JOURNAL OF APPLIED POLYMER SCIENCE VOL. 15, PP. 1493-1505 (1971)

Influence of Compacting Pressure on the Permeability of Vectorized Membranes for Liquids

A. PETERLIN and JOEL L. WILLIAMS, *Camille Dreyfus Laboratory, Research Triangle Institute, Research Triangle Park, North Carolina 27709*

Synopsis

The theory of liquid diffusive flow through graded membrane under applied pressure difference is developed and demonstrated on four simple models. The grading of the membrane, caused by a gradient of chemical composition or physical structure, results in a gradient of liquid uptake (hydration) which in turn is reduced by the compacting pressure existing in the membrane during the permeation experiment. The hydration established in equilibrium between the swelling tendency and compacting pressure determines the local permeability. It has different values $K_+ = K_-$ for opposite flow direction. The total membrane permeability $\langle K \rangle$, however, depends on the current direction only in the case that the relative depression of local hydration, and hence of permeability by pressure, is not uniform but has a gradient. In mathematical formulation, the directionality of membrane requires the local permeability to be an irreducible function of location and pressure p, continuously increasing or decreasing with x. Th permeability of the membrane is higher if the driving pressure is applied at the side of the membrane with higher relative reduction of hydration and permeability by compacting pressure.

INTRODUCTION

Vectorized membranes having a different permeability for flow in the opposite direction may be of value as permeation valves. Such asymmetric membranes for permeation of gases and vapors can be constructed, for instance, from two layers of different films, the permeability constants of which exhibit different pressure dependence[1] or by radiation-initiated grafting of sorbed polymer during permeation through the film which produces a concentration gradient of permeant.[2] Recent experiments[3] on flow of water through membranes of poly(styrene-pyridine) random copolymer with a quaternization gradient demonstrated an asymmetric permeability, i.e., a nearly 50% larger flow at the same pressure difference if the applied pressure and quaternization gradient had the same direction. In the membranes investigated, the permeability properties of each volume element are mainly determined by hydration which increases with quaternization. The permeability of the volume element extremely rapidly increases with hydration,[4] so that the membrane with a quaternization gradient exhibits a large permeability gradient. On the other hand, the membrane is exposed to a compacting pressure which reduces the hydration and hence the permeability.[5] The gradients of the driving and compacting pressure are exactly equal and opposite at every location in the membrane.

To our knowledge, there is in the literature no theoretical treatment of liquid permeation through such graded membranes under a pressure gradient taking into account the effect of composition and compaction gradient which could be used for explanation and understanding of experimental observations. Therefore, in that which follows, a study of some simple models is presented, demonstrating separately the role of both factors in producing the directional dependence of permeability. It turns out that vectorization occurs only in the case that the pressure dependence of the local permeability of the swollen membrane material has a gradient. A solvation (hydration) gradient alone, i.e., at constant compressibility, does not impart directionality to the transport properties of membrane for pure liquids.

HOMOGENEOUS MEMBRANE

The steady-state flow density j through a membrane of thickness l^* and permeability K^* under an applied pressure difference $\Delta p = p_0$ is usually described by Darcy's law (Fig. 1).

$$j = -K^* \frac{\Delta p}{\Delta x^*} = K^* p_0 / l^*. \qquad (1)$$

This equation can be immediately derived from the chemical potential of the permeant

$$\mu = \mu^0 + pV - RT \ln c \qquad (2)$$

where V is the molar volume and c is the molar fraction. Inside the membrane, the permeant is in equilibrium with outside liquid under the same macroscopic conditions, i.e., the same p and T. Since the membrane can be considered as a component with infinitely large molecular weight, its molar fraction vanishes yielding unity, i.e., a constant value for the molar

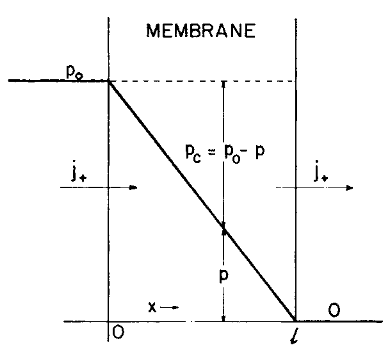

Fig. 1. Pressure p and compacting pressure $p_0 - p$ distribution in an ideal homogeneous membrane with j_+ (the current flows in the positive x-axis direction).

fraction of permeant inside the membrane. Hence, the transport velocity of the permeant in the membrane is

$$v = -(1/f)d\mu/dx^* = -(V/f)dp/dx^* \quad (3)$$

where f is the molar friction coefficient of the permeant in the medium and x^* is the location in the swollen membrane. The density of transport current is the product of local concentration ρH and velocity v,

$$j = -(\rho VH/f)dp/dx^* = -K^*dp/dx^* \quad (4)$$

with the local permeability

$$K^* = (\rho VH/f) = MH/f \quad (5)$$

where ρ is density, the swelling (hydration) H is the volume fraction at x^*, and M is molecular weight of the permeant. The main effect of H is not in the explicit factor as appearing in eq. (5) but in the drastic reduction of the friction coefficient f. Indeed, the value H/f varies by many orders of magnitude from that of nearly dry membrane to that of pure liquid if H goes from 0.01 to 1. A rather good approximation is given by

$$K^* \sim e^{-A/H} \quad (5a)$$

suggested by measurements of effective membrane permeability of water in a very wide hydration range.[4]

Since in steady state j is constant, eq. (4) can be integrated throughout the membrane, yielding

$$j = (1/l^*)\int_0^{p_0} K^*dp = \langle K^*\rangle\cdot p_0/l^* = K^*p_0/l^*. \quad (6)$$

In an ideal homogeneous membrane, the permeability K^* of the membrane material is a constant independent of pressure and location x^*. In any real membrane, however, the permeant swells and the pressure $p_c = p_0 - p$ which the membrane has to sustain (Fig. 1) compacts the material. The compacting pressure is maximum, and hence the swelling minimum at the low pressure side of the membrane. As a consequence, under the conditions of the permeability experiment the membrane becomes inhomogeneous as far as composition (membrane and swelling permeant) and permeant mobility are concerned.

The compacting pressure $p_c = p_0 - p$ is based on the mechanical equilibrium in the membrane. The applied pressure p_0 at $x^* = 0$ has to be borne by the membrane support at $x^* = l^*$. The transmittal to the support is effected by the membrane and by the local pressure of the permeant. That means that at any location x^* the membrane is exposed to a compaction pressure $p_0 - p$, which together with the permeant pressure p just adds up to the total transmitted pressure p_0. As a consequence the membrane is more compressed and the hydration more reduced at the low than at the high pressure side. This analysis is just the reversal of that by Bert[4] who assumes that the compaction is caused by p, being hence maximum at the high and minimum at the low pressure side of the membrane. Since he treats only membranes homogeneous in the dry state, his final results and the analysis of observable membrane permeability as function of applied pressure are not affected by his choice of $p_c = p$ as compared with ours, $p_c = p_0 - p$. One has merely to reverse the sign of the current in his Figure 1 or the normalized position in his plots of hydration (Fig. 4) and flow conductivity (Fig. 5). The integral in eq. (6) is, of course, independent of such a reversal.

The mobility increases extremely rapidly with permeant volume concentration H. On the other hand, H decreases with increasing p_c. The constant permeability of the dry homogeneous membrane becomes in the swollen state under the applied driving pressure p_0 a function of $p_c(x^*)$ or $p(x^*)$. Moreover, the membrane increases nonuniformly in thickness as a consequence of nonuniform swelling $H(p)$. The observed permeability in eq. (1) is an average of $K^*[p(x^*)]$ over the whole thickness of the membrane see eq. (6). It is not more a constant, but as a rule it decreases with p_0 as a consequence of increasing compaction with higher pressure.

If one assumes that swelling does not change the lateral dimensions but only the thickness of the membrane, one has a local deformation

$$dx^* = dx/(1 - H) \tag{7}$$

where x and x^* denote the location in the dry and swollen membrane, respectively. Hence, the equation for the current density in the volume element at x^* of the swollen membrane, eq. (4), can be transcribed in coordinates of the dry membrane

$$j = -K^*(P)\frac{dp}{dx}\cdot\frac{dx}{dx^*} = -K^*(p)(1 - H)\frac{dp}{dx} = K(p)\frac{dp}{dx} \tag{8}$$

with the local permeability

$$K(p) = (1 - H)K^*(p) \tag{9}$$

dependent exclusively on p. The dependence on x is not direct but merely through $p(x)$. The integration over x yields Darcy's law in terms of dry membrane

$$j\cdot l = \int_0^{P_0} K(p)dp = \langle K\rangle p_0 \tag{10}$$

which is independent of the direction of pressure gradient. Therefore, a membrane homogeneous when dry even after inhomogeneous swelling caused by the gradient of compaction pressure $p_c = p_0 - p$ does not acquire directionality. This result is trivial because one does not expect a change in $\langle K\rangle$ by turning around a homogeneous membrane.

VECTORIZED MEMBRANE

The situation is different if the dry membrane has already a built-in longitudinal gradient of transport properties caused by a gradient of chemical composition and/or physical structure (crosslinking, crystallinity). In equilibrium with a liquid (water), such a membrane will swell (hydrate) more on one side than on the other. High swelling (hydration) means high local permeability and compressibility, but also a longer way to travel for the permeant as a consequence of expansion in the x axis direction. One can expect that such a membrane will show a directionality, i.e., a difference in current j and hence in permeability K if the direction of the pressure difference p_0 is reversed.

Let us consider a few simple model cases which demonstrate the effect of single parameters even if they do not correspond very closely to the situation in actual membranes. In all models, the local permeability $K(x,p)$ already contains the correction factor $(1 - H)$ taking into account the membrane expansion by swelling as shown in eqs. (7)–(10).

I. The membrane has a hydration gradient producing an increase of local permeability K with x, i.e., $dK/dx > 0$. There is no effect of pressure on K. In the simplest case, K is a linear function of x,

$$K(x) = K_0(1 + \alpha x), \tag{11}$$

with no dependence on p.

II. The membrane has a permeability gradient as in model I. But the permeability is reduced at each location by the same function of compaction pressure, i.e., by a location independent function of p:

$$K = K_0 f_1(x) f_2(p). \tag{12}$$

Again $f_1(x)$ increases with x as with the first model. Since the compaction pressure decreases with p and the compaction decreases the permeability $f_2(p)$ is an increasing function of p but decreasing with p_0. A simple case of eq. (12) would be

$$K(x,p) = K_0(1 + \alpha x)/(1 + \beta(p_0 - p)) \tag{13}$$

containing only linear functions of x and p.

III. The effect of hydration and compaction is described by an irreducible function of x and p. The simplest expression for the permeability in such a case, containing only linear terms in x and p, can be written as

$$K = K_0\left(1 + \frac{\alpha x}{1 + \beta(p_0 - p)}\right) = K_0\left(1 + \frac{ax}{1 - bp}\right) \tag{14}$$

with

$$a = \alpha l/(1 + \beta p_0) \tag{15}$$
$$b = \beta/(1 + \beta p_0).$$

The permeability and compressibility increase with x.

IV. The effect of hydration and compaction is described by an irreducible function of x and p as in model III, but the compressibility decreases

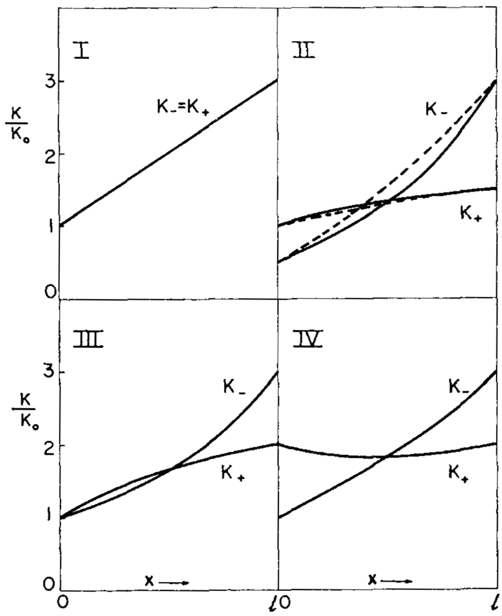

Fig. 2. Schematic plot of local permeability K_+ and K_- as function of x for the four models of eqs. (11), (13), (14), and (16) ($\alpha l = 2$ and $\beta p_0 = 1$) under the assumption that p is proportional to $l - x(+)$ or $x(-)$, respectively. This is correct for model I and the values at $x = 0$ and l for models II through IV. The correct data for model II are shown by broken line. Hence the correct data for models III and IV will be to the right of K_+ and to the left of K_-.

with increasing x. The simplest expression containing only linear terms in x and p reads

$$K + K_0\left(\frac{1}{1 + \beta(p_0 - p)} + \alpha x\right) = K_0'\left(\frac{1}{1 - bp} + ax\right) \quad (16)$$

with

$$\begin{aligned} K_0' &= K_0/(1 + \beta p_0) \\ a &= \alpha(1 + \beta p_0) \\ b &= \beta/(1 + \beta p_0). \end{aligned} \quad (16a)$$

A schematic representation of K_+ and K_- for the four cases represented by eqs. (11), (13), (14), and (16) is given in Figure 2. In order to make the plotting simpler, one has chosen proportionality between p and x or $l - x$. This is certainly not correct. Therefore the plots do not represent the actual changes of K with x. But they pretty well inform about the trend of permeability changes in a swollen graded membrane. The differences between the correct and simplified values are not very large, as can be concluded from the comparison of correct and simplified curves for model II.

The integration of eq. (4) can be performed in all four model cases, eqs. (11), (13), (14), and (16). One obtains for model I

$$p_0 = j \int_0^l \frac{dx}{K(x)} \tag{17}$$

$$j = p/\int_0^l = \langle K(l) \rangle \, p_0/l$$

$$\langle K(l) \rangle = l/\int_0^l \frac{dx}{K(x)}$$

and, in the special case,

$$p_0 = j \, \frac{\ln (1 + \alpha l)}{\alpha K_0} \tag{18}$$

$$j = K_0 \frac{\alpha p_0}{\ln (1 + \alpha l)} = \langle K(l) \rangle p_0/l$$

$$\langle K(l) \rangle = \frac{\alpha l}{\ln (1 + \alpha l)} K_0 = K_0(1 + \alpha l/2 - (\alpha l)^2/12 + \ldots)$$

The permeability $K(l)$ is independent of the value and direction of pressure difference. It increases with membrane thickness as a consequence of the assumed linear increase of K with x.

A similar result is obtained for the second model (II)

$$j \int_0^l \frac{dx}{f_1(x)} = K_0 \int_0^{p_0} \frac{dp}{f_2(p)} \tag{19}$$

$$j = K_0 \int_0^{p_0} \Big/ \int_0^l = \langle K(l,p_0) \rangle p_0/l$$

$$\langle K(l,p_0) \rangle = (K_0 l/p_0) \int_0^{p_0} \Big/ \int_0^l,$$

and, in the special case,

$$\frac{j}{\alpha} \ln (1 + \alpha l) = \frac{K_0}{\beta} \ln (1 + \beta p_0) \tag{20}$$

$$j = K_0 \frac{\alpha}{\beta} \frac{\ln (1 + \beta p_0)}{\ln (1 + \alpha l)} = \langle K(l,p_0) \rangle p_0/l$$

$$\langle K(l,p_0) \rangle = K_0 \frac{\alpha l}{\ln (1 + \alpha l)} \cdot \frac{\ln (1 + \beta p_0)}{\beta p_0}$$

$$= K_0 \left(1 + \frac{\alpha l}{2} - \frac{(\alpha l)^2}{12} + \ldots \right) \left(1 - \frac{\beta p_0}{2} + \frac{(\beta p_0)^2}{3} \ldots \right).$$

The permeability increases with l as in case I and decreases with p_0 as a consequence of membrane compaction under applied driving pressure. But there is no directionality. The current and the observed permeability $K(l,p_0)$ are independent of the orientation of the membrane and pressure gradient. One can formulate the result quite generally that the swollen inhomogeneous membrane does not show any directionality in current if the actual local permeability $K(x,p)$, including the swelling factor, eq. (9),

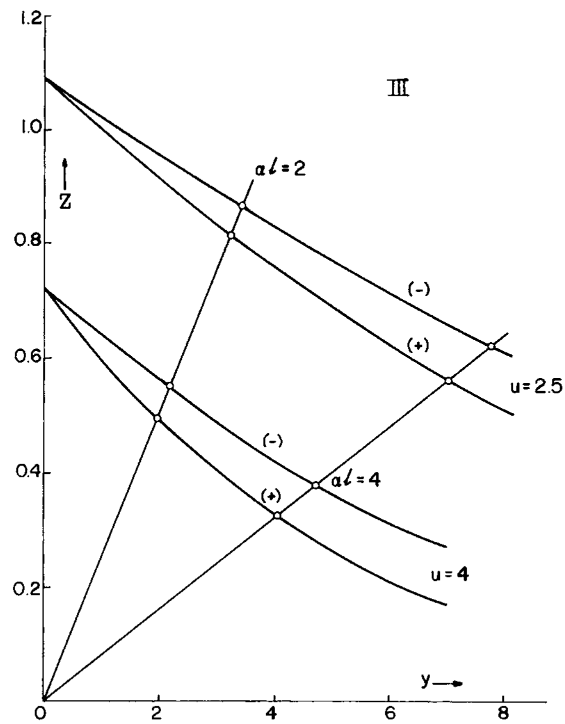

Fig. 3. Plot of $z_+ = K_0/\beta l j_+$ of model III vs. $y_+ = \alpha K_0/\beta |j_+|$ according to eq. (19) with the parameter $u = 1 + \beta p_0$. The intersection with the straight line $z = (K_0/\alpha l)y$ yields y_+ and y_- corresponding to the average pressure gradient p_0/l.

can be represented as a product of a function of x by a function of p, i.e., if the differential equation for the current can be integrated by straightforward separation of the coordinates p and x.

The third model (III) is indeed irreducible. In most cases the differential equation with a nonseparable $K(x,p)$ has to be solved by numerical integration. In the particularly simple case as represented by eq. (13), one obtains as intermediate solution of the differential equation

$$\frac{\beta l}{K_0} j_+ = \frac{1}{y-1} (u^{y-1} - 1) = 1/z_+ \tag{21}$$

$$\frac{\beta l}{K_0} j_- = \frac{1}{y+1} (u^{y} - u^{-1}) = 1/z_-$$

with

$$y_{\pm} = \frac{\alpha K_0}{\beta |j_{\pm}|} \tag{22}$$
$$u = 1 + \beta p_0.$$

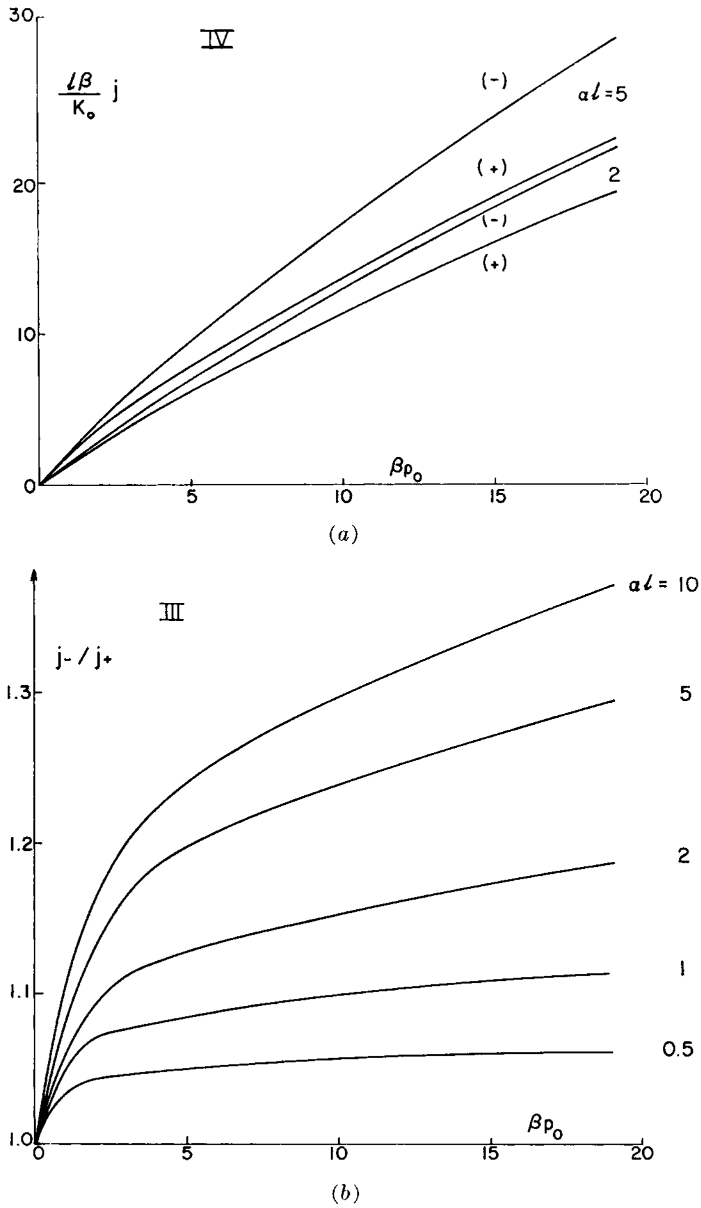

Fig. 4. The currents j_+ and j_- (a) and the ratio j_-/j_+ (b) as function of p_0 for different values of αl (model III).

In a plot of z versus y (Fig. 3), one obtains two curves z_+ and z_- for each u. By intersecting them with the straight line $z = (K_0/\alpha l)y$, one obtains the values y_+ and y_- corresponding to the membrane of thickness l at the applied pressure p_0. From them, one derives j_+, j_-, and the ratio $j_-/j_+ = y_+/y_-$, plotted in Figure 4 as functions of u, i.e., of the inverse maximum membrane compaction factor. With a choice of β, the abscissa can be also read in p_0 so that the curves $j(p)$ immediately yield the effective permeability of the membrane as function of applied pressure,

$$\langle K_{\pm}(l,p_0)\rangle = j_{\pm}l/p_0, \tag{23}$$

plotted in Figure 5. As expected $K_{\pm}$ decreases with increasing pressure as a consequence of membrane compaction.

Since j_-/j_+ is larger than 1 for positive α one has the general conclusion that the permeability is enhanced if the driving pressure is applied to the side of the membrane where the local hydration and hence the permeability is most reduced by compacting pressure, i.e., to the more compressible side of the swollen membrane. In our model with positive α, this is also the side with higher swelling. This result agrees with the experimental data by Williams et al.,[3] which shows a higher permeability with the pressure applied at the higher quaternized side of the membrane.

Negative α values reverse the situation, $j_+ > j_-$. Higher permeability is obtained if the pressure is applied to the less compressible side. But one must not forget that negative α means an increase of permeability with compaction which does not seem a very realistic model. Therefore, this case was not included in Figures 3–5.

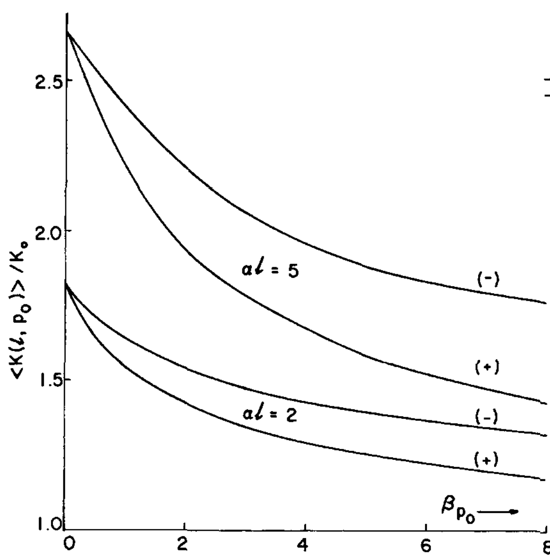

Fig. 5. Effective permeability $<K_{\pm}(l, p_0)>$ as function of p for different values of αl (model III).

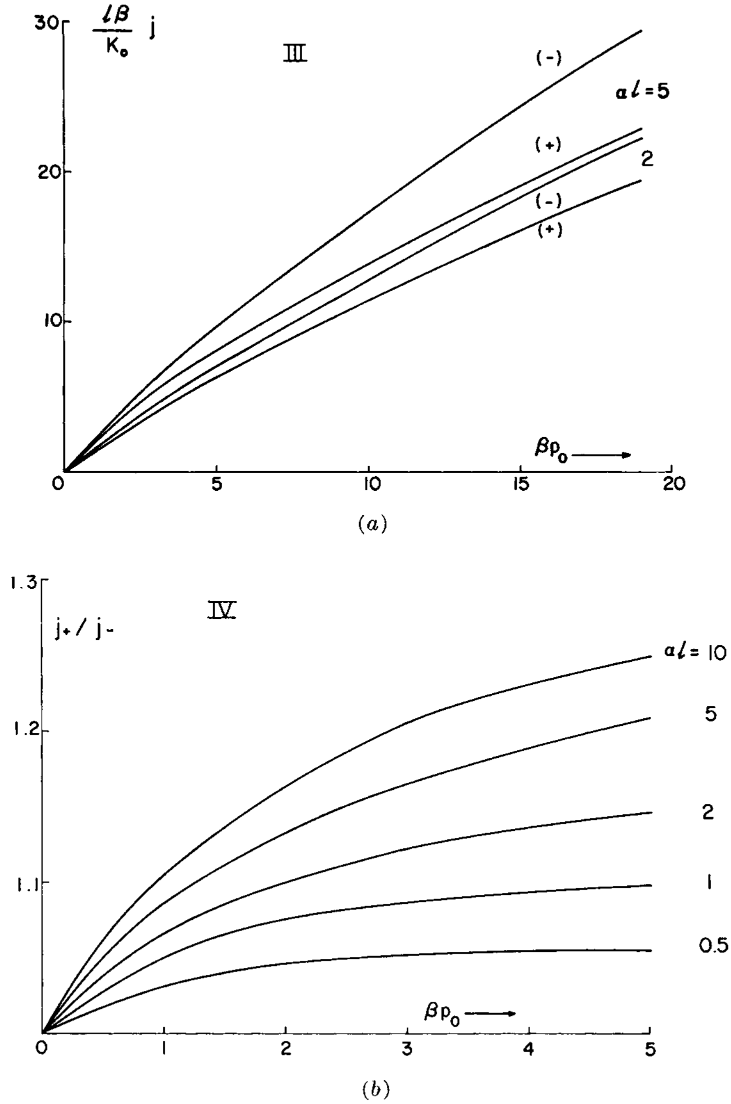

Fig. 6. The currents j_+ and j_- (a) and the ratio j_+/j_- (b) as function of p_0 for different values of αl (model IV).

One is certainly interested in the case where the reduction of hydration is similar to that in case III. One first obtains

$$\frac{\beta l}{K_0} j_+ = e^{uy}[Ei(-uy) - Ei(-y)] = 1/z_+ \tag{24}$$

$$\frac{\beta l}{K_0} j_- = e^{-y}[\overline{Ei}(uy) - \overline{Ei}(y)] = 1/z_-$$

with the definition of y_+ and u from eq. (22). Ei and $\overline{Ei}$ are exponential integrals[6]

$$Ei(-x) = -\int_x^\infty \frac{e^{-t}}{t} dt \tag{25}$$

$$\overline{Ei}(x) = \int_{0.3725}^{x} \frac{e^t}{t} dt.$$

The currents j_+ and j_- and the asymmetry j_+/j_- are plotted in Figure 6 as functions of u and p_0.

The permeability of such a membrane is higher if the pressure is applied at $x = 0$, i.e., at the side of low hydration but high compressibility. Together with the results of model III, one concludes that the decisive factor for membrane directionality is not the gradient of hydration but that of compressibility. The flux through the membrane is maximum if the pressure is applied at the side with maximum compressibility. This is easy to understand because the compacting pressure is smallest at the pressure side and maximum at the opposite side of the membrane. Hence the applied pressure compacts the membrane the least if the most compressible side of the membrane is exposed to p_0, i.e., $p_c = 0$ and the least compressible side to $p = 0$ with $p_c = p_0$.

In most membranes, high compressibility occurs at the side with high hydration (model III) so that one has a good rule of thumb that the permeability will be higher if the higher swollen side is exposed to the applied pressure. But the example of model IV just demonstrates that one must be careful in predicting or expecting the higher flux on the basis of local hydration only without paying attention to the compaction effect.

The assumption of linear permeability increase with hydration strongly underestimates the effect of quaternization and compacting pressure. In the actual membranes the permeability is correlated with hydration, as shown in eq. (5a). Such an exponential dependence would significantly increase the asymmetry of the membrane, i.e., the values j_-/j_+ and $\langle K_-\rangle/\langle K_+\rangle$ of Figures 4, 5, and 6 would show a much stronger dependence on pressure.

CONCLUSIONS

The four models calculated demonstrate two important aspects of inhomogeneous membranes:

1. Directionality of permeability exists only in the case where the dependence of local swelling and hence of permeability on pressure is a function of location (K is an irreducible function of x and p).
2. Higher permeability occurs in the flow direction with the high pressure applied to the membrane side with higher compressibility.

These conclusions are quite general although they were mainly deduced from and demonstrated on very simple models, including merely linear functions of x and p. Such a choice, dictated by mathematical expediency, does not limit the generality of conclusions.

This work was generously supported by the Camille and Henry Dreyfus Foundation.

References

1. C. E. Rogers, V. Stannett, and M. Szwarc, *Ind. Eng. Chem.*, **49,** 1933 (1957).
2. C. E. Rogers, *J. Polym. Sci.*, **C4,** 93 (1965).
3. J. L. Williams, A. Schindler, and A. Peterlin, *Makromol. Chem.*, in press.
4. H. Yasuda, C. Lamaze, and A. Peterlin, *J. Polym. Sci.*, in press.
5. J. Bert, *J. Polym. Sci.*, **B7,** 685 (1969).
6. E. Jahnke and F. Ende, *Tables of Functions*, Dover Publ., New York, 1945.

Received February 2, 1971