilde{t}$.
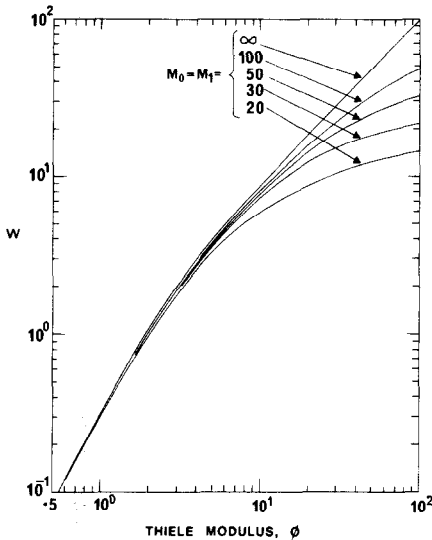

Fig. 1. Plots of W (eqn. (33b)) versus Thiele modulus ϕ, with Biot numbers M_0 and M_1 in the two reservoirs as parameters.

The unknown long time function $F_0(\tilde{t})$ of the expression for the intra-membrane concentration given in eqn. (29) can be found by taking the transform of eqn. (23a), substituting eqn. (29) into the resulting transform and eliminating the secular terms. The result is

$$F_0(\tilde{t}) = \frac{[\beta T'_n(1;\xi_n) - \alpha T'_n(0;\xi_n)]\,\exp(-\delta_n\tilde{t})}{\xi_n^2 + \phi^2} \qquad (37a)$$

where

$$\delta_n = \frac{[T'_n(0;\xi_n)]^2 + (N_1/N_0)[T'_n(1;\xi_n)]^2}{(\xi_n^2 + \phi^2)(T_n, T_n)} \qquad (37b)$$

DISCUSSION

The effect of the degree of chemical reaction and the initial reservoir concentrations α and β on the transient response of the bulk concentrations a and b versus long time Nt are shown in Figs. 2 and 3, respectively.

The following parameters are used in generating Fig. 2: $M_0 = M_1 = 100; N_0 = N_1 = 0.1; \alpha = 0.1; \beta = 1;$ and $\phi = 0.2, 0.5, 1, 2, 5$. As is shown in Fig. 2, the reservoir concentration a rises to a maximum and eventually decays to zero for small values of the Thiele modulus. This is so because the concentration difference between the two reservoirs, to which the overall diffusive flux between the two reservoirs is related, overcomes the chemical reaction inside the membrane during the initial period. However, after the reservoir concentration $a(t)$ rises to a certain level, the concentration difference between the two reservoirs decreases, the chemical reaction inside the membrane eventually dominates and, therefore, the reservoir concentration $a(t)$ decreases.

For the case of fast reaction ($\phi = 5$), the reservoir concentration $a(t)$ decreases monotonically at all times because the concentration difference between the two reservoirs is not great enough to overcome the fast chemical reaction inside the membrane.

Figure 3 shows the effect of the initial concentration α while other parameters remain constant ($M_0 = M_1 = 100; N_0 = N_1 = 0.1; \phi = 1; \beta = 1$). A similar argument as for Fig. 2 is applicable in this case. For the same degree of chemical reaction inside the membrane, increase in the initial reservoir concentration α reduces the concentration difference between the two reservoirs and, therefore, eliminates the rise of the reservoir concentration $a(t)$.

CONCLUSION

We have presented in this paper a formalism of solutions of a reactive membrane
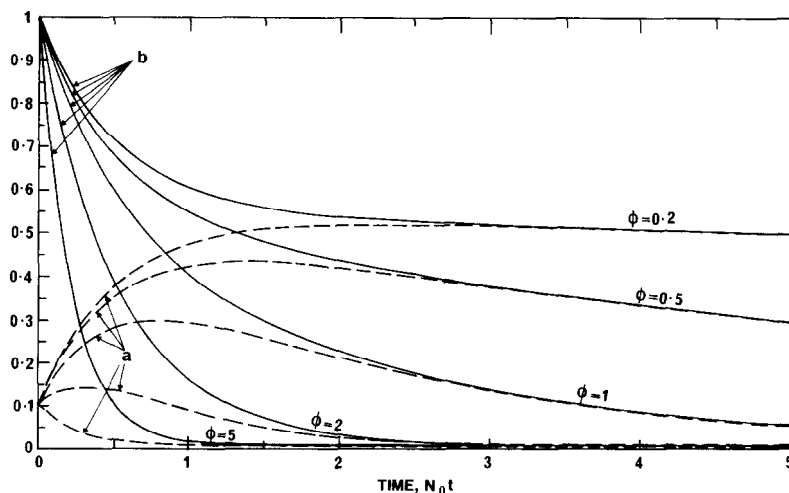
Fig. 2. Plots of the reservoir concentrations a (broken curves) and b (full curves) versus long time $N_0 t$ for $M_0 = M_1 = 100$, $N_0 = N_1 = 0.1$, $\alpha = 0.1$ and $\beta = 1$.
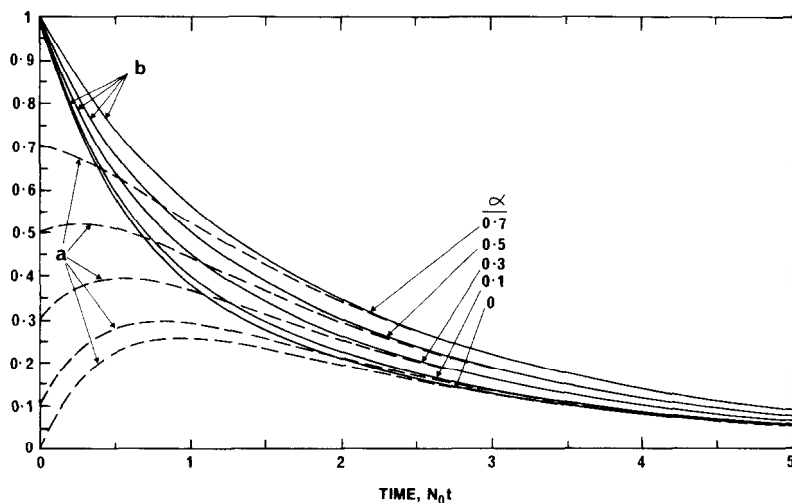

Fig. 3. Plots of the reservoir concentrations a (broken curves) and b (full curves) versus long time $N_0 t$ for $M_0 = M_1 = 100$, $N_0 = N_1 = 0.1$, $\phi = 1$ and $\beta = 1$.

bounded by two finite reservoirs. A generalized Sturm–Liouville integral transform is applied to obtain solutions, but in most practical cases in which either the membrane is thin or the reservoir is large, an ordinary Sturm–Liouville integral transform, which is simpler than its generalized counterpart, is used to obtain solutions. Solutions obtained in this way can be used to estimate either the effective diffusivity or the chemical reaction rate constant of the membrane.

NOMENCLATURE

a nondimensional reservoir concentration at $x = 0$

A matrix, defined in eqn. (21)

b nondimensional reservoir concentration at $x = 1$

c_n coefficient, defined in eqn. (13)

C_1, C_2 defined in eqns. (35a, b)

f auxiliary function, defined in eqn. (11)

f_n^* integral transform of f

F_0 long time function

F_1, F_2 defined in eqns. (18) and (19)

G_1, G_2 defined in eqns. (18) and (19)

H_1, H_2 defined in eqns. (18) and (19)

K_n transform kernel

M_0, M_1 Biot number for mass transfer

N_0, N_1 ratio of membrane volume to that of reservoirs

r_1, r_2 characteristic roots, defined in eqn. (35c)

T_n transform kernel

Greek symbols

α initial reservoir concentration at $x = 0$

β initial reservoir concentration at $x = 1$

δ_n defined in eqn. (37b)

Δ defined in eqn. (35d)

ζ_n eigenvalue

θ defined in eqn. (33a)

ξ_n eigenvalue

ϕ^2 Thiele modulus

Other symbols

$(,)$ defined in eqn. (31)

$\langle , \rangle$ defined in eqn. (14)

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