AN APPROXIMATE SOLUTION OF TRANSIENT DIFFUSION THROUGH LAMINATED MEMBRANES

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Approximate relations have been derived for the initial transient diffusion through laminated membranes of the AB or ABC type for boundary conditions corresponding to the time-lag method. It is shown that in the initial stages of diffusion the behaviour of laminated membranes can be approximated by hypothetical simple membranes of the same thickness, the diffusion and partition coefficient of which can be determined from the corresponding characteristics (and thicknesses) of the constituent layers.

Due to the importance of laminated structures as barriers preventing the undesired penetration of permeants in a number of applications (packaging technique, food technology, anticorrosion protection, health safety in dealing with harmful substances, and the like), considerable attention has been devoted in the literature to the phenomenology of diffusion through laminated membranes. Obviously, in the stationary state the diffusion flow is the same in all constituent layers of the lamina, and simple relations hold[1-4] between the permeation coefficient of the laminated structure and the respective diffusion (D_i) and solubility (S_i) parameters of the constituent layers. Assuming that for none of the layers the characteristics D_i, S_i are dependent on the concentration of the diffusant, relations have also been derived for the calculation of a quantity called time-lag for a number of structures important for practice: AB and ABA (Barrie and coworkers[5]), ABABAB... (Ash and coworkers[6]), ABC... (Ash and coworkers[2]). These data are sufficient to characterize the stationary diffusion through the laminated layer in an arrangement corresponding to the time-lag method[3,4]. On the other hand, comparatively little is known for laminated structures about the initial transient diffusion in the time-lag method or for other boundary conditions. For a lamina of the AB type an exact solution of transient diffusion has been derived[7] in the form of an infinite series containing roots of rather complicated transcendental equations, which therefore is not very convenient for practical calculations. For a symmetrical membrane of the ABA type the solution of transient diffusion has been derived[8] for the special case of a linear concentration gradient in both outer layers. A complete solution of transient diffusion in more complicated laminated structures meets with considerable mathematical difficulties and has not been offered yet. For some applications, however, the knowledge of the initial stages of permeation is of decisive importance, *e.g.* in the design of barriers against penetration of substances dangerous even in minute concentrations. On the contrary, in these cases the boundary conditions corresponding to the time-lag method are very well satisfied, and also the concentration dependence of the diffusion and partition coefficients can be safely neglected in approximate calculations.

In this study we derive approximate solutions to the problem of transient diffusion through laminated membranes of the AB or ABC type, valid for small times (before the stationary state is reached). It is shown that in this stage the composite membrane may be approximated by a hypothetical single layer, the characteristics of which (the diffusion and partition coefficients) may be calculated from the respective quantities (and thicknesses) of the constituent layers forming the real laminated membrane.

THEORETICAL

Let us consider only the arrangement used in the time-lag method, where the membrane (initially free of permeant) is exposed at time $t = 0$ on the one side to a medium in which the concentration is maintained at a constant level, while on the other side of the barrier the concentration remains virtually zero; all diffusion and partition coefficients are regarded as constant, concentration-independent quantities.

Membrane AB

In this case the boundary problem to be solved is described by equations

$$D_a \frac{\partial^2 C_a}{\partial x^2} = \frac{\partial C_a}{\partial t}, \tag{1}$$

$$D_b \frac{\partial^2 C_b}{\partial x^2} = \frac{\partial C_b}{\partial t} \tag{2}$$

with the boundary conditions

$$t = 0 \qquad 0 \leqq x \leqq a + b \qquad C_a = C_b = 0, \tag{3a}$$

$$t > 0 \qquad x = 0 \qquad C_a = 0, \tag{3b}$$

$$x = a \qquad D_a \frac{\partial C_a}{\partial x} = \frac{\partial C_b}{\partial x} D_b, \tag{3c}$$

$$x = a \qquad S_b \cdot C_a = S_a \cdot C_b, \tag{3d}$$

$$x = a + b \qquad C_b = S_b \cdot C_0, \tag{3e}$$

where D is the diffusion coefficient, C is concentration, x is the spatial coordinate perpendicular to the membrane surface, t is time and S is the partition coefficient. The indices refer to the two layers of the laminated membrane, a and b respectively are their thicknesses; C_0 is the (constant) concentration on one side of the membrane. Condition (*3c*) describes the continuity of flow at the boundary of both layers, while (*3d*) expresses the assumption that the local concentrations at the boundary satisfy the condition of thermodynamic equilibrium. The sought quantity is the overall amount of the permeant, $q_{ab}(t)$, which has passed through a unit area of the membrane at $x = 0$ from the beginning of the experiment,

$$q_{ab}(t) = \int_0^t D_a \left|\frac{\partial C_a(x, t')}{\partial x}\right|_{x=0} dt' . \quad (4)$$

This boundary-value problem is solved by the Laplace–Carson (L.–C.) integral transformation. Let us introduce L.–C. transforms of concentrations C_a, C_b by the equations

$$\mathscr{L}\{C_a(x, t)\} = s_a(x, p) = p \int_0^\infty e^{-pt} C_a(x, t)\, dt , \quad (5a)$$

$$\mathscr{L}\{C_b(x, t)\} = s_b(x, p) = p \int_0^\infty e^{-pt} C_b(x, t)\, dt . \quad (5b)$$

The solutions of the subsidiary equations are

$$s_a = U_a \cosh(x \sqrt{(p/D_a)}) + V_a \sinh(x \sqrt{(p/D_a)}) , \quad (6)$$

$$s_b = U_b \cosh(x \sqrt{(p/D_b)}) + V_b \sinh(x \sqrt{(p/D_b)}) . \quad (7)$$

The integration constants U_a, U_b, V_a, V_b must be determined from the boundary conditions (*3*).

For the transform $r_{ab}(p)$ of the sought quantity $q_{ab}(t)$ we have, in accordance with Eq. (*4*),

$$\mathscr{L}\{q_{ab}(t)\} = r_{ab}(p) = (D_a/p)(ds_a/dx)_{x=0} \quad (8)$$

which in view of the fact that $U_a = 0$ (*cf.* Eq. (*3b*)) and using (*6*) may be written as

$$r_{ab}(p) = V_a \sqrt{(D_a/p)} . \quad (9)$$

The integration constant V_a which is needed in Eq. (*9*) is determined by a straightforward but tedious algebra; the transform of the sought quantity thus becomes

$$r_{ab}(p) = \sqrt{\left(\frac{D_a D_b}{p}\right)} \frac{S_a S_b C_0}{S_b \sqrt{(D_b)} \sinh(\lambda_a a) \cosh(\lambda_b b) + S_a \sqrt{(D_a)} \sinh(\lambda_b b) \cosh(\lambda_a a)} , \quad (10)$$

where

$$\lambda_a = \sqrt{(p/D_a)} , \quad \lambda_b = \sqrt{(p/D_b)} .$$

Up to this point the procedure has been exact. Since, however, we seek an approximate solution valid for small times, let us utilize the properties of the L.–C. transformation and substitute in Eq. (*10*) for the hyperbolic functions their approximations valid for large values of the argument:

$$\sinh(x) \approx \cosh(x) \approx e^x/2 \quad (\text{for large } x)\,.$$

This gives an approximate resulting transform

$$r_{ab}(p) \cong \frac{4S_aS_bC_0}{S_b/\sqrt{D_a} + S_a/\sqrt{D_b}}\, p^{-1/2} \exp\left[-\left(\frac{a}{\sqrt{D_a}} + \frac{b}{\sqrt{D_b}}\right)\sqrt{p}\right] \tag{11}$$

which has its corresponding original in[9]

$$q_{ab}(t) = 2C_0(a + b)\,\bar{S}_{ab}\left[(1/\bar{\Psi}_{ab}\sqrt{\pi})\exp(-\bar{\Psi}_{ab}^2) - \operatorname{erfc}(\bar{\Psi}_{ab})\right], \tag{12}$$

where erfc is the error function complement, and we have introduced

$$\bar{\Psi}_{ab} = \frac{a + b}{2(\bar{D}_{ab}\,.\,t)^{1/2}}\,, \tag{12a}$$

$$(\bar{D}_{ab})^{1/2} = \frac{a + b}{a/\sqrt{D_a} + b/\sqrt{D_b}}\,, \tag{12b}$$

$$\bar{S}_{ab} = (\bar{D}_{ab})^{-1/2}\,\frac{2S_aS_b}{S_a/\sqrt{D_a} + S_b/\sqrt{D_b}}\,. \tag{12c}$$

The corresponding solution for a simple membrane with thickness l characterized by the diffusion coefficient D and the partition coefficient S may be written (ref.[9], p. 310) in the form

$$q(t) = 4SC_0\sqrt{(Dt)}\sum_{m=0}^{\infty}\operatorname{ierfc}\left[\frac{(2m + 1)\,l}{2\sqrt{(Dt)}}\right], \tag{13}$$

where the function ierfc is defined by the integral

$$\operatorname{ierfc}(z) = \int_z^{\infty}\operatorname{erfc}(x)\,\mathrm{d}x\,. \tag{14}$$

In an approximation for small times we restrict ourselves to the first term of the series in Eq. (*13*), and use the relation

$$\operatorname{ierfc}(z) = \pi^{-1/2} e^{-z^2} - z \operatorname{erfc}(z)$$

which is derived from Eq. (*14*) by integration by parts. This yields

$$q(t) = 2SC_0l[(1/\psi\sqrt{\pi})\exp(-\psi^2) - \operatorname{erfc}(\psi)]\,, \tag{15}$$

where we have introduced

$$\psi = l/2\sqrt{(Dt)}\,. \tag{15a}$$

A comparison between (*15*) and (*12*) reveals that in this approximation the laminated membrane AB behaves as a simple membrane characterized by the diffusion coefficient $\bar{D}_{ab}$ and by the partition coefficient $\bar{S}_{ab}$ which can be calculated from parameters of the two layers on the basis of Eqs (*12b*) and (*12c*).

Membrane ABC

Here, the problem is described by the equations

$$D_a \frac{\partial^2 C_a}{\partial x^2} = \frac{\partial C_a}{\partial t}\,, \tag{16}$$

$$D_b \frac{\partial^2 C_b}{\partial x^2} = \frac{\partial C_b}{\partial t}\,, \tag{17}$$

$$D_c \frac{\partial^2 C_c}{\partial x^2} = \frac{\partial C_c}{\partial t} \tag{18}$$

with the boundary conditions

$$t = 0 \quad 0 \leqq x \leqq a + b + c \quad C_a = C_b = C_c = 0\,, \tag{19a}$$

$$t > 0 \quad x = 0 \quad C_a = 0\,, \tag{19b}$$

$$x = a \quad D_a \frac{\partial C_a}{\partial x} = D_b \frac{\partial C_b}{\partial x}\,, \tag{19c}$$

$$S_b \,.\, C_a = S_a \,.\, C_b\,, \tag{19d}$$

$$x = a + b \qquad D_b \frac{\partial C_b}{\partial x} = D_c \frac{\partial C_c}{\partial x}\,, \tag{19e}$$

$$S_c \,.\, C_b = S_b \,.\, C_c\,, \tag{19f}$$

$$x = a + b + c \qquad C_c = S_c \,.\, C_0\,, \tag{19g}$$

in which the symbols represent an obvious extension of the preceding case. By employing a completely analogous procedure, we derive for the L.–C. transform of $q_{abc}(t)$ (which again represents the amount of the permeant which has passed through the unit area of the laminated membrane at $x = 0$) the formula

$$r_{abc}(p) = \mathscr{L}\{q_{abc}(t)\} = \frac{S_a S_b S_c \sqrt{(D_a D_b D_c)}\, C_0 p^{-1/2}}{S_b \sqrt{(D_b)} \sinh(\lambda_c c) \,.\, F + S_c \sqrt{(D_c)} \cosh(\lambda_c c) \,.\, G}\,, \tag{20}$$

where

$$F = \sqrt{(D_a)}\, S_a \,.\, \cosh(\lambda_a a) \cosh(\lambda_b b) + \sqrt{(D_b)}\, S_b \sinh(\lambda_a a) \sinh(\lambda_b b)\,, \tag{20a}$$

$$G = \sqrt{(D_a)}\, S_a \,.\, \cosh(\lambda_a a) \sinh(\lambda_b b) + \sqrt{(D_b)}\, S_b \sinh(\lambda_a a) \cosh(\lambda_b b) \tag{20b}$$

and the meaning of λ's is analogous to that in Eq. *(10)*.

An approximate calculation analogous to that used before gives, after inverse transformation,

$$q_{abc}(t) = 2(a + b + c)\, C_0\, \overline{S_{abc}} \left[\frac{1}{\sqrt{\pi}} \frac{1}{\overline{\psi_{abc}}} \exp\left(-\overline{\psi^2_{abc}}\right) - \operatorname{erfc}\left(\overline{\psi_{abc}}\right)\right], \tag{21}$$

where (in analogy to the earlier case)

$$\overline{\psi_{abc}} = \frac{a + b + c}{2\sqrt{(\overline{D_{abc}}\, t)}}\,, \tag{21a}$$

$$(\overline{D_{abc}})^{1/2} = \frac{a + b + c}{\dfrac{a}{\sqrt{D_a}} + \dfrac{b}{\sqrt{D_b}} + \dfrac{c}{\sqrt{D_c}}} \tag{21b}$$

and, eventually,

$$\overline{S_{abc}} = \frac{4\, S_a S_b S_c}{\dfrac{S_a S_b}{\sqrt{D_c}} + \dfrac{S_b S_c}{\sqrt{D_a}} + \dfrac{S_a S_c}{\sqrt{D_b}} + \dfrac{S_b^2 \sqrt{D_b}}{\sqrt{(D_a D_c)}}} \,.\, \frac{1}{\sqrt{\overline{D_{abc}}}}\,. \tag{21c}$$

Hence, also in this case we proved that in the initial stages of transient diffusion the laminated membrane ABC behaves as a simple barrier characterized by the diffusion coefficient $\overline{D_{abc}}$ and the partition coefficient $\overline{S_{abc}}$ which may be calculated from the parameters of the individual layers by means of Eqs (*21b*) and (*21c*).

RESULTS AND DISCUSSION

Both approximate solutions, Eqs (*12*) and (*21*), are based on the relation (*15*). Accordingly, the range of validity of approximation (*15*) was tested first: for a simple membrane the exact solution – Eq. (*13*) – was compared with the approximate formula (*15*). The results are summarized in Table I and indicate that Eq. (*15*) is an excellent approximation, not only throughout the initial stages of transient diffusion, but also rather deep in the range of the stationary state; usually, $\varphi = Dt/l^2 \simeq \simeq 0.45$ is taken as the transition value (ref.[4], p. 51).

When assessing the quality of the derived approximate relations at various combinations of parameters which characterize the constituent layers of a composite membrane, one must be able to determine the true time dependence of transient diffusion through laminated membranes of both types. Since, however, the exact solution[7] for lamina AB is not very convenient and no exact solution is known to exist for lamina ABC, the true quantities $q(t)$ have been calculated numerically, by a numerical inversion of the exact L.–C. transforms (10) or (20) employing the Gaver method[10,11]. The accuracy of this method is excellent as illustrated by Table I, where

TABLE I

Comparison of the exact course of diffusion through a simple membrane with the approximation according to Eq. (*15*) and with results of numerical inversion of the Laplace–Carson transform

Dt/l^2	$q(t)/2\,SC_0l$ (Eq. *13*)	Δq_{appr} [a] %	Δq_{inv} [b] %
0·101	0·004090	0·006	0·021
0·221	0·0386024	−0·002	0·001
0·293	0·0687869	−0·022	0·002
0·413	0·124886	−0·185	0·002
0·557	0·195582	−0·713	0·001
0·581	0·207494	−0·838	0·008

[a] Per cent deviation of approximate Eq. (*15*) from the exact course. [b] Per cent deviation of the value calculated by numerical inversion of the L.–C. transform from the exact course.

the last column contains deviations in per cent of values obtained by the numerical inversion of the L.–C. transform from the exact solution for the simple membrane.

All numerical calculations in this work were carried out using a desk-top, programmable computer Wang 2 200 B.

The accuracy of the derived approximate solution for the binary laminated membrane was tested for a number of combinations of the input parameters (D_a, D_b, S_a, S_b, a, b) shown in Table II. Since the main region of application of the approximate relation (*12*) may be expected in the interval before the stationary state is reached (as already mentioned, the position of the straight line characterizing the stationary diffusion may be found by using known relations for the permeation coefficient of the laminated membrane – the slope of the straight line – and for the time-lag – its intercept with the time axis), in the interactive mode of calculation with the desk-top minicomputer the computation was interrupted as soon as the slope of $q(t)$ obtained by numerical inversion of the L.–C. transform (10) stabilized to four digits. The corresponding time of onset of the steady state is denoted by t_s; the diffusion in the transient state will be characterized by a dimensionless time $\tau = t/t_s$ ($\tau < 1$).

The error involved in the derived approximate formula is illustrated in Fig. 1, in which the quantity δ, representing the per cent deviation of $q_{ab}(t)$ determined from Eq. (*12*) for a given combination of input parameters from the correct value obtained by the numerical inversion of the exact transform (*10*), is plotted against τ.

TABLE II

Tested combinations of parameters of lamina AB with thickness $a + b = 0{\cdot}1$ cm

Code	$D_a \cdot 10^7$ $cm^2 s^{-1}$	$D_b \cdot 10^7$ $cm^2 s^{-1}$	S_a	S_b	a cm	$\overline{D_{ab}}$ $cm^2 s^{-1}$	$\overline{S_{ab}}$
2D1	0·5	1	1	1	0·05	0·686	1
2D2	0·2	1	1	1	0·05	0·382	1
2S1	1	1	0·5	1	0·05	1	0·667
2S3	1	1	0·2	1	0·05	1	0·333
2S2	1	1	0·1	1	0·05	1	0·182
2S4	1	1	0·01	1	0·05	1	0·020
2A1	1	0·5	1	1	0·03	0·601	1·069
2A2	1	0·5	1	1	0·01	0·531	1·137
2A3	0·5	1	1	1	0·03	0·791	0·931
2A4	0·5	1	1	1	0·01	0·922	0·863

The figure shows that the deviation never exceeds 15% being thus comparable with the error involved in the experimental determination of the diffusion coefficient. The largest deviations are typical of large differences in the thicknesses of both layers (2A2, 2A3, 2A4); on the contrary, the error of the approximation is rather insensitive to differences in the partition coefficients (series 2S). In some cases the error δ passes through a flat extreme (2A1, 2A2, 2D1) which is real as has been demonstrated by calculations with $\tau > 1$.

TABLE III

Tested combinations of parameters of lamina ABC with thickness $a + b + c = 0{\cdot}09$ cm

Code	$D \cdot 10^7$, $cm^2 s^{-1}$			S_a	S_b	S_c	a cm	b cm	c cm	$\overline{D_{abc}} \cdot 10^7$ $cm^2 s^{-1}$	$\overline{S_{abc}}$
	D_a	D_b	D_c								
3A1	1	0·5	1	1	1	1	0·03	0·03	0·03	0·772	1·105
3A2	1	0·5	1	1	1	1	0·04	0·01	0·04	0·914	1·015
3A3	1	0·5	0·1	1	1	1	0·01	0·07	0·01	0·410	0·800
3B1	1	0·07	1	1	1	1	0·01	0·01	0·07	0·584	0·866
3B2	1	0·07	1	1	1	1	0·03	0·01	0·05	0·584	0·866
3B3	1	0·07	1	1	1	1	0·04	0·01	0·04	0·584	0·866
3S1	1	0·5	0·1	2	1	0·5	0·03	0·03	0·03	0·289	0·710
3S2	1	0·5	0·1	2	0·5	1	0·03	0·03	0·03	0·289	1·055
3S3	1	0·5	0·1	1	2	0·5	0·03	0·03	0·03	0·289	0·438
3S4	1	0·5	0·1	1	0·5	2	0·03	0·03	0·03	0·289	1·246
3S5	1	0·5	0·1	0·5	2	1	0·03	0·03	0·03	0·289	0·502
3S6	1	0·5	0·1	0·5	1	2	0·03	0·03	0·03	0·289	1·028

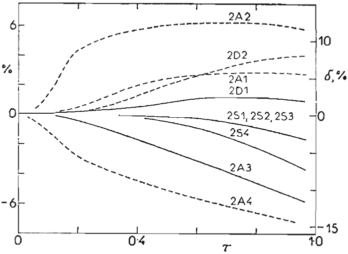

FIG. 1

Per cent deviation δ of the approximate Eq. (*12*) from the correct function obtained by numerical inversion of transform (10) for a laminated membrane AB. The scale to the right belongs to broken curves; code designations of the membranes are explained in Table II

A similar procedure was employed in verifying the validity of the approximate expression (*21*) for a three-layer membrane having an overall thickness $a + b + c = 0{\cdot}09$ cm. The parameters and code designations of tested membranes are summarized in Table III. In series 3A, the effect of thickness of the constituent layers was examined, while in series 3B the position of the central, thin and rather impermeable layer B sandwiched between two outer layers A was varied; finally, in series 3S the constituent layers had the same thickness while differing to a greater extent in their diffusion and partition coefficients.

The error of approximation, again expressed as a per cent deviation δ of the dependence calculated by using Eq. (*21*) from the numerical inversion of the transform (20), is plotted against τ for all tested combinations in Fig. 2. In series 3A, 3B (Fig. 2*a*) the error of approximation was always lower than 20% and in several cases lay below 10%. This holds also for some instances of series 3S (Fig. 2*b*), but for some combinations (3S1, 3S2, 3S5) the error was much higher and approached 40%.

It can be concluded that the relations derived in this study may be employed to predict approximately, with an accuracy sufficient for engineering calculations, the transient diffusion through laminated membranes AB – Eq. (*12*) – and ABC – Eq. (*21*) – using the knowledge of diffusion and partition coefficients of the constituent layers.

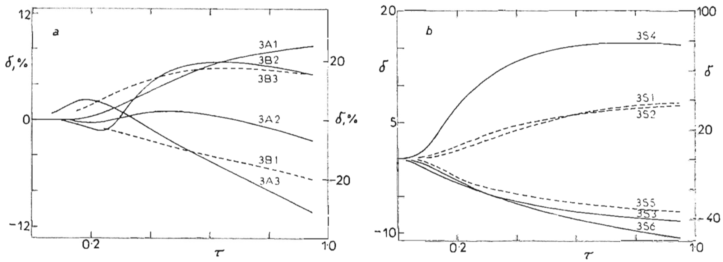

FIG. 2

Error of approximation (*21*) for a laminated membrane ABC. *a* Series of membranes 3A and 3B; *b* series of membranes 3S (*cf.* Table III). The scale to the right belongs to broken curves; code designations of membranes are explained in Table III

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