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SOLUTION OF THE EQUATIONS DESCRIBING THE FLOW OF ^{22}Na IN A SEMI-INFINITE COMPOSITE SYSTEM CONTAINING A MEMBRANE

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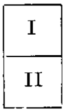
SUMMARY

Solutions to the flow equations in a semi-infinite composite system consisting of protein solution and a phospholipid sol with a membrane at the interface are described in this paper. The composite system was contained in a length of precision bore capillary tubing and the flow rate in the system was followed by using labelled NaCl and a continuous monitoring apparatus.

In a previous publication[1] we described a method for measuring the permeability coefficient of ^{22}Na$^+$ in a synthetic phospholipid membrane formed in a length of precision bore capillary tubing. In these experiments measurements of the radioactivity contained in the capillary tube were not made until the system was finite, *i.e.* 2 days after the start of the experiment. In this paper we describe solutions to the flow equations when the system is semiinfinite and we suggest a way in which the permeability coefficient can be calculated from measurements of the radioactivity during the first few hours of the experiment.

THEORY

A semi-infinite system with a membrane at the interface.



x = —h (open end)
x = o (membrane)
x = *l* (closed end)

The application of Fick's second law to each layer gives

$$\left(\frac{\partial C_i(x,t)}{\partial t}\right)_x = D_i\left(\frac{\partial^2(C_i(x,t)}{\partial x^2}\right) \quad i = (1,2) \tag{1}$$

where C_i and D_i represent the radioactivity and diffusion coefficient in layers I ($i = 1$) and II ($i = 2$). Eqn. 1 was solved to comply with the initial condition

$$C_1(x,t) = C_2(x,t) = C(x,0) \quad -h \leqq x \leqq l,\ t = 0 \tag{2a}$$

and the boundary conditions

$$C_1(x,t) = 0 \qquad \text{at } x = -h \qquad t > 0 \tag{2b}$$

$$D_1 \frac{\partial C_1(x,t)}{\partial x} = D_2 \frac{\partial C_2(x,t)}{\partial x} \qquad \text{at } x = 0, \qquad t > 0 \tag{2c}$$

$$\frac{\partial C_2(x,t)}{\partial x} = 0 \qquad \text{at } x = l, \qquad t > 0 \tag{2d}$$

$$D_1 \frac{\partial C_1(x,t)}{\partial x} = H(C_2(x,t) - C_1(x,t)) \qquad \text{at } x = 0, \qquad t > 0 \tag{2e}$$

where H is the permeability coefficient.

Using the notation of CARSLAW AND JAEGER[3] the Laplace transform of Eqn. 1 is

$$\frac{d^2\bar{C}_i}{dx^2} - q_i\bar{C}_i + \frac{C(x,0)}{D_i} = 0 \qquad (i = 1,2) \tag{3}$$

where $\bar{C}_i = \dfrac{C_i(x,t)}{p}$ and $q_i = \left(\dfrac{p}{D_i}\right)^{\frac{1}{2}}$

and $i = 1$ refers to layer I, and $i = 2$ refers to layer II. The transformed boundary conditions become

$$\bar{C}_1 = 0 \qquad \text{at } x = -h \tag{3a}$$

$$D_1 \frac{d\bar{c}_1}{dx} = D_2 \frac{d\bar{c}_2}{dx} \qquad \text{at } x = 0 \tag{3b}$$

$$\bar{C}_2 = \frac{C(x,0)}{p} \qquad \text{at } x = \infty \tag{3c}$$

$$D_1 \frac{d\bar{c}_1}{dx} = H(\bar{C}_2 - \bar{C}_1) \qquad \text{at } x = 0 \tag{3d}$$

Solutions of the differential Eqns. 3 are:

$$\bar{C}_1 = R_1 \cosh(q_1x) + S_1 \sinh(q_1x) + \frac{C(x,0)}{p} \tag{4}$$

$$\bar{C}_2 = A_2 e^{-q_2x} + \frac{C(x,0)}{p} \tag{5}$$

The coefficients R_1, S_1 and A_1 were evaluated using the transformed boundary conditions and Eqns. 4 and 5 become:

$$\bar{C}_1 = \frac{C(x,0)}{p} - \frac{C(x,0)}{p}\left(\frac{kH\cosh(q_1x) + D_1q_1\cosh(q_1x) - H\sinh(q_1x)}{Z}\right) \tag{6}$$

$$\bar{C}_2 = \frac{C(x,0)}{p} - \frac{C(x,0)}{p}\left(\frac{kHe^{-q_2x}}{Z}\right) \tag{7}$$

where $Z = kH \cosh(q_1h) + D_1q_1 \cosh(q_1h) + H\sinh(q_1h)$
and $k = (D_1/D_2)^{\frac{1}{2}}$.

The Complex Inversion Theorem was used to obtain the transforms of Eqns. 6 and 7 and yielded expressions for $C_1(x,t)$ and $C_2(x,t)$. Thus

$$C_2(x,t) = C(x,0) - \frac{C(x,0)}{2\pi i} kH \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{e^{-\lambda t-\mu_2 x}\mathrm{d}\lambda}{\lambda[E]} \tag{8}$$

where $E = kH\cosh(\mu_1h) + D_1\mu_1 \cosh(\mu_1h) + H\sinh(\mu_1h)$; $p \to \lambda$; $q_i \to \mu_i = \sqrt{\lambda/D_i}$ $(i = 1,2)$; and $\mu_2 = k\mu_1$.

The integrand in Eqn. 8 has a branch point at $\lambda = 0$, and therefore the Bromwich contour as used in the finite system had to be modified (*e.g.* Fig. 40 given in ref. 4) so that the singularity lay outside the contour. The evaluation of the line integral gave

$$C_2(x,t) = \frac{2C(x,0)kH}{\pi} \int_0^\infty \frac{e^{-D_1u^2t}(G)\mathrm{d}u}{u(F)} \tag{9}$$

where $F = k^2H^2\cos^2(uh) + D^2{}_1u^2\cos^2(uh) + H^2\sin^2(uh) + 2D_1uH\cos(uh)\sin(uh)$ and $G = kH\cos(uh)\sin(ukx) + D_1u\cos(uh)\cos(ukx) + H\sin(uh)\cos(ukx)$.

The inversion of Eqn. 6 yielded

$$C_1(x,t) = \frac{2C(x,0)kH^2}{\pi} \int_0^\infty \frac{e^{-D_1u^2t}\sin(u(x+h))\mathrm{d}u}{u(F)} \tag{10}$$

Integration of Eqns. 9 and 10 with respect to x over the interval 0 to $-h$ and 0 to l gave the total concentration of radioisotope in layers I and II, respectively,

$$C_1 = \frac{2Co}{(h+l)} \frac{kH^2}{\pi} \int_0^{-h} \int_0^\infty \frac{e^{-D_1u^2t}\sin(u(x+h))\mathrm{d}u\mathrm{d}x}{u(F)} \tag{11}$$

$$C_2 = \frac{2Co}{(h+l)} \frac{kH}{\pi} \int_0^{l} \int_0^\infty \frac{e^{-D_1u^2t}(G)\mathrm{d}u\mathrm{d}x}{u(F)} \tag{12}$$

In Eqns. 11 and 12 $C(x, 0)$ has been replaced by $C_0/(l+h)$ where C_0 is the total initial count rate in the capillary tube when $t = 0$. The integrations in Eqns. 11 and 12 were obtained numerically using Simpson's 1/3 rule.

Semi-infinite system without a resistance at the interface

Since there is no interfacial resistance at $x = 0$, the boundary conditions 2d and 3d are not applicable and are replaced by the conditions that

$$C_1 = C_2 \qquad \text{at } x = 0, \qquad t > 0 \tag{2e}$$

and the transformed boundary condition $\bar{C}_1 = \bar{C}_2$ at $x = 0$

The coefficients R_1, S_1 and A_2 were solved for Eqns. 4 and 5 using the boundary conditions described above. Thus

$$\bar{C}_1 = \frac{C(x,o)}{p} - \frac{C(x,o)}{p}\left(\frac{\cosh(q_1x) - \sigma\sinh(q_1x)}{\cosh(q_1h) + \sigma\sinh(q_1h)}\right) \qquad (13)$$

$$\bar{C}_2 = \frac{C(x,o)}{p} - \frac{C(x,o)}{p}\left(\frac{e^{-q_2x}}{\cosh(q_1h) + \sigma\sinh(q_1h)}\right) \qquad (14)$$

where $\sigma \Rightarrow (D_2/D_1)^{\frac{1}{2}} = 1/k$.

Eqns. 13 and 14 were inverted as described in the preceding section and the concentrations of radioisotope in layers I and II, *i.e.* C_1 and C_2, respectively, are given by Eqns 15 and 16

$$C_1 = \frac{2Co}{(l+h)}\frac{\sigma}{\pi}\int_o^{-h}\int_o^{\infty}\frac{e^{-D_1u^2t}\sin(u(h-x))\mathrm{d}u\,\mathrm{d}x}{u(\cos^2(uh) + \sigma\sin^2(uh)} \qquad (15)$$

$$C_2 = \frac{2Co}{(l+h)\pi}\int_o^{-h}\int_o^{\infty}\frac{e^{-D_1u^2t}(\sigma\cos(kux)\sin(uh) + \sin(kux)\cos(uh))\mathrm{d}u\,\mathrm{d}x}{u(\cos^2(uh) + \sigma^2\sin^2(uh))} \qquad (16)$$

RESULTS AND DISCUSSION

The double integrations in Eqns. 11, 12, 15 and 16 were obtained numerically using Simpson's rule on a C.D.C. 6600 computer. In the evaluation of the inner integral, u was increased in steps of one from 0 to 17 and the area obtained in each step was summed to give the total integral. In each step the interval was successively halved until the areas of two successive determinations differed by less than $1\cdot10^{-4}$ count·sec^{-1}. In the evaluation of the outer integral over x, the intervals were halved until each successive determination of the area differed by less than $1\cdot10^{-3}$ count·sec^{-1}.

In Table I the counts per second at various points in the capillary tube are tabulated for different values of H, the permeability coefficient at $t = 20997$ sec, for Expt. 32, part of finite series of experiments published previously[1].

If the upper layer had been removed at $t = 20997$ sec and the activity in layer II determined at this point, then by a comparison with the theoretical count in this layer for different values of H, it should be possible to determine the permeability coefficient. The experimental count, last column, Table I, can be determined to an accuracy of approximately 0.1 %, *i.e.* ±0.5 count·sec^{-1} for the count shown above, thus in the region in which H lies between $1\cdot10^{-4}$ and $1\cdot10^{-5}$ 0.5 count corresponds to $1.9\cdot10^{-5}$ unit in H.

Table II shows the calculated count rate in layers I and II for various times t, assuming that the permeability coefficient has a value of $1\cdot10^{-4}$ cm·sec^{-1}. The experimental count shown in the last column is reasonably close to the calculated count rate ($C_1 + C_2$) towards the end of the period when the system is semi-infinite (*i.e.* the count rate at l remains constant with respect to time). Columns 4 and 5 show the calculated count rate when the length of layer I has been increased by

TABLE I

COUNT RATE AT VARIOUS POINTS IN THE CAPILLARY TUBE

At t = 20997 sec (Expt. 32) $C_0 = 700.8$ counts·sec^{-1}, $h = 0.85$ cm, $l = 1.2965$ cm, $10^5 D_1 = 0.701$ cm^2·sec^{-1}, $10^5 D_2 = 1.116$ cm^2·sec^{-1}. x in cm.

H (cm·sec^{-1})	$x=l$	$x=l/2$	$x=0$	$x=0$	$x=-h/2$	$x=-h$	C_1	C_2	(C_1+C_2)	Exptl. count
0.01	321.8	319.6	290.4	290.3	184.5	0.0	145.1	408.9	554.0	554.0
0.001	321.8	319.7	290.8	289.2	184.4	0.0	144.9	409.1	554.0	
0.0001	321.6	320.0	294.5	284.8	183.4	0.0	143.7	410.1	553.8	
0.00001	320.0	320.1	309.3	264.0	179.9	0.0	138.8	412.8	553.7	

TABLE II

VARIATION OF THE COUNT RATE IN LAYERS I AND II WITH TIME

$H = 1 \cdot 10^{-4}$cm·sec^{-1}; $C_0 = 700.8$ counts·sec^{-1}; $10^5 D_1 = 0.701$ cm^2·sec^{-1}; $10^5 D_2 = 1.116$ cm^2·sec. Column 2–7, units: counts·sec^{-1}.

(1) t (sec)	(2) C_1	(3) C_2	(4) C_1	(5) C_2	(6) (C_1+C_2)	(7) C expt.
4670	209.9	418.6	213.2	415.3	628.5	605.9
7864	190.3	418.3	193.5	415.1	608.6	594.1
9392	182.6	417.9	185.8	414.7	600.6	587.7
12748	168.4	416.6	171.5	413.3	585.0	575.6
14373	162.6	415.6	165.7	412.5	578.2	571.6
20997	143.7	410.1	146.6	407.2	553.8	554.0
	$l_1 = 0.850_0$ $l_2 = 1.286_5$		$l_1 = 0.860_0$ $l_2 = 1.296_5$			

0.01 cm and layer II shows the corresponding decrease in 0.01 cm. This shows effect of errors in the measurement of the length of the layers of the composite system.

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