Studies with Thin Membranes. III. Measurement of Water Permeabilities of Parlodion Membranes Formed by the Dip Technique

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Synopsis

Thin Parlodion membranes whose preparation and electrochemical properties have already been described are used to study permeation of water through them. All the membranes allowed water to go through them when subjected to gradients of mechanical pressure or chemical potential. Thicker membranes were less permeable to water than thinner membranes. The total water flow observed under the influence of an applied pressure was analyzed in terms of an existing theory due to Ticknor and found inadequate to describe the flow in thicker membranes containing low quantities of water, whereas the flow in thinner membranes of moderate water content was found to be made up of both viscous and diffusional components. On the contrary, analysis of both the total and isotopic diffusional flows from the standpoint of another theory due to Mauro showed that all membranes gave flows which were composed of both diffusional and viscous components, the proportion of the former in the total flow increasing with increasing thickness of the membrane. The permeability data have been used to derive values for both the average radius of membrane pores and the total number of such pores present in different membranes.

INTRODUCTION

In the first two parts in this series,[1,2] the characterization of membranes prepared from solutions of Parlodion (purified pyroxylin, which is nitrated cellulose containing 10.5–12% nitrogen,[3] Mallinckrodt) in isoamyl acetate by the dip technique[1] and the electrical potentials arising across them when they separate electrolyte solutions[2] have been described. In this part, the results of permeation of water through them when subjected to osmotic or mechanical pressures and to gradients of chemical potential are presented and discussed in terms of the existing theories of water transport through membranes.

EXPERIMENTAL

Preparation of Membranes

Procedures already described[4] were followed to prepare membranes from Parlodion solutions at concentrations (w/v) in the range 0.25–3.0%.

Measurement of Osmotic Flow of Water

An apparatus of the type shown in Figure 1 was used. The membrane M was held between rigid Plexiglas disks, one of which had a hole (~7 mm. diameter) and the other a stainless steel mesh of similar diameter embedded in the center of the disk. A piece of filter paper was held between the mesh and the membrane to ensure complete wetting of the membrane surface. Two rubber gaskets with holes of similar diameter in the center were placed on the outer sides of Plexiglas disks. The whole membrane assembly was clamped between two pieces of industrial glass piping (~7 mm. I.D.). An exploded view of this arrangement is shown in Figure 2.

The half cells were filled, carefully displacing all air bubbles at the membrane surfaces, one with distilled water and the other (mesh side) with 0.5M sucrose or urea solution. The membrane assembly was covered with Plasticine clay to prevent membrane coming in contact with the thermostatic liquid when immersed in a thermostat. The precision bore capillaries C were placed on the mouths of the half cells and filled to a convenient
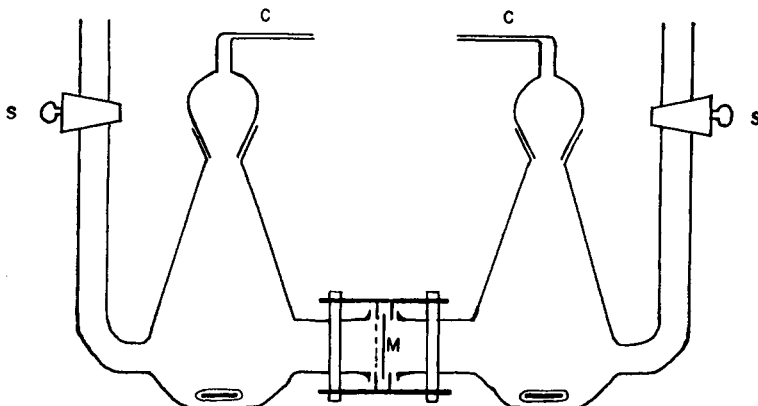
Fig. 1. Osmotic transport cell: (M) membrane held between Plexiglas disks and rubber gaskets; (C) precision-bore capillaries which are filled through the openings of the limbs containing stopcocks S.
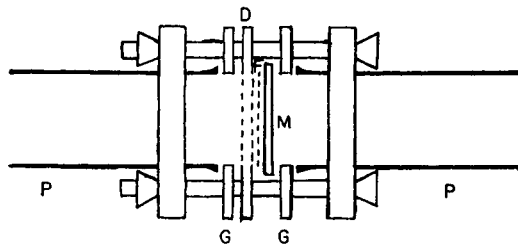
Fig. 2. Exploded view of the water transport cell containing the membrane assembly: (P) pieces of industrial glass piping holding the membrane M between rubber gaskets G; (D) Plexiglas disk containing the stainless steel mesh supporting the membrane; (F) filter paper held between D and M.

level with the respective liquids by using the openings of the limbs containing stopcocks S.   The whole cell was immersed in a water thermostat maintained at 22 ± 0.1°C.

The liquid in the cell was stirred by means of rotating magnets kept outside the thermostat but just below the iron-cored Teflon bars.   The movements of liquid with time in the two capillaries were followed on a travelling microscope.   The area of the membrane exposed to the solution was 0.38 cm.².   Membranes prepared from 3, 2, 1.5, and 1.0% Parlodion solutions were used in these measurements.   Other membranes prepared from 0.75, 0.50, and 0.25% Parlodion solutions gave almost zero flow for urea and sucrose solutions.

Measurement of Water Flow by Application of Mechanical Pressure

A cell similar to the one shown in Figure 1 with minor modifications was used.

The industrial glass pipings were bigger in diameter (~19 mm.), as also were the mouths of the two half cells which contained only water in these experiments.   The membrane assembly was as shown in Figure 2. The half cell in which membrane was in direct contact with water was connected to a nitrogen cylinder through a Hg manometer for application of pressure.   The precision bore capillary in the other half cell was vertical and the liquid movement in it when the membrane was subjected to a pressure gradient was followed with time on a cathetometer at 22 ± 0.1°C.
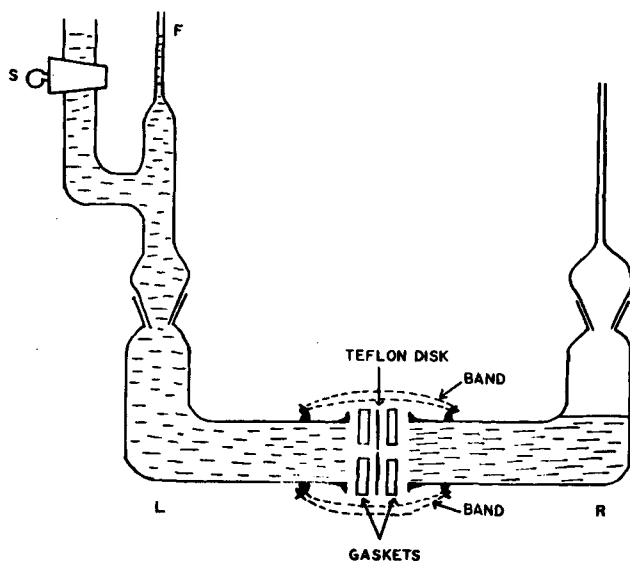

Fig. 3. Water transport cell used for measuring permeation of water through very thin Parlodion membranes: (R, L) glass pipings which hold the membrane and gaskets with the help of rubber bands; (F) capillary filled with water through the opening of its limb S.

The area of the membrane exposed to the liquid under pressure was 2.84 cm.². Here also membranes formed from 3, 2, 1.5, and 1% Parlodion solutions were used. A different experimental setup was used to follow water movements through more fragile structures formed from 0.75, 0.50, and 0.25% Parlodion solutions. These membranes could not be clamped in the way the other membranes were held for application of mechanical pressure. Nevertheless, they were handled in the following manner.

A circular Teflon piece ($\sim$18 mm. diameter) of thickness 0.8 mm., and containing a small hole (area $= 2.4 \times 10^{-3}$ cm.²) in the center was used to lift the membrane floating on water after being floated off from the glass plate on which the membrane was formed by dipping it into Parlodion solution and drying it under controlled conditions. The membrane was lifted in such a way as to cover the whole area of the Teflon disk and held between two rubber gaskets of similar diameters with holes ($\sim$3 mm. diameter) in the center. This whole assembly was held with the help of rubber bands between two pieces of industrial glass piping which were similar to the ones used in osmotic flow measurements. This arrangement is shown in Figure 3. The horizontal limb of the right half cell was filled with water and the left half cell was filled through its S limb almost to the top of the fine-bore capillary F (area $= 8.2 \times 10^{-3}$ cm.²) such that the difference in heights of levels of liquids in R and L was nearly 40 cm. water (height exactly known). Air bubbles at the membrane surfaces were carefully removed during filling. The apparatus was immersed in a thermostat as usual and the drop in the level of liquid in the capillary F was followed with time on a cathetometer. The success of these experiments depended on the success with which the fragile membrane was held securely but firmly between the gaskets and the two half cells. Very often the membrane broke during placement of rubber bands and less frequently during filling of the cell with water.

Measurement of Movement of Tritiated Water

A cell of the type shown in Figure 1 but without side arms was used. Each of the two half cells had a capacity of 200 ml. Glass piping of I.D. $\approx$19 mm. was used, and two of these pieces held the membrane assembly. The membrane whose surfaces were dried by blotting with filter paper was clamped with or without support as required and the liquid on either side was stirred using rotating magnets at very high speed. The "hot" solution, i.e., water containing 1 μc./ml. tritiated water (THO) was directly in contact with 2.84 cm.² of the membrane surface.

Exactly 150 ml. of distilled water was added to the "cold" side and exactly 150 ml. of THO was added to the "hot" side. When nearly 75 ml. of THO had been added a stop watch was started. At regular intervals of time, an aliquot (exactly 1 ml.) of liquid on the "cold" side was taken for counting. This loss in volume was compensated by adding 1 ml. distilled water.

The aliquot taken for counting was transferred to a polyethylene vial (capacity ~25 ml.) into which 20 ml. of Bray's solution,[5] was added and mixed. The samples were counted in a Packard TriCarb liquid scintillation counter. The experiments were done in an air-conditioned room at 22°C.

The above procedure was followed for membranes prepared from 3, 2, 1.5, and 1% Parlodion solution, while the following procedure was followed for membranes formed from the dilute solutions.

The membrane floating on water was lifted as described elsewhere[4] with a circular glass cup C (Fig. 4) provided with a glass handle H. The membrane M was left floating on the surface of water in C. The volume of water was brought to a marked level, previously calibrated, on C by
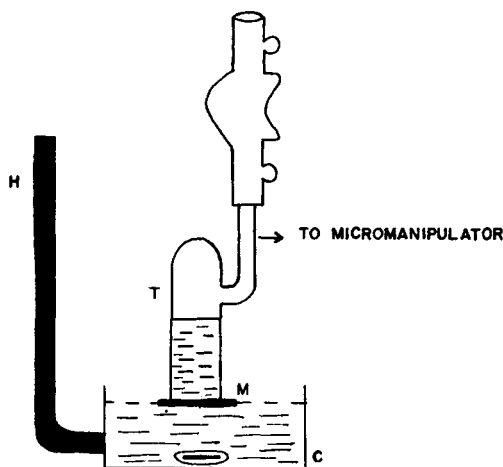

Fig. 4. Apparatus used for measuring isotopic water flux: (M) membrane resting on the surface of "cold" water contained in glass cup C provided with handle H; open end of glass tube T containing THO and held in micromanipulator contacted membrane surface to complete the cell arrangement.

removing some water by suction. The volume of this water ("cold" side) was 9.44 ml. A glass tube T of the form shown in Figure 4 and held in a micromanipulator was filled to a level already calibrated with THO solution by suction. The volume of this solution was 3.07 ml. By adjusting the manipulator, the open end of tube T was placed gently on the surface of the membrane and immediately the time was noted.

Even though the "hot" solution could not be stirred, the "cold" liquid at the bottom was gently stirred by using a tiny magnetic Teflon stirrer. At regular intervals of time, an aliquot of liquid (1 ml.) was taken from the bottom glass cup for counting as described already. As soon as an aliquot was removed for counting, 1 ml. of water was added immediately to compensate for the loss in volume.

RESULTS

Flow of Water Under Gradients of Osmotic and Mechanical Pressures

In Table I are given the results of measurements of water flow through membranes formed from 3, 2, 1.5, and 1% Parlodion solutions when they separated $0.5M$ sucrose or urea solutions and water. In columns 3 and 5 are given the same results expressed as millimeter Hg pressure by using the relation $\Delta P = RT\Delta C$, where ΔP is the theoretical osmotic pressure that would be exerted when ΔC concentration gradient acted on the membrane. The value of $RT\Delta C$ for the conditions under which the experiments were done was equal to 12.1 atm.

In this series some experiments were carried out without using the stainless steel mesh support for the membrane. The results were not significantly different from those given in Table I. The experimental error in these measurements was $\pm 15\%$.

In Table II are given the results of flow of water through membranes subjected to mechanical pressure gradients. It was convenient to work with membranes supported by stainless steel mesh. Unsupported membranes were very difficult to handle at pressures greater than 100 mm. Hg due to bulging. Only a limited number of experiments was done with

TABLE I

Osmotic Flow of Water through Parlodion Membranes

	Rate of water flow			
	0.5M sucrose		0.5M urea	
Parlodion solution, %	ml. $\dfrac{}{\text{min. area}}$	ml. $\dfrac{}{\text{min. area. mm. Hg}}$	ml. $\dfrac{}{\text{min. area}}$	ml. $\dfrac{}{\text{min. area. mm. Hg}}$
3.0	19.8×10^{-5}	2.2×10^{-8}	18.9×10^{-5}	2.1×10^{-8}
2.0	26.7×10^{-5}	2.9×10^{-8}	24.8×10^{-5}	2.7×10^{-8}
1.5	29.9×10^{-5}	3.3×10^{-8}	7.8×10^{-5}	0.9×10^{-8}
1.0	15.7×10^{-5}	1.7×10^{-8}	3.7×10^{-5}	0.4×10^{-8}

TABLE II

Flow of Water Through Parlodion Membranes Subjected to Mechanical Pressure Gradient

Parlodion solution, %	Rate of water flow, ml./min. area-mm. Hg $\times 10^8$
3.0	2.3
2.0	3.3
1.5	10.0
1.0	30.0
0.75	50,000
0.50	73,300
0.25	250,000

unsupported membranes at low pressures, particularly with 1.5 and 1% membranes. The results were identical to the values realized for supported membranes but the standard errors of the means were high, sometimes as high as 30–40% in the case of 1% membranes and about 20% in the case of thicker membranes (3%).

Some measurements of water flow through 3% supported membranes were done at different pressures and the flow rate J_v increased linearly with increase in applied pressure ΔP according to eq. (1):

$$J_v = L_p\Delta P \tag{1}$$

where L_p is the filtration or hydraulic permeability coefficient (see Table V).

The thinner structures formed from 0.75, 0.50, and 0.25% Parlodion solutions were all used unsupported, but as the pressure gradient and the area of the membrane were very small, bulging was no problem. The standard errors of the means, however, were again as high as 30–40%.

Flow of Tritiated Water Under Gradient of Chemical Potential

In the experiments where large and equal volumes (150 ml.) were used, removal of 1 ml. of solution for counting and addition of 1 ml. of distilled water did not introduce any significant error into the activity, i.e., counts per minute (cpm), that should have been present if 1 ml. aliquot had not been taken out, whereas removal of 1 ml. when small but unequal volumes were used did affect the activity (cpm). Therefore, necessary correction to the activity counted for samples taken out at regular intervals, except the activity of the first aliquot, was applied according to the relation

$$\text{cpm (corrected)} = \frac{[(\text{Actual cpm}) \times 9.44 \ (\text{volume of vessel})] + [\text{Preceding corrected cpm}]}{9.44}$$

These corrections were made after subtracting the background counts from the sample counts.

The flux of THO according to Fick's law for diffusion may be written following Mauro[6] as

$$dn/dt = (D_w A_w/RT)C(d\mu/dx) \tag{2}$$

where dn/dt is the rate of transport of n (i.e., THO) and change in chemical potential $d\mu = \bar{V}dP$ and $C\bar{V} = 1$. $\bar{V}$ is the partial molar volume, C is the concentration, and dP is the change in pressure. D_w is the diffusion coefficient of THO in water contained in pore area A_w and pore length dx which THO should travel to cross the diffusion barrier.

On making substitutions and writing dP/dx as $\Delta P/\Delta x$, eq. (2) becomes

$$\frac{dn}{dt} = (D_w A_w/\Delta x)(\Delta P/RT) \tag{3}$$

Equating ΔP to osmotic pressure, i.e., $RT\Delta C_{THO}$, we get

$$(dn/dt)_{THO} = (D_wA_w/\Delta x)\Delta C_{THO} \qquad (4)$$

This equation was integrated originally by Northrup and Anson[7] and recently by Robbins and Mauro.[8] Dainty and House[9] have given a general integrated equation:

$$\frac{D_wA_w}{\Delta x} = \frac{2.303V_1V_2}{(V_1 + V_2)\Delta t} \log \frac{C'V_1 + C''V_2 - C''_{t_0}(V_1 + V_2)}{C'V_1 + C''V_2 - C''_{t_0 + \Delta t}(V_1 + V_2)} \qquad (5)$$

where V_1 and V_2 are the volumes of compartments 1 ("cold" side) and 2 ("hot" side), respectively. C' and C'' are the initial concentration (taken as counting rate per milliliter) of tritium in compartments 1 and 2, i.e., at $t = 0$. C''_{t_0} and $C''_{t_0 + \Delta t}$ are concentrations in compartment 2 at time $t = t_0$ and $t = t_0 + \Delta t$, respectively. Δt therefore is the time elapsing between samplings in seconds. t_0 is not zero time but the time at which the initial sample required for evaluation of $(D_wA_w)/\Delta x$ is withdrawn.

When $V_1 = V_2$, i.e., with equal volumes, eq. (5) reduces to the form given by Robbins and Mauro.[8]

For the conditions of our experiments, viz., $C' = 0$ and $V_1 = 9.44$, $V_2 = 3.07$, eq. (5) becomes

$$\frac{D_wA_w}{\Delta x} = \frac{5.34}{\Delta t} \log \frac{3.07 \, C'' - 12.51 \, C''_{t_0}}{3.07C'' - 12.51C''_{t_0 + \Delta t}} \qquad (6)$$

A plot of log $(3.07C'' - 12.51C''_{t_0})/(3.07C'' - 12.51C''_{t_0 + \Delta t})$ against time shown in Figures 5 and 6 for both thick (3% membrane) and very thin (0.25% membrane) structures, respectively, gave straight lines in accordance with eq. (6). However $(D_wA_w/\Delta x)$ was evaluated numerically and $(A_w/\Delta x)$ values (Table III) were calculated by using the literature value for D_w:[10] (D_w, i.e., THO = 2.44×10^{-5} cm.[2]/sec.).

TABLE III
Diffusion of THO Through Parlodion Membranes

Parlodion solution, %	Membrane thickness, A.[a]	$D_wA_w/\Delta x$ for unsupported membrane, cm.[3]/sec.		$A_w/\Delta x$ pore area pore length, cm.
		Unequal volumes $(V_1 \neq V_2)$	Equal volumes $(V_1 = V_2)$	
3.0	4000	2.2×10^{-5}	2.6×10^{-4}	10.7
2.0	1300	2.6×10^{-5}	3.1×10^{-4}	12.7
1.5	640	3.0×10^{-5}	3.5×10^{-4}	14.3
1.0	325	3.2×10^{-5}	3.8×10^{-4}	15.6
0.75	225	3.4×10^{-5}	4.1×10^{-4b}	16.8
0.50	205	3.6×10^{-5}	4.3×10^{-4b}	17.6
0.25	95	5.8×10^{-5}	7.0×10^{-4b}	28.7

[a] See references 1 and 4.
[b] Inferred values.

In Table III are given the values of $(D_w A_w/\Delta x)$ calculated according to eq. (6) for the different membrane setups.

The values of $(D_w A_w/\Delta x)$ calculated by using different time intervals for any given membrane agreed to better than $\pm 1\%$ when large and equal volumes were used and to $\pm 5\%$ when small and unequal volumes were used. The standard error of means computed for a number of membranes of any one kind however was $\pm 15\%$, the order of variability noted for the method of preparation of membranes itself.[1,4]
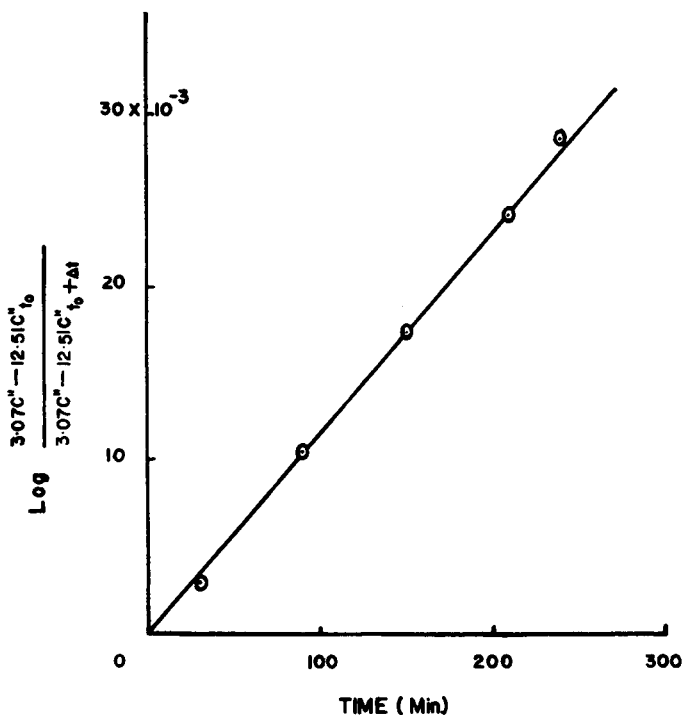

Fig. 5. Plot of log $[(3.07\ C'' - 12.51\ C''_{t_0})/(3.07\ C'' - 12.51\ C''_{t_0 + \Delta t})]$ against time for a 3% Parlodion membrane.

$(D_w A_w/\Delta x)$ values were also determined for supported 3–1% membranes. These values did not differ significantly from the values realized for the unsupported membranes given in Table III. This behavior, also noted in the case of water flow under the influence of mechanical pressure, is unusual in view of the fact that in general a stagnant layer of liquid trapped between the membrane and the support would add its thickness and thereby lower the value for $(D_w A_w/\Delta x)$. Such lowering has been observed[11] for a cation-exchange membrane containing about 60% water, and this lowering decreased when another cation-exchange membrane of lower water content (21%) was used. Consequently, in the present case the ineffectiveness of the stagnant layer is due to low water content[2] and high electrical resistance

of these Parlodion membranes employed under conditions of very high rates of stirring.

Because good stirring was difficult in the experimental setup where unequal and small volumes of liquids were used, the values of $(D_w A_w/\Delta x)$ were lower (Table III). The membranes formed from 3–1% Parlodion solutions were used in both the experimental setups. The $D_w A_w/\Delta x$ values for all these membranes employed under conditions of good stirring are higher than corresponding values obtained under conditions of inefficient stirring by a factor of 12. This factor was used to obtain values given in Table III, for 0.75, 0.50, and 0.25% membranes.

DISCUSSION

In Figure 7 are given plots of membrane thickness against flow rates induced under unit pressure and maintained by osmotic and mechanical forces. The osmotic flows both for sucrose and urea increase with thickness, reach a maximum, and then decrease with further increase in thickness. Ideally, when the flow rate has reached a maximum, it should have stayed
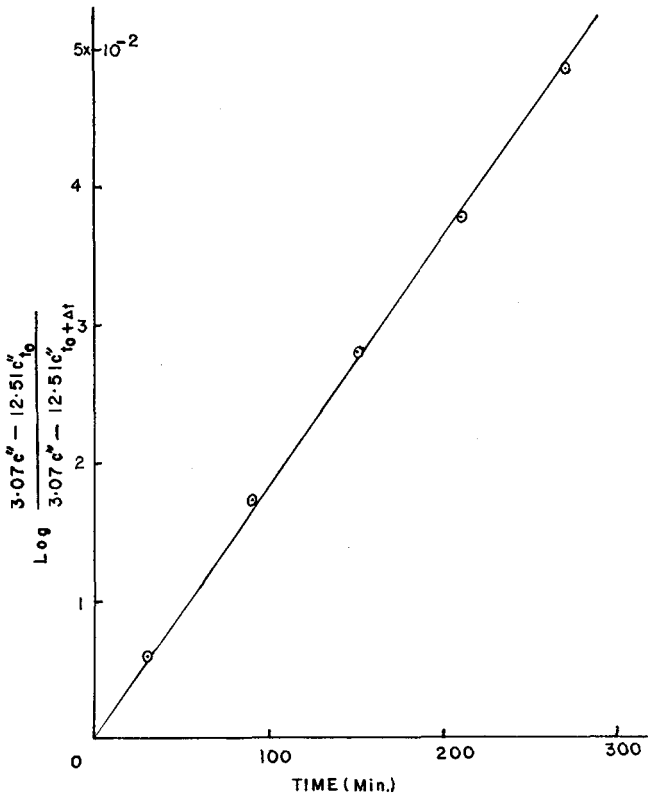
Fig. 6. Plot of log $[(3.07\ C'' - 12.51\ C''_{t_0})/(3.07\ C'' - 12.51\ C''_{t_0 + \Delta t})]$ against time for 0.25% Parlodion membrane.

at that level even when the membrane thickness was increased as shown by the hypothetical curve.   This part of decrease in flow rate observed with increase in thickness may be attributed to the presence of a force, frictional in character, opposing the flow of water through the membrane.   This frictional drag that exists between mobile water and the membrane material will increase as the membrane is made tighter.   The fact that thicker membranes formed from concentrated Parlodion solutions have less water
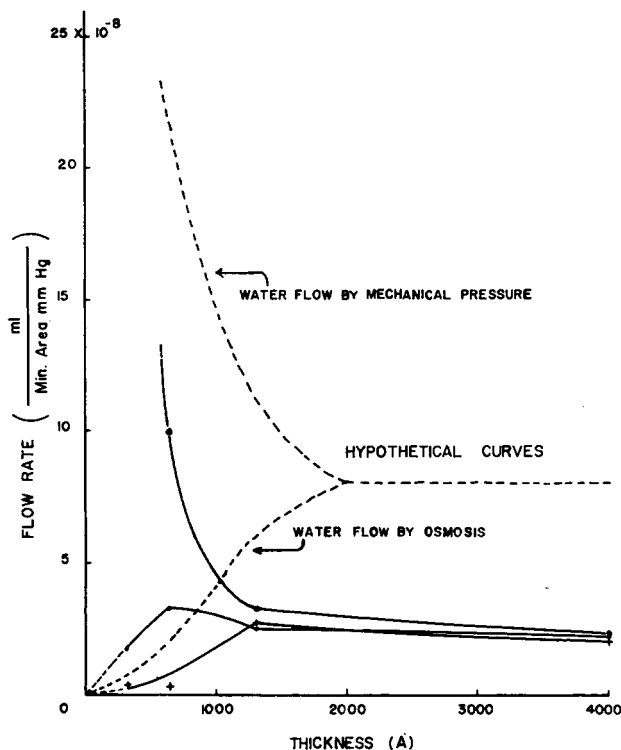

Fig. 7. Plots of membrane thickness against rates of flow of water through Parlodion membranes: (●) osmotic flow induced by 0.5M sucrose solution; (+) osmotic flow induced by 0.5M urea solution; (O) bulk flow induced by application of mechanical pressure; (– – –) hypothetical curves drawn in arbitrary units to indicate qualitatively the ideal nature of flows induced in a perfectly semipermeable membrane by gradients of osmotic and mechanical pressures.

indicates presence of smaller water channels which therefore exert increased drag on moving water, decreasing the flow rate.

In perfectly semipermeable membranes, the rate of flow of water due to osmosis will be equal to the rate of flow observed when membranes are subject to gradients of mechanical pressure.   The ratio of these two flows, called the reflection coefficient σ (introduced by Staverman[12]), the values of which are given in Table IV for the two solutes, indicates that the 3% membrane is almost impermeable to both sucrose and urea in contrast to

TABLE IV
Reflection Coefficient σ for Sucrose and Urea
in Parlodion Membranes

Parlodion solution, %	σ	
	Sucrose	Urea
3.0	0.96	0.91
2.0	0.88	0.82
1.5	0.33	0.09
1.0	0.06	0.01

other membranes which are more permeable to both the solutes. The two hypothetical curves drawn in Figure 7 depict the nature of the flow rates that would be observed across an ideal and semipermeable membrane. The departure of the experimental curves from the shapes of the hypothetical curves therefore indicated non-ideality and incomplete semipermeability in a very qualitative way.

Nature of Water Flow Through Membranes

The nature of water flow occurring across a membrane subjected to a pressure gradient is difficult to assess on ordinary grounds. Both Mauro[6] and Ticknor[13] have analyzed this problem. The type of flow should depend on the relative sizes of the permeating species and of the capillaries of the membrane and on the degree of bonding the mobile species had for the material of the membrane. Ticknor on theoretical grounds estimated that the rates of both diffusional and viscous flows would be equal when the pore radius of the membrane capillaries was nearly twice the radius of the permeating molecules. It was surmised that when the pore radius was larger than the radius of the permeating molecule, the flow would be laminar in nature and when the radii became equal the flow would be mostly

TABLE V
Flux Data (Total Flow and Diffusion) for the
Different Parlodion Membranes

Parlodion solution, %	Bulk flow due to ΔP $(L_p/18)$, mole-cm.^{2}/dyne-sec.	$\dfrac{D_w A_w}{\Delta x}$	Diffusion $(dn/dt)_{THO}$, mole-cm.^{2}/dyne-sec.	Flux ratio, diffusion / total
3.0	4.6×10^{-14}	2.6×10^{-4}	1.1×10^{-14}	1/4
2.0	6.5×10^{-14}	3.1×10^{-4}	1.3×10^{-14}	1/5
1.5	19.7×10^{-14}	3.5×10^{-4}	1.4×10^{-14}	1/14
1.0	59.4×10^{-14}	3.8×10^{-4}	1.5×10^{-14}	1/40
0.75	84.3×10^{-14}	4.1×10^{-4}	1.7×10^{-14}	1/49
0.50	122.2×10^{-14}	4.3×10^{-4}	1.8×10^{-14}	1/68
0.25	416.6×10^{-14}	7.0×10^{-4}	2.9×10^{-14}	1/144

diffusional. A statistical treatment of diffusion in such narrow pores has been recently given by Longuet-Higgins and Austin.[14]

Analysis by Robbins and Mauro[8] has shown that the solvent flow under a pressure gradient is composed of both viscous and diffusional components. For most barriers the predominant component was the viscous flow. Application of this analysis to our experimental data (Tables II and III) gave the results presented in Table V. The diffusion results were obtained from eq. (3) for the case $\Delta P = 1$ dyne/cm.^{2}. It is evident from the flux ratio that the viscous flux, always larger than the diffusional flux, increased as the membrane water content increased, i.e., thinner membranes.

By applying the analysis of Ticknor[13] to the data of Table II, the values of K_s and D given in Table VI were obtained from his equations, viz.

TABLE VI
Diffusion Coefficients for the Permeation of Water
Calculated According to the Theory of Ticknor

Membrane thickness, A.	Fractional void volume ϵ	$K_s \times 10^{18}$, cm.^{2}	$D \times 10^6$, cm.^{2}/sec.
4000	0.06	0.10	0.26
1300	0.09	0.05	0.08
640	0.11	0.07	0.10
325	0.12	0.11	0.14
225	0.14	126	137
205	0.15	168	170
95	0.19	266	213

$$K_s = Vl\eta/tA \Delta P = L_p l\eta/A \tag{7}$$

and

$$D = RTK_s/\epsilon \overline{V}\eta \tag{8}$$

Here K_s is the hydraulic permeability constant for the membrane of area A and thickness l, V is the volume of water of viscosity η flowing through the membrane in time t under the influence of a pressure gradient ΔP, D is the diffusion coefficient, and ϵ is the fractional void volume. The values of ϵ given in Table VI were computed by using the membrane water content data presented in our earlier publication[2] and the value of 1.6 for the density of Parlodion.

The values of K_s and D increase with decreasing membrane thickness except for the anomalous value obtained for the 3% membrane, the anomalous value being due to a very large increase in thickness of the membrane. However the increase in the values is not gradual. A sudden jump is noticed for 0.75% membrane, and the values gradually increase for 0.5 and 0.25% membranes. It is very likely that this sudden jump is associated with the uncertainty with which the membrane area in the case of thinner membranes is estimated. The value of 2.4×10^{-3} cm.^{2} was the

estimated area of the hole in the Teflon sheet holding the membrane. The jump in the values of K_s and necessarily so of D indicates that a much larger area than the estimated value for the hole is involved.   It is possible that the membrane may have bulged without being ruptured under the influence of the hydrostatic pressure head and thereby increased the membrane area.   The other membrane parameters, like L_p (Table V) and $A_w/\Delta x$ (Table III), which do not involve the membrane area term, follow almost a gradual rise with decrease in thickness.

The D values for the different membranes compared to the self-diffusion coefficient of water (2.5×10^{-5} cm.^{2}/sec.) are lower in the case of thicker membranes (3–1%) by a factor of nearly 200 and higher in the case of thinner membranes by a factor of nearly 8.   According to theory, it was shown that when D values approached the self-diffusion coefficient of water, the nature of flow through the membrane changed from viscous to diffusional.   So, it is inferred that the flow in very thin membranes (0.75–0.25%), being greater than the self-diffusion of water, is composed of both diffusional and viscous components.   On the contrary, the flow of thicker membranes being neither diffusional nor viscous, it is concluded that the theory is completely inapplicable to membranes whose water content is very small.   It should, however, be remembered that the calculations of K_s in the case of thinner membranes involved a doubtful term, the membrane area.   If the actual area of the membrane through which permeation took place was about eight times the actual area used in the calculations due to bulging, the value of D would approach the self-diffusion coefficient of water.   As this degree of bulging is very unlikely to occur, it is concluded that in very thin membranes the flow observed is composed of both diffusional and viscous components.

In view of the discussion given above for these Parlodion membranes whose specific resistance is of the order of 10^9 ohm-cm.,[1] the experimental finding that the two water-permeability coefficients, viz., osmotic and isotopic, derived for the phospholipid bilayer membrane (electrical resistance = 10^9 ohm-cm.^{2} or specific resistance = $10^9/6 \times 10^{-7} = 10^{15}$ ohm-cm.) by two groups of workers[15–18] are different is attributable to the different mechanisms of water transport operating under conditions of bulk flow and isotopic exchange flow.   Nevertheless, Hanai et al.[16] considered this difference to be due to the presence of stagnant layers of liquid at the two membrane–solution interfaces in isotopic flux measurements.   This explanation has been rejected by Huang and Thompson[17] on a detailed consideration of the extent to which these diffusional layers would control the diffusional flux across the membrane.   On the basis of this study where diffusional fluxes were measured under extreme conditions of stirring, the diffusional flow of water never reached the bulk flow under conditions of high speeds of stirring, even though the corresponding value for diffusion was considerably less when slight stirring was employed. The specific resistance of the phospholipid bilayer membrane being of the order of 10^{15} ohm-cm., even if stagnant liquid layers are present, the flux

across the membrane would be controlled completely by the membrane itself, and as a result to assign all the difference between the two permeability coefficients to stagnant layers alone becomes untenable.

Determination of Average Pore Radius

The applicability of various permeability equations used by different workers to derive an average value for the radius of membrane pores has been discussed by Lakshminarayanaiah in a recent revew article.[19] It was shown by Renkin[20] that the equation

$$r = \sqrt{8L_p\eta/(A_w/\Delta x)} \tag{9}$$

where r = radius of pores gave reasonable values for r, whereas the equation

$$r = \sqrt{8K_s/\epsilon} \tag{10}$$

gave values for r which were considered low and therefore to be in error. The values of r calculated for the different membranes using eqs. (9) and (10) are given in Table VII. It is seen that the values obtained for r according to eq. (10) for 3–1% membranes are less than the radius of the permeating water molecule (1.5 A.). The fact that water does move through these membranes makes these values of r quite absurd. So if one makes an analysis of the nature of flow through membranes by using eqs. (7)–(10), one is likely to be in error. For example, in the study of permeation of water through different heterogeneous hydrophylic membranes, Refojo[21] came to the conclusion that the type of flow which existed in his HEMA and PGMA membranes containing 39, 41, and 63% water was only diffusional. Application of eq. (10) to derive the radius of pores gave additional proof for the substance of Ticknor's theory in that the radii of pores of different membranes were twice the radius of the permeating species, a prediction made by the theory. In the context of the present study where even membranes containing only about 20% water produced flows which were mostly laminar in character containing diffusional component only to about 0.7%, it becomes resonable to expect the nature of flow of water in membranes of high water content (used by Refojo[21] and also by White,[22] who used acrylamide polymer gels) to be mostly viscous, containing an insignificant fraction of the diffusional component. This line of reasoning founded on an independent measurement of diffusion in Parlodion membranes of different water contents contradicts the conclusions which both Refojo and White reached on the basis of their analysis of experimental data by using eqs. (7)–(10).

Application of eq. (9) to derive the pore size for the membranes does not take into account steric hindrance at the pore entrance and frictional resistance with the pores felt by the penetrating molecules. Paganelli and Solomon,[23,24] taking these factors into account, have given a simple

equation for the effective radius of the pores present in the membrane. The equation is

$$r = -a + \sqrt{2a^2 + [8L_p\eta/(A_w/\Delta x)]} \qquad (11)$$

where a is the radius of the permeating molecule. The values for r, i.e., the effective pore radius, obtained for the different membranes by using

TABLE VII
Pore Radii, Fractional Pore Area, and the Number of Pores Present
in Parlodion Membranes

Parlodion solution, %	Pore radius r from eq. (10), A.	Pore radius r from eq. (9), A.	Effective pore radius r from eq. (11), A.	Fractional pore area $A_w/A \times 10^5$	Number of pores per cm.^{2} membrane
3.0	0.37	7.4	5.9	15.1	1×10^{10}
2.0	0.21	8.1	6.6	5.8	4×10^{9}
1.5	0.23	13.3	11.6	3.2	8×10^{8}
1.0	0.27	22.2	20.4	1.8	1×10^{8}
0.75	8.5	25.3	23.5	1.33	8×10^{7}
0.50	9.5	29.9	28.1	1.27	5×10^{7}
0.25	10.6	43.3	41.4	0.96	2×10^{7}

eq. (11) and the value of 1.97 A. for a are given in Table VII. As the values of r for 1–0.25% membranes from eqs. (9) and (11) do not differ very much, the factors mentioned above do not seem to operate in these membranes, where the pore sizes are large compared to the size of the diffusing molecule; where as the factors do affect the pore sizes of tighter membranes.

From the values of $A_w/\Delta x$ (Table III) and the effective pore radii (Table VII) for the various membranes, the fractional pore areas, i.e., A_w/A, and the number of pores present per unit area of membrane surface may be calculated. These values are given in the last two columns of Table VII. These values, according to expectations, indicate existence of a larger number of smaller pores in membranes of low water content and a smaller number of larger pores in membranes of high water content.

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Résumé

Des membranes fines de Parlodion dont la préparation et les propriétés électrochimiques ont déjà été décrites précédemment ont été utilisées pour étudier la perméation de l'eau à travers ces membranes. Toutes les membranes permettaient le passage de l'eau lorsqu'elles étaient soumises à des gradients de pression mécanique ou de potentiel chimique. Des membranes plus épaisses étaient moins perméables à l'eau que les membranes plus fines. Le flux total de l'eau observé sous l'influence d'une pression appliquée a été analysé sur la base des théories existantes dûes à Ticknor et trouvé inadéquat pour décrire le flux dans des membranes plus épaisses contenant de faibles quantités d'eau; alors que le flux au sein des membranes plus étroites d'une teneur en eau modérée a été trouvé composé de facteurs visqueux et diffusionnels. Par contre, l'analyse des écoulements totaux et isotopiques diffusionnels du point de vue d'une autre théorie due à Mauro montrait que toutes les membranes donnaient un écoulement qui était composé à la fois de facteurs diffusionnel et visqueux, la proportion du premier dans l'écoulement total dépendant de l'épaisseur croissante de la membrane. Les résultats de perméabilité ont été utilisés pour dériver des valeurs à la fois pour le rayon moyen des pores de la membrane et pour le nombre total de tels pores présents dans les différentes membranes.

Zusammenfassung

Dünne Parlodionmembranen, deren Darstellung und elektrochemische Eigenschaften schon beschrieben wurden, werden zur Untersuchung der Wasserpermeation durch dieselben verwendet. Alle Membranen erlaubten bei Einwirkung eines mechanischen Druckgradienten oder eines chemischen Potentialgradienten den Durchtritt von Wasser. Dickere Membranen waren für Wasser weniger durchlässig als dünnere. Der gesamte unter dem Einfluss eines angewendeten Druckes beobachtete Wasserfluss wurde mittels einer von Ticknor gegebenen Theorie analysiert; es war unmöglich, den Fluss in dickeren Membranen mit einem geringen Wassergehalt richtig zu beschreiben; dagegen konnte der Fluss in dünneren Membranen mit mässigem Wassergehalt in Viskositäts- und Diffusionskomponenten zerlegt werden. Im Gegensatz dazu zeigte die Analyse des totalen und des isotopen Diffusionsflusses vom Standpunkt einer anderen, auf Mauro

zurückgehenden Theorie, dass in allen Membranen ein Fluss auftritt, der aus Diffusions- und Viskositätskomponenten zusammengesetzt ist, wobei der Anteil der ersteren am totalen Fluss mit steigender Membrandicke zunimmt. Die Permeabilitätsdaten wurden zur Ableitung von Werten für den mittleren Membranporenradius und für die Gesamt- zahl solcher in verschiedenen Membranen vorhandener Poren herangezogen.