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EFFECT OF HETEROPOROSITY ON FLUX EQUATIONS FOR MEMBRANES

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An investigation is made of the possible errors in simple integrated equations for solute flux across both non-sieving and sieving porous membranes that can result from variations in the membrane structure. Detailed structural models are used, beginning with a membrane consisting of a parallel array of pores and progressing to series–parallel combinations of pore segments of various lengths and cross-sectional areas, with internal cross connections among pore segments allowed. It is shown that there are both upper and lower mathematical bounds on the possible variations that can be produced in a curve of solute flux versus volume flow by arbitrary variation in the membrane structure, subject only to certain general conditions. In particular, the flux equation for a homoporous membrane is a lower bound. The maximum deviations from this lower bound for a membrane of arbitrary structure are only moderately large, and require rather extreme pore size distributions; most distributions introduce only small errors. Implications of these results in studies of real membrane structure and in the design of experiments are discussed.

1. Introduction

In a preceding paper [1] we have discussed the range of applicability of equations for describing combined diffusion and convection across membranes, and shown that it is not in general possible to write an exact equation for solute flux without more information on membrane structure than is contained in the usual three overall parameters. In this paper we investigate the errors in simple transport equations that can arise from variations in the membrane structure, and show that there are definite bounds on the inaccuracies introduced, subject to certain general conditions. Somewhat surprisingly, the maximum relative deviations from homoporous behavior result only from rather bizarre pore size distributions, and are only moderately large; most distributions introduce only small errors. Implications of these results in studies of real membranes are discussed.

Our results are based on one fundamental assumption and one restriction on membrane pore geometry. The assumption is that the transport inside the membrane can be treated as one-dimensional in a locally averaged sense. The restriction is that for sieving membranes, pore geometry must not be such as to cause internal concentration polarization at any solute-rejecting interface. In such cases we cannot establish error bounds without more detailed knowledge of membrane structure, and D'Arcy's law does not hold for the volume flow.

We begin with a very simple mechanical model of a membrane consisting of a parallel array of non-sieving pores, and then build up more complicated membrane geometries by series–parallel combinations of pore segments of various lengths, cross-sectional areas, and sieving coefficients. Finally we allow internal cross connections among pores, so that the model hopefully embodies sufficient geometric complexity to mimic structures of real membranes. We discuss only nonelectrolyte solutions consisting of one solute and one solvent, and consider only the steady state.

2. Heteroporous open membranes: Parallel arrays

For simplicity we consider the membrane to consist of a parallel array of separate pores, each with its own cross-sectional geometry along its entire length. All pores are open to the given solute; that is, they do not sieve the solute, nor can osmosis result from a solute concentration difference across any pore.

The solute flux density $j_s^{(i)}$ across a pore of any particular type i at the steady state is given by the integrated equation,

$$j_s^{(i)} = j_V^{(i)} c_s' - \frac{j_V^{(i)} \Delta c_s}{\exp(j_V^{(i)}/P_i) - 1}, \tag{1}$$

where $j_V^{(i)}$ is the volume flux density, c_s is the solute concentration, and P_i is the diffusive permeability coefficient, equal to the solute–solvent diffusion coefficient in the pore divided by the effective pore length. The solute concentrations at the entrance and exit of the pore are c_s' and c_s'', and $\Delta c_s \equiv c_s'' - c_s'$. The measured solute flux density across unit area of the whole membrane, J_s, is related to $j_s^{(i)}$ by

$$J_s = \sum_{i=1}^{N} n_i A_i j_s^{(i)}, \tag{2}$$

where n_i is the number of pores of type i per unit membrane area, and A_i is the area of a pore of type i. The sum runs over all types of pores that are completely open to solute and solvent; thus $\Sigma_i n_i A_i$ does not necessarily equal a unit area since there may be regions of the membrane totally impermeable to solute and solvent. Combining eqs. (1) and (2) we obtain

$$J_s = c_s' \sum_i n_i A_i J_V^{(i)} - \Delta c_s \sum_i \frac{n_i A_i j_V^{(i)}}{\exp(j_V^{(i)}/P_i) - 1}. \tag{3}$$

We note that the measured volume flux density, J_V, is given by

$$J_V = \sum_i n_i A_i j_V^{(i)}, \tag{4}$$

so that the first term on the right-hand side of eq. (3) could be replaced by the measurable quantity $c_s' J_V$. But the second term cannot be simply expressed, nor can it be evaluated without knowledge of n_i, A_i, P_i and $j_V^{(i)}$. It thus appears that we cannot write a simple integrated flux equation for a heteroporous membrane without considerable information about the membrane structure. However, it turns out that the summation of the second term can usually be replaced by a single term to a good approximation, and definite bounds can be placed on the resulting error.

Consider first the special case of a homoporous membrane, for which eq. (3) does reduce to a simple form. The $j_V^{(i)}$ are then all equal, as are the P_i, which can be written in terms of an overall permeability coefficient, $P_s = \Sigma_i n_i A_i P_i$. Then eq. (3) reduces to

$$J_s^{\circ} = c_s' J_V - \frac{\Delta c_s J_V}{\exp(J_V/P_s) - 1}, \tag{5}$$

where the superscript ° designates the homoporous result for open membranes. This equation is identical with the result from irreversible thermodynamics if the reflection coefficient, σ, of the latter is set to zero. An interesting question is now as follows: how good (or how bad) is J_s° as an approximation to the true J_s of eq. (3)? The coefficient P_s for a heteroporous membrane would of course be determined experimentally by measurement of J_s in the pure diffusion limit, where all $j_V^{(i)}$ are zero, for which eq. (3) becomes

$$J_s = -\Delta c_s \sum_i n_i A_i P_i = -\Delta c_s P_s. \tag{6}$$

We shall show that $J_s \geqslant J_s^{\circ}$ at any given values of c_s', c_s'', and J_V; that is, the curve of J_s° versus J_V is a lower bound for all possible curves of J_s versus J_V (with the same c_s' and c_s''), obtained by varying the pore size distribution.

It is convenient to use dimensionless variables, defined as follows:

$$\alpha_i \equiv j_V^{(i)}/P_i, \tag{7}$$

$$\beta_i \equiv n_i A_i P_i / P_s, \tag{8}$$

$$Y \equiv J_s / c_s' P_s. \tag{9}$$

We may consider α_i as a statistical variable and the β_i as weight factors, and define α as an average of α_i with these weight factors,

$$\alpha = \langle \alpha_i \rangle \equiv \sum_i \beta_i \alpha_i = J_V / P_s. \tag{10}$$

Note that $\Sigma_i \beta_i = 1$. Similarly, if we define a function $\phi(\alpha_i)$ as

$$\phi(\alpha_i) \equiv \alpha_i - \frac{\Delta c_s}{c_s'}\left(\frac{\alpha_i}{\exp(\alpha_i)-1}\right), \tag{11}$$

then we see from eq. (3) that Y is the average of $\phi(\alpha_i)$ with β_i as weight factors,

$$\begin{aligned} Y &= \sum_i \beta_i \alpha_i - \frac{\Delta c_s}{c_s'} \sum_i \beta_i \left(\frac{\alpha_i}{\exp(\alpha_i)-1}\right) \\ &= \sum_i \beta_i \phi(\alpha_i) \equiv \langle \phi(\alpha_i) \rangle. \end{aligned} \tag{12}$$

From eq. (5) we see that Y^0 is

$$Y^0 \equiv J_s^0/c_s'P_s = \alpha - \frac{\Delta c_s}{c_s'}\left(\frac{\alpha}{e^{\alpha}-1}\right), \tag{13}$$

where α is given by eq. (10). That is, Y^0 is a function of α with the same functional form as ϕ,

$$Y^0 = \phi[\langle \alpha_i \rangle]. \tag{14}$$

In other words, in comparing Y with Y^0 we are comparing the average of a function of α_i with the function of the average of α_i. These two averages are related through a mathematical theorem known as Jensen's inequality [2].

In its simplest form, Jensen's inequality states that the average of a function of a set of variables x_i is always greater than or equal to the function of the average of x_i, provided only that the function of x_i is everywhere concave upward (second derivative positive). The set of x_i may be continuous or discreet and any set of non-negative weighting factors may be chosen to define the averages. As a simple example we might consider the function $\exp x_i$, with a set of $x_i = 1$, 3, 5, 6 and with unit weight factors. Then $\langle \exp x_i \rangle = \frac{1}{4}\, \Sigma_i \exp x_i = 143.7$, and $\exp \langle x_i \rangle = \exp\left[\frac{1}{4}\, \Sigma_i x_i\right] = 42.5$, and we see that Jensen's inequality is followed, since $\langle \exp x_i \rangle > \exp \langle x_i \rangle$. The function $\phi(\alpha_i)$ considered here is everywhere concave upward provided that $\Delta c_s = c_s'' - c_s' < 0$, as illustrated in fig. 1 and can easily be proved analytically, so Jensen's inequality applies,

$$\langle \phi(\alpha_i) \rangle \geqslant \phi(\langle \alpha_i \rangle), \tag{15}$$

or

$$Y \geqslant Y^0, \qquad J_s \geqslant J_s^0. \tag{16}$$

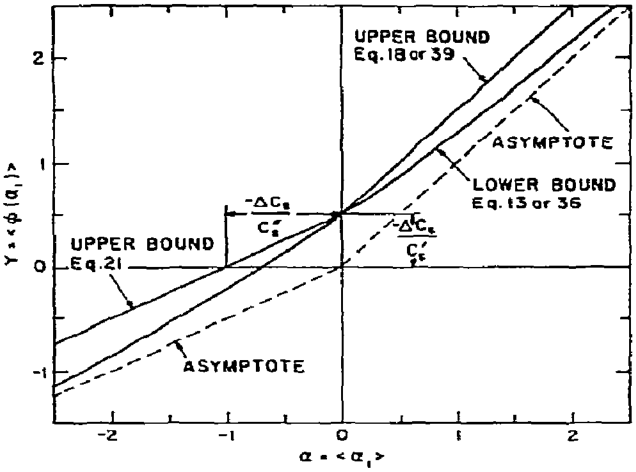

Fig. 1. Solute flux versus volume in dimensionless form, showing bounds for membrane heteroporosity. The curve for a heteroporous membrane of any pore-size distribution must lie within the indicated regions. The lower bound curve is given by the equation for a homoporous membrane. The dimensionless variables are $Y = J_s/c_s'P_s$ and $\alpha = J_V/P_s$, and the concentration difference illustrated is $-\Delta c_s/c_s' = 0.5$.

That is, the homoporous result is a *lower bound* to the exact but impractical result given by eq. (3) or eq. (12). If we can also find an upper bound for Y, then we can establish the maximum error possible when Y^0 (or J_s^0) is used as a flux equation for heteroporous membranes.

An upper bound in the region $\alpha \geqslant 0$ can be determined from the behavior of Y for $\alpha \to 0$ and $\alpha \to \infty$, and by noting that Y is always concave upward because it is a sum of everywhere concave-upward functions $\phi(\alpha_i)$ multiplied by positive numbers β_i. First we consider the case where all the α_i become large. Then the second summation in eq. (12) becomes negligible and $Y \to \alpha$; thus the slope $\mathrm{d}Y/\mathrm{d}\alpha$ of the curve of Y versus α approaches unity for large α. Next we consider the other end of the curve, where all $\alpha_i \to 0$. Then the exponential in eq. (12) can be expanded to show that Y becomes linear in α,

$$Y \to \left(\frac{c_s' + c_s''}{2c_s'}\right)\alpha - \frac{\Delta c_s}{c_s'}, \qquad \alpha \to 0. \tag{17}$$

This is the equation of a straight line whose intercept is $-\Delta c_s/c_s'$ and whose slope is $(c_s' + c_s'')/2c_s'$, which is less than unity since $c_s' > c_s''$. Thus the curve of Y versus α must start at $Y = -\Delta c_s/c_s'$ with a positive slope less than unity, and must eventually reach a constant slope of unity, irrespective of the values of β_i and hence independent of the nature of the pore distribution. Furthermore, Y must always remain concave upward. We conclude from these statements that Y versus α must always lie *below* a straight line passing through $Y = -\Delta c_s/c'_s$ at $\alpha = 0$ and having a slope of unity. That is, in the region $\alpha \geqslant 0$, the *upper bound* on Y is the straight line,

$$Y = \alpha - \Delta c_s/c'_s, \tag{18}$$

as shown in fig. 1. Thus to find the maximum possible error in using $Y^{\rm o}$ to approximate Y for $\alpha > 0$, we must maximize the function

$$\begin{aligned}\frac{Y - Y^{\rm o}}{Y} &= \left[\alpha - \frac{\Delta c_s}{c'_s} - \alpha + \frac{\Delta c_s}{c'_s}\left(\frac{\alpha}{e^{\alpha}-1}\right)\right]\left(\alpha - \frac{\Delta c_s}{c'_s}\right)^{-1} \\ &= -\frac{\Delta c_s}{c'_s}\left(1 - \frac{\alpha}{e^{\alpha}-1}\right)\left(\alpha - \frac{\Delta c_s}{c'_s}\right)^{-1},\end{aligned} \tag{19}$$

with respect to α at a given $\Delta c_s/c'_s$. The condition for a maximum turns out to be

$$e^{2\alpha} - e^{\alpha}\left(\alpha^2 - \alpha\frac{\Delta c_s}{c'_s} + \frac{\Delta c_s}{c'_s} + 2\right) + \frac{\Delta c_s}{c'_s} + 1 = 0. \tag{20}$$

Values for non-zero roots of this equation, and the corresponding maximum relative errors calculated according to eq. (19), are given in table 1 for several values of $-\Delta c_s/c'_s$. The *largest* possible relative error that can occur if the homoporous flux equation is used for heteroporous membranes is seen to be 23%, which occurs at $\alpha = 1.793$ for $-\Delta c_s/c'_s = 1$ (i.e., for $c''_s = 0$). At smaller values of $-\Delta c_s/c'_s$ the maximum relative error decreases.

For negative values of α, i.e., when the bulk flow J_V is directed against the concentration difference, the lower bound for Y is still $Y^{\rm o}$ but now the upper bound is the straight line

$$Y = [c''_s/c'_s]\,\alpha - \Delta c_s/c'_s = [1 + \Delta c_s/c'_s]\,\alpha - \Delta c_s/c'_s, \tag{21}$$

as shown in fig. 1. Here $c''_s/c'_s = 1 + \Delta c_s/c'_s$ is the limiting slope obtained from eq. (12) when all the α_i are large but negative. The difference between the upper and lower bounds is now

$$Y - Y^{\rm o} = -\frac{\Delta c_s}{c'_s}\left(1 - \frac{\alpha e^{\alpha}}{e^{\alpha}-1}\right). \tag{22}$$

A relative error calculation analogous to eq. (19) is not reasonable here, since the upper-bound straight line for Y crosses the α-axis at $\alpha = \Delta c_s/c''_s$ and the relative error would become infinite. However, the maximum absolute error, $Y - Y^{\rm o}$, will still be $-\Delta c_s/c'_s$, the same as it was when α was positive.

Table 1
Maximum possible relative errors from use of the homoporous flux equation for a heteroporous membrane

$-\Delta c_s/c'_s$	Max. $\alpha = J_V/P_s$	Max. $(Y - Y^{\rm o})/Y =$ Max. $[J_s - J_s^{\rm o}]/J_s$
0	0	0
0.2	0.935	0.070
0.4	1.251	0.121
0.6	1.472	0.163
0.8	1.647	0.195
1.0	1.793	0.230

An example of a pore distribution that would result in a true solute flux equation approximately the same as the upper bound line for $\alpha > 0$, eq. (18), is a few large pores (designated by 1) and a large number of small pores (designated by 2). In such a case most of the open area of the membrane consists of small pores, but most of the volume flow is through the large pores. For a numerical example suppose 95% of the open area is small pores, so that $\beta_2 = 0.95$ and $\beta_1 = 0.05$ if we assume all P_i are equal. Suppose that the radii of the two sets of pores are such that at any given pressure difference across the membrane one large pore carries 1000 times as much volume flow as one small pore, so that $\alpha_1 = 1000\,\alpha_2$. Then direct numerical computation with eq. (12) shows that the true $Y(\alpha)$ curve is never more than about 5% below the upper bound straight line. That is, the flux J_s for a membrane with a few relatively large pores will quickly deviate from the homoporous approximation and become linear in J_V.

Although the above example shows that the upper bound can be approached, the pore-size distribution involved is rather special. A more reasonable distribution, at least for synthetic membranes, is one falling off smoothly from some most probable pore size. Since a sharply peaked distribution of this type approaches homoporosity, we choose as an extreme example a flat distribution such that each size pore represents the same total open membrane area as any other size pore (i.e., $n_i A_i$ = constant). For this example we also assume that the pore area increases linearly with the index number i designating pore type, $A_i \propto i$ up to the maximum size at $i = N$, and that all the diffusive permeability coefficients P_i are the same. We further suppose that the volume flow through any pore type follows Poiseuille's law, so that $j_V^{(i)} \propto A_i$, and that the distribution is smooth enough that summations can be replaced by integrations. Although this set of assumptions probably corresponds to no real membrane, it serves to indicate the magnitude of the deviations from the lower bound that one might expect for heteroporous membranes with a smooth unimodal dispersion of pore sizes. On applying these assumptions to eq. (12) and carrying out some straightforward mathematical manipulations, we obtain, for $-\Delta c_s/c_s' = 1$,

$$Y = \alpha + \frac{1}{2\alpha}\int_0^{2\alpha} \frac{x\,dx}{e^x - 1}. \tag{23}$$

This integral is not an elementary one, but does correspond to one of the tabulated Debye functions [3]. By direct numerical computation we find that the maximum deviation of eq. (23) from the lower bound, Y^0, is less than 4%. Thus the homoporous approximation will be quite accurate for many types of heteroporous membranes.

3. Heteroporous sieving membranes: Parallel arrays

There is controversy over the form of the flux equations for diffusion and convection across (presumably) homogeneous membranes that are partially impermeable to a given solute. However, for the present purpose we will accept as correct for transport across a single pore the integrated flux equation as given by Patlak et al. [4]:

$$j_s^{(i)} = j_V^{(i)}(1-\sigma_i)c_s' - \frac{j_V^{(i)}(1-\sigma_i)\Delta c_s}{\exp[j_V^{(i)}(1-\sigma_i)/P_i] - 1}, \tag{24}$$

where σ_i is the reflection coefficient for pore i, which also appears in the volume flux density equation,

$$j_V^{(i)} = -L_p^{(i)}(\Delta p - \sigma_i \Delta\pi). \tag{25}$$

Here $L_p^{(i)}$ is the hydraulic conductivity coefficient, Δp is the pressure difference across the pore, and $\Delta\pi$ is the osmotic pressure due to a solute concentration difference that would exist across the pore if the pore were totally impermeable to the solute.

The exact flux equation is obtained, as before, by summing eq. (24) over all pores, but now we cannot use Jensen's inequality to prove that the homoporous form of the resulting flux equation is a lower bound. The reason is that the sum $\Sigma_i n_i A_i j_V^{(i)}(1-\sigma_i)$ does not equal $J_V(1-\sigma)$, where σ is the reflection coefficient observed for the whole membrane, and we must slightly modify the procedure used for open membranes in order to find a lower bound. The difficulty is related to the fact that the Onsager reciprocal relation does not necessarily hold in an overall sense for a heteroporous membrane, although it holds for each individual pore. Onsager reciprocity requires *strict* homogeneity or locality, and a heteroporous membrane is not homogeneous in this strict sense, as discussed in a preceding paper. It is not always appreciated how strict this requirement of locality can be. As an extreme example, the usual extension of Enskog's dense gas theory to mixtures [5] was recently found to violate Onsager reciprocity because of the failure of locality by only a fraction of a molecular diameter [6,7]. That is, the contact point between two rigid spheres does not lie halfway between their centers if the spheres are of different size, and this is the source of the trouble in mixtures of different size spheres.

It is again convenient to use dimensionless variables; we use the same definitions of β_i, Y, and $\phi(\alpha_i)$ as given by eqs. (8), (9), and (11), respectively, but redefine α_i as

$$\alpha_i \equiv j_V^{(i)}(1-\sigma_i)/P_i. \tag{26}$$

The exact solute flux equation is then found to be

$$Y = J_s/c_s'P_s = \sum_i \beta_i\alpha_i - \frac{\Delta c_s}{c_s'}\sum_i \beta_i\left(\frac{\alpha_i}{\exp(\alpha_i)-1}\right)$$

$$= \langle\phi(\alpha_i)\rangle, \tag{27}$$

which differs from the result for open pores only in the definition of α_i. The essential difference arises in the expression to be used for $\alpha = \langle\alpha_i\rangle$.

To find an explicit expression for α that can be used in Jensen's inequality we write

$$\alpha \equiv \langle\alpha_i\rangle = \sum_i \beta_i\alpha_i = J_V/P_s - \sum_i n_i A_i j_V^{(i)}\sigma_i/P_s. \tag{28}$$

Now if we accept

$$J_V = -L_p(\Delta p - \sigma\Delta\pi), \tag{29}$$

as a correct expression for observed overall volume flux density, as well as the operational definition of σ, then the observed hydraulic conductivity for the array of parallel pores is

$$L_p = \sum_i n_i A_i L_p^{(i)}, \tag{30}$$

and the observed reflection coefficient is

$$\sigma = \sum_i n_i A_i L_p^{(i)} \sigma_i / L_p. \tag{31}$$

With these expressions we can evaluate the summation on the right-hand side of eq. (28) for α; replacing $j_V^{(i)}$ in eq. (28) by its equivalent from eq. (25) and using eqs. (30) and (31), we obtain

$$\sum_i n_i A_i j_V^{(i)} \sigma_i = g\sigma J_V, \tag{32}$$

where

$$g = [\Delta p - [\langle\sigma_i^2\rangle/\sigma^2]\,\sigma\Delta\pi]/(\Delta p - \sigma\Delta\pi), \tag{33}$$

$$\langle\sigma_i^2\rangle = \sum_i n_i A_i L_p^{(i)} \sigma_i^2 / L_p. \tag{34}$$

Thus α is given by

$$\alpha = J_V(1 - g\sigma)/P_s, \tag{35}$$

and the *lower-bound* approximate equation for Y is

$$Y^s \equiv \phi(\langle\alpha_i\rangle) = \alpha - \frac{\Delta c_s}{c_s'}\left(\frac{\alpha}{e^\alpha - 1}\right), \tag{36}$$

where the supercript ^{s} designates the result for sieving membranes. Notice that $g = 1$ for $\Delta\pi \ll \Delta p$ (dilute solutions or high pressures), and also for a homoporous array with all σ_i identical (so that $\langle\sigma_i^2\rangle = \sigma^2$). In these cases Y^s reduces to the homoporous result of non-equilibrium thermodynamics, namely eq. (24) with the index i deleted.

The factor g defined by eq. (33) is in principle an observable quantity for sieving membranes. Expanding Y^s about $J_V = 0$ and rearranging the resulting linear equation, we obtain

$$J_s = \tfrac{1}{2}(c_s' + c_s'')J_V(1 - g\sigma) - P_s\Delta c_s. \tag{37}$$

This result is of course identical with that obtained by expanding each $j_s^{(i)}$ about $j_V^{(i)} = 0$ in eq. (24) and summing over all pores. The factor g could be determined from eq. (37) by performing experiments over the same range of small J_V but with several different values for $\Delta\pi$, the coefficient σ being found independently from eq. (29). The value of g so obtained could then be used in Y^s to approximate the behavior at higher volume flows. Since g depends on $\langle\sigma_i^2\rangle/\sigma^2$, it would give some information about the pore-size distribution of the membrane. Comparison of eqs. (29) and (37) shows that $g \neq 1$ represents a breakdown of the Onsager relation for the overall membrane, because the requirement of *strict* homogeneity is not met. In this connection it is interesting to note that eq. (37) differs from the result obtained by expanding the overall equation of Patlak et al., which yields

$$J_s = \tfrac{1}{2}(c_s' + c_s'')J_V(1 - \sigma) - P_s\Delta c_s, \tag{38}$$

in which the factor g does not appear.

Once α has been evaluated according to eq. (35), the remaining mathematical analysis proceeds as for the open membrane. In particular, the *upper bound* for positive α is the straight line,

$$Y = \alpha - \Delta c_s / c_s', \tag{39}$$

and the maximum relative error in using eq. (36) to approximate the true Y is 23%. Similarly, the upper bound for negative α has the same form as eq. (21) for the open membrane.

Note that heteroporous sieving membranes require four, rather than three, overall parameters in order to establish rigorous accuracy bounds, namely P_s, L_p, σ, and g. Only three would be needed if Onsager reciprocity held.

4. Open pores in series

We consider now the integrated solute flux equation for a single independent pathway consisting of n open pores in series, as shown in fig. 2. Each segment i has its particular values of $j_s^{(i)}$, $j_V^{(i)}$, and P_i. Boundary conditions are such that $c_s' = c_1$, the solute concentration at the entrance to pore 1; c_2 is the concentration at the end of pore 1 and the beginning of pore 2; and so forth until $c_{n+1} = c_s''$, the concentration at the end of the last pore. We shall show that the solute flux equation for such a series-pore model is exactly the same as for a single uniform pore.

At steady state the total solute flux, Q_s, and the total volume flux, Q_V, must be the same in each pore

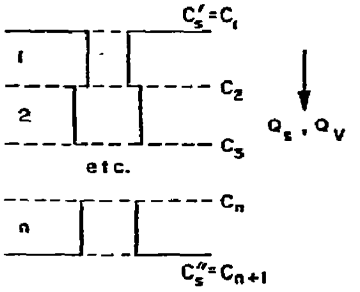

Fig. 2. Open-pore segments in series, with no internal concentration polarization.

segment,

$$Q_s = A_1 j_s^{(1)} = A_2 j_s^{(2)} = \ldots = A_n j_s^{(n)}, \tag{40}$$

$$Q_V = A_1 j_V^{(1)} = A_2 j_V^{(2)} = \ldots = A_n j_V^{(n)}. \tag{41}$$

The flux through any pore segment i is obtained from eq. (1) as

$$Q_s = Q_V c_i - \frac{Q_V (c_{i+1} - c_i)}{\exp(Q_V/A_i P_i) - 1}, \tag{42}$$

which can be solved for c_{i+1} to yield

$$c_{i+1} = c_i \, e^{\alpha_i} - [e^{\alpha_i} - 1] \, [Q_s/Q_V], \tag{43}$$

where $\alpha_i = j_V^{(i)}/P_i = Q_V/A_i P_i$, as previously defined in eq. (7). We wish to eliminate algebraically all the intermediate concentrations c_i, leaving only the concentrations at the boundaries, c_1 and c_{n+1}. From eq. (43) we obtain

$$c_2 = c_1 \, e^{\alpha_1} - [e^{\alpha_1} - 1] \, [Q_s/Q_V],$$

$$c_3 = c_2 \, e^{\alpha_2} - [e^{\alpha_2} - 1] \, [Q_s/Q_V]$$
$$= c_1 \, e^{\alpha_1 + \alpha_2} - [Q_s/Q_V] \, e^{\alpha_1 + \alpha_2} + [Q_s/Q_V],$$

whence by induction it is easy to prove that

$$c_{n+1} = c_1 \exp\left(\sum_i^n \alpha_i\right)$$
$$- [Q_s/Q_V] \exp\left(\sum_i^n \alpha_i\right) + [Q_s/Q_V]. \tag{44}$$

This can be rewritten, with $c_1 = c_s'$ and $c_{n+1} = c_s''$, as

$$Q_s = Q_V c_s' - \frac{Q_V [c_s'' - c_s']}{\exp(\Sigma_i^n \alpha_i) - 1}. \tag{45}$$

This is of the same mathematical form as the corresponding expression for a single uniform pore; all that is needed to prove mathematical identity of the two expressions is a suitable identification of $\Sigma_i^n \alpha_i$.

Since $\Sigma_i^n \alpha_i$ represents the effect of diffusion in eq. (45), we identify it with measurable quantities by passing to the pure diffusion limit, $Q_V \to 0$,

$$Q_s = -Q_V \, \Delta c_s \Big/ \sum_i^n \alpha_i = -\Delta c_s \Big/ \sum_i (1/P_i A_i). \tag{46}$$

Let the "measured" area of the pore be A; the observed permeability, P_s, would then be defined by

$$Q_s = -A P_s \Delta c_s. \tag{47}$$

Comparing eqs. (46) and (47) we find

$$1/AP_s = \sum_i (1/A_i P_i), \tag{48}$$

or

$$\sum_i \alpha_i \equiv Q_V \sum_i (1/A_i P_i) = Q_V/A P_s = J_V/P_s. \tag{49}$$

Thus the solute flux equation for a pathway consisting of open pores in series is identical with that for a single uniform pore. It is trivial to show that a similar result holds for the volume flux, since the equations are linear; that is,

$$Q_V = A L_p \Delta p, \tag{50}$$

$$1/AL_p = \sum_i [1/A_i L_p^{(i)}]. \tag{51}$$

5. Sieving pores in series

For this case the situation is considerably more complicated than for open pores, since solute may be rejected (sieved) at the entrance to each pore segment. As a result, solute concentration at the end of one segment will not necessarily equal solute concentration on the inner side of the entrance to the following segment. Patlak et al. (4) have analyzed this problem in great detail for two sieving membranes in series. We focus attention here on some results which, although not new, are needed to complete our discussion of heteroporous membranes.

For simplicity we consider only two segments having reflection coefficients σ_1 and σ_2, respectively. The upstream concentration is fixed at c_s', the downstream concentration fixed at c_s'', and the concentration c_2 at the end of segment 1 depends on the conditions of the experiment. We write eq. (24) for each pore segment,

$$\frac{Q_s}{Q_V} = c_s'(1-\sigma_1) - \frac{(1-\sigma_1)(c_2-c_s')}{e^{\alpha_1}-1}, \tag{52}$$

$$\frac{Q_s}{Q_V} = c_2(1-\sigma_2) - \frac{(1-\sigma_2)(c_s''-c_2)}{e^{\alpha_2}-1}, \tag{53}$$

where

$$\alpha_i = Q_V(1-\sigma_i)/A_i P_i . \tag{54}$$

Eliminating c_2 between eqs. (52) and (53), after some rearrangement we obtain

$$Q_s/Q_V = (1-\sigma_1)(1-\sigma_2)[c_s' - c_s'' e^{-\alpha_1-\alpha_2}] \tag{55}$$
$$\times\ [(1-\sigma_2)[1-e^{-\alpha_1}] + (1-\sigma_1)e^{-\alpha_1}[1-e^{-\alpha_2}]]^{-1} .$$

There does not seem to be any simple form, such as Y^s of eq. (36), that can be used to approximate this Q_s. To illustrate the difficulties involved, we imagine the first segment to be open ($\sigma_1 = 0$) and only the second segment to have sieving properties ($\sigma_2 \neq 0$), and compare the behavior of this series model with the corresponding parallel model of an open pore and a sieving pore. In the limit of low volume flows ($Q_V \to 0$), both models exhibit pure diffusion and thus behave similarly. However, at high volume flows ($Q_V \to \infty$) eq. (55) gives the limit

$$Q_s \to c_s' Q_V , \tag{56}$$

whereas the limit for the parallel-pore model according to eq. (36) is (assuming $\Delta\pi \ll \Delta p$)

$$Q_s = c_s'(1-\sigma) Q_V . \tag{57}$$

That is, for an open pore preceding a sieving pore in series, there is *no* sieving at the high flow limit, in contrast to the *existence* of sieving at the same limit for one open and one sieving pore in parallel. Thus the series array behaves like an open membrane at very low and very high Q_V, but behaves as a partially sieving membrane at intermediate Q_V. It does not seem possible to carry through an analysis for any series array of segments with different reflection coefficients similar to the analysis for parallel arrays. At any rate, we have been unable to establish any useful or lower bounds for a general series array. It is unlikely that one simple integrated solute flux equation can be found that can be used in general as an approximation to the exact equation for a series of sieving pores. Even the volume flow equation behaves in a complicated manner. As the pressure difference across a series array is increased, the increasing internal concentration polarization sets up an increasing osmotic pressure opposing the applied pressure, and Q_V does not increase linearly with Δp. However, this somewhat gloomy prospect may be brightened to some extent by noting that lateral diffusion within a membrane having interconnected pores may often relieve the effects of internal concentration polarization.

6. Interconnections of pores

Very complicated structures can be built up by internally cross-connecting a series–parallel array of pore segments of various lengths and cross sections. A mathematical analysis of such structures would at first sight seem impossible, but we shall show that the same bounds hold for them as hold for the simpler structures considered thus far, provided of course that no internal concentration polarization occurs and that we can use a one-dimensional treatment in each pore segment.

Because pores in series obey the same equations as a single uniform pore, we first note that every nonbranching segment in the structure can be replaced by

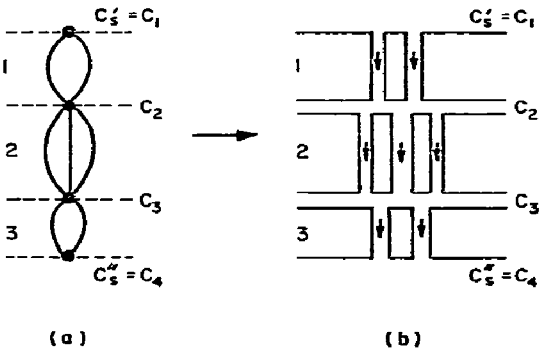

Fig. 3. Schematic diagram of a membrane with internally connected pore segments. In this special case the internal junctions are lumped together so that each junction is connected to at most two other junctions; this is equivalent to a series array of submembranes, as shown.

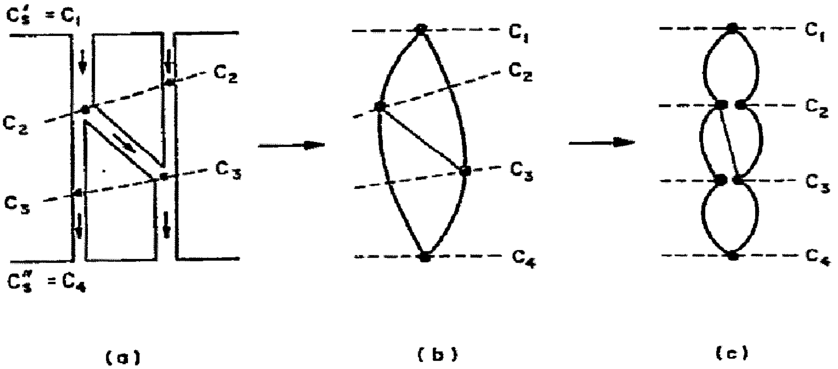

Fig. 4. Schematic diagram of a membrane whose internal connections are more complex than those of fig. 3. This is equivalent, in a sense discussed in the text, to a peculiar kind of series array of submembranes, as shown.

an equivalent uniform pore segment. This first step in the analysis removes from consideration all non-uniformities of cross section between internal junction points. We also note that unequal pore lengths are simply absorbed into the individual P_i.

We next consider an apparently special case with the junction points lumped together as shown schematically in fig. 3a. The characteristic property of this arrangement is that each junction point is connected by pore segments to *at most* two other junction points. Inspection shows that this is equivalent to a series array of submembranes, each submembrane consisting of a parallel array of pore segments, as shown in fig. 3b. The spaces between the submembranes are imagined to be sufficiently well stirred to maintain the concentrations uniform at the values corresponding to the junction points. It is now fairly straightforward to prove that the same bounds on J_s versus J_V hold for this series array of submembranes as hold for a single membrane. Without going into mathematical details, we can give the gist of a proof as follows. Compare the given array with a similar array consisting of homoporous submembranes, each homoporous submembrane having the same permeability coefficient as its corresponding heteroporous in the original array. The flux equation for the whole homoporous array is then obviously given by the previously-obtained lower bound, eq. (13). In the initial linear regime of very low J_V, both membrane arrays behave the same, because of the choice of permeability coefficients. Now as J_V is increased into the nonlinear regime, J_s tends to increase more for a heteroporous submembrane than for a homoporous one, with the result that the overall J_s for the heteroporous array can only be more than that for the homoporous array. (The fact that the intermediate concentrations c_i between the submembranes become different at higher J_V for the two arrays does not affect the sign of this inequality.) Thus the homoporous array gives a lower bound for the solute flux through the heteroporous array, and we have the same lower bound as before. The same upper bound as before, eqs. (18) and (21), can also be shown to hold. We note that $J_s \to c_s' J_V$ as $J_V \to \infty$ for the heteroporous array, and then the argument proceeds exactly as for the single membrane.

The final step in the general proof is to show that any interconnected pore structure can be reduced to the foregoing special case of a series array of submembranes. We shall give an explicit demonstration of this for the simple case of two parallel pores connected by one internal shunt, as shown in fig. 4a; the extension of the proof to more elaborate structures should then be obvious. In fig. 4b the membrane is redrawn schematically to emphasize the junction points. This structure apparently differs in a fundamental way from the previous one shown in fig. 3a, for two of the junction points are each connected to three other junction points. However, a simple construction shows that the two structures are in a sense equivalent. Suppose the concentration at the upper internal junction point is c_2; there is then some point in the parallel pore that also has the concentration c_2, and we pass a hypothetical plane through these two points as shown in figs. 4a and b. Similarly, we pass another hypothetical plane through the points of concentration c_3, the concentration at the lower internal junction point. These two planes divide the membrane structure into three submembranes as shown in fig. 4c. It should be recognized that this is not entirely the same as the special case of fig. 3. The pressures at the points of equal concentration are not necessarily equal, and we could not connect these points physically without altering the flow through the membrane. In other words, the structures in figs. 3 and 4 really are fundamentally different, in that their concentration and pressure distributions cannot in general both be made similar, although one or the other can be. But we are not concerned about pressure distribution here, we are concerned only with solute and volume flow, and eq. (1) shows that pressure difference do not explicitly enter the expression for solute flux in a given pore segment. Thus we are entitled to compare the upper "submembrane", between concentration surfaces c_1 and c_2 in fig. 4, with a hypothetical homoporous membrane having the same total volume flow, since the mathematical expressions for solute flux depend only on the variable J_V and not on the pressure distribution. This comparison shows that the solute flux in the upper submembrane is equal to or greater than the solute flux in the hypothetical homoporous membrane, by exactly the same reasoning as was used earlier to prove the lower bound for pores in parallel.

Continuing this line of reasoning for the rest of the "submembranes" in fig. 4, we conclude that the same lower bound on solute flux holds for a membrane with internal interconnections as holds for one without interconnections. A similar conclusion is reached for the upper bound, by the same method. That is, we note that the division of the interconnected membrane into an array of submembranes establishes that the curve of J_s versus J_V must always be concave upward, and that $J_s \to c_s' J_V$ as $J_V \to \infty$; the remainder of the argument then proceeds as before.

The generalization of the simple case shown in fig. 4 should now be apparent. A more complex membrane is divided into effective submembranes as follows. Proceeding downstream from the membrane face at $c_1 = c_s'$, we find the internal junction point with the highest solute concentration; we call this concentration c_2, and pass a hypothetical surface through all the points in the membrane where the solute concentration is c_2. This splits off the first submembrane. We then find the junction point downsteam that has the next highest solute concentration, call it c_3, pass a hypothetical surface through all the points having concentration c_3, and thereby split off the second submembrane. Continuing through the membrane in this fashion, we eventually divide it into as many submembranes as there are internal junction points having different solute concentrations, plus one more submembrane, as shown in fig. 4 for a membrane with only two internal junction points. Once this subdivision is made, the rest of the argument proceeds exactly as for the membrane of fig. 4.

Thus the bounds on solute as a function of volume flux hold for membranes with internal connections. In our discussion we did not have to be concerned with matters such as dead-end pore segments, because we dealt only with steady-state operation. Our arguments obviously do not hold for transients, or for various other kinds of time-dependent operation. Such cases are very much more complicated to analyze in detail, although a successful analysis would presumably yield information on membrane structure not available from analysis of just the steady state.

7. Discussion

The preceding paper [1] answered *No* to the question, "Can an exact transport equation for solute flux across an inert porous membrane be written without detailed knowledge of the membrane structure?" The present paper shows that the answer can be changed to *Yes* if the first few words of the question are changed to, "Can a useful approximate transport equation ...", provided that internal concentration polarization does not take place. In cases where internal concentration polarization occurs, error bounds cannot be established without detailed knowledge of membrane structure, and D'Arcy's law for volume flow does not hold. In fact, this last condition can serve as an operational test for the presence of internal concentration polarization.

We have shown, in other words, that solute flux depends only weakly on distribution of pore size. It follows that for heteroporous membranes solute flux is an insensitive probe of structure, unless perhaps the latter is rather bizarre.

A skeptical reader may well ask whether there is much practical import in the foregoing detailed analyses of transport equations based on special microstructural models. After all, it is only demonstrated that, save for cases of internal concentration polarization or for very bizarre pore size distributions (conditions not likely to be found in most synthetic membranes), a simple exponential function provides a close approximation to actual solute flux. The importance of the detailed structural approach, in our opinion, lies principally in exposing the danger of attempting to apply simplified transport equations to predict solute flux across biological membranes. Here a highly ordered rather than a random distribution of pore sizes may be encountered, with discrete sets of pores of widely different structures. Under such circumstances not only will the usual equations fail to predict solute flux properly, but measurements of hydraulic conductivity using solutes of different size to generate osmotic gradient may lead to widely varying results. Of particular importance is the fact that sieving coefficients may become markedly dependent upon the boundary conditions. It should also be appreciated that across biological membranes, or even synthetic membranes of mosaic structure, the condition of zero overall J_V does not preclude the existence of two opposite but equal convective fluxes, a condition that can lead to useless values for σ.

Finally, we may justify this primitive attempt on our part to construct a detailed (model) theory on other grounds. The beginnings of a detailed theory as outlined already provide a basis for designing experiments that allow some inferences to be drawn regarding the structural make-up of a given membrane, which is regarded largely as a black box in many previous approaches.

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