

Concentration and Pressure Dependence of Rate of Membrane Permeation

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Synopsis

The permeation of water and sodium chloride in cellulose acetate membranes has been examined over a wide range of concentration and pressure. The results obtained from reverse osmosis experiments have been used to evaluate relations derived on the assumption that permeation of both solution components takes place by diffusion down a concentration gradient in the membrane. With the aid of equilibrium and radioactive tracer measurements, most of the deviations could be attributed to nonconstancy of the diffusion, and, especially, the distribution coefficients of water. A comparison of the net flux in reverse osmosis with the rate of tracer permeation in the same membrane provided positive evidence to show that hydrodynamic flow under pressure cannot account for the water flux through the membrane. Differences in the shape of the distribution isotherms for salt and water between solution and membrane provide an explanation for the high selectivity of cellulose acetate membranes in favor of water.

INTRODUCTION

When hydrostatic pressure is applied to a solution located on one side of a permeable membrane a permeate of different composition may appear on the other side. The manner in which such partial separation of the components of a solution comes about remains a subject of controversy. The recent strong interest in this subject has been centered primarily on salt solutions. The present work was confined to water and sodium chloride solutions and cellulose acetate membranes. It was postulated that permeation of both species takes place by simple diffusion. Some evidence has been reported^{1,2} which supports a diffusion mechanism in general, but which also presents a number of difficulties.

If the permeate is more dilute in sodium chloride, it can be seen that the salt which does pass through the membrane can do so by diffusion down a concentration gradient. It is shown elsewhere³ that, with a hydrostatic pressure on the concentrated side of a nonporous membrane, the permeation of water can similarly be understood by diffusion down a concentration gradient inside the membrane. The reversal of this gradient can result from the effect of pressure on the partition of water between

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solution and membrane. The main purpose of this paper was to compare the expectations of this model with experimental results on water and sodium chloride flux in cellulose acetate membranes.

EXPERIMENTAL

Membrane Preparation

The membranes used were cast from solutions of Eastman cellulose acetate polymers. Solvents used were acetone or dioxane for the secondary acetates (~ 38 – 40% acetyl) and dichloromethane for the cellulose triacetate. The membranes were cast at room temperature from 10% solutions of polymer and were allowed to air dry after casting for $1/2$ hr to remove the volatile solvent. The membranes were then immersed in water and the water temperature raised to 80 – 90°C for 1 hr to "set" the membranes. This heat setting step helped to prevent changes in the membrane structure during use. The triacetate solution also contained 3% tetramethylene sulfone and 2% tetramethylene glycol as nonvolatile additives. The membranes were kept wet until the end of the experiment. The thicknesses of the membranes were determined by averaging 10 measurements made with an Ames dial indicator accurate to 0.0001 in.

Apparatus and Procedure

The reverse osmosis apparatus consisted of a two-piece circular Monel cell⁴ containing two chambers separated by a porous Monel plate on which the membrane was placed. The effective membrane area was 58 cm². The salt solution in the high-pressure chamber was agitated by means of a magnetic stirring bar which rotated about a pin in the center of the cell. The salt solutions were pumped into the high pressure chamber through an inlet port on the periphery of the cell and removed through an outlet port near the center. The effluent solution was reduced to atmospheric pressure with a Monel needle valve. The solutions were pumped by means of a Lapp Pulsafeeder (Model LS-20 with Monel head). The pressure fluctuation caused by the pump strokes were damped to $< \pm 2$ psi by means of an accumulator attached immediately after the outlet check valve on the pump. All high pressure lines were $1/8$ -in. copper tubing and low pressure lines of $1/8$ -in. Saran tubing. The pressure was controlled to $\sim \pm 2$ psi. This was accomplished with a calibrated Monel bourdon gauge to which was attached an adjustable differential transformer. The transformer was connected through a servomotor system and amplifier to the dc motor drive on the pump. The pressure could be varied and controlled accurately over the range 50 – 2000 psi. The permeation rate was determined by collecting a volume (measured to ± 0.02 ml) of liquid for a known time. The salt concentrations were determined by titration for chloride concentration utilizing an Aminco-Cotlove chloride titrator. As a check on these titrations, duplicate samples were taken, in many instances, and the

Na content determined by atomic absorption and the two results compared. In general, the two analyses agreed well.

The apparatus and techniques used in the radioactive tracer studies have been described elsewhere.⁵ All measurements were made at $25 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

Flux Equations

Both water and salt are considered to move through the membrane by diffusion. It is shown elsewhere³ that, if the water is not in continuous channels open to the surfaces, the concentration gradient prevailing inside the membrane in normal osmotic flow can be reversed by application of a sufficiently high pressure. The expression obtained for the water flux, J_w , is

$$J_w = (K_w D_w \bar{V}_w / LRT) (\Delta p - \Delta \pi) \quad (1)$$

L is the membrane thickness, R the gas constant, T the absolute temperature, \bar{V}_w the partial molar volume in solution, and π the osmotic pressure. If I represents the side with higher hydrostatic pressure, then (for positive J_w) $\Delta p = p^I - p^{II}$ and $\Delta \pi = \pi^I - \pi^{II}$. The distribution coefficient

$$K_w = \frac{K_{N,w}}{\gamma'_{m,w}}$$

where $K_{N,w}$ is a constant determined by the standard chemical potentials of water in the two phases. The activity coefficient $\gamma'_{m,w}$ in the membrane at $p = 1$ was assumed to be independent of concentration and the diffusion coefficient D_w independent of both concentration and pressure.

At high pressures it may be necessary to use the more exact equation³

$$J_w = \frac{K_w D_w \bar{V}_w}{L(RT + p_m \bar{V}_m)} (\Delta p - \Delta \pi) \quad (1a)$$

where p_m and \bar{V}_m are the pressure and partial molar volume of water in the membrane.

Although eq. (1) was derived for an ideally semipermeable membrane, the only qualification necessary for a real membrane is that the salt (solute) concentration in the membrane be low enough not to affect appreciably the behavior of water inside the membrane. This appears to be reasonable in most experimental situations encountered with the present highly selective membranes. On the other hand, both diffusion and distribution coefficients of salt may be expected to depend to a great extent on the water content of the membrane. According to Fick's law, with the diffusion coefficient, D_s , of salt independent of salt concentration and position in the membrane, the steady-state salt flux is given by

$$J_s = (K_s D_s / L) (a_{\sigma,s}^I - a_{\sigma,s}^{II}) \quad (2)$$

TABLE I
Effect of Concentration and Pressure on Flux in Reverse Osmosis (43.2% Acetyl)

Feed concn, <i>m</i>	Δp , atm	$C_{\sigma,s} \times 10^3$, <i>m</i>	$C_{\sigma,s}^{II}$ $\times 10^2, m$	$J_w \times 10^7$, mole/cm ² -sec	$\Delta p - \Delta \pi$, atm	$\frac{J_w \times 10^8}{\Delta p - \Delta \pi}$, moles/cm ² sec-atm	$J_s \times 10^{12}$, mole/cm ² -sec	$\frac{J_s \times 10^{10}}{\Delta a_{\sigma,s}}$, moles/cm ² -sec
0.01	6.8	1.25	0.039	1.46	6.3	2.32	1.0	0.011
	13.6	1.28	0.023	3.32	13.0	2.55	1.4	0.011
	27.2	1.36	0.014	6.81	26.6	2.56	1.7	0.012
	40.8	1.27	0.012	10.5	40.3	2.61	2.3	0.011
	54.4	1.28	0.011	14.2	53.9	2.64	2.9	0.011
0.1	68.1	1.29	0.010	17.8	67.5	2.64	3.2	0.011
	6.8	10.0	0.595	0.40	2.5	1.6	4.29	0.0720
	13.6	10.7	0.232	1.89	8.8	2.15	7.93	0.0808
	27.2	10.3	0.099	5.26	22.6	2.33	12	0.079
	40.8	10.6	0.079	9.07	36.1	2.51	13	0.081
0.5	54.4	10.7	0.075	12.6	49.6	2.54	17	0.082
	68.1	11.3	0.072	16.3	63.0	2.59	19	0.086
	27.2	48.4	2.09	0.80	6.1	1.3	30.1	0.314
	40.8	50.5	0.751	3.64	18.4	1.88	49.4	0.336
	54.4	51.7	0.520	6.46	31.3	2.06	59.4	0.346
1.0	68.1	52.0	0.366	10.0	44.7	2.24	66.8	0.349
	34.0	99.5	33.3	0.11	3.4	0.32	64.4	0.419
	40.8	98.7	27.9	0.28	7.8	0.36	140	0.449
	54.4	104	6.64	1.09	11.7	0.93	130	0.624
	68.1	102	2.14	3.79	23.3	1.63	146	0.648
81.7	101	3.35	10.3	37.5	2.75	622	0.635	

if $\gamma'_{m,s}$ is independent of concentration. The symbols are the same as those used for water, with w replaced by s ; $a_{\sigma,s}$ is the activity of salt in solution (σ). Another simple expression is obtained if $\gamma'_{\sigma,s}/\gamma'_{m,s}$ is assumed to be constant (e.g., unity). Then

$$J_s = (K'_s D_s / L) (C_{\sigma,s}^I - C_{\sigma,s}^{II}) \quad (3)$$

where C is the concentration.

Flux Variations with Concentration and Pressure

The results of the reverse osmosis experiments, all obtained on the same membrane are summarized in Table I. The variation of water flux with $\Delta p - \Delta \pi$ was approximately linear (columns 5-7). Especially the results at the lowest concentration are close to the behavior predicted by eq. (1).

The deviations observed are thought to be real, however. With increasing concentration there is an increasing curvature convex to the pressure axis. Two of the points at the highest concentration were obtained with a hydrostatic pressure substantially below the osmotic pressure of the feed solutions, but according to eq. (1) there is no *a priori* reason to expect¹ that linearity should not extend down to $\Delta p - \Delta \pi = 0$.

The salt flux J_s increased with increasing salt activity in the feed solution as shown in columns 8-10 of Table I (the small effect of pressure on a $a_{\sigma,s}^I$ is neglected). For the pressures at which there are a sufficient number of points the variation appears to be linear, with the exception of the highest concentration. J_s also increased with hydrostatic pressure, as reported earlier.^{1,4}

Radioactive Tracer Experiments

Since radioactive tracer permeation can be studied at chemical equilibrium, complications in the evaluation of results due to concentration dependence in diffusion and partition coefficients are avoided.⁵ Rate measurements at different solution concentrations in conjunction with equilibrium concentration measurements in the membrane make possible an evaluation of the concentration dependence of the coefficients. Such dependence could account for the peculiarities observed in reverse osmosis, if the latter indeed results from diffusion in a homogeneous medium. The data were obtained on membranes (38.4% acetyl) cast without extractable nonvolatile additives with average thicknesses varying between 92 and 101 μ . They were considerably less swollen and permeable than the membrane on which the reverse osmosis data were obtained. This, and also the scatter resulting from the use of different membrane samples for the different data points,⁵ substantially reduces the significance of the absolute values obtained, but the trends were expected to be similar. As described in detail earlier,⁵ the steady-state fluxes of the labeled solution components (far from equilibrium) are given by

$$J_i = (D/L)C_m \quad (4)$$

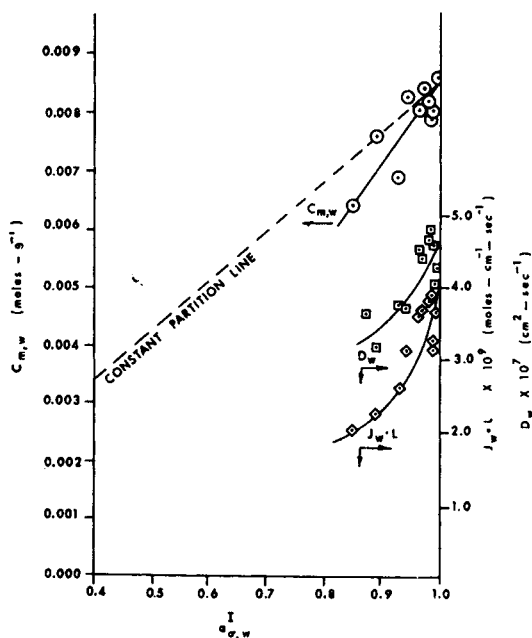


Fig. 1. Variation of water equilibrium concentration, tracer-labeled flux, and diffusion coefficient with water activity in solution; 38.4% acetyl.

Substituting for $C_m = (K_N/\gamma'_m)a_\sigma$ yields

$$J_w L = (DK_N/\gamma'_m)a_\sigma \quad (5)$$

Figure 1 shows an increase in the product of thickness L and the labeled water flux J_w as $a_{\sigma,w}$ increases. The upward curvature indicates an increase in permeation coefficient, $P = K_N D/\gamma'_m$, with water concentration, $C_{m,w}$, in the membrane. The departure from Henry's law ($C_{m,w}$ and dotted line) indicates that this curvature results, at least in part, from a concentration dependence of the partition coefficient $K_w = K_{N,w}/\gamma'_{m,w}$. Resolution of the origin of the decrease of γ'_m with increasing concentration is of central concern to a more detailed understanding.

When the diffusion coefficients of water are determined from experimental values of $C_{m,w}$ according to eq. (4), the scatter in the above plot is added to that from the permeation experiments. Nevertheless, there is little doubt of an increase of D_w with water concentration.

Figure 2 plots equilibrium salt concentration, $C_{m,s}$, in the membrane against salt activity, $a_{\sigma,s}$, in solution. The plot appears to be linear, as reported previously.^{1,2,6} It is taken to indicate that the degree of ionization in the membrane is similar to that in the solution, despite the predominantly organic composition of the membranes. This indication is compatible with the view,⁵ based on the experimental dependence of salt diffusion coefficients on membrane water content and on temperature,

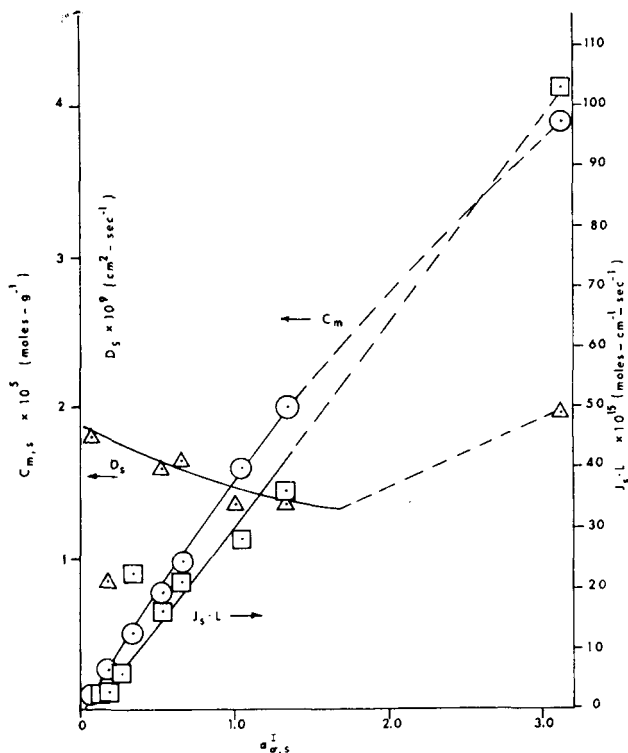


Fig. 2. Variation of salt equilibrium concentration, tracer-labeled flux, and diffusion coefficient with salt activity in solution; 38.4% acetyl.

that the salt requires multiple water contacts in the membrane. Closely associated ion pairs in the membrane should have given rise to strong upward curvature. A constant ratio of mean ionic activity coefficients, $\gamma_m^\pm/\gamma_{\sigma^\pm}$, is also implied by the linear plot, but a constant γ_m^\pm cannot be excluded within the precision of the data. The same indications are given by the approximately linear dependence of the flux on solution concentration in both tracer permeation (Fig. 2) and reverse osmosis experiments (Table I), but the highest concentration in the latter is considerably out of line. No clear preference for eq. (2) or (3) was apparent from these experiments.

The decrease of the diffusion coefficient of the salt with increasing salt concentration was expected, but the reason for the increase at the highest concentration, if real, is not clear. Diffusion of both water and salt have been attributed⁵ to the presence in the membrane of free volume which increases with increasing low molecular weight diluent content. Since the predominant effect of decreasing salt concentration on total diluent concentration is the increase in membrane water content, the decrease of D_s with increasing $a_{\sigma,s}$ provides added support for the validity of the free volume treatment.

Permeation Coefficients

Water Flux Deviations from Equation (1). The assumptions made in the derivation³ of eq. (1) confine its validity to systems in which the diffusion coefficient D_w and the activity coefficient $\gamma'_{m,w}$ in the membrane are independent of concentration. It must therefore be regarded as an ideal relation to which the cellulose acetate membranes examined by tracer permeation cannot be expected to adhere strictly. By extrapolating these findings to the membrane used in the reverse osmosis experiments, the deviations of the results in Table I from eq. (1) can be explained. This extension is further justified by earlier work on vapor sorption. Although constancy of D_w in cellulose acetate has been reported,⁷ that finding was based on experiments at much lower water activity. In any case, the deviations encountered here are mainly attributable to the concentration dependence of the distribution coefficient. There is ample evidence⁸⁻¹⁰ to show that the distribution isotherms on all cellulose acetates exhibit strong curvature concave to the C_m axis over almost the entire concentration range. We have also carried out further measurements from NaCl solutions on cellulose acetates varying in acetyl content from 29.9% to 43.6% and confirmed the same tendency in all cases.

If $\gamma'_{m,w}$ is allowed to vary with $C_{m,w}$ while all the other approximations³ made in the derivation of eq. (1) are retained, then

$$\frac{LRT}{DK_N} J_w = \frac{1}{\gamma'_I} [RT + (p^I - \pi^I) \bar{V}_\sigma - p_m \bar{V}_m] - \frac{1}{\gamma'_{II}} [RT + (p^{II} - \pi^{II}) \bar{V}_\sigma - p_m V_m] \quad (6)$$

In semipermeable or highly selective membranes, where π^{II} is so small that the second term on the right can be regarded as constant, a plot of J_w against $(-\Delta\pi)$ at constant Δp should exhibit upward curvature as a result of the variation of γ'_m with π^I . Where changes in the back flux cannot be neglected, the effect should be lessened, but it is well discernible in the results of Table I. It can also be seen, without alternative interpretation, in the paper by Michaels et al.¹

A similar effect is also expected for the variation of J_w with Δp at constant π^I , but it was much weaker, and almost absent in the most dilute solution examined (Table I). Among the factors that could counteract this tendency to upward curvature is the decrease of the diffusion coefficient with increasing pressure. The strong dependence of D_w on p^I which has been claimed elsewhere¹ is based on calculations which are inadmissible by the present treatment; it is also very unlikely on physical grounds. The effect of these moderate pressures on D , especially in glassy polymers, should be very small. A more important contribution comes from the increased energy required to introduce a water molecule into a membrane under pressure. Substitution for J_w of $J_w (1 + p_m \bar{V}_m / RT)$ according to

the more exact eq. (1a) introduces additional curvature in the same direction as found for the variation with π^I .

The nonconstancy of γ'_m can account for other apparent peculiarities. Lonsdale et al.² have reported that their diffusion coefficients from reverse osmosis experiments were much higher than they expected from literature data based on vapor sorption experiments. They are also substantially higher than those reported later from radioactive tracer measurements on similar membranes in 0.5*m* NaCl solution.⁵ Their calculation of D_w is nearly equivalent to that from eq. (1), and most of the discrepancy can again be explained by the concentration dependence of K . Closer agreement should be obtainable from eq. (1) by substituting for K the slope $\Delta C_m/\Delta a_\sigma$ at $a_\sigma \simeq 1$. For fuller agreement with the vapor sorption results it may also be necessary to correct for concentration dependence of D_w .

After this emphasis on departures from the relation for an ideal membrane, it should be reiterated that eq. (1) provides a reasonably good description which may be adequate for many purposes even with cellulose acetate membranes. In a search for an exact mechanism, however, they cannot be neglected.

Variation of Salt Flux with Pressure. Since an increase in p^I increases water flux, and hence salt activity gradient, some increase in salt flux with pressure should be expected according to eqs. (2) or (3) even at constant salt permeability. Substituting from eqs. (1) and (2) yields

$$\begin{aligned} C^{II} &= J_s/18J_w \\ &= \frac{RT}{18\bar{V}_w} \frac{P_s}{P_w} \frac{a_{\sigma,s}^I - a_{\sigma,s}^{II}}{\Delta p - \Delta\pi} \end{aligned} \quad (7)$$

or from eqs. (1) and (3):

$$R'/(1 - R') = (C^I/C^{II}) - 1 = (18\bar{V}_w/RT)(P_w/P_s)(\Delta p - \Delta\pi) \quad (8)$$

The salt rejection R'

$$R' = (C_{\sigma,s}^I - C_{\sigma,s}^{II})/C_{\sigma,s}^I$$

is generally used to characterize the effectiveness of desalination. According to eq. (8) a plot of $R'/(1 - R')$ against $\Delta p - \Delta\pi$ should be linear if the permeability coefficients, P_w and P_s , are constant. Figure 3 shows a consistent downward curvature which is reduced only slightly by use of eq. (7). The dependence of the salt flux on water flux is, thus, not sufficient to account for the pressure dependence of J_s , and it seems necessary to conclude that the apparent permeability coefficient of the salt increases with increasing pressure.

Michaels et al.¹ have suggested that part of the salt permeates by hydrodynamic flow through pores with occasional constrictions. Even in the absence of an alternative explanation, however, it is considered preferable to leave the question open pending more specific evidence. In view of the large number of parameters that can be, and have been, used with the pore

model, there is very little that can be predicted or that cannot be explained by it. Some independent physical evidence for at least the existence of such pores should be presented before any conclusions based on them can be accepted with confidence. Michaels et al. made clear the tentative nature of their suggestion. Also, the fairly close correspondence of their activation energies for the contributions from pores and diffusion, respectively, may be construed as evidence for correspondence of underlying mechanisms.

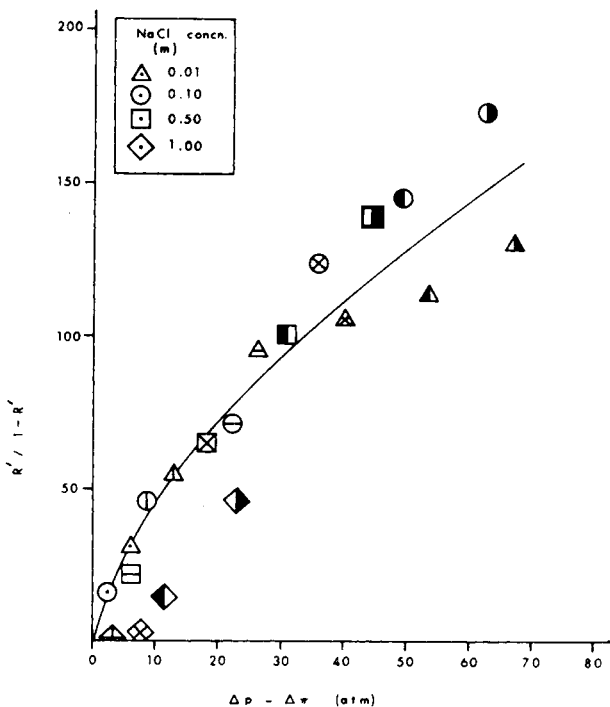


Fig. 3. Dependence of the selectivity function $R'/(1 - R')$ on $\Delta p - \Delta \pi$; 43.2% acetyl

A number of alternative explanations for the unexpectedly large increase of J_s with pressure have been considered, among them the possibility that the water content of the membrane (hence, the partition and diffusion coefficients of salt) increases with increasing pressure. This would be expected only if the partial molar volume of water in the membrane were less than half that in the liquid phase (e.g., if more than half of the volume required to introduce a water molecule into the membrane were already present as small voids resulting from lack of close fit between adjacent units of the polymer). From our inadequate evidence on this point it appears, however, that the steady-state water content does not increase with pressure and, more specifically, that the equilibrium salt content decreases with increasing pressure.

Increasing concentration polarization resulting from the increase of water flux with increasing pressure would provide another reasonable explanation, but our preliminary experiments had shown little or no effect of stirring speed on the flux of water or salt. However, in view of the emphasis placed by a number of authors¹¹⁻¹³ on the importance of these effects, we prefer not to exclude them as a possible explanation of the unexpectedly large increase of salt flux with hydrostatic pressure.

Comparison of Reverse Osmosis and Tracer Permeation Rates

The extreme flexibility of the pore model makes it very difficult to devise definitive, diagnostic experiments to differentiate it from diffusion in a homogeneous medium. For water permeation, however, a comparison of the rate of tracer permeation (in the absence of hydrostatic pressure) with the net flux measured by the volume of permeate in reverse osmosis does provide such a test. The data obtained in such an experiment are shown in Table II. To avoid ambiguity, the same membrane was used for both experiments.

TABLE II
Comparison of Net Water Flux in Tracer Permeation and Reverse Osmosis
(68 atm, Δp ; 38.4% Acetyl)

NaCl concn, <i>m</i>	Reverse osmosis		Radioactive tracer
	$J_w \times 10^7$, mole/cm ² -sec	$\Delta p - \Delta \pi$, atm	$J_w \times 10^7$, mole/cm ² -sec
0.1	0.24	63	2.6
0.5	0.17	48	3.9
1.0	0.06	24	3.7

As seen from Table II, the rates of water permeation measured by the radioactive tracer method in the absence of pressure were 10-60 times higher than those measured in reverse osmosis at 68 atm. At higher $\Delta p - \Delta \pi$ the discrepancy is lower and vice versa. It is difficult to see how pores can provide an understanding of such a result. Similar results were obtained with a number of different cellulose acetate membranes using the same membrane for both measurements.

If it is accepted, however, that the pressure serves only to modify the concentration gradient inside a homogeneous membrane, it can readily be understood why the net flux under pressure should be much lower than the flux in the tracer experiment. For simplicity, the diagram in Figure 4 was drawn for the case where \bar{V}_m is zero; the actual value of \bar{V}_m is not important for the purposes of this discussion. A profile of the membrane is shown by the solid vertical lines to the right. Interface I represents the high pressure side in reverse osmosis, or the spiked side in the tracer experiment. The ordinate shows the concentration of water in the membrane.

otherwise equivalent polymer (equal water solubility) in which γ'_m is constant. The salt flux should depend⁵ on total water content, but (almost) not on the shape of the water isotherm. The net result is a higher selectivity of flux in favor of water by comparison to a membrane with constant γ'_m and equal water solubility. This effect is in addition to factors conducive to selectivity operating also in the absence of a chemical concentration gradient.⁵

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