Permeation of Water and Sodium Chloride Through Cellulose Acetate

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Synopsis

The factors contributing to the selective permeation of water and sodium chloride through cellulose acetate membranes have been examined by the use of radioactive tracers. With decreasing acetyl content both the partition coefficient (solubility) and diffusion coefficient of water increased, the latter the more sharply. The effect was even more pronounced for salt, indicating that increasing selectivity with acetyl content stems mainly from increasingly preferential restrictions on salt mobility. Trends identical with those mentioned for decreasing acetyl content were found for increasing amounts of cellulose acetate solvents that had been extracted with water to yield more highly swollen membranes. A free-volume treatment for diffusion of small molecules below the glass transition temperature with the aid of subgroup motion in the polymer is used for both components. The water content of the membrane at (or near) saturation emerged as the predominant factor in the permeation behavior. In view of the similarity in the activation energies of water and salt diffusion the far steeper dependence of the salt diffusion coefficient on water content could not be accounted for by size differences between the diffusing species and has been attributed to confinement of salt ions to locations at which multiple water contacts are feasible.

INTRODUCTION

Whereas early work on diffusion in cellulose acetate was concerned mostly with vapor sorption and permeation, more recent interest has been concentrated on permeation from liquid mixtures. The osmotic flow of solvent to the concentrated side of a membrane placed between two solutions of unequal concentration can be reversed by application to the concentrated solution of a hydrostatic pressure exceeding the difference in osmotic pressure. Differences in permeability, such as those between water and dissolved salts, through a number of polymeric materials, notably cellulose acetates, result in partial separation of the solution components. The major objective of the present work was to examine the factors governing such selective permeation by more readily interpretable radioactive tracer methods, with emphasis on features of polymer composition and structure contributing to selectivity. It was assumed at the outset that both tracer and pressure-induced transport occur by simple diffusion through mobile free volume. Good evidence in support of simi-

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larity in the underlying processes is obtained by a comparison of reverse osmosis data reported in the literature[1-3] and obtained here[4] with the tracer results.

EXPERIMENTAL

Membranes

All the cellulose acetate powders were obtained from the Eastman Chemical Company. They were dissolved in a Waring Blendor, passed through a medium-fritted filter, and cast onto glass plates. The solvents used were 2-methoxyethanol for acetyl contents below 30% and dioxane for those above. Cellulose triacetate membranes with nonvolatile solvent additives were cast from dichloromethane. The membrane (38.4% acetyl) used for the study of temperature dependence was cast from acetone. After being cast the membranes were allowed to air dry for 1 hr. and then were immersed in water. The membranes cast from dioxane were dried as indicated later in the text. A preliminary study of reproducibility showed permeabilities different by a factor of about 2 for different castings of similar membranes, of less than 5% for membranes from the same casting, and of less than ±0.5% for repeated permeability measurements on the same membrane. The experiments regarded as most important were carried out on more than one series of membranes. The later results (most of those reported) did appear to show substantially better reproducibility, for unknown reasons, but this has remained the least satisfactory aspect of the work, severely limiting the definition of the conclusions, as will be evident from the discussion.

Membranes used for the measurement of temperature dependence were heated in water for 1 hr. at 90°C. to effect any changes that might otherwise have occurred during the permeation experiment. Such treatment was found to reduce the permeability.

The thickness of the wet membranes was determined after the permeation experiment with a dial gage graduated in units of 10^{-4} in. The values reported are averages of ten measurements taken at different points in a systematic pattern.

Permeation Cell

A major effort was spent on optimization of cell design for the purpose at hand. The drawing (Fig. 1) indicates most of the features. The two sections of the Lucite cell were held together with four bolts. The recessed cavities in the upper part of both chambers provided an air space above the liquid level, to ensure good liquid movement across the membrane area (57 cm.²). Liquid volume was usually about 125 ml., making the water aliquot negligible while not allowing excessive dilution of the tracer. In all experiments the liquid volume was sufficient to cover the whole membrane area.
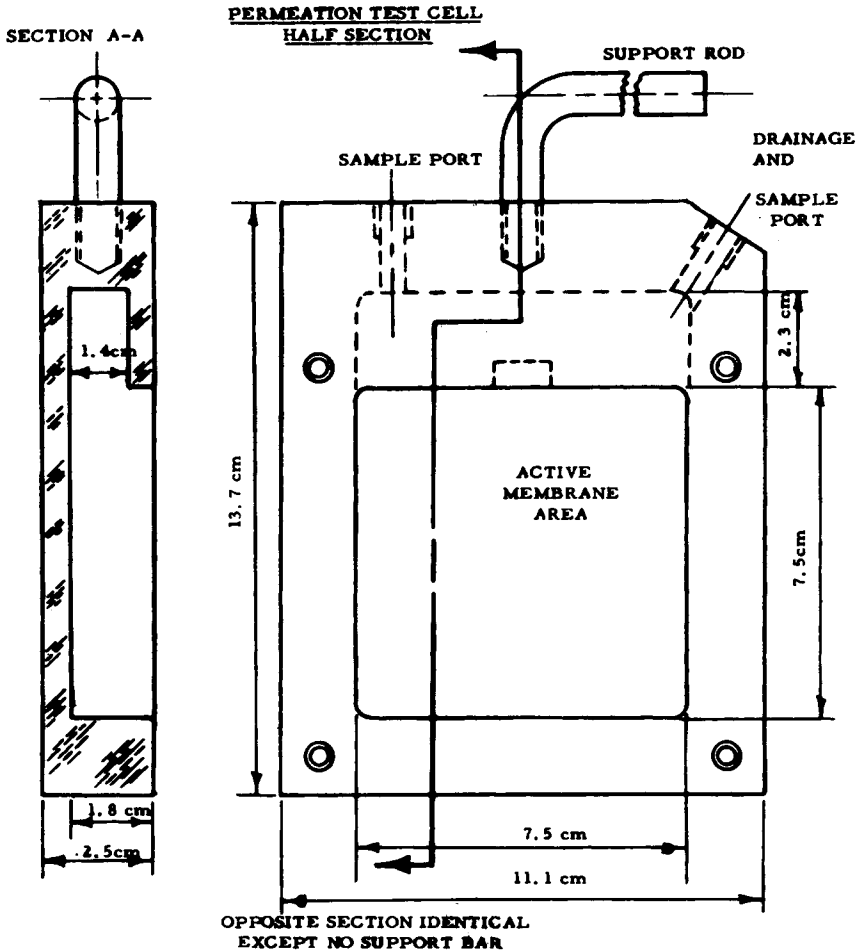
PERMEATION TEST CELL
HALF SECTION

SECTION A-A

SUPPORT ROD

SAMPLE PORT

DRAINAGE
AND

SAMPLE
PORT

2.3 cm

1.4cm

13.7 cm

ACTIVE
MEMBRANE
AREA

7.5cm

1.8 cm

2.5cm

7.5 cm

11.1 cm

OPPOSITE SECTION IDENTICAL
EXCEPT NO SUPPORT BAR

Fig. 1. Permeation test cell half-section.

Measurement of Permeation Rates

The membranes were clamped between the two halves of the cells in such a way that the outer parts of the gaskets were in contact with one another. Coating the vulcanized neoprene gaskets with unvulcanized neoprene from benzene solution eliminated small leakages to the bath. The cells were immersed in an Aminco (Model 4-8615) constant-temperature ($\pm 0.03°$C.) bath provided with an overhead rod to which the cell arm was connected. Rotary oscillation of the rod by an eccentric drive provided agitation that could be varied in amplitude by changes in effective length of the cell arm or in the eccentricity of the drive and varied in frequency by changes in motor speed. The agitator settings used were determined by preliminary experiments in a range in which the fastest membranes showed no effect of agitation on permeation rate. The area of the

central gasket cut-off, which could not be less than that of the compressing cell wall, defined the effective membrane area.   After assembly the membrane was tested for leaks with Sky Blue 6B, a direct (cellulose) dye, and equilibrated overnight in the shaking bath with the solution to be used. Agitation was started immediately after tracer introduction; after 30 sec. a sample from the spiked side was withdrawn for counting (N^*).   The steady-state permeation rate J was determined from the variation with time t of the count N of samples from the unspiked side by

$$J = (V_d C \text{v}^*/A N^*)(\Delta(N/\text{v})/\Delta t)$$

where C is the total concentration (water or salt) in moles per cubic centimeter, A the membrane area, V_d the volume of the unspiked solution, and v the volume of the aliquot with N counts per minute; the asterisk denotes the corresponding quantities for the initial measurement on the spiked side.   Measurements were confined to times short enough to enable neglect of back-permeation of tracer, as indicated by the absence of downward curvature in plots of N versus t.   Water (THO) was counted on a Packard Tri-Carb Liquid scintillation spectrometer (Model 4322) with a 0.2 ml. aliquot.   Salt (^{22}NaCl) was measured on a Nuclear Chicago 181A counter with 5 ml. aliquots, which were returned to the cell immediately.

Where possible, a direct measurement of the diffusion coefficient D_τ was obtained from the time lag τ in approach to the steady state.[5]

$$D_\tau = L^2/6\tau \tag{1}$$

where L is the membrane thickness.   Unless specified otherwise, all measurements were at 25.0°C.

Equilibrium Concentration Measurements

Equilibrium concentrations of water were determined at the end of the permeation experiments by blotting sections of the membrane between towels, weighing in tared containers, and then drying to constant weight. Preliminary experiments indicated that even for the most permeable membrane there was no measurable effect of the number of 2-sec. blottings between a total of 4 and 16 sec.   The blotting time was fixed at 10 sec. Salt concentration in the membrane was obtained by elementary analysis for Na.

RESULTS AND DISCUSSION

The same basic treatment is applied to the permeation of both water and salt.   According to Fick's law, the flux J at any point x along the direction of permeation is

$$J = -D\partial C/\partial x \tag{2}$$

The diffusion coefficient D should be constant in any given experiment, if the properties of the membrane do not change along x.   Isotope effects,

hence concentration dependence, are highly unlikely here, and time effects should have been avoided by the (chemical) equilibration before the beginning of the permeation experiment.

For either component, water or salt, C may be regarded as the concentration of the labeled portion; e.g., for water it is the concentration at x of the (H_2O + THO) which had been in the labeled solution immediately after the tracer was introduced. This arbitrary definition of a species unrecognizable by chemical methods greatly facilitates the discussion.

Since the experiments are confined to times short enough to enable neglect of the concentration on the unlabeled side, the steady-state flux through a film of thickness L is then given by

$$J = (D/L)C_m \qquad (3)$$

Strictly, C_m represents the concentration (of labeled species) just inside the membrane at its interface with the labeled solution. That interfacial layer may be regarded as at equilibrium with the solution, if diffusion in the membrane is much slower than other steps. Agitation was provided to contribute to that end. C_m is then equivalent to the total concentration of the component in the film and can be measured by conventional chemical methods at the end of the permeation rate measurements, which yield J. With a separate measurement of L this leads to a determination of the diffusion coefficient. When the time lag for approaching steady state is large enough, especially with thick membranes, the steady-state diffusion coefficient may be compared with D_r independently established from the intercept τ of the linear steady-state permeation rate plot on the time axis.[5] In general, the steady-state values appeared to be more consistent and somewhat higher.

Since C_m depends on the salt concentration in solution, it is convenient to define a distribution coefficient

$$K = C_m/a_s \qquad (4)$$

related to the distribution constant $K_N = a_m/a_s$ by $K = K_N/\gamma_m$, where a_s and a_m are the activities in solution and membrane, respectively, and γ_m is the activity coefficient in the membrane. In the case of NaCl it appears[2,4] that K is constant. With a proper choice of standard state it becomes numerically equivalent to K_N. For water K should be very close to its solubility in the membrane, if the salt concentration is not high (e.g., at $0.5m$ at which most of this work was carried out) and with pure water as the standard state. If γ_m is independent of concentration or if salt concentration is zero, then K is equivalent to the solubility. Substituting eq. (4) in eq. (3) gives

$$J = DKa_s/L \qquad (5)$$

Here K characterizes the membrane (almost) independently of solution concentration. The product $P = KD$ is closely related to Barrer's permeability coefficient.[5]

Effect of Acetyl Content on Permeation

Most of the cellulose acetate available is obtained[6] by partial deacetyla-
tion of the triacetate (44.8% acetyl) to an acetyl content varying down to
about 38%. The effect of progressive deacetylation on permeation be-
havior is summarized in Table I. The permeability of water and salt both
increase with ϕ_{OH}, the weight fraction of hydroxyl groups in the polymer
(Figs. 2 and 3). As shown more clearly in Figure 4, the permeation se-
lectivity ($S_p = 18(P_w/P_s)$) between water and salt increases sharply with
increasing acetyl content (the factor of 18 compensates for the different
standard state for water in solution). The selectivity S_p does not suffer
from strong dependence on concentration and pressure and the insensitivity
at high selectivity, as does the per cent salt rejection usually used as a
measure of selectivity.[4] It is a measure of the preference with which a
membrane allows a water molecule at the interface to pass through it by
comparison to salt. Selectivity of partition and diffusion can be defined
by analogy, but the plots are omitted for the sake of brevity.

Figure 5 shows a continuous decrease in K_w with increasing acetyl
content. The diffusion coefficient D_w decreases more steeply (Fig. 6).
The decrease in water permeability is, then, due more to increased con-
straint on motion than to a lowering of the affinity of water for the polymer.
All these statements also apply to salt (Figs. 3 and 7), but the effects are
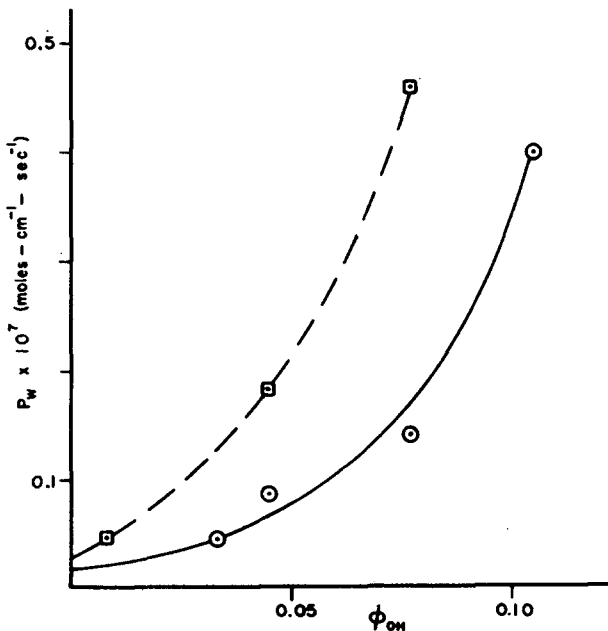

Fig. 2. Dependence of permeation coefficient of water on acetyl content; ϕ_{OH} is
hydroxyl weight fraction: (□) membrane dried 2 days; (○) membranes dried 7 days.

TABLE I
Effect of Acetyl Content on Permeation

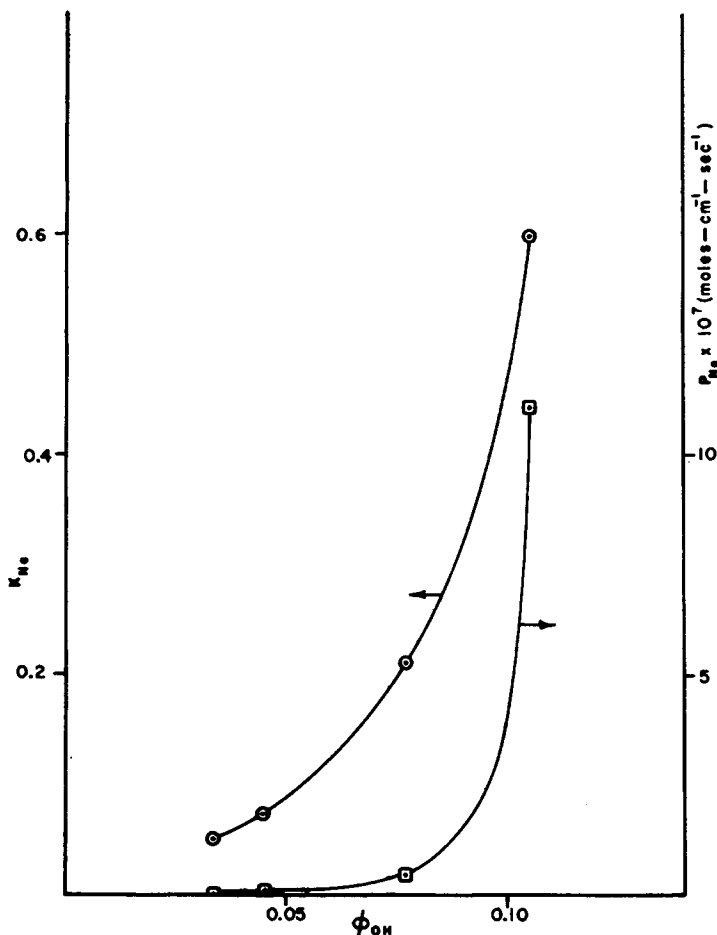| Membrane no.	Acetyl, %	[NaCl], molal	L, cm.	J, moles cm.$^{-2}$ sec.$^{-1}$		$\tau_s \times 10^3$, sec.	C, moles/g. dry membrane	
				$J_w \times 10^7$	$J_{Na} \times 10^{10}$		$C_w \times 10^2$	$C_{Na} \times 10^4$
1	33.8	0.5	0.0523	8.63	4.0	—	2.15	1.13
2	38.4	0.5	0.0449	4.01	—	—	1.60	0.695
3	43.6 (CTA)	0.5	0.0303	1.46	—	—	0.80	0.434
4	29.9	0.5	0.0122	32.3	31	—	2.45	2.04
5	33.8	4.0	0.0495	2.47	3.1	8.9	1.39	6.69
6	38.4	4.0	0.0614	1.21	0.40	45	1.19	2.31
7	40.0	4.0	0.0627	0.62	0.083	180	0.86	1.65

Fig. 3. Variation of permeation and partition coefficients of salt with acetyl content.

sharper in all cases; i.e., the increase in selectivity derives to a greater extent from increasing differences in mobility than from those in affinity.

Several factors could play a part in the increase in permeability with increasing deacetylation. Cellulose triacetate can be obtained with sufficiently pronounced crystallinity to yield a sharp x-ray diffraction pattern. It has been reported repeatedly,[7,8] though not invariably,[9] that penetrants such as water may be excluded from the regions responsible for the sharp lines. Partially deacetylated polymers have greatly reduced crystallization tendencies. This corresponds to the generally lower regularity of structure of copolymers. Even when the homopolymer does not appear crystalline, copolymers generally can be dissolved and swollen more readily. In the present case the most important factor should be the hydrophilic nature of the OH groups on the units that serve as comonomers, which will contribute greatly to the swelling tendency by water. The
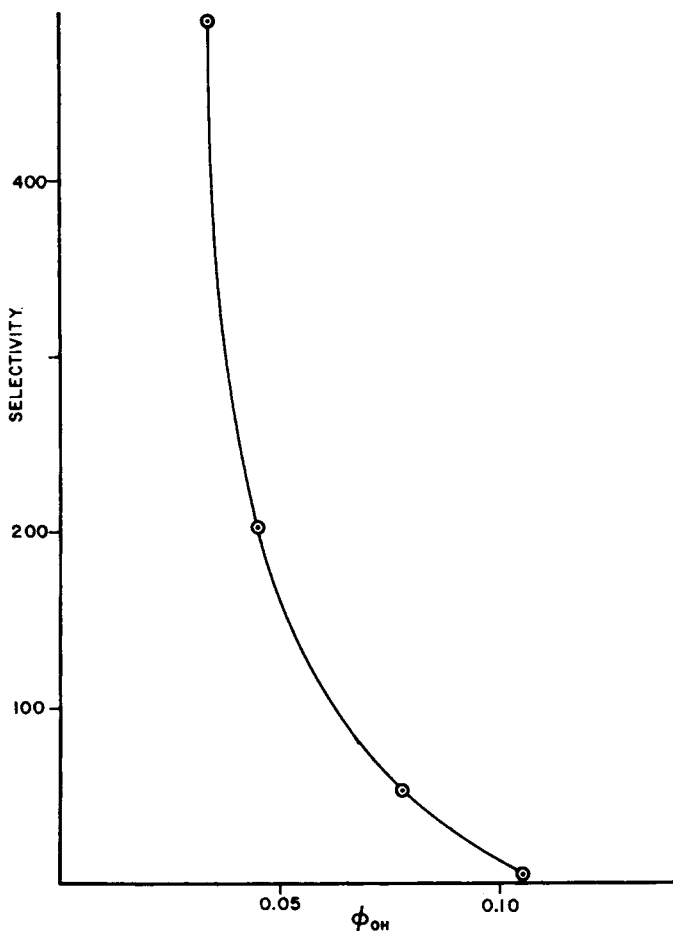
Fig. 4. Variation of permeation selectivity $P_{Na}/18P_w$ between salt and water with acetyl content.

common feature in these factors is that deacetylation results in an increase in K_w and hence in an increased equilibrium water content C_w from a given solution.

The uptake of salt would be affected by the same factors, but the predominant effect is likely to be an indirect one. If the dry membrane is regarded as an organic solvent, the wet membrane is a mixed organic–aqueous solvent, and the affinity of salt for that solvent will increase with water content. The variation of the diffusion coefficients of both water and salt can also be related to variations in water content, as discussed below.

It has been suggested[3] that the hydroxyl groups are essential for the selective diffusion of water by serving as sites to which water can attach by hydrogen bonds. The water moves by exchanging one site for an ad-
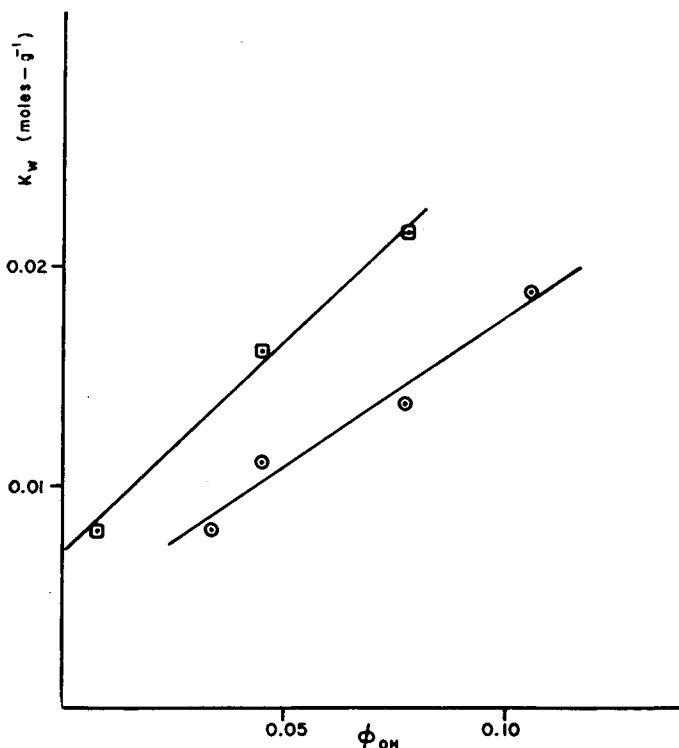
Fig. 5. Variation of partition coefficient of water with acetyl content.

jacent one. A treatment of diffusion, in which the penetrant is confined to a limited number of such specific sites,[10] shows that a plot of D versus site content should extrapolate to the origin. That is not confirmed by the plots of D versus ϕ_{OH} (Fig. 6).

Where comparable data are available from reverse-osmosis experiments,[2,3] the trends with varying acetyl content agree with those reported here. This may be regarded as evidence of similarity in mechanisms underlying pressure-induced and tracer permeation. The absolute magnitude of the permeabilities in the work of Lonsdale and his co-workers[2] are somewhat higher. As shown elsewhere,[4] this can be understood on the basis of "chemical" concentration gradients[11] in reverse-osmosis experiments.

Effect of Extracted Solvents

When a membrane containing a water-soluble solvent for the polymer is placed in excess water until the solvent is removed, the resulting membrane contains more water than a solvent-free one similarly immersed (Fig. 8). The excess water is lost irreversibly on drying, but as long as the membranes are kept wet, they appear sufficiently stable to allow a valid study of their permeation properties. Dimethyl sulfoxide (DMSO), for which systematic results are reported here, has a vapor pressure suffi-
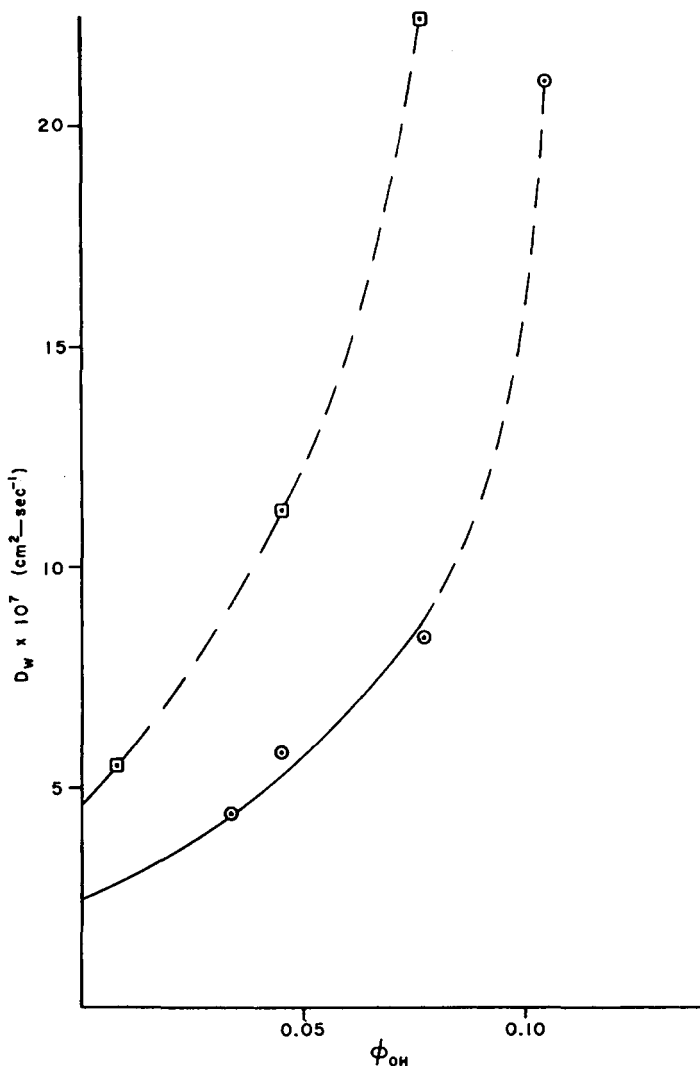
Fig. 6. Variation of diffusion coefficient of water with acetyl content.

ciently lower than dichloromethane to allow casting from a solution of the latter and evaporating it while the DMSO is retained. Cellulose triacetate (CTA), which was used throughout, is soluble in DMSO, which in turn is soluble in water. The permeation results are reported in Table II.

As seen from Figures 8 and 9, in comparison with Figures 2–7, all trends discussed for increasing ϕ_{OH} hold also for increasing (extracted) DMSO at constant acetyl content. They can again be attributed to the differences in water content.

The incremental water may be distributed fairly evenly between all polymer molecules,[12] or it may prefer to segregate in certain regions. The

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TABLE II

Effect of DMSO Content (Extracted) on Permeation Properties

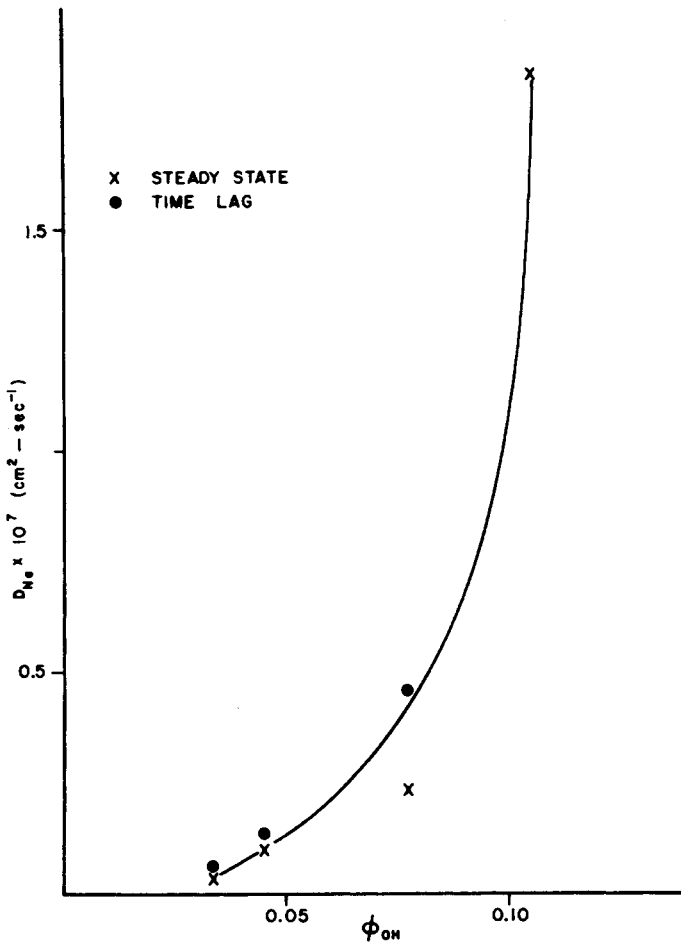| Membrane no.	DMSO, g./g. dry polymer	[NaCl], molal	L, cm.	J, moles cm.$^{-2}$ sec.$^{-1}$		C, moles/g. dry membrane	
				$J_w \times 10^7$	$J_{Na} \times 10^{10}$	$C_w \times 10^2$	$C_{Na} \times 10^4$
8	0.1	0.5	0.0168	1.25	—	1.06	0.044
9	0.2	0.5	0.0197	3.67	0.006	1.40	0.40
10	0.4	0.5	0.0145	4.81	0.10	1.74	0.48
11	0.8	0.5	0.0220	16.2	16	2.07	1.0
12	1.2	0.5	0.0239	36.8	160	3.48	2.9
13	0	0	0.0175	0.994	—	0.739	—
14	0.4	0	0.0198	1.42	—	0.831	—
15	0.6	0	0.0214	2.41	—	1.10	—
16	0.8	0	0.0259	31.9	—	2.15	—
17	1.0	0	0.0229	20.7	—	2.48	—
18	1.2	0	0.0255	22.8	—	3.18	—
19	1.6	0	0.0312	45.6	—	4.59	—

Fig. 7. Variation of diffusion coefficient of salt with acetyl content.

latter is more likely in the highly swollen membranes. With increasing (extracted) DMSO the ability of the membranes to separate water and salt decreases; however, membranes of this type might be effective in the dialysis of polymer solutions.

Membranes with heterogeneities along the direction of permeation can have a thin layer that will effect the separation (which evidently is independent of thickness) and the rest as a highly swollen gel. Membranes exceeding in permeation rate any of those reported here but having high selectivity to aqueous salt solutions have been made[13] and shown to exhibit such heterogeneity.[14] They are prepared from a secondary cellulose acetate with an amount of solvent substantially higher than those reported herein and immersed in water after a brief drying. During the drying (acetone) solvent can evaporate from the surface to form a less permeable skin. After immersion a rate of entrance of water faster than
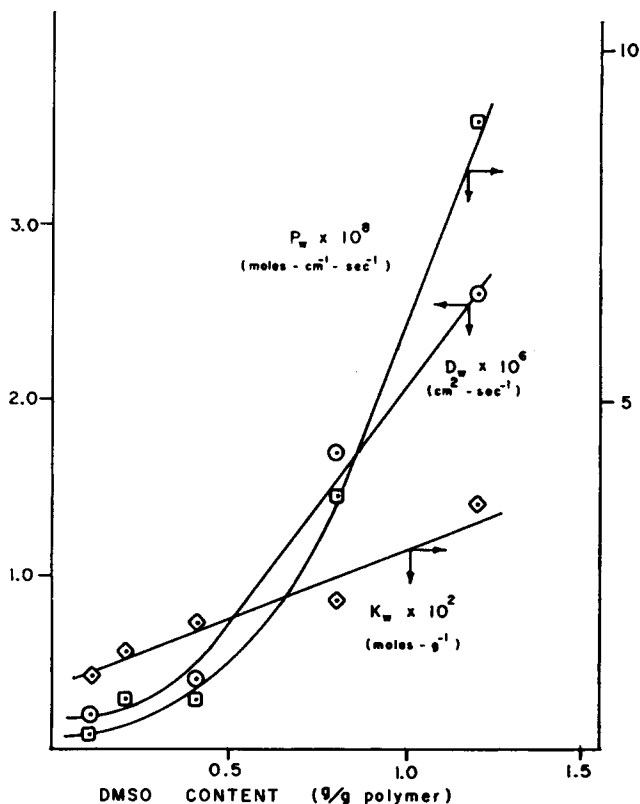
Fig. 8. Effect of DMSO content (extracted) on permeation properties of water.

that of removal of acetone should eventually result in a nonsolvent mixture and hence in gelation with high liquid content.   In this laboratory such a high-flux, but reasonably selective, heterogeneous membrane was obtained by casting a membrane of low acetyl content (29.9%) directly from a 1:1 acetone–water mixed solvent.   After evaporation of some of the more volatile acetone the casting became turbid.   The final membrane had a thick, white part on the side near the glass and a very thin, shiny layer at the air interface.   Most of our discussion should apply to the selective portion of such membranes.   The other part may be approximated by the membranes represented by the points at the extreme right of Figures 2 to 9, in which turbidity was also observed.

The water permeability was also examined on a longer series with varying DMSO content, to relate to a simultaneous study of nuclear magnetic relaxation.   The results are similar but less scattered than those shown in Figure 9.   In addition, a number of membranes were prepared with an equal amount of different water-soluble CTA solvents, with the results shown in Table III.   Plots of permeation properties versus

TABLE III
Effect of Nonvolatile Solvents (Extracted) on Permeation Properties

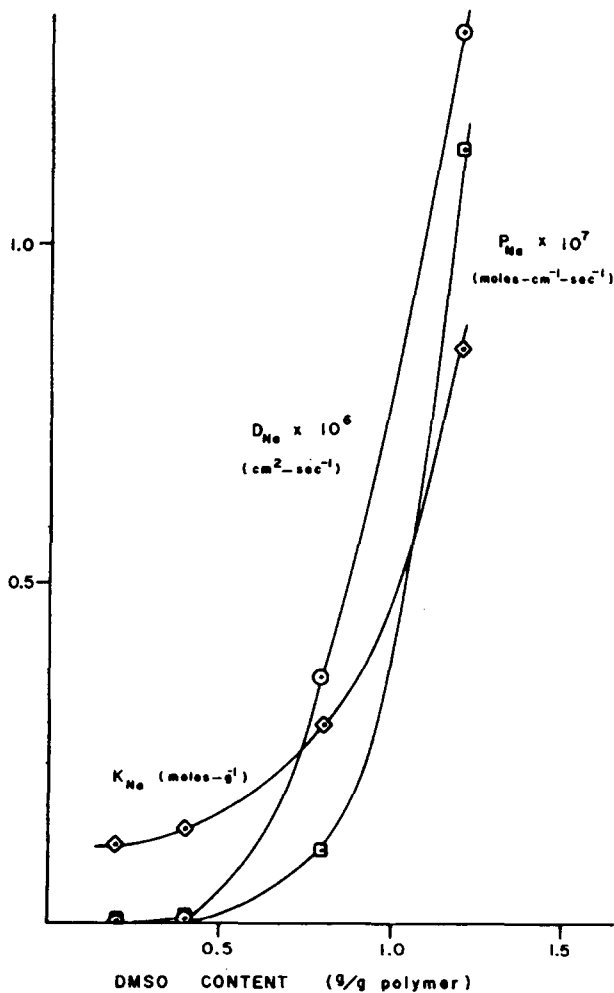| Mem-brane no.	Solvent (29%)	[NaCl], molal	L, cm.	$J_w \times 10^7$, moles cm.$^{-2}$ sec.$^{-1}$	$\tau_w \times 10^{-3}$, sec.	$C_w \times 10^2$, moles/ g. dry membrane
20	None	0	0.0745	0.411	6.6	0.81
21	Sulfolane	0	0.106	0.380	1.3	0.89
22	DMSO	0	0.0932	1.44	3.2	1.51
23	Ethylene carbonate	0	0.0910	0.766	5.1	1.21

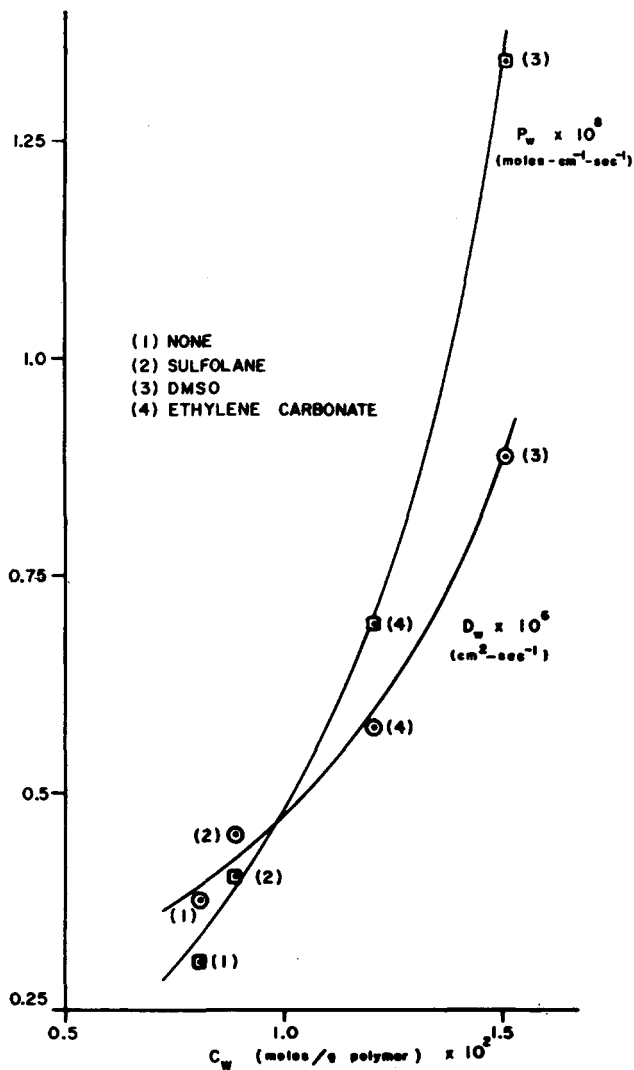Fig. 9. Effect of DMSO content (extracted) on permeation properties of salt.

Fig. 10. Effect of nonvolatile solvents (extracted) on permeation properties.

water content C_w (Fig. 10) give reasonably smooth curves of the general shape of Figures 2–9.

For characterizing the effect of water content and isolating intrinsic effects of varying polymer compositions and structure, a free-volume treatment of motion in polymers was used.

Diffusion of Foreign Species and Free Volume

The rubbery behavior of polymers above their glass transition temperature T_g, reflecting motion of large segments of the polymer molecule, is attributed[15-17] to the presence of large units of unoccupied volume. If a hole of adequate size is located next to a segment, the latter can jump

into it by cooperative rotation about single bonds. The free volume thus moves around at random by the consecutive jumps of different segments. Foreign molecules smaller than the largest free-volume units can evidently move by similar jumps. Such guest molecules will also contribute additional free volume[18-20] especially if they are small and flexible.[21] The incremental free volume usually results in a pronounced concentration dependence of the diffusion coefficient.[20,22]

The predominant evidence indicates that at room temperature cellulose acetate polymers are below their glass–rubber transition temperature even after swelling by (moderate amounts of) diluents. While the segmental motion outlined has been applied to diffusion of small gas molecules below T_g, this hardly appears justified when the required motion ceases as the temperature is lowered below T_g. For a case of guest molecules of a size comparable to such a segment, it has indeed been shown that the rate of diffusion becomes negligible in the vicinity of T_g.[23] It does not follow, however, that all motion in the polymer molecule ceases, as evidenced by the mechanical toughness of many glassy polymers. The mobility of the relatively small groups involved here may in turn disappear at one or more subtransitions. This has recently been reviewed in detail.[24] It now appears that the free volume left at T_g is not a uniform 1/40 for all polymers[16] but is substantially higher and somewhat variable. A value of 0.12 cited[35] for cellulose acetate is close to that expected from Simha and Boyer's treatment.[26]

The free volume present below T_g does not accumulate to the point at which rubberlike motion or diffusion of relatively large guest molecules is feasible, but there is no *a priori* reason why it cannot govern diffusion of small enough molecules or ions, as long as the free volume is sufficiently mobile. This will require mobility of small constituent groups of the polymer.

Observation of multiple transitions in cellulose acetates has indeed been reported.[27-29] Rotation of acetyl side groups has been suggested[30] as a possible source. Conformational changes in the glucoside rings may also deserve attention.

The most specific evidence of motion in the membranes under examination and its relation to permeation behavior was obtained from pulsed proton magnetic resonance experiments on membranes in which the H_2O had been replaced by D_2O. The proton relaxation times increased with increasing diffusion coefficient of water determined in parallel permeation experiments. The correlation times estimated for the polymer protons involved, e.g., on the acetyl side groups, indicate a mobility somewhat lower than, but of the same order of magnitude as, that of water. This work may be reported in detail at a later date.

Free Volume and Water Content

The relation of diffusion to free volume has been examined by a number of somewhat different methods.[17,31-33] Here use will be made of the de-

velopment of Fujita.[20]   To avoid the assumption of a fractional free volume f_0 at zero diluent content and constant temperature common to all membranes, one wet membrane will be used as a reference (r).   The tentative assumption is then made that differences in fractional free volume f of different membranes saturated with water (or nearly so) are proportional to the differences in volume fraction of water, v, the small amounts of salt being neglected:

$$f = f_r + \beta(v - v_r) \tag{6}$$

The implied assumption of negligible intrinsic effect of underlying polymer composition and structure can be attenuated, if indicated by the results, by treating β as a parameter and by the use of more than one reference membrane.   This should certainly be necessary for completely different classes of polymers (some change in structure quite generally results from sorption or even changes in temperature).   An additional assumption involved is that the functional form is the same below as above T_g, although the coefficient β may be different.   Following Fujita's treatment, the diffusion coefficient is given by

$$D = ART \exp \left\{ -B/f \right\} \tag{7}$$

where B is a measure of the size required for motion of the diffusing molecule, and A is the proportionality constant between its mobility and the probability of a hole of that size, obtained by generalization of Cohen and Turnbull's expression.[17]   We shall use a (non-existent) reference membrane with $f_r = 0$.   By combination of eqs. (6) and (7) one then obtains:

$$1/(\ln D - \ln D_r) = M + N/v \tag{8}$$

where $M = f_r/\beta$ and $N = f_r{}^2/\beta B$.   For D_r a value of 1.0×10^{-7} cm.^{2} sec.$^{-1}$ was tried.   The exact choice was somewhat arbitrary, since exact extrapolation from the plot of log D versus C was impossible.   Fujita[20] made a point of these difficulties even for data from a single membrane. The value used was a convenient compromise between what looked like a reasonable extrapolation and the value obtained by Long and Thompson[34] from vapor-sorption measurements at much lower v.   A choice closer to the latter data would have given somewhat better linearity.   A common value of 1.3 was used for the density ratio of polymer to water.

   The results are shown in Figure 11.   The points represent membranes from the different series described in earlier figures.   It should be pointed out that the nature of the function hides the scatter at low $1/v$ (one point at 3.3 for $1/v = 5.03$ has been omitted).   In general, the membranes from which a solvent was extracted tend to be somewhat above the line drawn, while those immersed without solvent are usually below.   The reasons for this are not clear.   It may reflect minor differences in homogeneity, possibly involving macroheterogeneities of the type discussed earlier and resulting from the different rates of diffusion of water into, and solvent out of, the membrane being extracted.   Most of the points are unexpect-
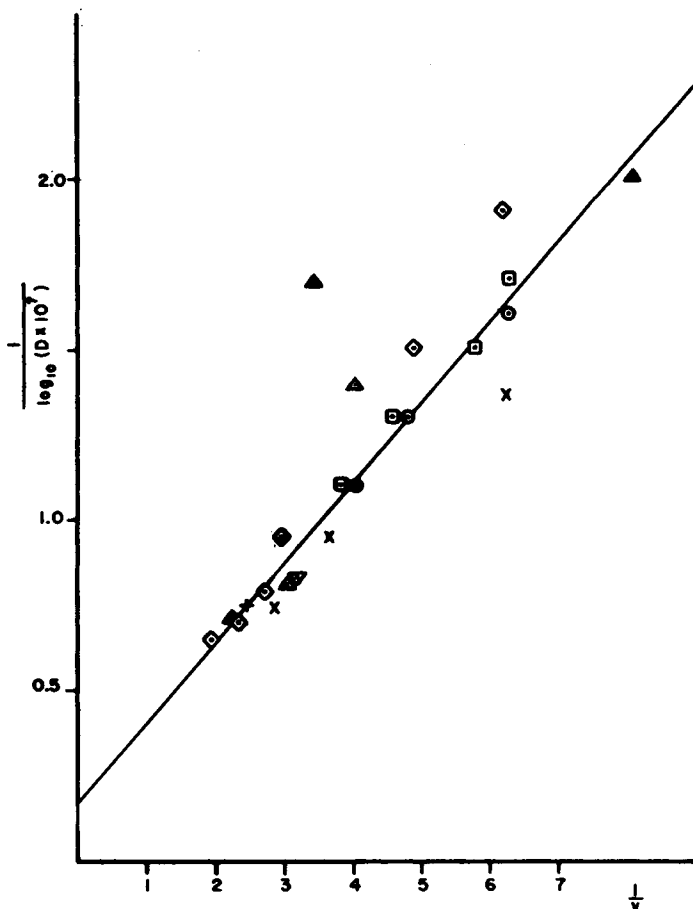
Fig. 11. Plot according to eq. (8): variation of shift factor on volume fraction of water.

edly close to the line, however. A membrane (without solvent) of 25.1% acetyl content, run in connection with a special experiment, fell exactly on the line. Regardless of the small systematic differences mentioned, the water content of the membrane is clearly the major factor governing diffusion. The line drawn extrapolates to a diffusion coefficient of 3×10^{-5} cm.^{2}/sec.$^{-1}$ for pure water at $1/v = 1$; the slope is 0.10, and the intercept gives a value of 0.08 for f_r/β.

The diffusion of salt is discussed after a description of the temperature dependence. In principle, it should also be governed by the free volume created (mainly) by the water in the membrane, but our data are inadequate for a systematic treatment. Any increase in free volume due to increases in salt content of the membranes, e.g., by variations in solution concentration, should be minor by comparison to the contribution of water. From what has been shown of the effect of deacetylation and solvents it is evident that the salt diffusion coefficients do increase with water content.

Moreover, the dependence is much stronger than for water itself. It appeared reasonable at first to attribute this to differences in the required free-volume accumulation B. Diffusion jumps of hydrated ions comparable to those in aqueous solution could well necessitate such larger hole size. In the early stages of the work it was even considered possible that transport of salt requires mobile free-volume units larger than provided below T_g and that this is the reason for the selectivity to salts of cellulose acetate membranes.

Temperature Dependence

Increases in temperature affect the diffusion coefficient mainly through changes in free volume f. If the differences in the dependence on water content of salt and water are due to differences in B, there should then be corresponding differences in the activation energies.

The membranes used for these measurements (38.4% acetyl content cast without nonvolatile solvents) were heat-set in water for 1 hr. at 90°C., in order to effect any physical changes, such as crystallization, that might otherwise take place during the experiment. At first one membrane was to be used over the whole temperature range, in order to eliminate scatter known to result from different samples, but preliminary experiments indicated the probability of an unacceptable amount of degradation. It was then decided to run the series in duplicate and to use each membrane at two different temperatures. After the second temperature the membrane was used for determination of the equilibrium concentration C_m. The same value of C_m was used for both rate experiments at that temperature. All membranes were from the same casting with a 10% solution in acetone.

The results are given in Table IV. The logarithmic plots of the diffusion coefficients against reciprocal temperature (Figs. 12 and 13) show no evidence of a sharp transition. Just above the glass transition temperature

TABLE IV
Temperature Dependence of Permeation Properties

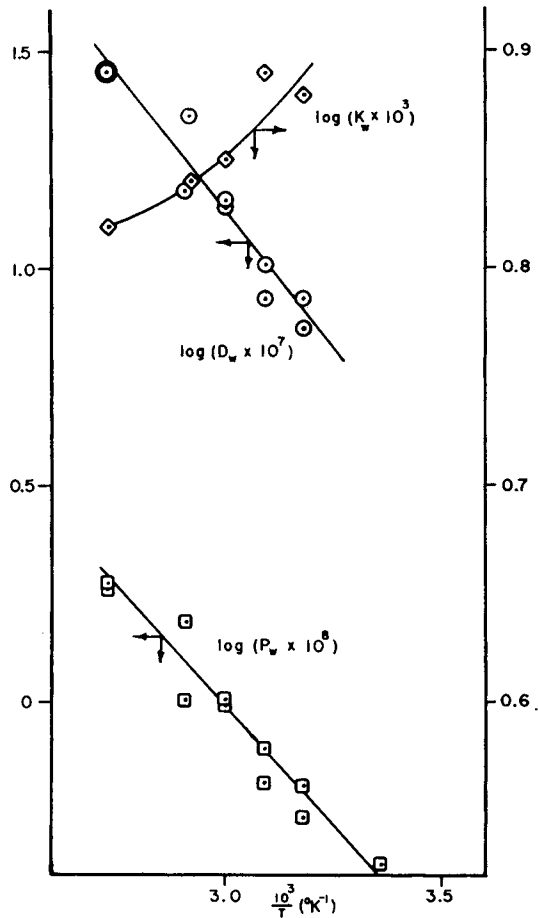| Temp., °C.	[NaCl], molal	L, cm.	J, moles cm.$^{-2}$ sec.$^{-1}$		C, moles/ g. dry number	
			$J_w \times 10^7$	$J_{Na} \times 10^{10}$	$C_w \times 10^2$	$C_{Na} \times 10^4$
24.5	0.5	0.0099	4.22	0.014	0.822	0.22
41	0.5	0.0099	5.38	0.012	0.767	0.19
	0.5	0.0099	6.38	0.022	—	—
50	0.5	0.0098	7.85	0.023	0.699	0.14
	0.5	0.0098	6.56	0.032	—	—
60	0.5	0.0099	10.1	0.032	0.680	0.14
	0.5	0.0099	10.0	0.035	—	—
70	0.5	0.0099	15.3	0.041	0.757	0.14
	0.5	0.0098	10.1	0.029	—	—
90	0.5	0.0098	18.7	0.055	0.651	0.11
	0.5	0.0099	18.5	0.057	—	—

Fig. 12. Temperature dependence of permeation properties of water.

the energies of activation of processes depending on free-volume units of the size of the segments released at T_g are very high[23,33] and then decrease toward a fairly constant value with increasing temperature. The experimental plots show no consistent curvature. This, and also the relatively low activation energies of diffusion, about 5.8 kcal. for water and 6.1 kcal. for salt, show that the polymer is either far above T_g, which is very unlikely, or below it and subject to subgroup motion. The high absolute values of the diffusion coefficients are in line with the latter argument. Cellulose triacetate membranes cast without extractable solvents may be a partial exception in this respect. In spite of major efforts and time spent we were unable to measure permeation of salt through it. If we assume that the equilibrium uptake can be extrapolated, the salt diffusion coefficient cannot be above a 10^{-11} cm.^{2} sec.$^{-1}$ order of magnitude, and it may well be lower.
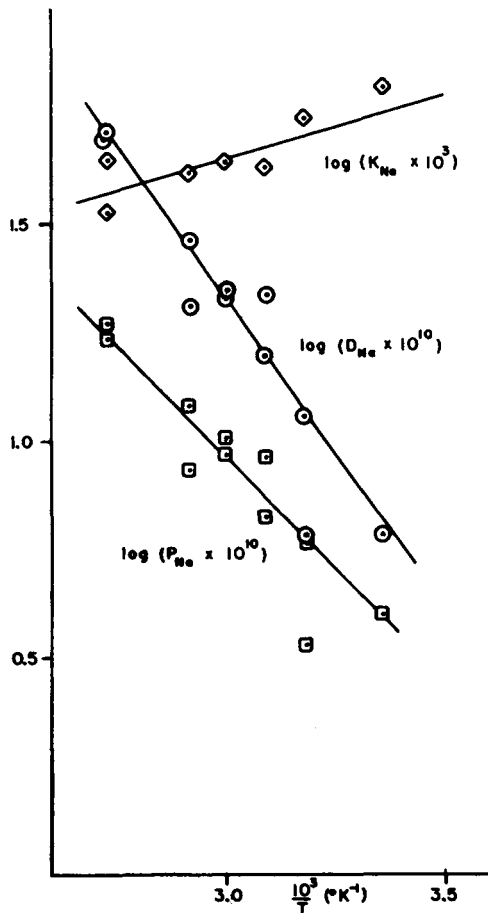
Fig. 13. Temperature dependence of permeation properties of salt.

The activation energy of salt diffusion was very similar to that of water, indicating that the differences in the dependence of the diffusion coefficients on water content are not due to differences in B. If the salt species moving were unhydrated ions, there would really be no major size difference by comparison to water, but this need not be postulated. Similar activation energies in systems in which major differences in size as well as in diffusuon coefficients are known to exist are readily accounted for by the similar size of the polymer unit that has to move away to create an adjacent hole, if no continuous guest channels exist. The NMR results cited earlier are in line with this.

From the slope of the K_w plot in Figure 12 a negative integral heat of solution of water is obtained, indicating more favorable interaction of water molecules with those of the membrane than interaction of respective like molecules.

Permeation Selectivity

The closeness of the activation energy of salt diffusion to that of water prevents assignment of the steeper dependence of its diffusion coefficient on water content to a difference in size B of free-volume unit required. It must be concluded that the pre-exponential factor A in eq. (7) is a function of water content. It is suggested that this arises from a necessity of accumulation of enough water contacts to serve as sites for solution of salt ions. It was shown earlier[10] that such confinement to limited sites leads to a proportionality of diffusion coefficient to site concentration at constant free volume. The variation of K_{Na} with water content (e.g., from deacetylation), steep but less than that of D_{Na}, conforms to this necessity for multiple contacts. It has, in fact, been suggested[3] that the salt needs regions of "unbound" water with which it can interact more readily. The requirement here can be understood less specifically, e.g., by an increase with water content of fluctuations in local dielectric constant. This should be facilitated by weaker interactions of incremental water.

The negative heat of solution of salt can hardly be construed as showing interaction of salt with the polymer more favorable than with water. It corresponds to the suggestion given above by showing indirectly the effect of temperature on water content.

The high selectivity of cellulose acetate membranes to the components of aqueous salt solutions can then be attributed to a number of features. They contain a large number of moderately hydrophilic groups, they are below T_g at the temperature of interest, and they allow for small group motion within their rigid framework. The latter provides a means of transport below T_g. A substantial amount of water uptake without accumulation is made possible by the many polar groups with which it can interact favorably. The absence of the relatively large holes formed in rubbery polymers should also work against accumulation of water that can act as sites for salt. It is possible that the location of polar groups on the mobile side chains further contributes[10] by preferential transport of water.

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Résumé

Les facteurs contribuant à la pénétration sélective d'eau et de chlorure de sodium au travers de membranes d'acétate de cellulose ont été examinés à l'aide de traceurs radioactifs. En diminuant la teneur en groupe acétyle, le coefficient de partition (la solubilité) et le coefficient de diffusion de l'eau croissent tous deux, le dernier plus fortement. L'effet est plus fortement prononcé pour le sel, ce qui indique qu'une sélectivité croissante en fonction du nombre de groupes acétyles, résulte principalement de restrictions préférentielles croissantes à la mobilité des sels. Des tendances identiques à celles mentionnées pour la décroissance de la teneur en groupe acétyle ont été trouvées par des quantités croissantes en solvant de l'acétate de cellulose qui ont été extraites avec de l'eau pour fournier des membranes plus fortement gonflées. Un traitement basé sur la notion de volume libre pour la diffusion des petites molécules en-dessous de la température de transition vitreuse à l'aide du mouvement des sous-groupes au sein du polymère est utilisé pour les deux composants. La teneur en eau de la membrane à la saturation ou au voisinage de celle-ci est apparemment le facteur principal du comportement à la perméation. Vue la similitude des énergies d'activation pour la diffusion de l'eau et du sel, la dépendance beaucoup plus forte des coefficients de diffusion du sel vis à vis de la teneur en eau ne peut pas être expliquée par des différences de tzille entre les espèces diffusantes; elle a été attribuée au confinement des ions salins à des endroits où de nombreux contacts avec l'eau sont possibles.

Zusammenfassung

Die zur selektiven Permeation von Wasser und Natriumchlorid durch Celluloseacetatmembranen beitragenden Faktoren wurden mittels radioaktiver Markierung untersucht. Mit abnehmendem Acetylgehalt stiegen Verteilungskoeffizient (Löslichkeit) und Diffusionskoeffizient von Wasser an, und zwar letzterer stärker. Der Effekt war bei Salz noch stärker ausgeprägt, was zeigt, dass die Zunahme der Selektivität mit dem Acetylgehalt hauptsächlich auf ein Anwachsen der präferentiellen Beschränkung der Salzbeweglichkeit zurückgeht. Ein mit demjenigen bei abnehmendem Acetylgehalt gefundenen identisches Verhalten wurde bei zunehmenden Mengen an Celluloseacetatlösungsmitteln angetroffen, welche zur Bildung höher gequollener Membrane mit Wasser extrahiert worden waren. Für beide Komponenten wird eine Behandlung mittels des freien Volumens für die Diffusion kleiner Moleküle unterhalb der Glasumwandlungstemperatur mit Hilfe der Subgruppenbewegung in Polymeren verwendet. Der Wassergehalt der Membrane bei (oder nahe bei) der Sättigung erwies sich als der wichtigste Faktor für das Permeationsverhalten. Im Hinblick auf die Ähnlichkeit der Aktivierungsenergie für Wasser- und Salzdiffusion konnte die weitaus steilere Abhängigkeit des Salz-Diffusionskoeffizienten vom Wassergehalt nicht den Grössenunterschieden zwischen den diffundierenden Spezies zugeschrieben werden; sie wurde auf die Beschränkung der Salzionen auf Stellen, wo multiple Wasserkontakte möglich sind, zurückgeführt.