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Kinetic model for membrane transport

1. Effects of membrane volume and partitioning kinetics

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Equations for the transport of solutes through a membrane are derived, taking into account both the membrane volume and the partitioning kinetics, and have been found to involve two rate constants for solute transport, namely, those corresponding to solute transport from the solution to the membrane (k_1) and from the membrane to the solution (k_2). The time course followed before partitioning equilibrium has been attained, which is usually ignored, is shown to depend strongly on the relative magnitudes of k_1 and k_2.

1. Introduction

A number of studies have been reported on the kinetics of solute transport through membranes [1–4]. When a membrane which is permeable to solutes separates two solutions, 1 and 2, the time course of the variation in solute concentrations in the respective solutions under steady-state conditions [2] is often described by (see, e.g., ref. 1):

$$V_1 \frac{dC_1(t)}{dt} = -PA(C_1(t) - C_2(t)), \quad (1)$$

$$V_2 \frac{dC_2(t)}{dt} = -PA(C_2(t) - C_1(t)), \quad (2)$$

where A represents the membrane area, P the permeability coefficient of the solute, $C(t)$ the solute concentration at time t, V the solution volume and subscripts 1 and 2 refer to solutions 1 and 2, respectively. Under the initial conditions

$$C_1(0) = C_0, \quad (3)$$

$$C_2(0) = 0, \quad (4)$$

the solution to eqs. 1 and 2 gives

$$C_1(t) = C_0(\phi e^{-at} + 1 - \phi), \quad (5)$$

$$C_2(t) = C_0(1 - \phi)(1 - e^{-at}), \quad (6)$$

where

$$\phi = V_2/(V_1 + V_2) \quad (7)$$

is the volume fraction of solution 2 and a is defined by

$$a = PA(1/V_1 + 1/V_2). \quad (8)$$

Note that eqs. 5 and 6 satisfy the following relationship:

$$V_1C_1(t) + V_2C_2(t) = V_1C_0 \quad (9)$$

Eq. 9 does not involve the membrane volume,

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which means that eqs. 1 and 2 are applicable only in the case where the membrane is sufficiently thin to justify the assumption of the amount of solute within the membrane being negligible. Also, in eqs. 1 and 2, the partition coefficient, K, of the solute between the solution phases and the membrane phase is incorporated solely into the permeability coefficient, i.e., $P = KD/d$ (D, diffusion coefficient of solute; d, thickness of membrane), which implies that thermodynamic equilibrium with respect to partitioning of solute is maintained. Although Zentner et al. [3] proposed an equation which takes into account the finite volume of membranes, their expression still assumes attainment of partitioning equilibrium to take place.

In the present paper, in order to study the initial stages of solute transport before partitioning equilibrium has been attained, we present a simple kinetic model for the entire time course of membrane transport, with the introduction of the average concentration of solutes in the membrane phase. This model takes into account appropriately both the finite volume of the membrane and the kinetics of partitioning without assuming equilibrium to be reached.

2. Theory

Consider transport of solute through a planar membrane of volume V_m separating two solutions (solutions 1 and 2), the volumes of which are V_1 and V_2, respectively (fig. 1). Let the concentrations of solute in solutions 1 and 2 at time t be $C_1(t)$ and $C_2(t)$, respectively, with the average concentration in the membrane phase being $C_m(t)$.

The time course of the variations in solute concentration may be described as follows,

$$V_1 \frac{dC_1(t)}{dt} = -k_1 C_1(t) + k_2 C_m(t) \tag{10}$$

$$V_2 \frac{dC_2(t)}{dt} = -k_1 C_2(t) + k_2 C_m(t) \tag{11}$$

$$V_m \frac{dC_m(t)}{dt} = k_1 (C_1(t) + C_2(t)) - 2k_2 C_m(t) \tag{12}$$

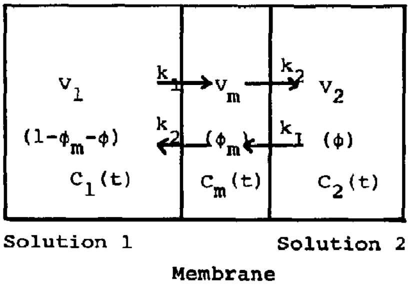

Fig. 1. A membrane of volume V_m separating two solutions, 1 and 2, whose volumes are V_1 and V_2, respectively. ϕ and ϕ_m, volume fractions of solution 2 and the membrane, respectively; $C_1(t)$, $C_2(t)$ and $C_m(t)$, solute concentrations of the respective phases; k_1 and k_2, rate constants.

where k_1 denotes the rate constant relating to transport of solute from the solution into the membrane phase, k_2 corresponding to that from the membrane phase to the solution.

The solutions to eqs. 10–12, subject to the initial conditions

$$C_1(0) = C_0 \tag{13}$$

$$C_2(0) = 0 \tag{14}$$

$$C_m(0) = 0 \tag{15}$$

are expressed as

$$\begin{aligned} \frac{C_1(t)}{C_0} = {} & \{1 - \phi - \phi_m\}/\{1 + (K-1)\phi_m\} \\ & + \{g(\phi + FK\phi_m)\exp(-f\alpha t) \\ & -f(\phi + GK\phi_m)\exp(-g\alpha t)\}/ \\ & \{(g-f)(1 + (K-1)\phi_m)\} \end{aligned} \tag{16}$$

$$\begin{aligned} \frac{C_2(t)}{C_0} = {} & \{1 - \phi - \phi_m\}/\{1 + (K-1)\phi_m\} \\ & \times (1 - \{g\exp(-f\alpha t) - f\exp(-g\alpha t)\}/ \\ & \{g - f\}) \end{aligned} \tag{17}$$

$$\begin{aligned} & \frac{C_m(t)}{C_0} \\ & = \{K(1 - \phi - \phi_m)\}/\{1 + (K-1)\phi_m\} \\ & \quad \times (1 - \{gF\exp(-f\alpha t) - fG\exp(-g\alpha t)\}/ \\ & \quad \{g - f\}) \end{aligned} \tag{18}$$

with

$$\alpha = \frac{k_1}{2}\left(\frac{1}{V_1} + \frac{1}{V_2}\right) = \frac{1-\phi_m}{2(1-\phi-\phi_m)\phi}\gamma \tag{19}$$

$$\gamma = k_1/(V_1 + V_2 + V_m) \tag{20}$$

$$\phi = V_2/(V_1 + V_2 + V_m) \tag{21}$$

$$\phi_m = V_m/(V_1 + V_2 + V_m) \tag{22}$$

$$K = k_1/k_2 \tag{23}$$

$$f = 1 + \frac{2\phi(1-\phi-\phi_m)}{K\phi_m(1-\phi_m)} - \left(\left(1 - \frac{2\phi}{1-\phi_m}\right)^2 + \left(\frac{2\phi(1-\phi-\phi_m)}{K\phi_m(1-\phi_m)}\right)^2\right)^{1/2} \tag{24}$$

$$g = 1 + \frac{2\phi(1-\phi-\phi_m)}{K\phi_m(1-\phi_m)} + \left(\left(1 - \frac{2\phi}{1-\phi_m}\right)^2 + \left(\frac{2\phi(1-\phi-\phi_m)}{K\phi_m(1-\phi_m)}\right)^2\right)^{1/2} \tag{25}$$

$$F = 1 - \frac{(1-\phi_m)f}{2(1-\phi-\phi_m)} \tag{26}$$

$$G = 1 - \frac{(1-\phi_m)g}{2(1-\phi-\phi_m)} \tag{27}$$

where ϕ and ϕ_m denote the volume fractions of solution 2 and the membrane, respectively, and K can be interpreted as the solute partition coefficient, since at equilibrium ($t \to \infty$) eqs. 16–18 yield:

$$C_m(\infty) = KC_1(\infty) = KC_2(\infty) \tag{28}$$

Note that eqs. 10–12 satisfy

$$V_1C_1(t) + V_2C_2(t) + V_mC_m(t) = V_1C_0 \tag{29}$$

which signifies that the total amount of solute remains constant throughout.

3. Results and discussion

We have derived a system of equations describing the time course for variation in solute concentrations in solutions 1 (eq. 16) and 2 (eq. 17) and within the membrane (eq. 18), which take into account both the membrane volume and the partitioning kinetics. It should be emphasized that these equations involve two different exponential functions of time t: $\exp(-\alpha ft)$ and $\exp(-\alpha gt)$. These functions represent the relaxation time for reaching equilibrium in each case. This contrasts with the fact that the conventional transport equations, eqs. 5 and 6, involve a single function of time, $\exp(-at)$. Since $f < g$, $\exp(-f\alpha t) > \exp(-g\alpha t)$, indicating that $\exp(-f\alpha t)$ corresponds to the slower relaxation while $\exp(-g\alpha t)$ refers to the faster one, as shown in fig. 2a. Fig. 2b demonstrates the effect of the partition coefficient

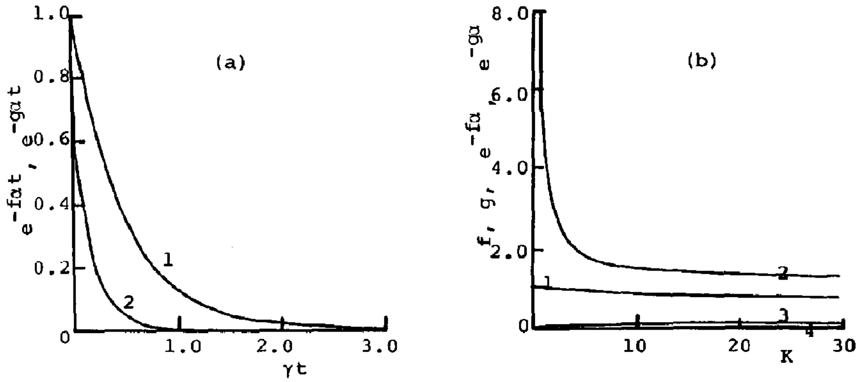

Fig. 2. (a) Relaxation of $\exp(-f\alpha t)$ and $\exp(-g\alpha t)$ as a function of γt, when $\phi = 0.2$, $\phi_m = 0.2$, $K = 10$. Curve 1, $\exp(-f\alpha t)$; curve 2, $\exp(-g\alpha t)$. (b) Effect of K on f (curve 1), g (curve 2), $e^{-f\alpha}$ (curve 3) and $e^{-g\alpha}$ (curve 4) when $\gamma t = 1$, $\phi = 0.5$, $\phi_m = 0.2$.

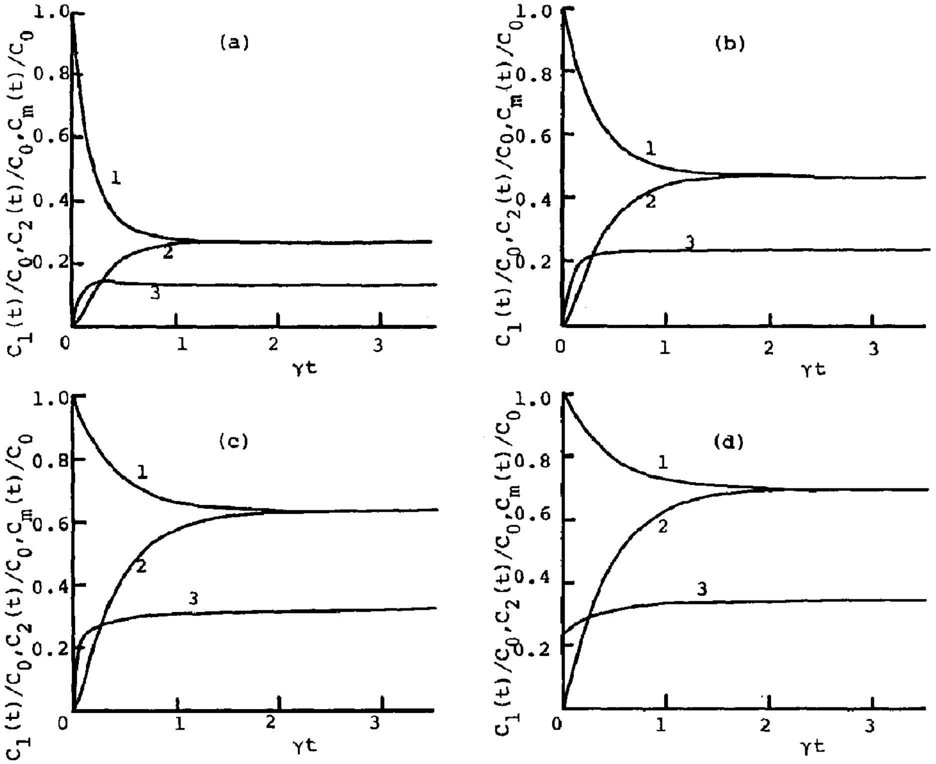

Fig. 3. Effect of ϕ_m on $C_1(t)/C_0$ (curve 1), $C_2(t)/C_0$ (curve 2) and $C_m(t)/C_0$ (curve 3) when $\phi = 0.3$, $K = 0.5$. ϕ_m: (a) 0.5, (b) 0.3, (c) 0.1, (d) 0.01.

on the values of f, g, $e^{-f\alpha t}$ and $e^{-g\alpha t}$ ($\gamma t = 1$). α remains unaffected by K and is always greater than zero, as indicated by eqs. 19 and 20. In the case of K decreasing to 0, f tends to 1 and g to ∞. Also, for K increasing, with f and g becoming smaller, $e^{-f\alpha}$ and $e^{-g\alpha}$ increase, demonstrating that both the slow and fast relaxation times grow longer. In the situation where K tends to zero, eqs. 16 and 17 simplify to forms that do not contain $\exp(-g\alpha t)$ although they do involve $\exp(-f\alpha t)$ (described below; eqs. 43 and 44). Assuming that $\phi_m = 0$ and $f = 1$, these equations can be further reduced to yield eqs. 5 and 6, indicating that in this situation $\exp(-f\alpha t)$ corresponds to $\exp(-\alpha t)$ in the conventional equations, as described later on in the present paper (eqs. 33 and 34).

In order to determine the general features of eqs. 16–18, we consider several limiting cases.

3.1. $\phi_m \rightarrow 0$

The time courses of $C_1(t)/C_0$, $C_2(t)/C_0$ and $C_m(t)/C_0$ depend on the membrane volume, V_m.

As shown in fig. 3, as time elapses, $C_1(t)/C_0$ and $C_2(t)/C_0$ reach the same value, and $C_m(t)/C_0$ tends to the value of $C_1(\infty)/C_0$ (or $C_2(\infty)/C_0$) multiplied by K. On the membrane fraction decreasing, $C_1(\infty)/C_0$ and $C_2(\infty)/C_0$ increase, and both $C_1(t)/C_0$ and $C_2(t)/C_0$ attain a value of $1 - \phi$ at $t = \infty$ when $\phi_m = 0$, as shown in the following:

In the limiting case where V_m tends to zero, we have

$$f \rightarrow 1 \qquad (30)$$

$$g \rightarrow \infty \qquad (31)$$

so that

$$C_m(t) = 0 \qquad (32)$$

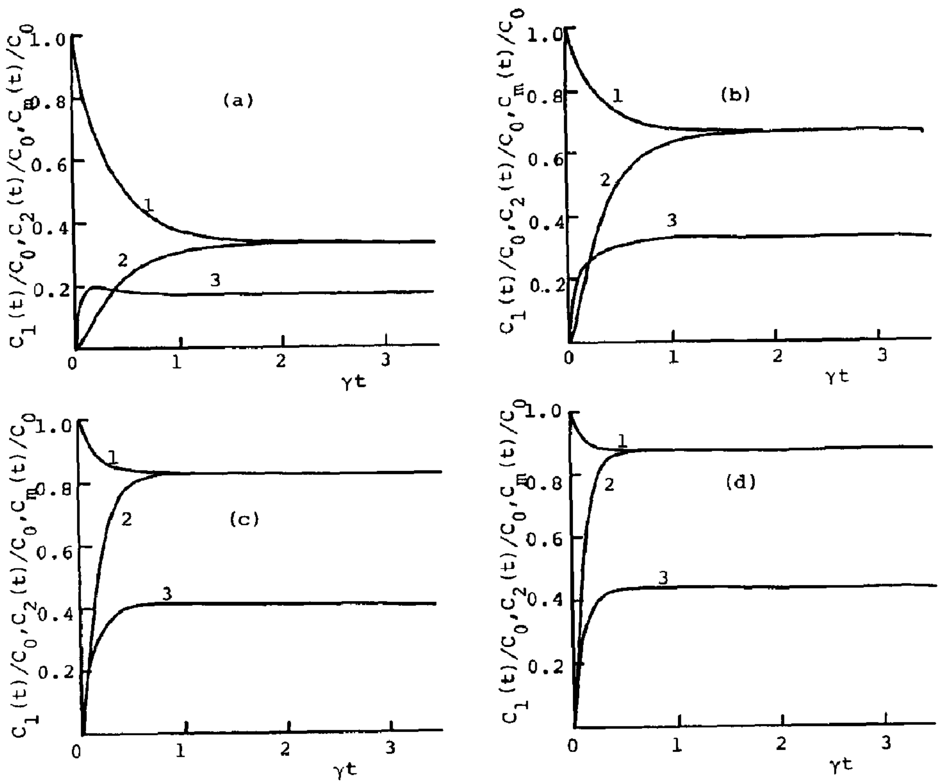

Fig. 4. Effect of ϕ on $C_1(t)/C_0$ (curve 1), $C_2(t)/C_0$ (curve 2) and $C_m(t)/C_0$ (curve 3) when $\phi_m = 0.2$, $K = 0.5$. ϕ: (a) 0.5, (b) 0.2, (c) 0.05, (d) 0.01.

and

$$\frac{C_1(t)}{C_0} = \phi \exp(-\alpha t) + 1 - \phi \tag{33}$$

$$\frac{C_2(t)}{C_0} = (1 - \phi)(1 - \exp(-\alpha t)) \tag{34}$$

As expected, when V_m is sufficiently small such that it may be ignored, eqs. 16 and 17 can be reduced to eqs. 33 and 34, respectively, which are of the same form as the commonly used membrane transport equations (eqs. 5 and 6). Comparison of eqs. 33 and 34 with eqs. 5 and 6 yields

$$\alpha = a \tag{35}$$

In addition, from eqs. 8 and 19,

$$k_1 = 2PA \tag{36}$$

Eq. 36 connects the conventional model with the present model, as discussed later in this article.

3.2. $\phi \to 0$

In the limiting case where the volume of solution 2 is zero, a situation arises where only the partitioning kinetics for solute from solution 1 into the membrane phase is considered. Fig. 4 depicts the influence of the volume fraction of solution 2 on $C_1(t)/C_0$, $C_2(t)/C_0$, and $C_m(t)/C_0$. The smaller the volume fraction of solution 2, the more rapid are the changes in $C_1(t)$, $C_2(t)$, and $C_m(t)$ with time γt, and, as a consequence, the duration of the period preceding attainment of equilibrium with regard to the solute concentrations in each of the respective phases becomes shorter.

In the limit of zero volume for solution 2, we obtain

$$C_2(t)=0 \tag{37}$$

and

$$\frac{C_1(t)}{C_0}=\frac{1-\phi_{\rm m}}{1+(K-1)\phi_{\rm m}}+\frac{K\phi_{\rm m}\exp(-\beta t)}{1+(K-1)\phi_{\rm m}} \tag{38}$$

$$\frac{C_{\rm m}(t)}{C_0}=\frac{K(1-\phi_{\rm m})}{1+(K-1)\phi}(1-\exp(-\beta t)) \tag{39}$$

where

$$\beta=k_1\left(\frac{1}{V_1}+\frac{1}{KV_{\rm m}}\right)=\frac{1+\phi_{\rm m}(K-1)}{K(1-\phi_{\rm m})\phi_{\rm m}}\gamma \tag{40}$$

Eq. 40 shows that the effective membrane volume is $KV_{\rm m}$. Apparently, from eq. 37, when $V_2=0$ and $t\to\infty$, $C_1(t)/C_0$ reaches a value of $(1-\phi_{\rm m})/(1+(K-1)\phi_{\rm m})$, and $C_{\rm m}(t)/C_0$ becomes equal to $C_1(\infty)/C_0$ multiplied by K.

3.3. $K\to 0$

In the limiting case where the partition coefficient, K, is very small, we again have

$$f=1-\frac{K\phi_{\rm m}(1-2\phi-\phi_{\rm m})^2}{4\phi(1-\phi_{\rm m})(1-\phi-\phi_{\rm m})}+O(K^2) \tag{41}$$

$$g=\frac{4\phi(1-\phi-\phi_{\rm m})}{\phi_{\rm m}(1-\phi_{\rm m})K}+O(1) \tag{42}$$

so that

$$\frac{C_1(t)}{C_0}=1-\frac{\phi}{1-\phi_{\rm m}}+\frac{\phi}{1-\phi_{\rm m}}\exp(-f\alpha t) \tag{43}$$

$$\frac{C_2(t)}{C_0}=\left(1-\frac{\phi}{1-\phi_{\rm m}}\right)(1-\exp(-f\alpha t)) \tag{44}$$

$$C_{\rm m}(t)=\frac{K(1-\phi-\phi_{\rm m})}{1-\phi_{\rm m}}\times\left(1-\frac{1-2\phi-\phi_{\rm m}}{2(1-\phi-\phi_{\rm m})}\exp(-f\alpha t)-\frac{1-\phi_{\rm m}}{2(1-\phi-\phi_{\rm m})}\exp(-g\alpha t)\right) \tag{45}$$

Eqs. 43 and 44 are formally equivalent to eqs. 5 and 6, respectively, since $\phi/(1-\phi_{\rm m})=V_2/(V_1+V_2)$.

However, it should be stressed that the effect of a finite volume $V_{\rm m}$ remains a contributory factor that may not be disregarded even when K is very small. In the case where $K\to 0$, f being equal to unity, and α decreases without extrema concomitant with $\phi_{\rm m}$ diminishing as described above, then $e^{-f\alpha}$ decreases as $\phi_{\rm m}$ becomes greater for the case where K is small. Therefore, the length of time required for the solute concentrations in the respective phases to reach equilibrium decreases with increasing $\phi_{\rm m}$.

Fig. 5 demonstrates that when k_2 increases, without k_1 being affected, the time period preceding the attainment of equilibrium by the solute concentration in the membrane diminishes (curve 3). Also, for $k_1=k_2$, the partitioning of solute between the membrane and solution phases reaches equilibrium at a much slower rate as compared to when $k_1/k_2=0.01$. In contrast, the time span corresponding to the case where the solute concentrations in both solution phases become equal in value is scarcely affected by the increase in k_2 (curves 1 and 2). The explanation is as follows: when K is small, f is altered to a lesser extent by K (eqs. 24 and 41) than is g (eqs. 25 and 42), as depicted in fig. 2b. $C_{\rm m}(t)/C_0$ includes both of the functions $\exp(-f\alpha t)$ and $\exp(-g\alpha t)$ (eq. 45) whereas $C_1(t)/C_0$ and $C_2(t)/C_0$ contain only a single exponential, $\exp(-f\alpha t)$ (eqs. 43 and 44). Consequently, the time required for the attainment of identical values of solute concentrations in solutions 1 and 2, being governed by $\exp(-f\alpha t)$, is now only weakly dependent on K. However, the corresponding period of time with respect to the membrane varies according to both $\exp(-f\alpha t)$ and $\exp(-g\alpha t)$, and hence behaves as a function of K. This time period shows its lowest value in the situation where $1-\phi-\phi_{\rm m}=\phi$.

3.4. $K\to\infty$

When the solute has a very large partition coefficient, if $1-\phi-\phi_{\rm m}>\phi$ (or $V_1>V_2$)

$$f\to\frac{2\phi}{1-\phi_{\rm m}} \tag{46}$$

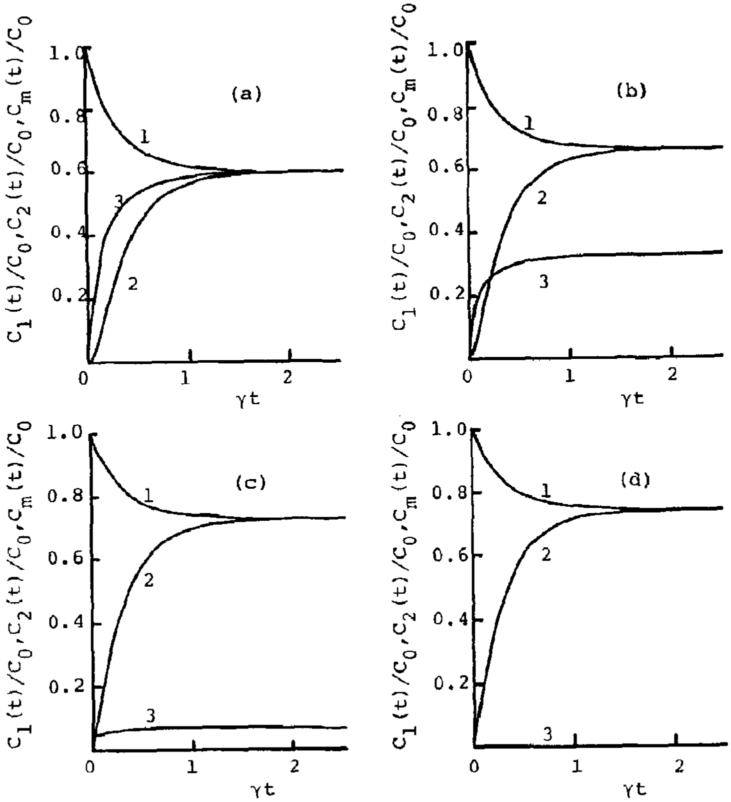

Fig. 5. Effect of K on $C_1(t)/C_0$ (curve 1), $C_2(t)/C_0$ (curve 2) and $C_m(t)/C_0$ (curve 3) when $\phi = 0.2$, and $\phi_m = 0.2$. K: (a) 1, (b) 0.5, (c) 0.1, (d) 0.01.

$$g \to 2\left(\frac{1-\phi-\phi_m}{1-\phi_m}\right) \tag{47}$$

and if $\phi > 1-\phi-\phi_m$ (or $V_2 > V_1$)

$$f \to 2\left(\frac{1-\phi-\phi_m}{1-\phi_m}\right) \tag{48}$$

$$g \to \frac{2\phi}{1-\phi_m} \tag{49}$$

and in both cases

$$\frac{C_1(t)}{C_0} = \exp(-2\phi\alpha t/(1-\phi_m)) \tag{50}$$

$$C_2(t) = 0 \tag{51}$$

$$\frac{C_m(t)}{C_0} = \frac{1-\phi-\phi_m}{\phi_m}(1-\exp(-2\phi\alpha t/(1-\phi_m)) \tag{52}$$

Eq. 51 indicates that, as a result of the high value of K, transport of solute is possible only in the direction from solution 1 to the membrane, and solute is unable to reach solution 2. At $t \to \infty$, all solute molecules are trapped within the membrane and no solute remains in solutions 1 and 2. Equilibrium of the partitioning between the membrane and solution phases cannot be attained unless the concentrations in solutions 1 and 2 have become identical, which is especially clear when $K > 1$. In other words, when $K > 1$, the usually employed assumption of partitioning being at equilibrium is not valid. From eqs. 51–53, it is apparent that the time interval required for the solute concentrations to reach equilibrium values becomes shorter as $1-\phi-\phi_m$ decreases, as illustrated by eq. 53:

$$-\frac{2\phi}{(1-\phi_m)}=-\frac{\gamma}{1-\phi-\phi_m} \tag{53}$$

3.5. $V_1 = V_2 = V$

In the case where the volumes of solutions 1 and 2 are equal ($V_1 = V_2 = V$), we have

$$f=1 \tag{54}$$

$$g=\frac{K\phi_m+1-\phi_m}{K\phi_m} \tag{55}$$

$$\frac{C_1(t)}{C_0}=\frac{1-\phi_m}{2(1+\phi_m(K-1))}+\tfrac{1}{2}\exp(-\alpha t)+\frac{K\phi_m}{2(1-\phi_m(K-1))}\times\exp(-(1+\phi_m(K-1))\alpha t/K\phi_m) \tag{56}$$

$$\frac{C_2(t)}{C_0}=\frac{1-\phi_m}{2(1+\phi_m(K-1))}-\tfrac{1}{2}\exp(-\alpha t)+\frac{K\phi_m}{2(1+\phi_m(K-1))}\times\exp(-(1+\phi_m(K-1))\alpha t/K\phi_m) \tag{57}$$

$$\frac{C_m(t)}{C_0}=\frac{K(1-\phi_m)}{2(1+\phi_m(K-1))}\times(1-\exp(-(1+\phi_m(K-1))\alpha t/K\phi_m)) \tag{58}$$

When $K\phi_m \ll 1$, g being greater than unity, the term involving $\exp(-g\alpha t)$ can be neglected, and hence eqs. 56–58 reduce to

$$\frac{C_1(t)}{C_0}=\tfrac{1}{2}(1+\exp(-\alpha t)) \tag{59}$$

$$\frac{C_2(t)}{C_0}=\tfrac{1}{2}(1-\exp(-\alpha t)) \tag{60}$$

$$\frac{C_m(t)}{C_0}=\frac{K}{2} \tag{61}$$

Eq. 61 indicates that

$$\frac{dC_m(t)}{dt}=0 \tag{62}$$

Hence, from eq. 12

$$C_m(t)=\frac{K}{2}(C_1(t)+C_2(t)) \tag{63}$$

$$\exp(-\alpha t)=\frac{2(C_1(t)(2V+KV_m)-VC_0)}{C_0(2V+KV_m)} \tag{64}$$

Eq. 64 is in agreement with the expression reported by Zentner et al. [3].

In the opposite case: $K\phi_m \gg 1$,

$$f\to 1 \tag{65}$$

$$g\to 1 \tag{66}$$

and

$$\frac{C_1(t)}{C_0}=\exp(-\alpha t) \tag{67}$$

$$\frac{C_2(t)}{C_0}=0 \tag{68}$$

$$\frac{C_m(t)}{C_0}=\frac{1-\phi_m}{2\phi_m}(1-\exp(-\alpha t)) \tag{69}$$

These equations signify that equilibrium for partitioning cannot be attained before the solute concentrations in both solutions have become equal when K is large. As described above, the lower the value of K, the smaller is the duration of time necessary for the solute concentrations to achieve equilibrium. In contrast, for $K\phi_m \ll 1$, with regard to the case for the membrane, this time span displays a minimum when $\phi = 1-\phi-\phi_m$.

3.6. *Relation of the conventional model to that of the present study*

As shown in eq. 36, the present model is related to the conventional model in terms of k_1 and P.

In the conventional model P is defined as

$$PA=\frac{V_1(dC_1(t)/dt)}{C_1(t)-C_2(t)} \tag{70}$$

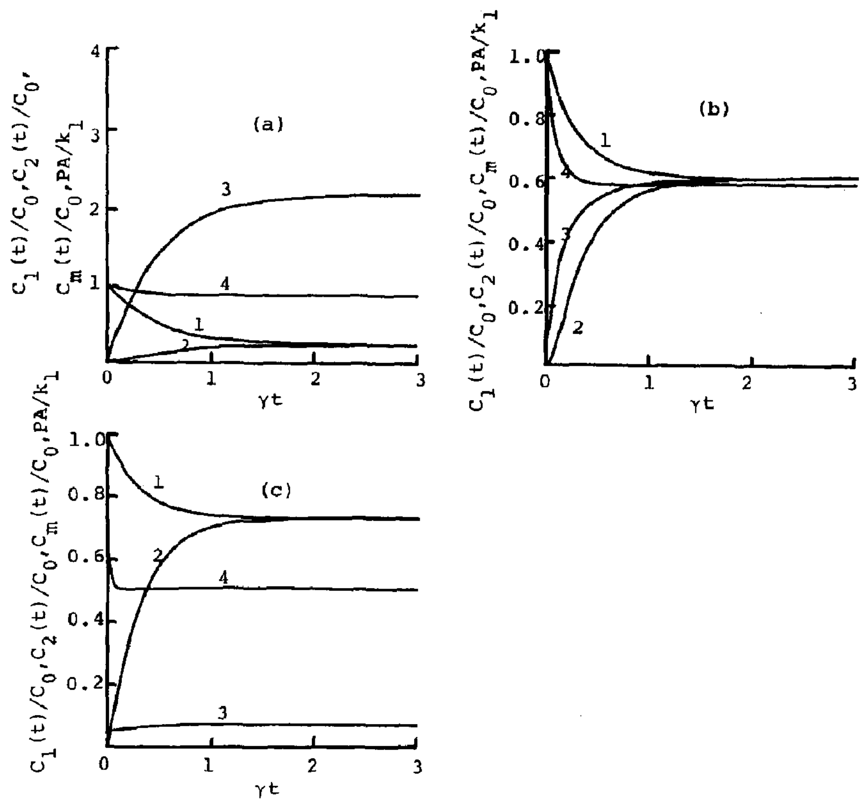

Fig. 6. Effect of K on $C_1(t)/C_0$ (curve 1), $C_2(t)/C_0$ (curve 2), $C_m(t)/C_0$ (curve 3) and PA/k_1 (curve 4) when $\phi = 0.2$ and $\phi_m = 0.2$. K: (a) 10, (b) 1, (c) 0.1.

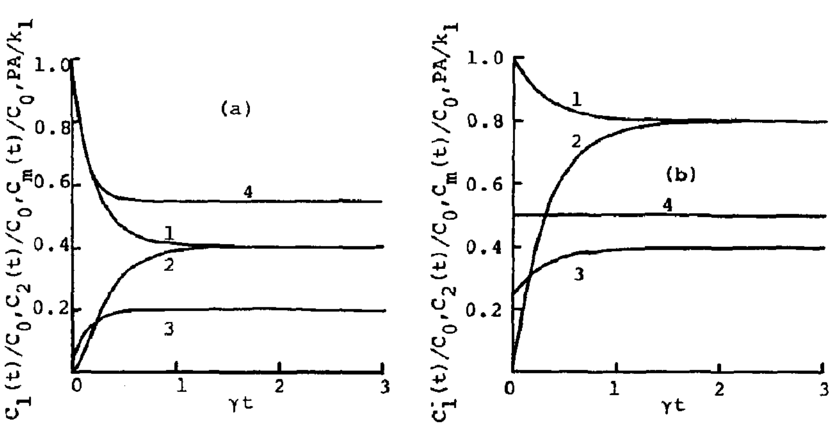

Fig. 7. Effect of ϕ_m on $C_1(t)/C_0$ (curve 1), $C_2(t)/C_0$ (curve 2), $C_m(t)/C_0$ (curve 3) and PA/k_1 (curve 4) when $\phi = 0.2$ and $K = 0.5$. ϕ_m: (a) 0.5, (b) 0.001.

Substituting eqs. 16 and 17 into eq. 70,

$$\begin{aligned} PA = k_1\big[&g(\phi + F(1-\phi-\phi_m+K\phi_m)) \\ &\times \exp(-f\alpha t) - f(\phi + G(1-\phi-\phi_m+K\phi_m)) \\ &\times \exp(-g\alpha t)\big]/\big[g(FK\phi_m - \phi_m + 1)\exp(-f\alpha t) \\ &- f(GK\phi_m - \phi_m + 1)\exp(-g\alpha t)\big] \end{aligned} \tag{71}$$

P being a function of αt, when $t \to 0$

$$\frac{PA}{k_1} = 1 - \frac{1}{K}\frac{2(1-\phi-\phi_m)\phi\alpha t}{\phi_m(1-\phi_m)} + O(t^2) \tag{72}$$

When $t \to \infty$

$$\frac{PA}{k_1} \to 1 - \frac{(1-\phi-\phi_m)(1-F)}{FK\phi_m - \phi_m + 1} \tag{73}$$

Only when $K \to 0$ and $t \to \infty$ (fig. 6), or when $\phi_m = 0$ (fig. 7), does the following hold true:

$$PA = \frac{k_1}{2} \tag{74}$$

As shown in fig. 6, as K decreases the value of PA/k_1 at $\alpha t = \infty$ decreases to 0.5. At $\alpha t = \infty$, PA/k_1 tends to 0.872 when $K = 10$, 0.581 when $K = 1$, and 0.508 when $K = 0.1$. Fig. 7 also shows that if ϕ_m is very small, PA/k_1 drops sharply to 0.5.

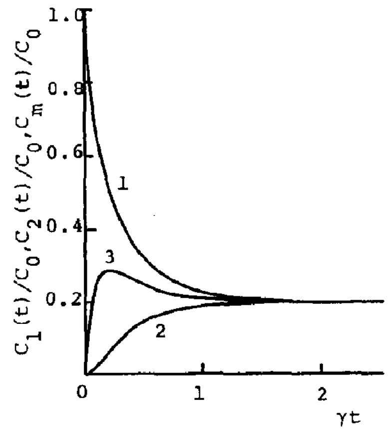

Fig. 8. Lag time during the increase in $C_2(t)/C_0$ and overshoot in $C_m(t)/C_0$. Curves 1–3 correspond to $C_1(t)/C_0$, $C_2(t)/C_0$, and $C_m(t)/C_0$, respectively.

3.7. *Initial stages of membrane transport*

Consider the initial stage of membrane transport,

$$\frac{C_1(t)}{C_0} = 1 - \frac{2\phi\alpha t}{1-\phi_m} + O(t^2) \tag{75}$$

$$\frac{C_2(t)}{C_0} = \frac{2\phi(1-\phi-\phi_m)^2}{(1-\phi_m)^2\phi_m}\frac{1}{K}\alpha^2 t^2 \tag{76}$$

$$\frac{C_m(t)}{C_0} = \frac{2\phi(1-\phi-\phi_m)}{(1-\phi_m)\phi_m}\alpha t + O(t^2) \tag{77}$$

It is interesting that the initial term in the expression for $C_2(t)$ is proportional to t^2, whereas those of $C_1(t)$ and $C_m(t)$ vary according to t. This property may be correlated with the lag time that is involved in the increase in solute concentration in solution 2 and the overshoot phenomenon that occurs with the membrane's solute level as depicted in fig. 8. The above-mentioned forms of behavior cannot be predicted on the basis of the conventional model and will be the subject of the second paper in this series of studies.

4. Conclusions

We have derived equations for the transport of solutes through a membrane, taking into account both membrane volume and partitioning kinetics. Unless the rate constant for the solute transport from the solution to the membrane (k_1) is much smaller relative to that from the membrane to the solution (k_2), equilibrium for the case of partitioning between the membrane and solution will be unattainable until the solute concentrations in both solution phases have reached an identical value, at variance with the conventionally accepted assumption of such equilibration taking place. For very high values of the ratio k_1/k_2, the aforementioned time span diminishes with decreasing volume fraction for the donor phase. By contrast, for k_1/k_2 of very small magnitude, the length of time required in the analogous situation for the membrane reaches its lowest value, whilst the values relating to the solution phases are at a peak when the volume of a donor solution phase is equal to that of the acceptor solution phase. Since k_2 decreases concomitantly with k_1 remaining constant, the period of time for reaching equilibrium for each of the respective phases lengthens. In some instances, a lag period was observed prior to the solute having reached the acceptor solution phase together with the solute concentration displaying behavior characteristic of the overshoot phenomenon in the membrane during the initial stages of permeation.

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