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# Resistance and Mass Transfer Control through Passive Porous Films. I. A Transport Model for Diffusive Permeability

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# Resistance and Mass Transfer Control through Passive Porous Films. I. A Transport Model for Diffusive Permeability

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## Abstract

The first part of this work describes a model for the passive transport of solutes through membrane systems formed by a low porosity film and the adjacent boundary layers. Model equations allow correlation of the overall phenomenological coefficient of diffusive resistance with the morphological and structural characteristics of the membrane system. Based on the general solution, the total resistance appears to be the result of three contributions related to the membrane itself, the associated boundary layers, and the pore end effects. Under specific conditions it is possible to obtain an explicit and simple functional dependence for each of these contributions as well as to express the solute concentrations in the membrane-boundary layer interfaces.

## INTRODUCTION

An important aspect of the behavior of membranes—either biological or artificial—in the presence of fluid phases, appears when the generalized force applied on them is a gradient of chemical potential associated with a solute concentration difference. This force induces a solute flux through the membrane barrier (the so-called diffusive permeation) that tends to make the concentrations of both sides equal. This process is usually characterized by the proportionality coefficient between the flux and the driving force (diffusive permeability in this case).

For a given difference of concentrations, the diffusive permeation of a chemical species is governed by the nature of the membrane and by the experimental conditions (*1*, *2*). In fact, it is known that the homogeneous or heterogeneous character of the membrane affects the flux in a different way, and also that the presence of hydrodynamic boundary layers (or stagnant layers) next to the membrane acts as an additional barrier to diffusion (*3*, *4*).

However, it is common practice to analyze the mass transfer through heterogeneous membranes as if they were homogeneous permeable membranes, that is to say, without considering the effects of interaction between the pores and the subsequent distortion of the flux. In other cases the effect of boundary layers is omitted (*5*), although at times they can control the flux. A phenomenological treatment of permeabilities (or associated resistances) is sometimes applied, but without relating each term to the intrinsic characteristics (geometrical, structural, etc.) of each element of the whole barrier.

Part I of this series is devoted to a theoretical study of diffusive permeation through a complete membrane system, i.e., a simultaneous consideration of the effects of the membrane itself, the pore end, and associated barriers such as stagnant layers. The treatment we use follows Keller and Stein (*6*) but is based on experimental results related to the structural and functional characterization of microporous track-etched membranes. Once the complex relationship between the mass transfer coefficient and the intrinsic parameters of the membrane system is established, we will obtain an approximation, valid in a wide range of conditions of work, which considerably simplifies the use of the model equations.

In Part II (*7*), the model is applied to the results of experiments of diffusive permeation on the aforementioned membranes, which will permit estimation of the value of certain parameters of interest and establishment of the concentration profiles through the membrane system.

## MORPHOLOGICAL CHARACTERIZATION AND MODELIZATION

From a morphological-structural point of view, microporous membranes are normally characterized by a small number of parameters: pore size, surface pore density, and thickness. These are generally considered sufficient because the thickness, $l$, is identified with the pore length and it is possible to obtain the porosity from the pore radius and the surface pore density.

In models for the fluxes, it is usually assumed that pores are so closely spaced that the membranes is homogeneously permeable and shows a diffusive resistance, $R_m$, related to its porosity, $\varepsilon$, by (*8, 9*)

$$R_m = l/\varepsilon D_p \tag{1}$$

where $D_p$ is the pore diffusivity.

For boundary layers of thickness $\delta$:

$$R_\delta = \delta/D_\delta \tag{2}$$

where $D_\delta$ is the corresponding diffusivity.

The overall resistance, $R_T$, is $R_T = R_m + 2R_\delta$, that is,

$$R_T = \frac{l}{\varepsilon D_p} + \frac{2\delta}{D\delta} \tag{3}$$

because it corresponds to an one-dimensional model of diffusion resistances in series.

Nevertheless, at times the problem is more complex because the membranes present irregularities in their morphologies (variations in the pore sizes, sloping in their trajectories, etc.) which require a deeper characterization and the introduction of these details in the models. It is also necessary to consider an additional effect which is characteristic of membranes with low or moderate porosities, and which has been commented on by several authors (*1, 5*). Due to the lack of homogeneity on the surface of these types of membranes, the streamlines of diffusive flux are distorted around the mouth of each pore.

This requires a component of the diffusive velocity parallel to the membrane surface, as well as the normal one, to be considered; i.e., treatment of a two-dimensional flux is required.

Our samples are a group of track-etched membranes of polycarbonate (Nuclepore) with nominal pore diameters of 5, 2, 0.8, 0.4, and 0.1 μm, denoted by N5, N2, N08, etc. in this paper. These membranes have been characterized in a previous study (*10*) by scanning electron microscopy (SEM) of their surfaces. We obtained results on the distribution of pore sizes, the surface pore radius, $r_s$, and the surface pore density, $N$, from which it was possible to obtain the fractional open area of the membrane, given by $\pi r_s^2 N$.

By using transmission electron microscopy (TEM) measurements, we have been able to determine the thickness, $l$, of the transverse sections and to detect the presence of internal widening of pores (*11*). Finally, from measurements of the hydrodynamic permeability coefficient, and taking into account the correction due to the angular tortuosity factor, the effective radius of the pores, $r_e$, and the corresponding porosities, $\varepsilon_e$, have been obtained by using the Hagen-Poiseuille law (*12*).

Table 1 summarizes the most relevant results for the present study. As can be seen, the values of the parameters that characterize the membrane surface differ considerably from those inside the membrane. This result will affect the membrane's functional behavior under the action of some generalized force and so must be taken into account when a proper model for fluxes is proposed.

## TWO-DIMENSIONAL MODEL

The membrane is considered as a film of thickness $l$, pierced by pores of approximately cylindrical shape (whose surface radius can differ from their effective radius, $a$) equally distributed on its surface, the distance between the centers of two adjacent pores being $2b$.

The steady-state diffusive flux, $J_d$, of a chemical species through the membrane appears between two homogeneous solutions of concentrations $c_1$ and $c_2$ ($c_1 > c_2$). The effect of the viscous resistance of the solvent in the vicinity of the membrane will be simulated by two fluid stagnant

TABLE 1
Results Obtained for the More Relevant Structural Parameters of the Membranes Studied (Nuclepore of polycarbonate)

| | Membrane | | | | |
|---|---|---|---|---|---|
| Parameter | N5 | N2 | N08 | N04 | N01 |
| $r_s$ (μm) | 1.81 | 0.79 | 0.344 | 0.188 | 0.044 |
| $\pi r_s^2 N$ (%) | 5.5 | 5.7 | 11.3 | 10.1 | 3.3 |
| $r_e$ (μm) | 2.07 | 1.11 | 0.52 | 0.258 | 0.065 |
| $\varepsilon_e$ (%) | 7.5 | 10.6 | 27.6 | 21.1 | 7.5 |
| $l$ (μm) | 10.7 | 10.6 | 10.9 | 10.9 | 6.4 |

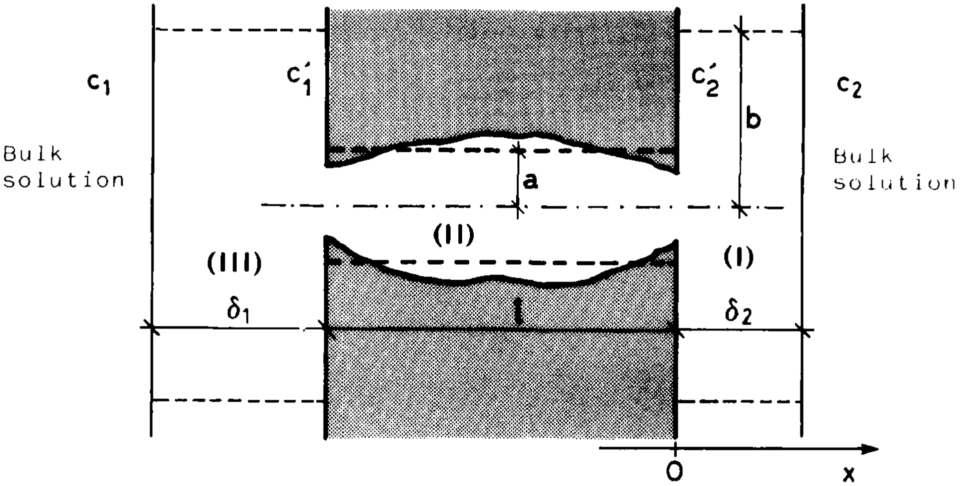

FIG. 1. Cross section of a unit cell of the porous membrane (shaded) and the associated boundary layers (Regions I and III), showing their characteristic geometrical parameters. In Region II the approximated profiles of a real pore (continuous line) and of the equivalent pore of radius *a*, with the same functional behavior (broken line), are included.

films (boundary layers) of thickness $\delta_1$ and $\delta_2$, respectively. Nevertheless, due to symmetry, they can be assumed to be of the same thickness, $\delta$, without loss of generality.

The concentrations in the two membrane–boundary layer interfaces are represented by $c'_1$ and $c'_2$, respectively (Fig. 1).

Let us suppose that the diffusive layers can be divided around each pore by fictitious surfaces perpendicular to the membrane plane and impermeable to the solute. The pattern of identical and independent cells, in which each pore has associated with it a part of the boundary layers, allows us to take as a base for the analysis only one such elemental cell.

Formally, each cell will be considered as subdivided into three cylindrically symmetrical regions: two regions corresponding to the stagnant films, where the diffusivity is $D_\delta$ [represented as (I) and (III) in Fig. 1] and the pore itself where the diffusivity is $D_p$ [represented by (II) in the same figure]. It is also convenient to represent the geometrical characteristics of the system by means of the following dimensionless parameters:

$$\beta = b/a; \qquad \lambda = \delta/a; \qquad \omega = l/a \tag{4}$$

In the steady state, Fick's second law is expressed (*13*) by

$$D\nabla^2 c = 0 \tag{5}$$

where $D$ is the diffusion coefficient of the diffusing substance and $c$ is the concentration.

In cylindrical coordinates ($\rho,\theta,x$), and supposing that because of axial symmetry, c is independent of the angular coordinate, Eq. (5) can be expressed by

$$\frac{\partial^2 c}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial c}{\partial \rho} + \frac{\partial^2 c}{\partial x^2} = 0 \tag{6}$$

Now, it is necessary to solve Eq. (6) for each of the regions mentioned previously, under the corresponding boundary conditions. In this case we have followed the procedure pointed out in Ref. *6*, which is based on the use of Hankel's finite transform (*14–16*). Later, the condition of steady-state flux will permit us to equate the solutions at the boundaries ($x = 0$ and $x = l$) and thus to obtain expressions for the overall diffusive resistance, $R_T$ (or the corresponding diffusive permeability, $P_T = 1/R_T$) and for the concentrations $c_1'$ and $c_2'$:

$$R_T \equiv \frac{1}{P_T} = \frac{c_1 - c_2}{J_d} = \frac{a\omega\beta^2}{D_p} + \frac{8a\beta^2}{D_\delta} H(\beta,\lambda) \tag{7}$$

where

$$H(\beta,\lambda) = \frac{1}{\beta^2}\sum_{n=0}^{\infty} \frac{J_1^2(\alpha_n a)\tan h(\alpha_n a\lambda)}{(\alpha_n a)^3 J_0^2(\alpha_n a\beta)} \tag{8}$$

$J_0$ and $J_1$ are the first kind Bessel functions of zero- and first-order, respectively, and the values $\alpha_n$ represent the zeros of the equation $J_1(\alpha_n b) = 0$. Also:

$$c_1' = c_1 - \frac{c_1 - c_2}{2 + \Gamma} \tag{9}$$

$$c_2' = c_2 + \frac{c_1 - c_2}{2 + \Gamma} \tag{10}$$

where Γ is given by

$$\Gamma \equiv \frac{\omega D_\delta}{4D_p H(\beta,\lambda)} \tag{11}$$

The use of Eq. (7), (9), and (10) in a particular case requires a previous evaluation of $H(\beta,\lambda)$, which can be laborious. In the study by Keller and Stein (*6*), this function was calculated for several values of β and λ in the range 1 to $10^3$; however, as we will see later, the function $H(\beta,\lambda)$ can be evaluated by a simple approximation valid for a wide range of cases of practical interest.

## LINEAR APPROXIMATION OF *H*(β,λ)

If we evaluate in an explicit form the zeroth-order eigenfunction in the series expansion of $H(\beta,\lambda)$, we obtain

$$H(\beta,\lambda) = \frac{\lambda}{4\beta^2} + \frac{1}{\beta^2} \sum_{n=1}^{\infty} \frac{J_1^2(\alpha_n a) \tan h(\alpha_n a\lambda)}{(\alpha_n a)^3 J_0^2(\alpha_n a\beta)} \tag{12}$$

This result suggests that, for limited values of the argument, the previous function can approximate to a simple expression. In fact, we have done a linear regression analysis on $H$ against $\lambda/\beta^2$, considering the intervals $1.4 < \beta < 10^3$ and $8 < \lambda < 10^3$, and we have obtained the following correlation:

$$H(\beta,\lambda) = 0.250(\lambda/\beta^2) + 0.164 \tag{13}$$

with a correlation coefficient of 0.9999 for a total of 100 data points.

As can be observed, the validity range of the above approximation corresponds to a wide range of porosity and pore size values. Because $\beta^2 = 1/\varepsilon$, the limit values $\beta = 1.4$ and $\beta = 10^3$ correspond approximately to values of $\varepsilon = 0.5$ and $\varepsilon = 10^{-6}$, respectively, thus including a wide range of membrane porosities. For λ, assuming an average value for δ of about 50 μm (*17–19*), the approximation would be valid for membranes with pore radii between 0.05 and 6 μm.

With that, substituting Eq. (13) in Eq. (7) gives

$$R_T \equiv \frac{1}{P_T} = \frac{a\omega\beta^2}{D_p} + \frac{2a\lambda}{D_\delta} + 1.312\,\frac{a\beta^2}{D_\delta} \tag{14}$$

where a third term appears which is obviously related to the pore end effects, which did not appear in the one-dimensional treatment.

Now, if we express Eq. (3) equally as a function of the dimensionless parameters, we have

$$R_T = \frac{a\omega\beta^2}{D_p} + \frac{2a\lambda}{D_\delta} \tag{15}$$

By comparison of Eqs. (15) and (7), we conclude that both models agree when $H(\beta,\lambda) = \lambda/4\beta^2$; but as we have stated in Eq. (12), this is the value which $H(\beta/\lambda)$ takes when we only consider the first term in their series expansion, that is, when the pore end effects included in the remainder terms of the expansion are not considered. So the one-dimensional model can be considered as a first-order approximation for the analyzed model and, therefore, as a particular case.

Finally, expressing Eq. (14) as a function of measurable properties:

$$R_T = \frac{l}{\varepsilon_e D_p} + \frac{2\delta}{D_\delta} + \frac{1.312}{\pi r_s N D_\delta} \tag{16}$$

or, simply:

$$R_T = R_m + 2R_\delta + 2R_e \tag{17}$$

Similarly, after substitution of Eq. (13) into Eq. (11), we obtain for the concentrations in the membrane–boundary layer interfaces $c_1'$ and $c_2'$:

$$c_1' = c_1 - \frac{c_1 - c_2}{2 + \Omega} \tag{18}$$

$$c_2' = c_2 + \frac{c_1 - c_2}{2 + \Omega} \tag{19}$$

with

$$\Omega \equiv \left(\frac{D_\delta}{D_p}\right) \frac{l}{\pi r_s^2 N \delta + 0.656 r_s} \tag{20}$$

In conclusion, we can say that the proposed model considers, besides the influence of the membrane and the boundary layers, the influence derived from the inhomogeneities in the pore surface distribution. Thus, a connection between the permeability results and the morphology of the membrane system has been established without compromising the classical phenomenological formalism of an arrangement of diffusive resistances in series, and including as a limiting case that in which the pore end effects are negligible.

On the other hand, the approximation used for $H(\beta,\lambda)$ does not include an important restriction in the utilization of the model, because it is valid for a great number of porous membranes.

## SYMBOLS

| | |
|---|---|
| $a$ | radius of the equivalent pore |
| $b$ | half-distance between the centers of two adjacent pores |
| $c_1, c_2$ | bulk solute concentrations |
| $c_1', c_2'$ | solute concentrations at the membrane-boundary layer interfaces |
| $D_p, D_\delta$ | solute diffusivities through the membrane pore and boundary layer, respectively |
| $H(\beta,\lambda)$ | function defined by Eq. (8) |
| $J_0, J_1$ | Bessel functions of zeroth and first order, respectively |
| $J_d$ | diffusive flux of solute |
| $l$ | membrane thickness |
| $N$ | surface pore density of membrane |
| $P_t$ | total diffusive permeability coefficient |
| $R_m, R_\delta, R_e$ | diffusive resistances of the membrane, boundary layer, and pore end, respectively |
| $R_T$ | diffusive resistance of the membrane system (total resistance) |

| | |
|---|---|
| $r_e$ | effective pore radius (evaluated from Hagen-Poiseuille law) |
| $r_s$ | surface pore radius |
| $t$ | time |
| $x$ | axial coordinate inside the pore |

## Greeks

| | |
|---|---|
| $\alpha_n$ | zeros of equation $J_1(\alpha_n b) = 0$ |
| $\beta$ | $b/a$ (dimensionless geometrical parameter) |
| $\delta$ | boundary layer thickness |
| $\varepsilon$ | fractional open area of the membrane. |
| $\varepsilon_e$ | effective porosity of membrane, calculated from $r_e$ |
| $\lambda$ | $\delta/a$ (dimensionless geometrical parameter) |
| $\omega$ | $l/a$ (dimensionless geometrical parameter) |
| $\rho$ | radial coordinate inside the pore |
| $\Omega$ | relationship between parameters of the membrane system, defined by Eq. (20) |
| $\Gamma$ | dimensionless relationship defined by Eq. (11) |
| $\theta$ | angle coordinate |
| $\nabla^2$ | Laplacian operator |

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