

Transport Properties of Cellulose Acetate Osmotic Membranes*

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Synopsis

Diffusion and distribution coefficients of water and sodium chloride have been measured in cellulose acetate osmotic membranes. These coefficients have been found to vary with the degree of acetylation of the cellulose ester. The diffusion coefficient of water varies from 5.7×10^{-6} to 1.3×10^{-6} cm.²/sec., and the diffusion coefficient of salt varies from 2.9×10^{-8} to 3.9×10^{-11} as the acetyl content is increased from 33.6 to 43.2 wt.-%. A homogeneous diffusion model is proposed which describes the observations in terms of Fick's law.

INTRODUCTION

Recent work done by Reid and Breton¹ and by Loeb and Sourirajan² has shown that cellulose acetate films act as highly selective membranes in the separation of water from salt solutions by reverse osmosis. The present study was undertaken in an attempt to obtain quantitative data on the permeability of such membranes to water and to sodium chloride under the conditions of interest in water desalination, and to interpret these data in terms of a reasonable membrane permeation model.

EXPERIMENTAL

The membranes used in this work were prepared from various grades of cellulose acetate supplied by Eastman Chemical Products, Inc. The membranes referred to as "normal" were cast with a Gardner film-casting knife on glass plates at room temperature and were stripped from the glass after they were quite dry. A solvent was chosen for each material which gave optically clear membranes, apparently free of imperfections. The casting solutions for the 37.6, 39.5, and 39.8 wt.-% acetyl cellulose acetates were prepared by dissolving a weighed quantity of the acetate powder in three times its weight of reagent-grade acetone. The solution of the 43.2 wt.-% acetyl material was made similarly but with *p*-dioxane as solvent, and the 33.6 wt.-% acetyl powder was added to three times its weight of absolute

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ethyl alcohol, and sufficient water was then added to effect complete solution.

The "modified" membranes were prepared by a procedure essentially similar to that described by Loeb and Sourirajan.² In this case, the casting solution consisted of 22.2 wt.-% cellulose acetate (39.8 wt.-% acetyl, Eastman No. 398-3), 1.1 wt.-% Baker anhydrous $\text{Mg}(\text{ClO}_4)_2$, 66.7 wt.-% reagent-grade acetone, and the balance distilled water. The solution was cooled to -5°C . and cast on cold glass plates in a deep freeze maintained at this same temperature. The membranes were allowed to dry for 4 min. after casting and were then immersed in ice water and kept there for at least 1 hr. Finally, the membranes were annealed in 81°C . water for 30 min.

The gross transport properties were measured in two types of experiments, one involving normal osmosis, the other reverse osmosis. In the normal osmosis experiments, a piece of the membrane of interest was supported between two coarse Monel grids in a circular hole (~ 15 cm. diameter) through a central dividing member in a rectangular plastic box. An O-ring seal was made around the perimeter of the hole. Aqueous solutions of different salt concentrations were then placed in each of the two chambers of the box. The solutions were stirred during the experiments. Water permeability was determined by measuring the rate of increase in water volume on the high-concentration side, with zero (i.e., <0.5 cm. water) pressure difference across the membrane. Salt permeability was calculated from the increase in salt concentration on the low-concentration side during the experiments. All the osmosis experiments were conducted at room temperature.

Properties of the modified membranes were also determined in a reverse osmosis apparatus. Here the membrane was supported on a piece of filter paper supported in turn on porous stainless steel. A salt solution of known concentration and under a pressure ranging from 3 to 140 atm. was circulated across the membrane, and the throughput water was collected from the porous plate. Water permeabilities were calculated from the throughput rate, and the salt permeability from the water throughput and the salt content of the effluent.

The water content of certain of the membranes was determined as a function of relative humidity by weighing over sulfuric acid-water solutions on an Ainsworth recording semimicrobalance. The chamber containing the sulfuric acid solution, with the membrane suspended above it, was immersed in a 25°C . constant-temperature bath. Following each measurement, the density of the solutions was measured pycnometrically, and the relative humidity was obtained from the literature.³

The solubility and diffusive behavior of NaCl in the membrane materials was determined by immersing relatively thick (~ 0.1 mm.) pieces of membrane (~ 2 cm. by 5 cm.), which had been previously saturated with water, in NaCl solutions of known concentration for varying lengths of time. After immersion, the pieces were quickly wiped dry with cleansing tissue

and then analyzed for sodium by a neutron-activation technique. The 1.37- and 2.75-m.e.v. γ -rays of 15-hr. Na^{24} were counted by using a NaI -(Tl) crystal and single-channel pulse-height analyzer. Sodium analyses were effected by comparing the results with appropriate standards.

RESULTS

Osmosis Experiments

A series of experiments was carried out in the osmosis cell at room temperature with normal membranes of various acetyl contents. A 5.0 wt.-% NaCl solution was used on one side of the membranes and distilled water on the other side. The water and salt fluxes observed are reported in Table I.

TABLE I
Permeability of Normal Cellulose Acetate Films

Acetyl content, wt.-%	Thickness, μ	Water flux, $\mu\text{g./cm.}^2\text{-sec.}$	Apparent permeability to H_2O , D_1C_1 , $\mu\text{g./cm.}^2\text{-sec.}$	Salt flux $\mu\text{g./cm.}^2\text{-sec}$	Apparent permeability to NaCl , D_2K , $\text{cm.}^2\text{/sec.}$
33.6	28	19	1.8	0.80	4.5×10^{-8}
	23	19	1.4	0.79	3.6×10^{-8}
37.6	19	9.0	0.57	0.044	1.7×10^{-9}
	19	9.1	0.57	0.031	1.2×10^{-9}
39.5	20	3.3	0.22	0.044	1.7×10^{-9}
	13	6.3	0.28	0.017	4.5×10^{-10}
	15	5.4	0.28	0.074	2.3×10^{-9}
39.8	28	2.7	0.26	0.0053	3.0×10^{-10}
	29	2.5	0.25	0.012	6.7×10^{-10}
	51	1.1	0.20	0.018	1.8×10^{-9}
	28	3.4	0.32	0.0046	2.6×10^{-10}
43.2	14	3.2	0.15	0.0079	2.2×10^{-10}

In all cases, the experiments were terminated while the NaCl concentration on the distilled water side was still small, i.e., less than ~ 0.1 wt.-%. The thicknesses reported are the average of several micrometer readings taken at various points on each membrane. The membranes were found to be uniform to $\pm 5 \mu$.

A similar series of measurements was made with normal membranes which had been heat-treated after preparation by the usual procedure. Heat treatments at 80 and 100°C. were carried out by soaking the membranes in a water bath at the desired temperature for 30 min.; the 160°C. heat treatment was performed in air for a period of 72 hr. The results of these experiments are indicated in Table IIA. Permeability measurements were also carried out on membranes which were cast from solutions prepared from solvents other than those reported above. The quality of these mem-

TABLE II
Effect of Some Process Variables on Water Permeability of Normal Membranes

Acetyl content, wt.-%	Treatment/solvent	Thick-ness, μ	Water-flux, $\mu\text{g./cm.}^2\text{-sec.}$	$\text{H}_2\text{O, D}_1\text{C}_1$, $\mu\text{g./cm.}^2\text{-sec.}$	Salt flux, $\mu\text{g./cm.}^2\text{-sec.}$	Apparent permeability to $\text{H}_2\text{O, D}_1\text{C}_1$, $\mu\text{g./cm.}^2\text{-sec.}$	Apparent permeability to $\text{NaCl, D}_2\text{K}$, $\text{cm.}^2\text{/sec.}$
A. 39.5	Heated to 80°C.	22	2.2	0.17	0.024	1.1×10^{-9}	
		18	2.7	0.16	0.0014	4.8×10^{-11}	
39.8	Heated to 80°C.	32	1.2	0.13	0.011	7.1×10^{-10}	
		18	4.0	0.24	0.033	1.2×10^{-9}	
	Heated to 100°C.	35	0.78	0.091	0.0013	9.0×10^{-11}	
	Heated to 160°C.	26	2.5	0.22	0.012	6.0×10^{-10}	
B. 33.6	Pyridine	42	13	1.8	0.52	4.4×10^{-8}	
	Pyridine-H ₂ O (6.6:1)	40	7.5	1.0	0.29	2.3×10^{-8}	
39.8	<i>p</i> -Dioxane	35	6.2	0.72	0.043	3.0×10^{-9}	
	<i>p</i> -Dioxane-H ₂ O (6.6:1)	35	1.44	0.17	0.00097	6.8×10^{-11}	
	Pyridine	31	2.6	0.27	0.0039	2.4×10^{-10}	
	Pyridine-H ₂ O (6.6:1)	32	2.3	0.25	0.0038	2.4×10^{-10}	
43.2	Pyridine	32	2.9	0.31	0.0061	3.9×10^{-10}	

branes was, in general, not as good as that of the membranes reported on above. The pertinent data are given in Table IIB.

An additional measurement was carried out on a normal, 39.8% acetyl membrane using more concentrated salt solutions. The 35- μ thick membrane was supported between solutions containing 22.6 and 25.1 wt.-% NaCl. The water flux observed was 0.76 $\mu\text{g./cm.}^2\text{-sec.}$

Finally, one measurement was made by using a modified membrane with a measured thickness of 100 μ and the usual 5.0 wt.-% NaCl versus distilled water arrangement. Very vigorous stirring was required to eliminate concentration gradients on the brine side, because of the high water flux observed. With this vigorous stirring, a water flux of 510 $\mu\text{g./cm.}^2\text{-sec.}$ and a salt flux of 0.45 $\mu\text{g./cm.}^2\text{-sec.}$ were measured.

Reverse Osmosis

Reverse osmosis experiments were performed on the modified membranes with results essentially similar to those already reported by Loeb and Sourirajan.² Results of water throughput measurements for four different pieces of membrane and with two different sodium chloride solutions in the high-pressure chamber are shown in Figure 1. All points were taken with circulation velocities in excess of 100 cm./sec., where boundary-layer effects in this apparatus and under these conditions have been shown to be negligible.⁴

The hysteresis loops shown indicate a significant loss of membrane permeability as a result of compression in the cell. Part of this loss was found to be recovered when the membrane was left at lower pressures for a few hours.

The water throughput data for these highly selective membranes can be extrapolated to zero at a pressure very close to the osmotic pressure (~ 1 atm. for the 0.13 wt.-% brine and 37 atm. for the 4.5 wt.-% brine). For

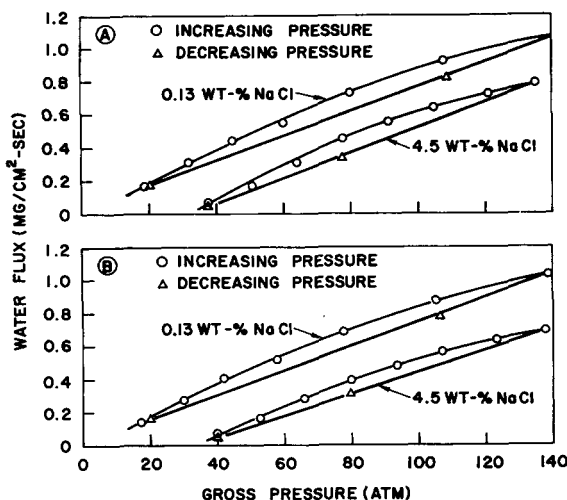


Fig. 1. Water flux vs. gross pressure for four modified cellulose acetate membranes.

purposes of comparison with other membrane properties, we can characterize the permeability of the membrane by the initial (i.e., before compression) value of the membrane constant, A , in the equation⁵

$$F_1 = -A(\Delta P - \Delta \pi) \quad (1)$$

where F_1 is the water throughput and ΔP and $\Delta \pi$ are the pressure difference and the osmotic pressure difference across the membrane, respectively. The initial slopes of the lines in Figure 1 yield values of A ranging from 0.9×10^{-5} to 1.2×10^{-5} g./cm.²-sec.-atm.

The selectivity of membranes like those used in these water throughput measurements is good, but somewhat variable. The salt permeabilities (defined as the salt flux divided by the difference in the salt concentrations of the solutions on the two sides of the membrane) of the membranes used in Figure 1 were 13×10^{-6} cm./sec. (Fig. 1A) and 17×10^{-6} cm./sec. (Fig. 1B) for the low-concentration experiments and 16×10^{-6} cm./sec. (Fig. 1A) and 12×10^{-6} cm./sec. (Fig. 1B) for the high-concentration experiments. These data were calculated from the salt flux at the highest experimental pressures. More detailed data are given for two similar membranes (but with slightly higher membrane constants, $\sim 1.5 \times 10^{-5}$

g./cm.²-sec.-atm.) in Figure 2 in the form of salt rejections. Salt rejection, S , is defined as

$$S = (\rho_2^i - \rho_2^0) / \rho_2^i \quad (2)$$

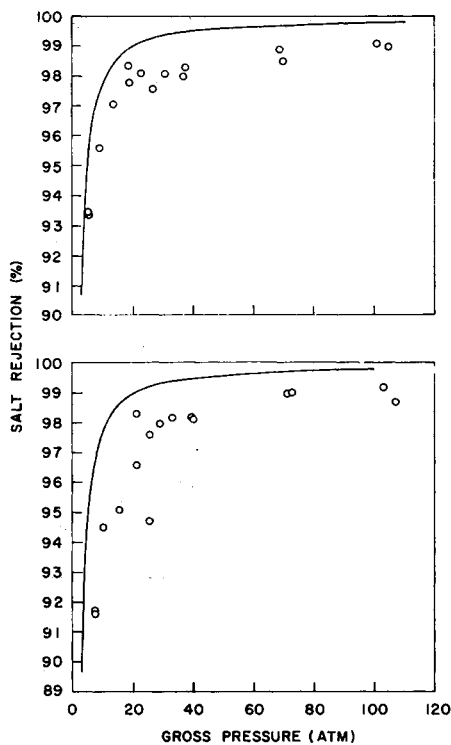


Fig. 2. Salt rejection of two modified membranes vs. gross pressure (for 1000 ppm NaCl feed brine).

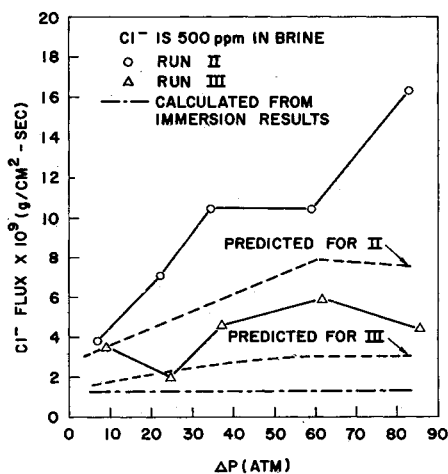


Fig. 3. Chlorine ion flux vs. pressure difference across a modified membrane.

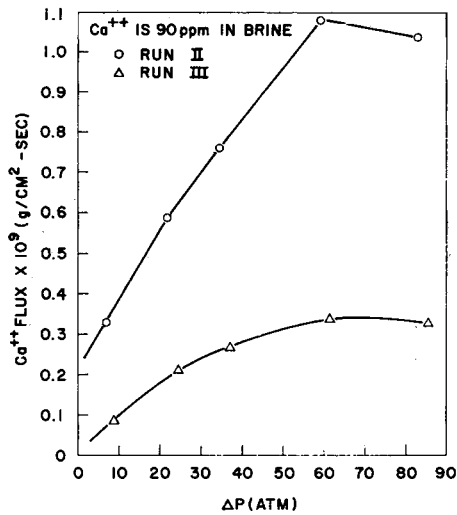


Fig. 4. Calcium ion flux vs. pressure difference across a modified membrane.

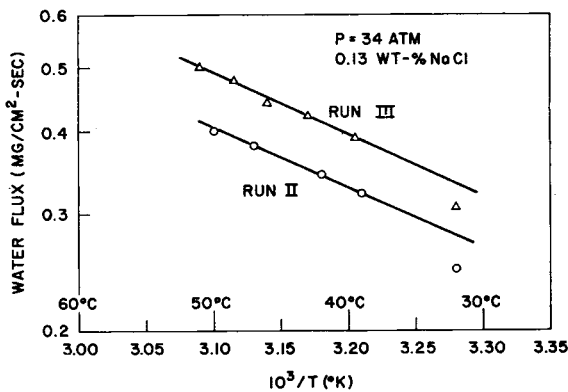


Fig. 5. Water flux vs. reciprocal temperature for modified membranes.

where ρ_2^i and ρ_2^0 are the brine-side and throughput salt concentrations, respectively.

In reverse osmosis experiments with CaSO_4 solutions in place of the usual NaCl brines, it was found that the membrane permeabilities for this divalent salt were substantially lower than those for the monovalent salt. An experiment was then performed with a solution containing 500 ppm Cl^- added as NaCl and 90 ppm Ca^{++} added as CaSO_4 . The observed pressure-dependent fluxes of the two ions are shown in Figures 3 and 4.

Measurements were also made of the water flux as a function of temperature for the modified membrane over the range 32–50°C. The results for two films are shown in Figure 5 in the form of Arrhenius plots. The flow increased with increasing temperature such that it doubled in approximately 33°C., but there was no significant change in salt rejection, which

was 98% under the experimental conditions of 34 atm. pressure and 0.13 wt.-% NaCl brine. From the slope of the lines one calculates an apparent activation energy for the water permeation process of 4.2 kcal./mole.

Water Content

Water sorption measurements were made on cellulose acetate membranes of two different degrees of acetylation. For the 39.8% acetyl material, the water sorption as a function of relative humidity for both a normal and a modified membrane is shown in Figure 6. The shape of these curves is typical of the curves observed in the water sorption behavior of a number of cellulosic materials.⁶ A similar measurement was carried out with a normal 33.6% acetyl film, and the water sorbed at 100% R.H. was 22.9 wt.-% or 0.285 g./cc. assuming that the molar volumes of water and cellulose acetate are additive.

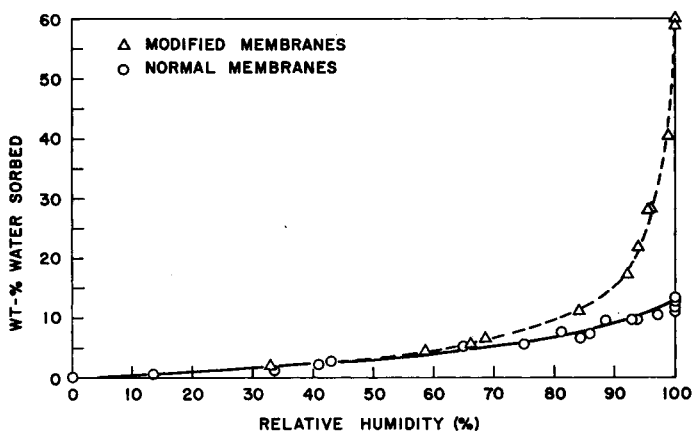


Fig. 6. Water sorption vs. relative humidity for normal and modified membranes.

Salt Permeation

Salt diffusion and distribution coefficients in normal cellulose acetate membranes were measured by following the approach to steady state of salt sorption when membranes were immersed in 5% NaCl solutions. Membranes were removed from the solution after several time periods, including essentially infinite time. The solution to a diffusion problem of this type is given by the equation⁷

$$(C_f - \bar{C})/C_f = (8/\pi^2) \exp\{-\pi^2 D_2 t / \Delta x^2\} \quad (3)$$

where \bar{C} and C_f are, respectively, the average salt concentration at any time t and the final or steady-state salt concentration, D_2 is the salt diffusion coefficient, and Δx is the membrane thickness. Equation (3) is valid when the initial salt concentration in the films is zero and at long times. The quantity $(C_f - \bar{C})/C_f$ is plotted against time for a normal 39.8%

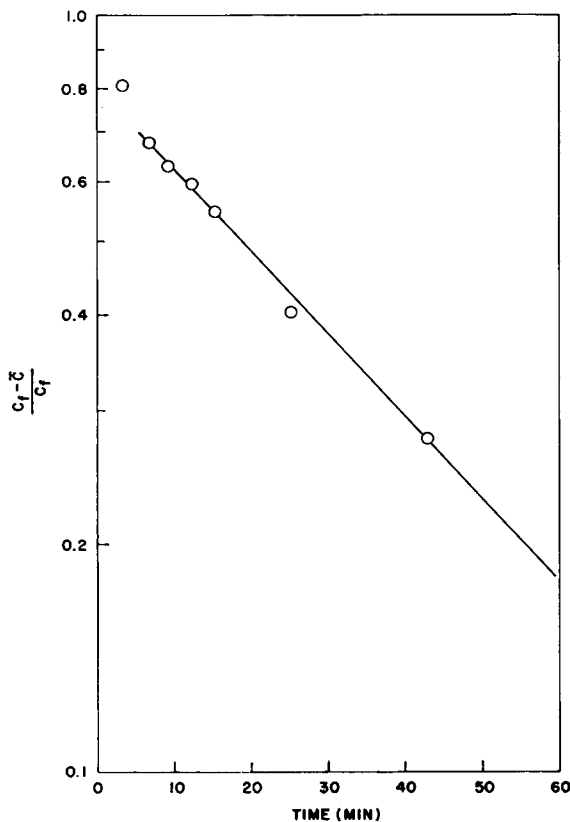


Fig. 7. Typical results for the approach to the steady state in a salt distribution coefficient experiment with normal membranes.

acetyl membrane in Figure 7, and eq. (3) is seen to be followed quite nicely. The slope of the line is $-\pi^2 D_2 / \Delta x^2$, from which a value of D_2 of 9.4×10^{-10} cm.²/sec. is obtained. One can obtain a distribution coefficient, K , where

$$K = \frac{\text{grams NaCl/cc. membrane}}{\text{grams NaCl/cc. solution}}$$

from the steady-state salt concentration. A summary of the diffusion coefficient and distribution coefficient values obtained in this way for several cellulose acetates is given in Table III. Because the membranes used in these measurements were of varying thickness ($\Delta x = 30 - 105\mu$), eq. (3) was solved for each piece of membrane and the diffusion coefficients given in Table III represent the averages of these values.

Similar experiments have been conducted on normal 39.8% acetyl membranes heated to 80°C. in a water bath prior to immersion. The average diffusion coefficient obtained with ten pieces of membrane was $8.6 \pm 2.0 \times 10^{-10}$ cm.²/sec., and the distribution coefficients obtained in two separate

TABLE III
Salt Distribution and Diffusion Coefficients in Normal Membranes

Acetyl content wt.-%	K	\bar{D}_2 , cm. ² /sec.	Number of points
33.6	0.17, 0.17	$2.9 \pm 0.6 \times 10^{-8}$	5
37.6	0.046, 0.077	$4.3 \pm 2.0 \times 10^{-9}$	9
39.8	0.035	$9.4 \pm 1.1 \times 10^{-10}$	5
43.2	0.014, 0.016	$3.9 \pm 1.3 \times 10^{-11}$	8

experiments were 0.031 and 0.027. These values are very close to those obtained with unheated membranes.

To study the dependence of D_2 and K on salt concentration, one series of measurements was conducted with a 0.5% NaCl solution; the \bar{D}_2 obtained, based on seven samples, was $1.26 \pm 0.37 \times 10^{-9}$ cm.²/sec., and K was 0.032. A number of other distribution-coefficient data have been obtained from steady-state salt concentrations at 1.6% and 10.6% NaCl. The range of K values was 0.036–0.040 and 0.030–0.043, respectively, in these two solutions. The results show no dependence on salt concentration and yield an average value for K of 0.037.

DISCUSSION

Transport Mechanisms

In theoretical treatments of semipermeable membranes, they are often viewed as porous sieves through which constituents of the solution in question may either diffuse or flow by viscous processes. A number of variants on this general scheme exist, including that in which strong adsorption on the pore walls is assumed to explain some of the observed properties. Much of the early thinking along these lines was summarized in an extensive review article by Ferry⁸ in 1936.

Discrimination between two substances by a sieve on the basis of size is readily imagined when the distinction to be made is between water and colloidal particles or dissolved substances of very high molecular weight.

It is more difficult, however, to believe that any sieve could make a sharp distinction between water molecules in various states of aggregation and small ions in various states of hydration, as has been pointed out by Breton.⁹

A more reasonable suggestion is that the ions are excluded by Coulomb forces arising from charges residing on the walls of the pores. It is likely that the membranes most commonly used in ultrafiltration and similar processes discriminate against ions in this way. For instance, Ambard and Trautmann¹⁰ have reported extensive measurements on cellophane membranes which show considerable discrimination against ions at low salt concentrations, but they find that the ability of the membrane to discriminate falls rapidly as the salt concentration increases. Since the effec-

tive range of the Coulomb forces in a medium containing charged particles varies inversely as the square root of the charge density, sieves of this kind would be expected to show this decreasing selectivity, and very small pores indeed would be required to achieve good selectivity for concentrated solutions. Crudely, one might expect that the pore radius would have to be of the order of a Debye length, which is $\sim 7 \times 10^{-8}$ cm. in a 5 wt.-% aqueous NaCl solution at room temperature. (Dresner and Kraus¹¹ have recently calculated the relationship between pore size and degree of semipermeability quantitatively for a specific model of this kind.)

It is not likely, therefore, that the same mechanism is effective in the particular cellulose acetate membranes of interest here because, as is evidenced by the work of Reid and Breton,¹ of Loeb and Sourirajan,² and that reported here, these membranes show a very high degree of discrimination against ions, even at high salt concentrations, and their degree of semipermeability is not strongly sensitive to salt concentration.

Ferry credits Lhermite¹² with suggesting, in 1855, as an alternative to the sieve idea, "the theory of partial solubility, which represents the solvent as dissolving into the membrane on one side and out on the other." The present work is best understood in these terms. In the present case, the transport of both solvent and solute can be described as molecular diffusion through the membrane under the chemical potential gradient existing across it.

Film Structure

In a concurrent report,¹³ electron microscopic studies of cellulose acetate membranes of both the normal and the modified variety have been described. These studies revealed that the normal membranes appear fully dense and without structure at the magnifications used ($\sim 8000 \times$), while the modified membranes appear to be quite porous throughout, with an irregular pore structure on the scale of about 0.1μ except for an apparently dense layer on the air-dried side which is about 0.25μ thick when the membrane is prepared as described above.

Many qualitative observations support the hypothesis that it is this "skin" which provides essentially all the resistance to salt and water flow through the modified membrane. Thus, the membranes are known to have directional properties, and Loeb¹⁴ has reported that disrupting the air-dried surface greatly increases the permeability of the membranes and destroys their selectivity.

The water-sorption measurements reported above give some further insight into the structure of the membranes. It is well known that the water sorption properties of cellulose and its derivatives⁶ may depend somewhat upon such factors as their degree of crystallinity; and a small amount of hysteresis was observed in the present measurements on the normal cellulose acetate membranes, in agreement with similar experience with cellulose reported in the literature.⁶ The magnitude of the effect was small, how-

ever, and the sorption process can safely be viewed as reversible for our purposes.

Tankard¹⁵ has characterized the water which is sorbed by organic polymers as "solvent" and "nonsolvent" water, depending upon whether the water is available to act as a solvent for ionic materials. He finds that the nonsolvent water in 36.9% acetyl cellulose acetate comprises 14.1 wt.-%, a value consistent with our results on normal membranes at 100% R.H. Since the electron microscope shows no porosity in these membranes, we may regard this water as dissolved in the membrane.

The water sorption curve for the modified membrane approaches that for the normal membrane at low relative humidity, as one might expect if the solubility of water in the cellulose acetate phase of this porous membrane

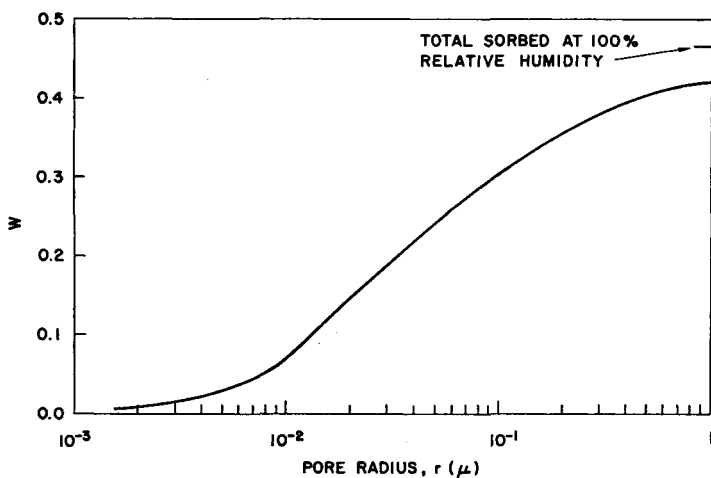


Fig. 8. Volume of water sorbed in capillaries in modified 39.8%-acetyl cellulose acetate membranes (w = cubic centimeters of water per gram of membrane held in pores of radius less than r).

is the same as it is in the normal membrane. The excess water in the modified membranes is believed to be held by capillary action in the pores which have been observed by means of electron microscopy. The difference between the two curves in Figure 4 gives the water sorbed in capillaries as a function of relative humidity. With this information, one can estimate the pore-size distribution in the modified membranes. Assuming the pores to be of circular cross section and the contact angle between cellulose acetate and water to be 0° , the water under the concave surfaces exposed in the pores will be under a negative pressure, due to surface tension, of ^{16a}

$$P = 2\gamma/r \quad (4)$$

where P is the negative pressure necessary to prevent the evaporation of the water at the reduced relative humidity, γ is the surface tension of the water,

and r is the radius of the exposed hemispherical surface of the water. Furthermore,^{16b}

$$P = (RT/\bar{V}_1) \ln(P_w^0/P_w) \quad (5)$$

where P_w^0 and P_w are the vapor pressures of pure water and of the water within the pore, respectively (i.e., P_w/P_w^0 is the relative humidity when the system is equilibrated); R is the gas constant; T is the absolute temperature; and \bar{V}_1 is the partial molar volume of water. One can solve eqs. (4) and (5) to give the relative humidity at which water is sorbed by pores of radius r . By comparing this result with the excess water found in the modified membranes at several relative humidities, one can compute the volume of water held in pores of radius less than any given radius. A plot of this result is shown in Figure 8. The dissolved water, as given by the curve for the normal membrane, was first subtracted from the total, and only the excess was assumed to be in the pores. It is clear that most of the pores are quite small and that the bulk of the water is held in pores in the 0.01–0.3 μ range. Thus, the conclusions reached here are in substantial agreement with the observations made from the electron micrographs.

Water Permeation

Accepting the view that water transport through the normal membranes is by diffusion through a single phase, we might expect to be able to characterize the process by means of a Fick's law diffusion coefficient, i.e., D_1 in the expression

$$J_1 = -D_1 dC_1/dx \quad (6)$$

where J_1 is the water flux through the membrane and C_1 is the concentration of water dissolved in the membrane.* Making the approximation that the cellulose acetate–water solution is Henrian, i.e.,

$$\mu_1 = \text{constant} + RT \ln C_1 \quad (7)$$

where μ_1 is the chemical potential of the water, eq. (6) becomes

$$J_1 = \frac{D_1 C_1}{RT} \frac{d\mu_1}{dx} \approx \frac{D_1 C_1}{RT} \frac{\Delta\mu_1}{\Delta x} \quad (8)$$

with Δx being the membrane thickness.

The last approximation is a reasonable one because the range of μ_1 covered here is very small; e.g., the relative vapor pressure of a 5 wt.-% NaCl solution compared with that of pure water at room temperature¹⁷ is 0.97. The chemical potential of water in the external phase of the present

* In setting down this simple expression for the flux of water and the equivalent expression for the flow of salt which is presented in eq. (13), it is assumed that the cross-terms, i.e., the effect of salt flow and water flow on one another, are negligible. That this is indeed the case is borne out experimentally by the agreement between the permeabilities of both salt and water as observed in the osmosis experiments and in the reverse osmosis experiments, as is discussed below.

experiment is varied by changing the total pressure and concentration of the solutions. The chemical potential difference is therefore conveniently written as

$$\begin{aligned}\Delta\mu_1 &= \int (\partial\mu_1/\partial C_2)_{T,P} dC_2 + \int (\partial\mu_1/\partial P)_{T,C_2} dP \\ &= \int (\partial\mu_1/\partial C_2)_{T,P} dC_2 + \bar{V}_1 \Delta P\end{aligned}\quad (9)$$

where C_2 is the salt concentration in the membrane. By definition,^{16c} when $\Delta\mu_1 = 0$, $\Delta P = \Delta\pi$, so

$$\int (\partial\mu_1/\partial C_2)_{T,P} dC_2 = -\bar{V}_1 \Delta\pi \quad (10)$$

$$\Delta\mu_1 = \bar{V}_1 (\Delta P - \Delta\pi) \quad (11)$$

where \bar{V}_1 is the partial molar volume of water in the external phase and ΔP and $\Delta\pi$ are the pressure and osmotic pressure differences across the membrane, respectively. Hence, eq. (8) becomes

$$J_1 = -D_1 C_1 \bar{V}_1 (\Delta P - \Delta\pi)/RT \Delta x \equiv -A(\Delta P - \Delta\pi) \quad (12)$$

In arriving at this result, we have implicitly assumed that D_1 , C_1 , and \bar{V}_1 are independent of P . This assumption is reasonable in the pressure range of interest here (up to 140 atm.) because these properties of condensed phases are quite generally insensitive to pressures until values of thousands of atmospheres are reached.

Equation (12) now allows us to calculate from the water-throughput measurements the apparent water permeability, $D_1 C_1$, which is shown in Table I. With the help of reported values for C_1 , we can obtain the diffusion coefficients for water in the membranes. Since the water activity in the external phases was close to unity in all the experiments but one, we should use for C_1 that value attained at 100% R.H. The values of C_1 have been obtained both from the present study and from a compilation by Eastman Chemical Products, Inc.¹⁸ The values reported by Eastman for 37.6, 39.5, and 43.2% acetyl membranes at 95% R.H. were increased by a factor of 1.05 to approximate the 100% R.H. condition. The Eastman values for acetyl contents in the neighborhood of 33.6 and 39.8% are in acceptable agreement with the values obtained in the present work for membranes of this acetyl content, and the latter values were used.

The results of these calculations are given in Table IV. The water content, the diffusion coefficient, and the permeability are all seen to decrease with increasing acetyl content. The fact that different solvents were used to effect the solution of these several cellulose acetates for use in the osmosis cell experiments is not believed to have a major bearing on this conclusion. A comparison of the water permeabilities reported in Table I with those in Table IIA reveals that the data generally differ by no more than a factor of two, indicating that the heat treatment does not significantly alter the

TABLE IV
Diffusion Coefficients for Water as Measured in Normal Membranes

Acetyl content, wt.-%	Average value of D_1C_1 , g./cm.-sec.	C_1 , g./cc.	D_1 , cm. ² /sec.
33.6	1.6×10^{-6}	0.29	5.7×10^{-6}
37.6	5.7×10^{-7}	0.20	2.9×10^{-6}
39.5	2.6×10^{-7}	0.17	1.5×10^{-6}
39.8	2.6×10^{-7}	0.16	1.6×10^{-6}
43.2	1.5×10^{-7}	0.12	1.3×10^{-6}

water permeability. The fact that some of the results of Table IIB do fall outside the apparent experimental uncertainties of Table I may be attributable in part to a real effect of the solvent and in part to the fact that the films prepared from these solvents were generally less perfect. The permeability result is in qualitative agreement with that reported by Reid and Breton,¹ but a quantitative check is not possible because some of the data needed to insert their results into eq. (12) are not available. A comparison can be made with the later report of Reid and Koppers.¹⁹ These authors used an expression similar to ours to calculate diffusion coefficients from permeability data, but apparently lumped the factor C_1 into their D_1 . To put their data on a 40 wt.-% acetyl material on a comparable basis, we have multiplied their reported diffusion coefficients for water by a factor of 1/0.16. On this basis, their values for D_1 range from 5×10^{-7} to 5×10^{-6} cm.²/sec., and hence are of the same order as those reported here. We did not observe the rapid changes in D_1 with increasing pressure reported by Reid and Koppers.

The 4.2 kcal./mole apparent activation energy given by the data of Figure 5 seems reasonable when compared with activation energies reported by Barrer²⁰ for water transport through a variety of membranes. The values reported range from 3 to 8 kcal./mole, and the value reported for cellulose nitrate, the only cellulosic material included in the Barrer compilation, is 4.7 kcal./mole. Reid and Koppers¹⁹ report values around 5 kcal./mole for 40 wt.-% acetyl membranes. These activation energies, of course, include the heat of sorption and are not the activation energies for the diffusion process. The heat of sorption of water in cellulosic materials is generally positive, which means that the activation energy for diffusion is somewhat greater than that for permeation.

The permeability of similar cellulose acetate membranes to water vapor has been determined by a number of workers. If the transport mechanism is indeed molecular diffusion, one would expect the diffusion coefficients determined from experiments involving transfer of liquid water and of water vapor to be identical. This does not, however, appear to be the case. Hauser and McLaren,²¹ for example, have measured the permeability of a 40.2% acetyl cellulose acetate film containing 9% plasticizer, which was

commercially made. They used the so-called cup method, in which the weight gain or loss of a membrane-covered cup is measured when the relative humidities inside and outside the cup are different. The weight change is followed until a steady state is attained, and the permeability is obtained from the steady-state rate of sorption or desorption. In this way, the permeability can be measured as a function of the average relative humidity of the system. Hauser and McLaren used Henry's law to obtain a diffusion coefficient from the permeability data and accompanying equilibrium water sorption measurements. They observed that the sorption behavior was quite non-Henrian at relative humidities in excess of 50%, and they therefore report diffusion coefficients only at 40 and 60% R.H. These values are both 3×10^{-8} cm.²/sec. at 25°C., in comparison with a value of 1.6×10^{-6} cm.²/sec. obtained in the present study at 100% R.H.

Long and Thompson²² have also measured the water diffusion coefficient in cellulose acetate. Their technique consisted of following the rate of change of weight of a suspended membrane as the environmental relative humidity was changed. A diffusion coefficient was then obtained at some average relative humidity from the rate of approach to the steady state using the same solution to the diffusion equation that was used in the present paper to obtain the diffusion coefficient of NaCl in the membranes. The membranes were cast from acetone solution of 37.9% acetyl material on a mercury surface and allowed to air-dry. Long and Thompson observed that on desorption (and occasionally on sorption) the behavior was non-Fickian at long exposure times in such a way as to lead to smaller calculated diffusion coefficients. They report diffusion coefficients under conditions where the relative humidity in the chamber surrounding the membrane varied from 0 to approximately 34% and from 0 to approximately 66%. The equilibrium water sorptions were 3.4 and about 8%, respectively, in these two cases. The diffusion coefficients reported range from 3×10^{-8} to 4.5×10^{-8} cm.²/sec. and are stated to be obtained from the initial, Fickian stage of diffusion. For a cellulose acetate of a similar acetyl constant, a value of 1.4×10^{-6} cm.²/sec. was obtained at 100% R.H. in the present study.

Several other reports have been made of the water permeability of cellulose acetate membranes, but there are insufficient experimental data given to make a complete comparison with the work reported above. Thomas²³ has conducted sorption studies on a cellulose acetate membrane of unspecified acetyl content and obtained a diffusion coefficient of 1.6×10^{-8} cm.²/sec. at 30°C. Kovacs²⁴ has used the method of following the approach to steady state in the weight change of cellulose acetate membranes of unspecified acetyl content on both sorption and desorption. The calculated diffusion coefficients are concentration-dependent, and in a membrane approximately 80% saturated with water, the reported value is 9×10^{-7} cm.²/sec. at 18°C. Korte-Falinski²⁵ has used the cup method to obtain the permeability of a membrane stated to be cellulose diacetate. At 77% assuming Henry's law holds, one can calculate a diffusion coefficient of

5×10^{-7} cm.²/sec. at 30°C. Taylor, Hermann, and Kemp²⁶ also used the cup method and the steady-state solution to obtain the permeability of a cellulose acetate membrane of unspecified acetyl content and origin. At a relative humidity difference across the membrane of 96% humidity on one side and zero on the other, the permeability was 1.6×10^{-6} g./hr.-cm.-mm. Hg, which, assuming Henrian behavior, yields $D = 7 \times 10^{-8}$ cm.²/sec. Finally in the *Handbook of Plastics*,²⁷ some permeability data are given which were obtained in an unspecified manner. The results can be used to calculate a diffusion coefficient by assuming Henry's law, and the result is $D = 5 \times 10^{-8}$ cm.²/sec. for materials stated to be both "cellulose acetate" and "cellulose triacetate."

It is difficult indeed to rationalize these several experimental results. One possible reason for the discrepancies is a difference in membrane preparation procedure, but the Long and Thompson membranes, for example, were prepared from acetone solution as were those used here, and the relative insensitivity of our membranes to heat treatment suggests that treatment after casting is not a sufficiently important variable to explain the discrepancy.

A second possibility is that the difference is to be ascribed to the differences in the chemical activity of the water encountered in the two experiments. Thus, the present measurements were made near 100% relative humidity, while other investigators with whose work a complete comparison can be made generally worked below 70%. The high salt-concentration osmosis experiment reported earlier was made to check this possibility. The relative humidities of the 22.6 and 25.1 wt.-% NaCl brines used are 78 and 81%, respectively.¹⁷ This experiment yielded a diffusion coefficient for water in 39.8% acetyl membrane of 7.9×10^{-7} cm.²/sec., a value significantly lower than the 100% humidity result, but still substantially larger than that obtained in the vapor-phase experiments.

There are several reports in the literature²⁸⁻³⁰ of discrepancies between permeabilities in polymer systems as determined in experiments carried out in the vapor phase as opposed to the liquid phase. In each case, the permeability to liquid was considerably greater than to the corresponding saturated vapor, in some cases by a factor of ten or more.²⁹ In the cellulose acetate-water system, the present experiments are the only ones known to have been carried out with liquid water, the rest having apparently been done with water vapor. Thus, while there is no satisfactory explanation for the discrepancy between liquid and vapor permeation behavior, there is a precedent for the effect; the discrepancy between the present results and those of previous workers may be a further manifestation of this effect.

The permeability of the membranes prepared by the "normal" procedure but with Mg(ClO₄)₂ and water added to the casting solution is only about a factor of two higher than that reported for the normal membranes, and the salt transmissions are similar; this despite the fact that electron microscopic examination of these films showed a porous structure similar in appearance to the substructure of the modified membranes.¹² Apparently,

the pores formed under these conditions are closed, so that their only importance is to increase the measured thickness of a membrane containing a given amount of cellulose acetate, and hence to increase its apparent permeability.

The permeability of the modified membrane, however, is obviously very much higher than would be expected for a normal membrane of the same gross thickness. Assuming, instead, that the permeability of its surface layer is just equal to that of a 39.8% acetyl normal film, and that the flow resistance of the porous substrate is negligible, we can calculate a film thickness of 0.15μ for the modified membrane used in the osmosis experiments. This value is in reasonable agreement with the "skin" thickness of $\sim 0.25 \mu$ observed in the electron microscopic work. The results of this osmosis experiment, when inserted in eq. (12), yield $A = 1.2 \times 10^{-5} \text{ g./cm.}^2\text{-sec.-atm.}$ for the membrane constant. This is in excellent agreement with the values obtained in the reverse osmosis experiments.

It has already been pointed out that the membrane constant A decreases somewhat at high pressures. This change in properties is believed to be due to compression of the porous substructure of the membrane during loading. A permanent compression of the membrane is known to occur during operation in the reverse osmosis cells, a membrane being only 80% of its initial thickness after use at 100 atm. This compression could lead to the development of a significant pressure drop due to viscous flow through the porous portion of the membrane, or could actually close some of the pores, thus increasing the effective membrane thickness.

Salt Permeation

As Clark³¹ has recently pointed out, if the salt flux through an osmotic membrane is viewed as diffusive, the driving force is almost entirely due to the salt concentration difference, since the chemical potential differences due to the pressures used are always negligible compared with those due to the concentration differences under conditions like those encountered in the present work. We might expect, then, that the salt flux, J_2 , can be written simply as

$$J_2 = -D_2(dC_2/dx) \approx -D_2(\Delta C_2/\Delta x) \quad (13)$$

where D_2 and C_2 are the diffusion coefficient for and concentration of salt in the membrane, and we have assumed D_2 to be independent of C_2 . The salt concentration in the membrane is determined by the salt concentration ρ_2 of the external phase, and if we assume that the distribution coefficient K for salt between the membrane and water is independent of concentration, then eq. (13) becomes

$$J_2 = -D_2K\Delta\rho_2/\Delta x \quad (14)$$

The distribution coefficient data show that K is, in fact, a good constant in the range of interest for the 39.8% acetyl membranes. Thomas and Barker³² have recently reported some data on the sorption of several salts

in 40% acetyl cellulose acetate. Films of 267 μ thickness were immersed in 0.1M solutions of a number of salts, including NaCl, for 48 hr. and analyzed for sorbed chloride ion. The distribution coefficient obtained for NaCl expressed in the units used in the present paper was 0.031, which is slightly less than, but nevertheless in good agreement with, the value reported above. The small discrepancy is explainable on the basis of the 48-hr. immersion used by Thomas and Barker; by using the diffusion coefficient for this material given in Table III, it can be shown that after this immersion time the films were undersaturated by about 10%, which correction puts their results in excellent agreement with those reported above. They also found that the distribution coefficient for KCl was independent of concentration over the range 0.1–1.0M, in excellent agreement with the present data for NaCl.

It is apparent from Tables I and II that the apparent salt permeability, D_2K , of the membranes used in the osmosis experiments was quite variable. This variability is believed to have resulted either from salt leakage around the seals in the osmosis cell or from salt leakage through defects in the membranes. These effects are greatly magnified here, as compared to their effect on water flux, because of the very low salt permeability of the intact film. The choice of solvent may well have an effect on the apparent salt permeability because of the introduction of defects. The quality of the casting solutions obtained with the several solvents varied over a wide range as judged from the opacity and viscosity of the solutions, and it was qualitatively observed in the osmosis experiments that the apparent salt permeability was lower with the better solutions.

The salt sorption measurements made in this study largely circumvent the problem of film imperfection because the very small volume of holes needed to completely invalidate osmosis experiments will accommodate too little salt water to affect the sorption measurements.

The low permeability of the membranes to CaSO_4 suggested that their permeability to divalent ions might be a good measure of their degree of perfection. The results of Figure 4 appear to support this hypothesis, in that the observed Ca^{++} fluxes are quite different for two nominally identical membranes and depend nearly linearly on applied pressure, as would be expected for viscous flow through holes. The zero pressure intercepts on this picture represent diffusive leakage of Ca^{++} through these holes, while the failure of linearity at the highest pressures may represent sealing of some of the imperfections as the membrane is deformed.

The same pores which leak Ca^{++} , of course, should leak other solutes as well, so that the NaCl flux in a reverse osmosis experiment should be the sum of the diffusive flux through the membrane and the leakage through the holes. In Figure 3, we have indicated the diffusive flux calculated from the results of the immersion experiments and then have drawn in a "calculated" curve for each of the two membranes. These were calculated from the Ca^{++} data by multiplying by the relative concentration of Cl^- and Ca^{++} and then adding the diffusive flux. The agreement with experiment is by

no means perfect, but it does appear that the bulk of the Cl^- flux can be accounted for on this basis.

An important parameter of reverse osmosis membranes is their salt rejection S , as defined in eq. (2). Equations (12) and (14) allow us to develop a theoretical expression for S :

$$S = 1 - \frac{J_2}{\rho_2^i J_1} = 1 - \frac{D_2 K R T}{D_1 C_1 \bar{V}_1} \cdot \frac{\Delta \rho_2}{\rho_2^i} \cdot \frac{1}{(\Delta P - \Delta \pi)} \quad (15)$$

In Figure 2, the salt rejection curve calculated from the osmosis and salt-water immersion experiments for a 5 wt.-% NaCl solution is contrasted with experimental results. The calculated curve presumably represents a limiting performance for 39.8% acetyl cellulose acetate membranes.

CONCLUSIONS

The present work indicates that the permeation of water and sodium chloride through perfect cellulose acetate membranes can be accounted for on the basis of a simple, homogeneous-diffusion model. Real membranes, in general, appear to have some imperfections, which have little effect on water permeation but contribute significantly to salt permeation under the conditions studied.

Three groups have suggested rather specific models for cellulose acetate membranes in recent years. Reid and Breton¹ proposed a model in which water and ion transport is diffusive in nature and occurs in amorphous regions between crystalline portions of the membrane. Stress was laid on the transient occurrence, due to Brownian motion, of pores which permit ion transport in these regions, and on the similarity between the bound water structure in cellulose acetate and in ice.

The present observation that a homogeneous model fits the experimental data rather well does not disprove the idea that the membrane is inhomogeneous. It is quite possible that some regions of the membrane are less pervious than others for structural reasons, and that the measured permeabilities are some average over all the regions.

On the other hand, it is clear from treatments like Clark's³¹ and our data that Reid and Breton's hypothesis of Brownian motion, and restriction thereof at high pressure, is unnecessary to explain the rapid increase in selectivity which is observed with increasing applied pressures in reverse osmosis experiments. On the contrary, this result is directly predictable from the transport equations, and, in fact, the slight pressure dependence of NaCl permeability observed in this work was opposite to that suggested by Reid and Breton, i.e., the permeability increased with increasing pressure.

The present interpretation of the available data also casts some doubt on the usefulness of the structural analogy to ice, since the diffusion coefficients observed for water are nearer those of typical liquids than those of crystalline solids. Thus, the self-diffusion coefficient for water in the liquid state has been measured by Wang³³ as 2×10^{-5} cm.²/sec. at 25°C., while

the self-diffusion coefficient in ice is reported to be only 1×10^{-10} cm.²/sec. by Kuhn and Thurkauf,³⁴ and the present work indicates a diffusion coefficient of 1.4×10^{-6} to 5.7×10^{-6} cm.²/sec. for water in the cellulose acetates studied. Olander³⁵ has tabulated diffusivities for water in various organic liquids near room temperature and lists values as low as 2×10^{-6} cm.²/sec.

Sourirajan³⁶ made the quite different suggestion, similar to that of Loeb,¹⁴ that the water transport occurs through small holes in the membrane and is selective because of negative adsorption of salt on the membrane surface. A salt-free layer is thus produced adjacent to the membrane, and the selectivity of the membrane is determined by the relationship between the pore radii and the thickness of the salt-free layer. As has already been pointed out, the fact that the salt permeability is independent of salt concentration is to be expected in the case of a homogeneous membrane, but probably not in the case of a sieve. Sourirajan points out that the thickness of this salt-free layer is concentration dependent; hence, his model predicts a concentration-dependent salt permeability; indeed, he presents some data which support this contention. However, these data were obtained on commercial membranes which were made by a process quite different from the one described above. The data of Reid and Breton,² of Loeb and Sourirajan,³ and those obtained in the present study on films prepared as described do not show a dependence of salt permeability on concentration.

No claims will be made here for general applicability of the model presented, but for the specific case of cellulose acetate membranes prepared as described, the model seems consistent with the results and is recommended by its simplicity as a means of treating permeability data. More detailed models are necessary to explain quantitatively such features of the results as the dependence of water and salt permeability on the acetyl content of the materials.

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Résumé

On a mesuré les coefficients de diffusion et de distribution de l'eau et du chlorure de sodium dans des membranes osmotiques d'acétate de cellulose. On a trouvé que ces coefficients varient avec le degré d'acétylation de l'ester de cellulose. Le coefficient de diffusion de l'eau varie depuis 5.7×10^{-6} cm²/sec et le coefficient de diffusion du sel varie entre 2.9×10^{-8} et 3.9×10^{-11} lorsque la teneur en groupement acétylé augmente de 33.6 à 43.2% en poids. On propose un modèle de diffusion homogène qui décrit les observations suivant la loi de Fick.

Zusammenfassung

Diffusions- und Verteilungskoeffizienten wurden für Wasser und Natriumchlorid in osmotischen Zelluloseacetatmembranen gemessen. Diese Koeffizienten zeigten eine Abhängigkeit vom Acetylierungsgrad des Zelluloseesters. Der Diffusionskoeffizient von Wasser ändert sich mit einer Zunahme des Acetylgehalts von 33,6 auf 43,2 Gewichts-% von $5,7 \times 10^{-6}$ auf $1,3 \times 10^{-8}$ cm²/sec und der Diffusionskoeffizient des Salzes von $2,9 \times 10^{-8}$ auf $3,9 \times 10^{-11}$. Ein homogenes Diffusionsmodell wird angegeben, welches die Beobachtungen anhand des Fick-Gesetzes beschreibt.

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