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NOTE

Permeation Properties in Laminated Membranes

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Abstract

The response of laminated membranes to permeation was investigated using simple permeation equations. The intrinsic permeability constant of the membrane was shown to be between the maximum or minimum intrinsic permeability constant of all component membranes. Thus the separation factor of the laminated membrane for any type of permeating molecules will be between the values of maximum and minimum separation factors of the component membranes. Permeation through the laminated membrane for a given species will depend on the direction of permeation if the intrinsic permeability constant of any permeating molecule is dependent on the concentration. A simple example for the concentration dependence of permeability constant shows the limits of anisotropic flow ratio.

INTRODUCTION

The laminated membrane (*1*) is one type of heterogeneous membrane. Although diffusion in laminated membrane was studied as early as 1959 by Frish (*2*), the application of laminated membranes as membrane valves (*3*, *4*) or other biological phenomena interpretation (*5*) was investigated only recently. Petropoulos (*3*, *4*) has studied theoretically the flow reversal effects in a simple laminated membrane using the fundamental diffusion equation. Graves et al. (*5*) have applied the principles of Fick's law of diffusion in a laminated membrane to explain bubble formation or, more precisely, the mechanism of maculopapular skin lesions in a helium–oxygen environment. It is the purpose of this paper to use similar but more simple permeation equations to describe all these phenomena.

PERMEATION EQUATION

The basic permeation equation for any permeating molecule, i, through a slab of n laminated membranes is given by (*1*)

$$\frac{l}{P_i} = \frac{l_1}{P_{i1}} + \cdots + \frac{l_n}{P_{in}} \tag{1}$$

where P_{i1} is the intrinsic permeability constant of the permeating molecule, i, in the component 1 membrane; l_1 is the thickness of the component 1 membrane; P_i is the average intrinsic permeability constant of permeating molecule i in the laminated membrane; and l is the total thickness of laminated membrane. Therefore:

$$l = \sum_{i=1}^{n} l_i \tag{2}$$

RANGE OF PERMEATION RATES AND SEPARATION FACTORS

Before deriving expressions for the ranges of permeation properties in a laminated membrane, we will first prove the following mathemathical relations. If

$$Z = \frac{\sum_{i=1}^{n} X_i}{\sum_{i=1}^{n} Y_i}$$

where

$$X_i, Y_i > 0 \quad \text{and} \quad \left(\frac{X}{Y}\right)_{\min} \leqq \left(\frac{X_i}{Y_i}\right) \leqq \left(\frac{X}{Y}\right)_{\max}$$

Then

$$\left(\frac{X}{Y}\right)_{\min} \leqq Z \leqq \left(\frac{X}{Y}\right)_{\max}$$

Since

$$\frac{X_i}{Y_i} \leqq \left(\frac{X}{Y}\right)_{\max}$$

therefore

$$X_{\max} Y_i \geqq X_i Y_{\max} \qquad \text{as} \quad X_i, Y_i > 0$$

Therefore

$$\sum_{i=1}^{n} X_{\max} Y_i \geqq \sum_{i=1}^{n} X_i Y_{\max}$$

and

$$\frac{\sum_{i=1}^{n} X_i}{\sum_{i=1}^{n} Y_i} \leqq \left(\frac{X}{Y}\right)_{\max}$$

Similarly

$$\frac{\sum_{i=1}^{n} X_i}{\sum_{i=1}^{n} Y_i} \geqq \left(\frac{X}{Y}\right)_{\min}$$

Therefore

$$\left(\frac{X}{Y}\right)_{\min} \leqq Z \leqq \left(\frac{X}{Y}\right)_{\max} \tag{3}$$

The separation factor (SF) for two permeation species, α and β, is the ratio permeability constant (*6*)

$$\mathrm{SF}_{\beta}^{\alpha} = P_{\alpha}/P_{\beta} \tag{4}$$

By combining Eqs. (1) and (4), one can obtain the separation factor in the laminated membrane;

$$\mathrm{SF}_{\beta}^{\alpha} = \frac{\sum_{i=1}^{n} \frac{l_i}{P_{\beta i}}}{\sum_{i=1}^{n} \frac{l_i}{P_{\alpha i}}} \tag{5}$$

Applying Eq. (3) to Eq. (5), one can obtain

$$\left(\frac{\dfrac{l_i}{P_{\beta i}}}{\dfrac{l_i}{P_{\alpha i}}}\right)_{\min} \leqq \mathrm{SF}_{\beta}^{\alpha} \leqq \left(\frac{\dfrac{l_i}{P_{\beta i}}}{\dfrac{l_i}{P_{\alpha i}}}\right)_{\max}$$

or

$$[\mathrm{SF}_{\beta}^{\alpha}(i)]_{\min} = \left(\frac{P_{\alpha i}}{P_{\beta i}}\right)_{\min} \leqq \mathrm{SF}_{\beta}^{\alpha} \leqq \left(\frac{P_{\alpha i}}{P_{\beta i}}\right)_{\max} = [\mathrm{SF}_{\beta}^{\alpha}(i)_{\max}] \tag{6}$$

where $[SF_\beta^\alpha(i)]_{max}$ and $[SF_\beta^\alpha(i)]_{min}$ are the maximum and minimum separation factor for component α relative to β in the set of all component membranes in a laminated membrane.

Equation (6) shows that the ranges of the separation factor for the laminated membrane is between the maximum and minimum separation factor of component membranes in the laminated membrane. For this reason, one cannot increase the separation factor more than that of individual membranes by laminating membranes.

Similarly, the intrinsic permeability constant in the laminated membrane can be shown to be

$$[P_i]_{min} \leqq P_i \leqq [P_i]_{max} \tag{7}$$

where $[P_i]_{max}$ and $[P_i]_{min}$ are the maximum and minimum permeability constant of all component membranes in a laminated membrane, respectively.

$$[P_i]_{max} \geqq P_i$$

Therefore

$$\frac{l_i}{P_i} \leqq \frac{l_i}{[P_i]_{max}}$$

Take the summation

$$\sum_{i=1}^{n} \frac{l_i}{P_i} \geqq \sum_{i=1}^{n} \frac{l_i}{[P_i]_{max}} = \frac{l}{[P_i]_{max}}$$

as

$$\frac{l}{P} = \sum_{i=1}^{n} \frac{l_i}{P_i}$$

Therefore

$$\frac{l}{P} \geqq \frac{l}{[P_i]_{max}}$$

and

$$P \leqq [P_i]_{max}$$

In the same way, one can show

$$P \geqq [P_i]_{min}$$

Thus both the intrinsic permeability constant and separation factor for the laminated membrane fall between the maximum and minimum values for the component membranes.

ANISOTROPIC FLOW

Consider one component of permeant through a simple laminated AB membrane. The permeation rate will be independent of the direction of flow if the permeation constant in each component membrane is independent of the concentration or activity. If the permeation constant is dependent on the concentrations or activities, there will be an anisotropic permeation rate. We will use the same case of concentration dependence of permeability constants as described by Petropoulos (*3*):

$$\begin{aligned} P_A(\alpha) &= P_a \quad && \text{if } \alpha_a \leqq \alpha \leqq 1 \\ P_A(\alpha) &= P_0 \quad && \text{if } 0 \leqq \alpha \leqq \alpha_a \\ P_B(\alpha) &= P_B \quad && \text{for all } \alpha \end{aligned}$$

where $\alpha = a/a_0$; a_0 is the activity of penetrant at the upstream face of the membrane; a is the activity of penetrant in the membrane.

By applying the above conditions to Eq. (1), one can derive the permeation flux in the direction of **AB** or **BA**, J_{AB} or J_{BA}, as follows, if the permeation activity profile in the laminated membrane is as shown in Fig. 1.

$$\frac{l}{P_{AB}} = \frac{l_A}{P_a} + \frac{l - l_A}{P_B} \tag{8}$$

$$\frac{l}{P_{BA}} = \frac{l - l_A}{P_B} + \frac{l_A - l_a}{P_a} + \frac{l_a}{P_0} \tag{9}$$

By substituting Eq. (8) into Eq. (9), one can obtain

$$\frac{l}{P_{BA}} = \frac{l}{P_{AB}} + \left(\frac{1}{P_0} - \frac{1}{P_a}\right) \tag{10}$$

The anisotropic flow ratio was defined as (*3*)

$$f = P_{AB}/P_{BA} \tag{11}$$

Combining Eqs. (10) and (11), one can obtain the anisotropic flow ratio;

$$f = 1 + \frac{l_a}{l}\left(\frac{P_{AB}}{P_0} - \frac{P_{AB}}{P_a}\right) \tag{12}$$

Thus, if P_a is larger than P_0, f will be larger than 1. In other words, the

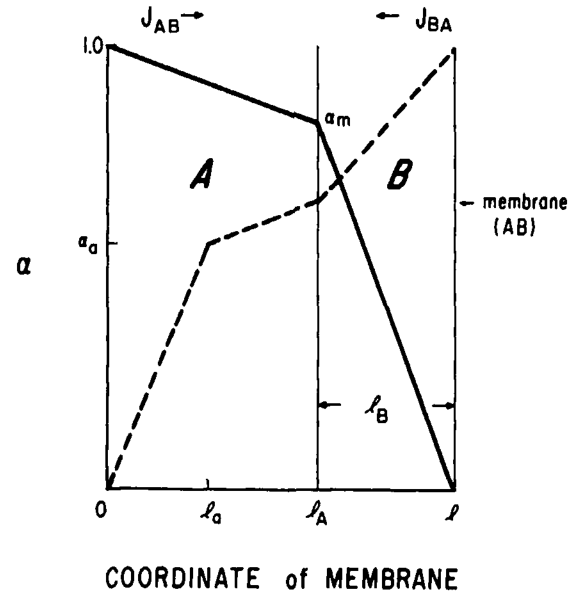

FIG. 1. Possible activity profile in a laminated membrane AB for the sense of AB and BA. (For meaning of symbols, see text.)

permeation rate will be larger in the **AB** direction than in the **BA** direction. The anisotropic value will depend on the value of P_0 and P_a. In the extreme case when P_0 is approaching zero and l_a is approaching l, f could become very large.

OTHER APPLICATIONS

Loeb and Sourirajan (7) type membranes and liquid/solid composite membranes are special cases of laminated membranes. The basic permeation equations for laminated membranes can be applied to those cases.

SUMMARY

We have used the simple permeation equation for the flat laminated membranes and discussed the ranges of permeation rates and separation factor. The possibility for anisotropic flow in the laminated membranes can be easily demonstrated by using a simple permeation equation. Thus one cannot expect a laminated membrane to be more selective toward permeant molecules through any component membranes. There are some experimental facts to substantiate the above conclusions (*8*).

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