Physical Characteristics of Osmotic Membranes of Organic Polymers*

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INTRODUCTION

The use of synthetic osmotic membranes for desalting saline waters was proposed by Reid[1] in 1953. This process involves reversal of osmotic flow from a solvent cell to a solution cell across a semipermeable membrane. Pressure more than sufficient to counterbalance the osmotic pressure of the solution applied to the solution cell will reverse the direction of flow. The feasibility of the process depends upon the discovery or the synthesis of a suitable semipermeable membrane. Such a membrane must: (a) be semipermeable with respect to an ionic solution; (b) resist chemical reaction with the solution; and (c) possess a physical structure which permits a reasonable rate of water diffusion.

Breton[2] investigated the semipermeability of films prepared from a variety of polymers and concluded that, among those tried, cellulose acetate film possessed the most desirable features as a semipermeable membrane for sodium chloride solutions: 96% of the ions were rejected from solutions ranging in concentration from $0.1M$ to $0.6M$. Nevertheless, cellulose acetate could not conceivably be used in an economic application of this process. The efficient flow rate was of the order of $25\mu l.$ l./hr. cm.^{2} for film one-half mil thick in contact with $0.1M$ sodium chloride under a pressure of 600 psi. Furthermore, the selectivity of the film failed after six to fourteen days. This failure was shown by Kuppers[3] to be associated with the hydrolysis of acetyl groups from polymer chains.

Although cellulose acetate was not suited to practical application of osmotic desalting of saline waters, it did offer a means of studying the mechanism by which water is selectively transported across such membranes. It was hoped that this mechanism could be elucidated to the extent that a more

practical membrane could be synthesized. Hence, Breton[2] initiated an investigation from which stemmed the following theory.

"Those ions and molecules that cannot enter into hydrogen bonding with the membrane are transferred by hole-type diffusion. The rate of diffusion appears to be governed by a water-cellulose acetate structure. The reaction between water and the cellulose acetate polymers to form bound water regions is induced by compressing the membrane. As pressure is applied on the membrane, more bound water is produced which causes the rate of hole-type diffusion to decrease."

"On the other hand, those ions and molecules that can associate with the membrane through hydrogen bonding actually combine with the membrane and are transported through it by alignment-type diffusion. The formation of the water-cellulose acetate structure does not appreciably diminish the diffusion rate of water through the membrane."

Hole-type diffusion was interpreted as a process with low activation energy wherein molecules migrated through free-volume between polymer chains with a diffusion coefficient differing little from the self-diffusion coefficient of the diffusing fluid. Alignment-type diffusion, on the other hand, was visualized as a process in which molecules migrated by discreet jumps from one hydrogen bonded site to another within a polymer-bound water system. The water was presumed to be incorporated in this structure in an icelike orientation. The activation energy for diffusion by the latter process would be high relative to hole-type diffusion.

This theory was supported by experimental work showing that: (*a*) salt rejection of cellulose acetate film was relatively poor at low pressures, increased rapidly in the interval of 150 to 250 psi, then approached 100% asymptotically with further increase in pressure; (*b*) the dielectric constant of moist film increased more rapidly under compres-

sion than that of dry film; (c) semipermeability was correlated, by means of electrical measurements, with resistance of these membranes to passage of ions incapable of forming hydrogen bonds, but not of ions which may participate in hydrogen bonding; and (d) transference numbers of sodium and chloride ions were such that semipermeability could not be attributed to an ion exchange reaction with the membrane, comparable to that described by McKelvey et al.[4]

The magnitude and sign of the activation entropy, according to the absolute reaction rate theory,[5] will depend upon the relative order associated with the reactant and the activated state. An increase in order in passing from the reactant state to the activated state will be indicated by negative activation entropy. If we now apply the absolute reaction rate theory to the diffusion of water across a cellulose acetate film, the liquid water on the side of the membrane maintained at the higher pressure will be the reactant, and the water-cellulose acetate structure will be the activated state. A simple hole-type diffusion, involving no disruption of the membrane, should have a positive activation entropy, since that for self-diffusion of water is positive.[5] On the other hand, alignment-type diffusion involving hydrogen bonding would imply a rather highly ordered activated state, and hence, a negative activation entropy. Therefore, if Breton's theory is essentially correct, it should be possible to observe a negative activation entropy for the diffusion of water through cellulose acetate films. Further-

more, a change in the mechanism of water transport across the membrane at higher pressures might be reflected in activation entropy values.

It is also reasonable to expect that water incorporated into the polymer structure would alter its mechanical properties in a manner dependent upon the nature of bonding forces involved.

The purpose, then, of this study was: (a) to determine diffusion coefficients and activation entropy values for the diffusion of various liquids and gases through cellulose acetate and other polymer films under high pressure differentials; (b) to study the compressive deformation and elastic properties of moist and dry cellulose acetate film; and (c) to interpret these findings in the light of Breton's theory regarding the mechanism of water and ion flow through cellulose acetate membranes.

EXPERIMENTAL

A. Diffusion Through Membranes

Apparatus

The essential elements of the diffusion apparatus (Fig. 1) were the film support of porous stainless steel inserted in Monel metal disks, the fluid reservoir tank, compressed nitrogen gas, and the flow meter (dilatometer) inserted in the effluent side of the film support. The film support and fluid reservoirs were immersed in a constant-temperature waterbath in which the temperature was controlled to within 0.05°K. Bypass metering accessories are shown to the left.
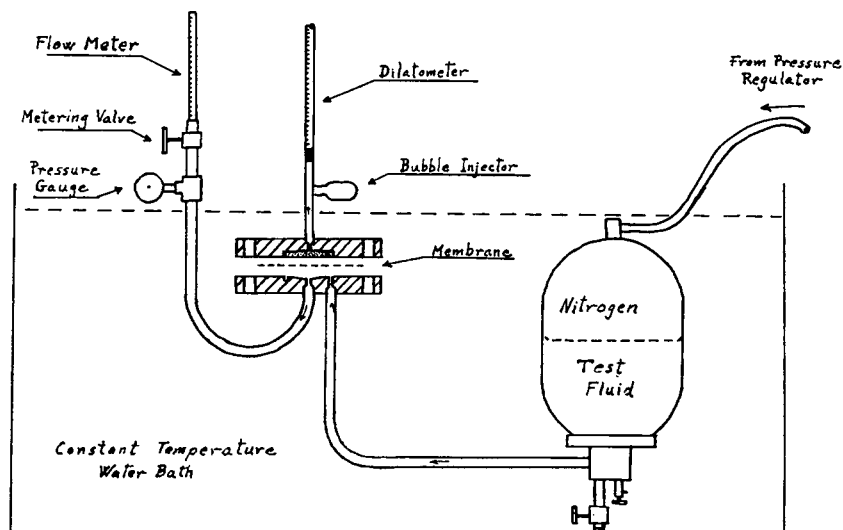

Fig. 1. Expanded view of apparatus used for kinetic studies.

Procedure

The flow rate of fluid diffusing through a film was measured over a temperature range of 290 to 330°K. and pressure differentials from 250 to 1000 psi. If, for a particular pressure differential, a straight line with no perceptible inflection was obtained from a plot of the logarithm of flow rate versus reciprocal temperature, it was assumed that an activated rate process involving but one rate-determining step was being observed. With this condition satisfied, the experimental activation energy was calculated from the slope which, in turn, was determined as a statistical regression coefficient from sets of 12 to 20 measurements (Fig. 2).

The diffusion coefficient, defined as the rate of material transfer across a unit surface per unit concentration gradient, was obtained by assuming that measured flow rates were the resultant of two opposing rates, each having the same rate constant, k, and each proportional to the activity of the diffusing fluid. Hence:

$$\text{Rate} = k(\alpha - \alpha_0)$$

where α is the activity of the fluid on the high pressure side of the film and α_0 that on the side of the film exposed to atmospheric pressure. The activity α of the liquid was calculated from the thermodynamic relation:

$$\Delta G = RT \log (\alpha/\alpha_0) = \int_{p_0}^{p} \bar{V} dp$$
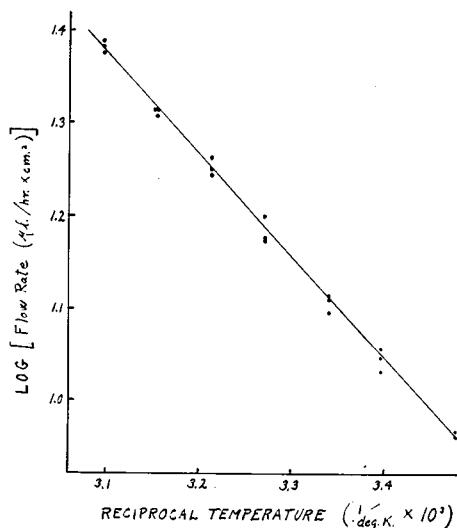

Fig. 2. A representative plot of the logarithm of flow rate vs. reciprocal temperature for the determination of diffusion activation energy. Water flow through cellulose acetate (40% acetyl) film, 0.44 mil thickness under a pressure of 750 psi.

The compressibility of water was neglected in the calculation of molar volume, $\bar{V}$, since this simplification resulted in an error of less than 0.5% in the value of $\bar{V}$.[6] Therefore

$$\log \alpha = \bar{V}_{273}(\rho_{273}/\rho_T)[(p - p_0)/RT]$$

If we assume the activity gradient to be linear, the film thickness multiplied by the specific rate constant k gives the experimental diffusion coefficient. General definitions of diffusion velocities and the absolute reaction rate theory[5] have made possible a theoretical formulation of the diffusion coefficient

$$D = e\lambda^2(\bar{k}T/h)e^{\Delta S^*/R}e^{-E_a/RT}$$

in which the entropy of activation ΔS^* and the mean free path λ are the only unknown quantities which were not submitted to experimental measurement in this study. Therefore, we assumed a value of λ in order to calculate ΔS^*. The mean free path is the distance a molecule moves from one equilibrium position to the next, and this must be the order of magnitude of the effective diameter of water molecules. A 50% error in the estimated λ would change the absolute values of activation entropy by approximately 1.5 cal./mole-°K. We chose λ equal to 10^{-7} cm., which is the value assumed by Levi[7] for the diffusion of water vapor through cellulose acetate.

Attention is called to the tacit assumption that the diffusing molecule encountered a homogeneous membrane barrier. If, however, there existed in the film crystalline regions the dimensions of which were large relative to those of diffusing molecules, the area of film through which diffusion could have occurred would have been reduced, and we then would have observed a rate process involving a fraction of the total film surface. Let us suppose this phenomenon prevailed and that but half of the film area was permeable. The effect of this would have been to increase activation entropy values by 1.3 cal./mole-°K. The difference would not have altered the interpretations made of these values, the most significant of which depended upon relative rather than absolute values.

B. Compressive Deformation of Membranes

Apparatus

A device (Fig. 3) was constructed for the purpose of measuring film deformation under compression. The base was a 10-in. I-beam, 48 in. long. A fulcrum arm, 30 in. long, was mounted so that its
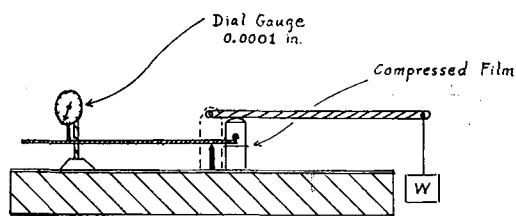
Fig. 3. Apparatus for measuring compressive deformation of thin films.

pivot point (at one end of the arm) was 7 in. above the midpoint of the upper surface of the I-beam. Weights were suspended from the other end of the arm by means of a stirrup. The fulcrum arm, in a horizontal position, was allowed to bear on matched steel cylinders, 1.5 in. in diameter, placed such that their axis was 3 in. from the pivot point of the fulcrum arm. The lower cylinder was securely welded to the I-beam support. The film to be compressed was placed between polished, flat, end surfaces of the steel cylinders. A light-weight aluminum alloy fork (extended in the direction opposite to that of the fulcrum arm) was mounted with bearing points on two lugs set in either side of the upper cylinder, and on a knife edge placed 1.25 inches from the cylinder axis. A dial gauge, calibrated in units of 10^{-4} in. was firmly supported from the I-beam so as to make contact with the aluminum fork. This fork magnified the displacement along the cylinder axis 11.47-fold. In the absence of a compressible membrane the elastic deformation of the apparatus itself was 8.4×10^{-4} in. on the cylinder axis per 1000 psi applied to cylinder end surfaces. The sensitivity of the apparatus was 8.7×10^{-6} in.

Procedure

The instrument was zeroed with 24 psi bearing on films. This pressure was increased stepwise to a maximum of 999 psi and then reduced to the original pressure of 24 psi. Friction in the displacement magnifying device and in the moving parts of the dial gauge itself were overcome by gently tapping the base of the instrument with a rawhide mallet. Repeated compression cycles could be made without any danger of disturbing the membrane, since a minimum of 24 psi was applied to the film at all times. Dry film was subjected to a number of cycles sufficient to demonstrate its completely elastic behavior.

Following the measurement of the compressibility of membranes in the dry state (in an atmosphere of approximately 65% R. H.) the film was allowed to

absorb water from a wick placed on the fringes of the film which extended outside the matched steel cylinders. The membrane was still under a pressure of 24 psi and had not been disturbed in any way since the completion of dry compression cycles. A period of 24 hr. was allowed for saturation of membranes with water under the aforementioned conditions. Subsequent compression cycles, with the water wick still in place, were repeated until another elastic state was demonstrated or until it became evident that plastic flow was occurring.

RESULTS

A. Diffusion Through Membranes

Preliminary diffusion trials with cellulose acetate film gave hysteresis loops which clearly indicated a need for an induction period at high pressure differentials to produce a stable state of the polymer capable of yielding reproducible flow rates. There was no further indication of hysteresis effects following an induction period of 24 hr. at 750 or 1000 psi and 320°K.

Diffusion coefficients, activation energies, and activation entropies for the diffusion of water through two thicknesses of cellulose acetate film at several pressure differentials are given in Table I. Corresponding data for cellophane film are contained in Table II.

Erratic flow rates were observed for the diffusion of water through unirradiated polyethylene (0.8–1.0 mil, DYNK-1) film supplied by the Bakelite Co. and nylon (1.0-mil Zytel 42X) film supplied by the du Pont Co. Activation energies were unattainable. The diffusion of water through irradiated polyethylene (1.5-mil Alathon 10) and Teflon (2 mil) films supplied by the du Pont Co. was less than

TABLE I

Diffusion of Water Through Cellulose Acetate (40% Acetyl) Films Cast on Plate Glass from Acetone Solutions

Film thickness, mils	Pressure differential, psi	Diffusion coefficient at 30°C., cm.²/sec. $\times 10^8$	Experimental activation energy, cal./mole	Activation entropy, cal./mole °K.
0.33	250	14.9	5160	−12.8
	500	10.0	5002	−14.0
	750	8.8	4975	−14.4
	850	9.5	5022	−14.1
0.67	250	13.2	7660	− 4.7
	500	11.7	4838	−14.2
	750	10.2	4906	−14.3
	1000	9.2	6105	−10.3

TABLE II

Diffusion of Water through Cellophane (du Pont PT-300)
0.88-mil Film

Pressure differential, psi	Diffusion coefficient at 30°C., cm.²/sec. × 10⁷	Experimental activation energy, cal./mole	Activation entropy, cal./mole °K.
250	16.5	4257	−10.9
500	19.0	4180	−10.9
1000	17.5	4894	−8.7

TABLE III

Diffusion of Methanol through Cellulose Acetate (40% Acetyl) Film Cast on Plate Glass from Acetone Solution. Film Thickness 0.67 mils

Pressure differential, psi	Diffusion coefficient at 30°C., cm.²/sec. × 10⁸	Experimental activation energy, cal./mole	Activation entropy, cal./mole °K.
250	not reproducible	—	—
500	not reproducible	—	—
750	3.3	4712	−17.2
1000	18.3	6960	−6.4

could be measured in our apparatus, i.e., the diffusion coefficients were less than 10^{-11} cm.²/sec.

Reliable data for the diffusion of methanol through cellulose acetate film resulted only at pressure differentials of 750 and 1000 psi (Table III).

An attempt was also made to obtain activation entropy values for the diffusion of nitrogen gas through cellulose acetate and cellophane. The diffusion coefficient for a 0.33-mil film of cellulose

acetate (40% acetyl) was approximately 8.8×10^{-7} cm.²/sec. at 500 psi and was essentially independent of temperature, while that through 0.88-mil cellophane was less than 7×10^{-12} cm.²/sec. at 750 psi. Reliable activation energies, and hence entropies could not be extracted from these data.

The experimental data described thus far are summarized in Table IV. It should be emphasized that these data were attained with film which had been stabilized at high pressure differentials. Thus, in the case of cellulose acetate, the film would have been "induced" into the semipermeable condition described by Breton.[2]

The induction process in which there was an important change in the semipermeability of cellulose acetate membranes was subjected to further study. With the use of 0.67-mil film of cellulose acetate (40% acetyl) cast from acetone solution, diffusion coefficients, activation energies, and activation entropies were determined, with pressure differentials ranging from 50 psi in increasingly small increments to 1000 psi, and then stepwise back to 200 psi.

Diffusion coefficients dropped sharply with increasing pressure (Fig. 4) up to about 250 psi where a sudden shift to a higher value occurred. As the pressure differential was increased beyond 250 psi, the coefficient decreased asymptotically. The coefficient increased but slightly on the return sequence of decreasing pressures, 1000 psi downwards.

Activation entropy values were relatively high at 50 and at 250 psi, the pressures at which diffusion coefficients were very sensitive to pressure change. Beyond the critical point of 250 psi the general trend of entropy values was toward more negative

TABLE IV

Diffusion Coefficients, Activation Energies, and Activation Entropies for the Diffusion of Water, Methanol, and Nitrogen through Several Polymer Films over a Range of Pressure Differentials

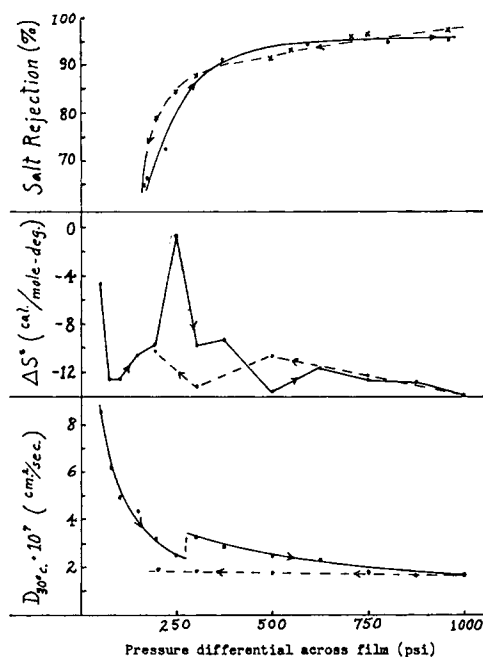| Film	Diffusant	Film thickness, mils	Range of pressure differentials, psi	Range of diffusion coefficients at 30°C., $D \times 10^8$	Range of activation energies, cal./mole	Range of activation entropies, cal./mole °K.
Cellulose acetate (40% acetyl)	water	0.33, 0.67	250–1000	9.2–15.0	4906–7660	−4.6 to −14.4
	methanol	0.67	750–1000	3.3–18.3	4712–6960	−6.4 to −17.2
	nitrogen	0.33	500	88		
Cellophane	water	0.88	250–1000	165–190	4180–4894	−8.7 to −10.9
	nitrogen	0.88	750	<0.001		
Polyethylene (non-irradiated)	water	1.0	1000	0.014		
Polyethylene Alathon 10 (irradiated)	water	1.5	1000	<0.001		
Teflon	water	2.0	1000	<0.001		
Nylon (Zytel 42X)	water	1.0	1000	∼0.1		

Fig. 4. Changes in the entropy of activation for diffusion and in the diffusion coefficient which occur as cellulose acetate film is "induced" to a semipermeable condition by means of water diffusion under high pressure differentials. Salt rejection data were taken from the work of Breton.[2]

values, reaching a minimum of -13.9 cal./mole-°K. at 1000 psi. All values on the return sequence (decreasing pressure) were less than -10/mole-°K.

B. Compressive Deformation of Membranes

Cellulose acetate (40% acetyl) film cast from acetone solution was elastically deformed by approximately 13% of its thickness at a pressure of 1000 psi (Table V). When the film was saturated with water, this deformation was less than 3%. Repeated cycles of compression and relaxation of cellulose acetate film in contact with excess moisture resulted in progressively greater film swelling and decreased compressive deformation up to what appeared to be the saturation point (Tables V and VI).

In contrast, dry cellophane (du Pont PT-300) underwent elastic deformation of less than 3% of the thickness, while wet cellophane was deformed plastically more than 70% of the original thickness. Plastic flow under compression did not occur when cellophane polymer chains were crosslinked with cupric ions. The copper-cellophane complex was formed by mercerizing cellophane in 15% sodium hydroxide solution and then rinsing with a 5% solution of cupric acetate. The elastic deformation of wet films of copper-cellophane was not much greater than that of cellulose acetate (Tables V–VII).

DISCUSSION

Negative entropy values (-14 cal./mole-°K. at 1000 psi) for the diffusion of water through cellulose acetate film suggest that water molecules are constrained to states of high order in their transport across the membrane. That this order is greater for compressed membranes is indicated by an activation entropy value of -9 cal./mole-°K. reported by Levi[7] for the diffusion of water vapor across noncompressed cellulose acetate film. Values for two different thicknesses of cellulose acetate film were in good agreement at 500 psi and above. However, at 250 psi, the thinner of the two films had decidedly the lower activation entropy. This difference was attributed to the greater ease with which the thinner film underwent polymer reorientation under compression.

TABLE V

Compressive Deformation of Cellulose Acetate (Three Layers of 0.67-mil Film). Dimensions Relative to Original Film Thickness

Pressure psi	Dry film		Wet film (in contact with excess moisture)[a]							
	Cycle 1	Cycle 2	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7	Cycle 8
24	1.000	0.987	1.052	1.100	1.118	1.139	1.157	1.179	1.214	1.214
293	0.913		1.052		1.122	1.139				
499	0.891		1.052		1.126	1.139				
753	0.882		1.030		1.131	1.157				
999	0.869	0.866	1.013	1.065	1.105	1.144	1.166	1.183	1.196	1.196
753	0.881		1.030	1.078	1.131					
499	0.917		1.065	1.105	1.144					
293	0.935		1.078	1.100	1.135					
24	0.987	1.000	1.100	1.118	1.139	1.157	1.179	1.214	1.214	1.214

[a] After 24-hr. period of water sorption *in situ* under 24 psi pressure.

TABLE VI

Compressive Deformation of Cellulose Acetate (Three Layers of 1-mil Film).   Dimensions Relative to Original Film Thickness

Pressure, psi	Wet film (in contact with excess moisture)						
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7
24	1.000	0.994	0.997	1.020	1.026	1.026	1.029
293	0.962	0.983	0.997	1.012	1.020		
494	0.934	0.962	0.985	1.009	1.020	1.020	1.020
753	0.930	0.962	0.980	1.003	1.006		
999	0.910	0.959	0.980	0.994	1.006	1.006	1.012
753					1.009		
499	0.942	0.971		1.003	1.009		1.026
293	0.956	0.985		1.012	1.017		
24	0.994	0.997	1.020	1.026	1.026	1.029	1.026

TABLE VII

Compressive Deformation of Copper-Cellophane Complex (Two Layers of 1-mil Film).   Dimension Relative to Original Film Thickness

Pressure, psi	Dry film			Wet film (in contact with excess moisture)[a]			
	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3	Cycle 4
24	1.000	1.000	1.004	1.074	1.061	1.035	1.035
499				0.987			
999	0.952	0.952	0.948		1.000	1.000	1.000
499							
24	1.000	1.004	1.000	1.061	1.035	1.035	1.035

[a] After 24-hr. period of water sorption in situ under 24 psi pressure.

The mechanism for the transport of water across cellophane film under high pressure differentials may be comparable to that for cellulose acetate film, as indicated by an activation entropy value as low as -12 cal./mole-°K. It is probable that the difference in the behavior of the two materials is mainly the greater Brownian movement of polymer chains in cellophane film, and hence greater chance for random diffusion to occur.

If water bridges (crosslinks) polymer chains of cellulose acetate, as suggested by Breton,[2] the corresponding increase in the order of the polymer-diffusant system, beyond that of single attachment, would be expected to render the activation entropy values more negative than in the case of methanol, where single attachments is possible but not bridging. Hence, the low activation entropy for the diffusion of methanol through cellulose acetate does not support the theory that polymer chains are actually crosslinked by hydrogen bonded water.

Although noncompressed cellulose acetate is not an effective semipermeable membrane for ionic solutions, the semipermeability increases rapidly as the pressure differential across the membrane asymptotically the behavior of an ideal semi-permeable membrane with further increase in pressure. The interval in which the diffusion coefficient and activation entropy values were most erratic (150–250 psi) corresponds to the interval in which the membrane semipermeability was most sensitive to pressure change (Fig. 2). It is presumed that random diffusion predominates at low pressures and that, during the induction of membranes to a semipermeable state, a significant reorientation of polymer chains occurs, random diffusion increases, and alignment-type diffusion remains at the predominant mechanism for water transport.

That wet cellulose acetate film is less deformable under compression than dry film (Table V) has two implications. First, it adds weight to the interpretation of Breton's measurements[2] at the dielectric constant of wet and dry film. Specifically, if these measurements were corrected for film deformation up to 1000 psi compression, the differences between the wet and the dry film would have been even greater than originally reported. This difference in dielectric constants was presented as evidence for the presence of hydrogen-bonded

water in the amorphous regions of membranes. Secondly, the greater elastic modulus of compressed wet film demonstrated a strong interaction between water and polymer chains in the cellulose acetate-water structure.

Successive compression and relaxation of cellulose acetate film in contact with excess moisture (Tables V and VI) has demonstrated that compression increases the capacity of film for bound water. This was predicted by Breton[2] from more theoretical considerations.

Although, the diffusion coefficient, under high pressure differentials, for water in cellophane is roughly 10-fold greater than that in cellulose acetate, nitrogen gas flows quite freely through the latter while cellophane is nearly impermeable to the gas under similar conditions. Since the deformation of cellophane under a pressure of 1000 psi is less than 3% film compaction cannot explain the impermeability of cellophane to nitrogen. It appears, rather, that the structure of dry cellophane is sufficiently dense that a polar molecule is required to separate the polymer chains to the extent that appreciable diffusion can occur. Obviously, amorphous regions of cellulose acetate are of a more open structure than cellophane. Nevertheless, the crystalline regions of cellulose acetate prevent plastic flow of wet film so characteristic of cellophane.

In view of the known properties of cellophane, in particular its capacity to support hydrogen bonding and its high permeability to water, one may ask what can be done to make this film a more effective semipermeable membrane for ionic solutions. A consideration of work reported herein and related investigations carried out in this laboratory suggest a partial solution. One defect of cellophane seems to be excessive Brownian movement of polymer chains when wetted and concurrent plastic flow under compression. Two observations[9] strongly support this contention: (1) an increase in pressure differential across the film from 600 to 1500 psi raised the salt rejection from 8 to 12%. It is reasonable to expect that greater film compression would restrict, to some degree, Brownian movement and hence random diffusion; (e) when cellulose polymer chains were crosslinked with cupric ions, the salt rejection was increased to 19% at 600 psi. Moreover, plastic flow did not occur. Thus it appears that crosslinking elements might be incorporated into cellophane in such a manner that an optimum spacing of polymer chains and sufficient constraint to Brownian movement would result in an efficient semipermeable membrane for ionic

solutions. An important drawback to such a modification of the cellulose structure is that it is apt to reduce significantly the favorable diffusion coefficient of water through cellophane.

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Synopsis

The mechanism of water transport across cellulosic membranes under high pressure differentials was studied in an attempt to explain the semipermeability of these films when used as osmotic membranes for ionic solutions. Diffusion coefficients and activation entropy values for the diffusion of water and other fluids through various polymer films were determined, and compressive deformation of cellulose acetate and cellophane films was measured. Activation entropy values for the diffusion of water across both cellulose acetate and cellophane films illustrated that water molecules are constrained to states of high order as they are transported across the membrane under high pressure differentials. Activation entropy values for the diffusion of methanol through cellulose acetate film failed to support the proposition that chains of this polymer may actually be crosslinked by hydrogen-bonded water. It appeared, rather, that but one hydrogen of the water molecule was involved in hydrogen bonding to the polymer. A significant reorientation of the polymer in the pressure interval in which cellulose acetate film is induced into a semipermeable condition was indicated by pressure-dependent fluctuations of diffusion coefficients and activation entropy values in this interval. The greater elastic modulus of wet cellulose acetate film under a compressive force applied normal to

the film surface demonstrated a strong interaction between water and polymer chains in the cellulose acetate-water structure. The capacity of the film for bound water was also increased by repeated compression while wet. Wet cellophane films deformed plastically under compression. Crosslinking polymer chains of cellophane film with cupric ions prevented plastic flow and, at the same time, increased the semipermeability of the film for sodium chloride solutions.

Résumé

On a étudié le mécanisme du passage de l'eau à travers des membranes de cellulose sous des grandes différences de pression dans le but d'expliquer la semiperméabilité de ces films lorsqu'on les utilise comme membranes osmotiques pour des solutions ioniques. On a déterminé les coefficients de diffusion et les valeurs de l'entropie d'activation pour la diffusion de l'eau et d'autres fluides à travers différents films de polymère et on a mesuré la déformation due à la compression de films d'acétate de cellulose et de cellophane. Les valeurs de l'entropie d'activation pour la diffusion de l'eau à travers des films d'acétate de cellulose et de cellophane montrent que les molécules d'eau sont réunies à des états d'ordre supérieur lorsqu'elles sont transportées à travers la membrane sous des différences de pressions élévées. Les valeurs de l'entropie d'activation pour la diffusion du méthanol à travers un film d'acétate de cellulose font supposer que les chaînes de ce polymère doivent être "pontées" par la liaison hydrogène de l'eau. Il apparait en outre qu'un hydrogène seulement de la molécule d'eau est impliquée dans la liaison hydrogène du polymère. Une réorientation appréciable du polymère, dans l'intervalle de pression où le film d'acétate de cellulose est rendu semiperméable, est indiquée par des fluctuations de la pression dépendant des coefficients de diffusion et des valeurs de l'entropie dans cet intervalle. Le très grand module d'élasticité du film d'acétate de cellulose mouillé sous une force de compression, appliqué normalement à la surface du film, montre une forte interaction entre l'eau et les chaînes de polymère dans la structure acétate de cellulose-eau. La capacité du film de "lier" de l'eau est aussi augmentée par des compressions répétées lorsqu'il est mouillé. Les films de cellophane mouillés se déforment d'un façon plastique sous la compression. Le pontage des chaînes polymériques du film de cellophane avec des ions cuivriques prévient l'écoulement plastique et du même coup, augmente la semiperméabilité du film pour les solutions de chlorure de sodium.

Zusammenfassung

Zur Aufklärung der Halbdurchlässigkeit von Cellulosefilmen bei Verwendung als osmotische Membranen für Ionenlösungen wurde der Mechanismus des Wassertransportes durch Cellulosemembranen unter Anwendung von hohen Druckdifferentialen untersucht. Diffusionskoeffizienten und Aktivierungsentropiewerte wurden für die Diffusion von Wasser und anderen Flüssigkeiten durch verschiedene Polymerfilme bestimmt und die Kompressionsdeformation von Celluloseazetat- und Cellophanfilmen wurde gemessen. Die Werte der Aktivierungsentropie für die Diffusion von Wasser durch Celluloseazetat- und Cellophanfilme zeigen, dass die Wassermoleküle beim Transport durch die Membran unter hohem Druck in hoch geordnete Zustände überführt werden. Die Werte der Aktivierungsentropie für die Diffusion von Methanol durch einen Celluloseazetatfilm sprechen nicht für die Annahme, dass die Ketten dieses Polymeren tatsächlich durch die Wasserstoffbrücken von Wasser vernetzt sein können. Es scheint eher so zu sein, dass nur ein Wasserstoff des Wassermoleküls an der Bildung von Wasserstoffbrücken zum Polymeren beteiligt ist. Eine signifikante Umorientierung des Polymeren im Druckintervall, in welchem der Celluloseazetatfilm zum halbdurchlässigen Verhalten "induziert" wird, liessen druckabhängige Schwankungen der Diffusionskoeffizienten und Aktivierungsentropien in diesem Intervall erkennen. Der grössere Elastizitätsmodul von feuchten Celluloseazetatfilmen, die unter einer, senkrecht zur Filmoberfläche wirkenden Kompressionskraft stehen, zeigt, dass eine starke Wechselwirkung zwischen Wasser und den Polymerketten in dem Celluloseazetat-Wassersystem besteht. Durch wiederholte Kompression im feuchten Zustand konnte auch die Kapazität des Filmes für "gebundenes" Wasser erhöht werden. Feuchte Cellophanfilme wurden bei der Kompression plastisch verformt. Eine Vernetzung der Polymerketten des Cellophanfilms mit Kupfer-(II)-ionen verhinderten das plastische Fliessen und erhöhten gleichzeitig die Halbdurchlässigkeit des Films für Natriumchloridlösungen.