Water and Ion Flow Across Cellulosic Membranes*

C. E. REID and E. J. BRETON†

Department of Chemistry, University of Florida, Gainesville, Florida

INTRODUCTION

Among the several processes currently under study for producing fresh water from saline sources is the reverse-osmosis, or ultrafiltration, process. In this process, salt water is held under pressure against a suitably supported semipermeable membrane which will pass water but block ions. If the pressure exceeds the osmotic pressure of the solution, fresh water will flow through, while the solution remaining behind becomes more concentrated.

Unfortunately, no membrane satisfactory for this purpose is known, but it is hoped that one may be developed from polymeric materials. This hope was strengthened by the discovery, reported below, that cellulose acetate shows the necessary semipermeability properties, though improvement in flow rate and durability are necessary before practical application is possible.

An understanding of the fundamental processes of water and ion transfer through the membrane appears to be a prerequisite to a rational attack on the problem of designing improved films. The research reported here was undertaken primarily to gain an understanding of these processes.

EVALUATION PROGRAM

In order to find a semipermeable membrane for strong electrolytes, a trial-and-error approach was used, although it was felt that the desired membrane should contain some hydrophilic groups. Various types of thin films were obtained from chemical manufacturers; some films were prepared in the laboratory.

The apparatus that was ultimately developed for measuring the semipermeability is shown in

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† Present address: E. I. du Pont de Nemours & Co., Wilmington, Delaware.

Figure 1. It embodied the following features. (1) Pressures up to 1500 psi could be obtained by means of compressed air or nitrogen. (2) Stirring was accomplished by convection; one leg was heated and the other cooled. (3) Monel was used throughout, which reduced corrosion to a minimum. (4) The membrane was supported by a ceramic disk which was recessed into the base plate and turned on a lathe to a flat surface. This design permitted the testing of very thin films at high pressures.

The reservoir was a 2-foot length of 3-inch schedule 80 Monel pipe, capped at both ends, with a capacity of 2.75 liters. The plates enclosing the membrane were ($^3/_4$-inch Monel circles, 4 in. in
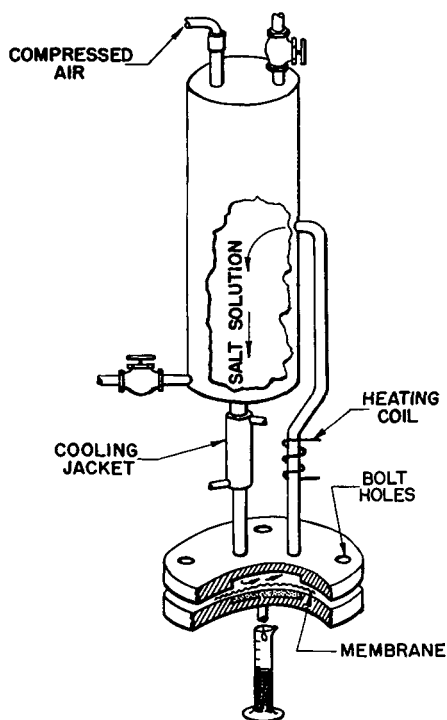

Fig. 1. Apparatus for determining the semipermeability of imperfect osmotic membranes.

diameter in one apparatus and 8 in. in another; the respective membrane diameters were 1⁵/₈ and 4 in. The connecting pipes were ¹/₄-in. Monel tubing.

To measure the semipermeability, a film was first clamped into place as illustrated in Figure 1. The apparatus was filled with salt solution and the pressure applied. Water that passed through the membrane was collected at the bottom and analyzed. From the concentration of salt in the apparatus and that in the water that had passed through the membrane, the percentage of salt rejected was calculated. The percentage of salt rejected is taken as a measure of semipermeability. All results reported here were taken near the beginning of the run, before appreciable increase of salt concentration in the reservoir had occurred.

Early in this investigation some concern was felt as to the effect of dissolved gases on the film. If solution saturated with gas at the high reservoir pressure enters the film with its gas concentration unchanged, bubbles must form as it moves toward the low-pressure side of the membrane. These might cause mechanical disruption of the film structure. Several unsuccessful attempts were made to separate the gas from the solution. These were abandoned when it was learned that, in the absence of electrolytes, films can function for several months at least without noticeable deterioration. Apparently dissolved gases are largely rejected by the membrane, though the degree of rejection has not been measured.

The results of the screening program are recorded in Table I.

As can be seen by Table I, the semipermeability of cellulose acetate far exceeded that of any other film tested. Consequently, further study was confined for the most part to cellulose acetate membranes. The semipermeability of cellulose acetate to various solutions is given in Table II.

THEORY FOR THE SEMIPERMEABILITY OF CELLULOSE ACETATE

Of the many theories proposed for the phenomenon of semipermeability, i.e., sieve, distillation, adsorption, solubility, and ion exchange,[1] none adequately explains why cellulose acetate is permeable in strong electrolytes, although in their most general sense, the solubility and adsorption theories would certainly cover the observed behavior of cellulose acetate. However, this question is then raised: Why is the solubility or adsorption of water in cellulose acetate so much

TABLE I
Semipermeability of Various Membranes to Aqueous Sodium Chloride Solutions

Membrane tested	Pressure on membrane, psi	Semipermeability, % rejection of dissolved NaCl by membrane[a]	Remarks
Polyvinyl alcohol (du Pont Elvanol 71-24)	100	None	Effluent pH 11
Polyvinyl alcohol (Baked at 145°C.)	600	22	No pH change
Polyvinyl alcohol (Baked at 145°C.)	780	26	No pH change
0% Polyvinyl alcohol, 50% phenol-formaldehyde	100	None	Effluent pH 12
75% Polyvinyl alcohol, 25% polytetraallylammonium bromide	100	19	Effluent pH 12
Polytetraallyl-ammonium bromide	70	20-35	
Amberplex A-1 anion membrane (Rohm and Haas)	700	None	
Amberplex C-1 cation membrane (Rohm and Haas)	700	None	
Ethyl cellulose	800	None	
Nylon (Plastex Process Co.)	800	None	
Cellophane (du Pont PT 300)	700	6	No pH change
Rubber hydrochloride	700	—	No flow through membrane[b]
Polystyrene (Dow Chemical Co.)	800	None	
Saran (Dow Chemical Co.)	800	None	Very low flow rate
Polyethylene	800	None	
Cellulose acetate butyrate	800	None	
Cellulose acetate (Celanese S-604)	800	—	No flow
Cellulose acetate (du Pont 88 CA-43)	850	96	
Cellulose acetate (du Pont 88 CA-43)	400	97.4	

[a] Per cent rejection was based upon the change in chloride concentration from influent to effluent.

[b] If after 48 to 72 hours, no water was collected, an entry of no flow was made.

TABLE II
Semipermeability of Cellulose Acetate to Aqueous
Solutions of Various Electrolytes

Membrane[a]	Pressure on membrane, psi	Electrolyte	Concentration	Semipermeability, % rejection of dissolved electrolyte by membrane
Cellulose acetate	850	NaCl	0.11 M	96
Cellulose acetate	715	MgCl$_2$	0.031 M	99
Cellulose acetate	800	CaCl$_2$	0.0054 M	98
Cellulose acetate	500	Na$_2$SO$_4$	0.018 M	97
Cellulose acetate	850	NaBr	0.0012 M	93
Cellulose acetate	840	NaF	0.0012 M	86
Cellulose acetate	800	H$_3$BO$_3$	0.0011 M	46
Cellulose acetate	800	NH$_3$	0.04 M	30
Same film as used for NH$_3$ experiment	830	NaCl	0.17 M	90
Cellulose acetate	800	Ocean water	4%	96

[a] Du Pont CA-48 cellulose acetate membrane, 0.88 mils thick, was used for this series of tests.

greater than that of strong electrolytes? If it could be attributed merely to the presence of hydrophilic groups, then cellophane and polyvinyl alcohol, which have a very high concentration of hydroxyl groups, should have a greater degree of salt rejection than cellulose acetate does. But they do not.

To formulate a theory which would explain the semipermeability of cellulose acetate, it was necessary to find out what unique combination of properties of cellulose acetate caused this phenomenon. Fortunately, a great amount of work has been done on cellulose chemistry. This work is well presented in Volume V of *High Polymers*,[2] and pertinent parts of it will be briefly reviewed here before the proposed mechanism is presented.

Cellulose-type membranes are made up of a network of long polymers averaging 15,000 A. in length and of the order of 10 to 20 A. in width.

These polymers have, for the most part, a random orientation in the membrane. When polymer chains run parallel to each other in an orderly manner, crystalline regions are set up. In these regions, the polymers are held together by hydrogen bonds and van der Waals forces and assume definite spacings. On the other hand, when the chains lie in a disorderly manner, the spaces between polymers are much greater. These are called amorphous regions.

This concept of the internal structure of membranes applies to all types of cellulose films. Baker, Fuller, and Pape[3] have shown, however, that cellulose acetate is unique in that it possesses a moderate degree of crystallinity. That is, the internal forces are numerous enough and strong enough to restrict Brownian motion and hold a large percentage of the polymer chains in highly ordered regions. Of necessity, the spacings in the amorphous regions are much smaller than they would be if there were little or no crystallinity.

When water molecules are introduced into cellulose acetate, they concentrate in the amorphous regions.[2] Here, it is postulated, they become associated by hydrogen bonding to the carbonyl oxygens in the cellulose acetate, thereby filling the voids with bound water. The tightness of these bound water regions depends upon the pore size in the membrane. When they are large, as in the case of cellophane, the bound water is loosely held together. In cellulose acetate, the pores are smaller, which causes the water that is present to be more tightly bound.

In a structure such as this, it is proposed that two different mechanisms of diffusion occur. Ions and molecules that cannot enter into hydrogen bonding are transported across the membrane by hole type diffusion. That is, their diffusion depends upon the probability of hole formation in the membrane. Filling the pores of cellulose with tightly bound water reduces the probability of hole formation, thereby reducing diffusion of this type.

Those ions and molecules that can combine with the membrane through hydrogen bonding and can fit into the bound water structure are presumed to be transported across the membrane by alignment of hydrogen bonds with the membrane. After these molecules combine with one side of the membrane, they migrate across by transferring from one hydrogen bonding site to another and are finally discharged from the other side.

On the basis of these concepts (i.e., bound water,

hole and alignment types of diffusion), it can now be deduced that the semipermeability of cellulose acetate is due to this situation: that within the membrane strong electrolytes diffuse very slowly compared to the rate of diffusion of water. In cellulose acetate, the high degree of crystallinity reduces Brownian motion and pore size sufficiently to permit bound water to fill the voids, which greatly reduces the probability of hole formation. Hence, the rate of diffusion of sodium chloride is very low. If the membrane were compressed, more crosslinking would occur, the bound water would become more stabilized, and the rate of diffusion would become even less.

On the other hand, the rate of diffusion of water through cellulose acetate is relatively high, since water is transported by a different mechanism. Compression of the membrane would not be expected to reduce appreciably alignment-type diffusion of water. Therefore, compression of the structure should increase the semipermeability of the membrane.

The hydrogen bonding mechanism does not exclude the sieve mechanism. The size of the holes that are continually appearing and disappearing plays a secondary role. The rates of diffusion of solutes that cannot enter into hydrogen bonding depend upon pore size. However, in the case of those ions and molecules that can enter into hydrogen bonding, the permeability depends upon their ability to fit into the icelike structure of the membrane.

Literature Support for Theory

Cellulose acetate provides excellent conditions for hydrogen bonding because there are large numbers of oxygen atoms in each polymer. That water is bound to cellulose acetate polymers is amply supported in the literature. Gruner,[4] Petitpas and Mathieu,[5] and others[2] have discussed chemical-type bonding between water and cellulose polymers.

If water were passing through cellulose acetate by combining with the bound water within the membrane, its reduction in entropy should be comparable to the conversion of liquid water to ice. Stamm and Loughborough[6] report that the first water sorbed by cellulose acetate has a $T \Delta S$ value equivalent to the heat of fusion of water, indicating that the water does have orientation (and, hence, bonding) comparable to that of ice. Neale and Williamson[7] have also reported that the bonding between cellulose and water is comparable to that of ice.

The work of Baumgartl[8] on ultrasonics suggests that strong electrolytes migrate in cellophane by hole-type diffusion. He observed that the rate of diffusion of NaCl in cellophane was increased twofold by the action of ultrasonics. It is assumed that the ultrasonic acoustical radiation increased the vibration of the cellulose polymers and this might be expected to increase the concentration of holes in the polymers. Consequently, hole-type diffusion would be increased.

Experimental Support of Theory Based Upon Semipermeability Determinations

Although there is abundant evidence to substantiate indirectly the theory presented in the previous section, little experimental work has yet been reported to support it directly. Consequently, a series of experiments was designed to test this concept. These experiments fall into two broad categories. The first group was based upon the determination of the semipermeability of cellulose acetate under various conditions. They are reported in this section. The second group of experiments was based upon the measurement of the electrical properties of cellulose acetate under various conditions. These experiments are reported in the following section.

The hydrogen bonding concept for the semipermeability of cellulose acetate is compatible with the results contained in Table II. Inasmuch as neither the cations nor the anions of NaCl and NaBr can enter into hydrogen bonding, these salts should be effectively rejected, and they are. The very high rejection of $MgCl_2$ and $CaCl_2$ may be attributed to the large size of the hydrated magnesium and calcium ions which would reduce their rate of diffusion.

Since the fluoride ion can enter into hydrogen bonding, this ion should have a greater rate of diffusion than the chloride ion. Sodium fluoride, therefore, should have a lower semipermeability than NaCl, and this was found to be true.

A very low salt rejection would be expected for those solutes that can enter into the water-cellulose acetate structure through hydrogen bonding. Ammonia is an example of this type of solute. As indicated in Table II, the semipermeability for NH_3 was only 30%—about one-third of that for NaCl.

Apparently the H_3BO_3 molecule can enter into the water-cellulose acetate structure with considerable ease, because its salt rejection was 46%.

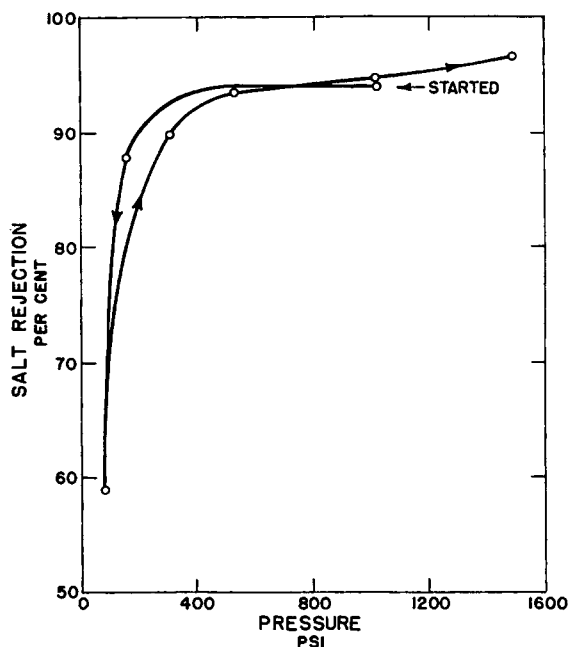The mechanism presented in the previous section

Fig. 2. Effect of pressure on the semipermeability of 40% cellulose acetate. Solution, 0.1 N NaCl.

and ethyl cellulose exhibit no semipermeability. Spence[9] has shown that, because of the plasticizing effect of the butyrate group, cellulose acetate butyrate has a much lower degree of crystallinity than cellulose acetate.

Effect of Pressure on Semipermeability

When the semipermeability of cellulose acetate (expressed as per cent salt rejection) was determined at various pressures, the relationship depicted in Figure 2 was obtained. An explanation for this phenomenon has already been suggested. As pressure is applied, the Brownian movement is restricted, and the structure of the polymer is compressed. The water within the amorphous region becomes more tightly bound, so the membrane becomes a more impenetrable barrier to sodium chloride.

Effect of Crystallinity on Semipermeability

Spence[9] has also shown that, as the acetyl content of cellulose acetate is increased, the degree of crystallinity likewise increases. Varying the acetyl content then becomes a means of varying the crystallinity.

Increasing the degree of crystallinity would have a twofold effect according to the hydrogen-bonding mechanism. First, as explained previously, the semipermeability should increase. Second, the flow rate of water through the membrane should decrease, since the percentage of amorphous regions (through which the water passes) is decreased.

Variations of salt rejection and flow rate with

is also compatible with the results presented in Table I. Polyvinyl alcohol and cellulose both have large concentrations of oxygen atoms that permit bound water regions to form. However, the degree of crosslinking through crystallinity of these two polymers is low; consequently, there is much Brownian movement and the concentration of holes is relatively large. For this reason these membranes have a low degree of semipermeability.

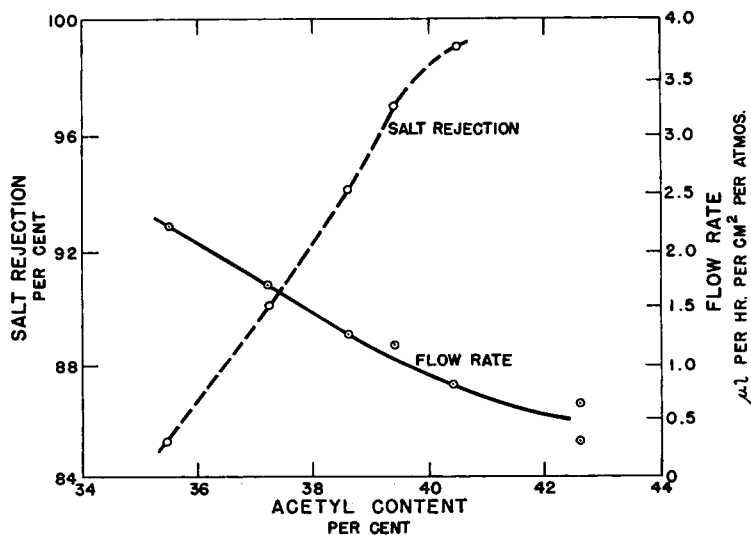For this same reason, cellulose acetate butyrate

Fig. 3. Effect of acetyl content on the semipermeability of cellulose acetate membranes and the flow rate across them. Thickness, 6 microns.

acetyl content have been determined. They are presented in Figure 3.

The role of crystallinity as depicted above is borne out by the data. Up to an acetyl content of 40% there was a continual increase in the semipermeability and a decrease in the penetration of water

Effect of Thickness

Film thickness appears to be at most only slightly related to salt rejection. In a typical series of runs, salt rejection decreased from 99% to 96% as thickness decreased from 22 microns to 3.7 microns. Thinner films show low rejection, but the likelihood of mechanical defects in very thin films is so great that the significance of this is questionable.

Flow rate increases, as expected, with decreasing thickness. The exact form of dependence is doubtful; in some trials an inverse proportionality was obtained, but in the most extensive run the equation

$$r = (744/t) - 14.71$$

held within 5% for films of thickness 5.6 microns or more. (Here r is flow rate in microliters/hr./cm.^{2}, and t is thickness in microns; see Table III.) In all cases, the rates for very thin films are less than those predicted by extrapolation of data from thicker films. This appears reasonable if one assumes that the total resistance to flow includes one or two interfacial resistances which are independent of film thickness.

Since even a thickness of only three microns corresponds to the width of several thousand cellulose acetate chains, it is not surprising that salt rejection is maintained in films as thin as this. The slight increase in salt rejection with increasing thickness, if significant, probably merely indicates that microscopic defects are less likely to extend all the way through a thick film than a thin one. The effect of thickness on flow rate does not appear to have any bearing on the theory presented here, since it is difficult to conceive of any mechanism that would predict substantially different results.

Electrical Measurements to Support Theory

In the previous section, semipermeability-type experiments were described which support the hydrogen-bonding concept of semipermeability. However, these experiments support only indirectly the crux of the theory—namely, that hydrogen bonding sets up an icelike structure impenetrable to strong electrolytes. More direct evidence was

needed, first, to establish the existence of the bound water regions and, second, to show that two different types of diffusion are involved in the transfer of water and sodium chloride ions across cellulose acetate.

TABLE III
Effect of Film Thickness on Flow Rate and Salt Rejection[a]

Thickness, microns	Flow rate, μl./hr. cm^2	Salt rejection, %
22	19.1	99
15	33.4	98
11	53.1	98
5.6	117.8	96
3.7	116.5	96

[a] Salt solution, 0.1 M NaCl; pressure, 600 psi; film composition: 100 parts by weight cellulose acetate, 18 parts Monsanto Santicizer M-17 (methyl ethylphthalylglycollate), 7 parts triphenyl phosphate, 1 part phenyl salicylate; cast as acetone solution.

Dielectric Measurements of Cellulose Acetate

Evidence for the existence of the water-cellulose acetate structure could be obtained by showing that compression of the membrane which sets up the structure and increases the amount of bound water is accompanied by an increase in hydrogen bonding. In order to detect an increase of hydrogen bonding, some observable property which depends upon hydrogen bonds was needed. The dielectric constant meets this requirement. It has been established that hydrogen bonding markedly increases the dielectric constant of some liquids. Pauling[10] has explained this effect on the basis that hydrogen bonding increases the dipole moment which in turn increases the dielectric constant.

Latimer,[11] on the other hand, explains this effect on the basis of atomic polarization. He presents arguments to show that the polarization of hydrogen atoms involved in hydrogen bonding causes a large contribution to the dielectric constant. Furthermore, using Raman spectra, he shows that the largest contribution to the dielectric constant is made when the axis of the hydrogen bond is parallel to the field intensity.

If Latimer's concept applies to water in cellulose, the dielectric constant of hydrated cellulose acetate should increase with pressure, since the amount of bound water is also increasing. If no additional hydrogen bonding were occurring when cellulose acetate is compressed, the dielectric constant of hydrated cellulose acetate should remain constant.

Experimental

The dielectric constant of du Pont CA-43 was measured by placing the film between two brass plates approximately one inch in diameter and measuring the capacity with a heterodyne beat apparatus. The instrument that was used had an error of less than one $\mu\mu f.$[12] Pressure was applied to the film with a 10,000-pound hydraulic press. The brass plates were insulated from the press.

As pressure was applied to the film, changes in apparent dielectric constant could have been due to four factors: (1) an increase caused by structural changes within the films, (2) a decrease caused by water squeezing out of the film, (3) an increase caused by better contact between condenser plates and the membrane, and (4) a change resulting from a change in the dielectric constant of water itself.

The change in apparent dielectric constant due to structural and dimensional changes was corrected for by measuring the capacity of a dry film as a function of pressure. The $\Delta\epsilon$-versus-pressure relationship for dry CA-43 also serves as a correction for any increase in apparent dielectric constant due to better contact between the brass plates and the membrane.

To insure that the change in dielectric constant was not caused by a difference in water content, the film was first subjected to the pressure at which the capacitance was to be measured. After the squeezed-out water had been removed, the condenser formed by the brass plates and the film was wrapped with cellophane tape to prevent evaporation losses. Then the pressure was reduced to atmospheric pressure. The dielectric constant was determined at atmospheric pressure and the pressure was again increased for the determination at the desired pressure. The difference between the dielectric constant at atmospheric pressure and at the desired pressure was used for the ordinate in Figures 4 and 7.

The relationship between the increase in dielectric constant and pressure for cellulose acetate is given in Figure 4. As shown, there was a decided increase in dielectric constant with pressure. This large increase in dielectric constant is due, not only to the formation of hydrogen bonds, but also to the large probability that they are formed in a direction parallel to the electric field intensity.

It is felt that these results furnish direct evidence of the existence of bound water regions in cellulose acetate.

Electrical Resistance Across Cellulose Acetate

Hole-Type and Alignment-Type Diffusion in Cellulose Acetate

Electrical resistance measurements were used to demonstrate that two different types of diffusion are occurring in cellulose acetate. In electrolytic conduction the current is carried out by anions and cations in solution. Both electrical resistance and rate of diffusion depend upon the mechanical resistance that these ions encounter during migration. Therefore, the electrical resistance across a membrane can serve as a quantitative index of their diffusion rates. Diffusion rate and electrical resistance, of course, vary inversely with each other.
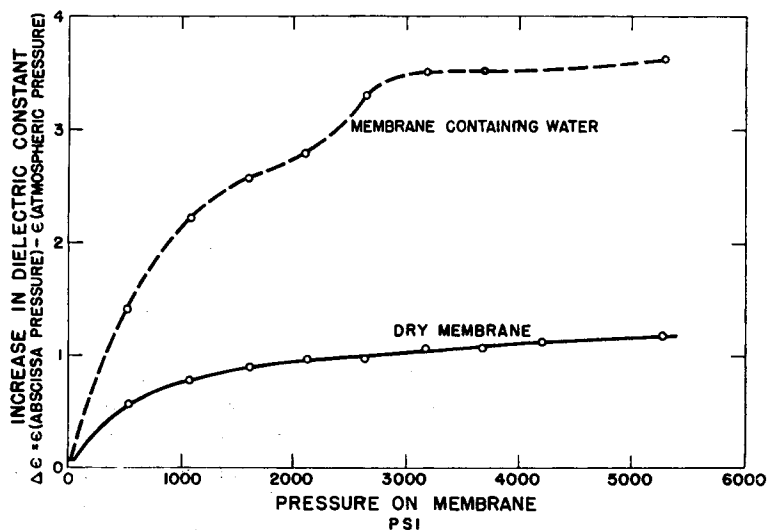

Fig. 4. Effect of pressure on the dielectric constant of cellulose acetate (du Pont CA-43).

In subsequent sections, the term, "membrane resistance," refers to the electrical resistance across the membrane.

Experimental

The membrane resistance of a specific ion was determined by placing an appropriate ion exchange membrane on each side of the semipermeable membrane. A drawing of the cell used for measuring resistances is shown in Figure 5. The circular carborundum whetstones serve two purposes. First, they compress the film uniformly, and, second, they act as electrolyte chambers. When saturated, each holds between 4 and 5 ml. of solution. With this apparatus, compressive stresses
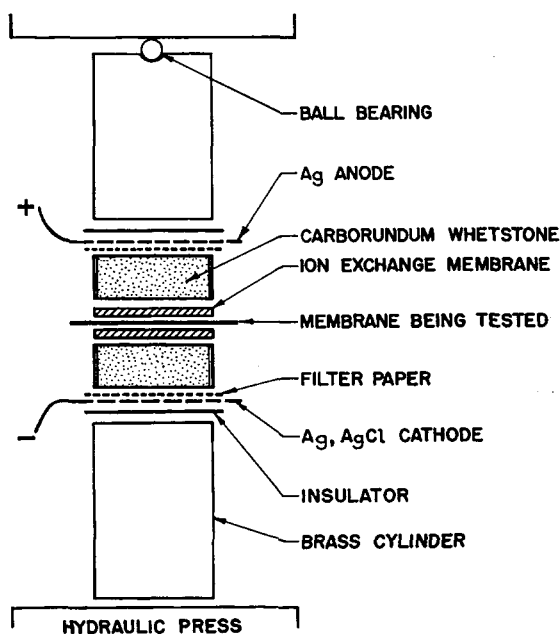

Fig. 5. Apparatus for measuring membrane resistances.

of over 8000 psi can be applied to a film. To eliminate evaporation losses, the sides of the carborundum stones were covered with wide elastic bands and wrapped with Presstite insulation tape. This tape, which is pliable like putty, was pressed to cover all cracks.

A Beckman Model G pH meter was used for measuring the voltage drop across the cell. The current passing through the cell was found by measuring the voltage drop across a known resistance. Ohm's law was used for calculating resistances. The membrane resistances used in Figures 6, 7, and 8 are the total resistances across the cell minus the resistance across the cell without the semipermeable membrane. The resistances across

the ion exchange membrane were low and did not vary significantly with pressure.

In the selection of electrodes, two factors were considered. First, the products of the electrode reactions had to be nongaseous. Second, the products of the electrode reactions should not introduce interfering ions into the system.

To measure the membrane resistance of chloride ions, disks of Amberplex anion permeable membranes in the chloride form were placed on both sides of the cellulose membrane. The cell was compressed to the maximum pressure at which resistances were to be measured, and the excess solution that squeezed out was removed. After wrapping the cell with Presstite tape, resistance
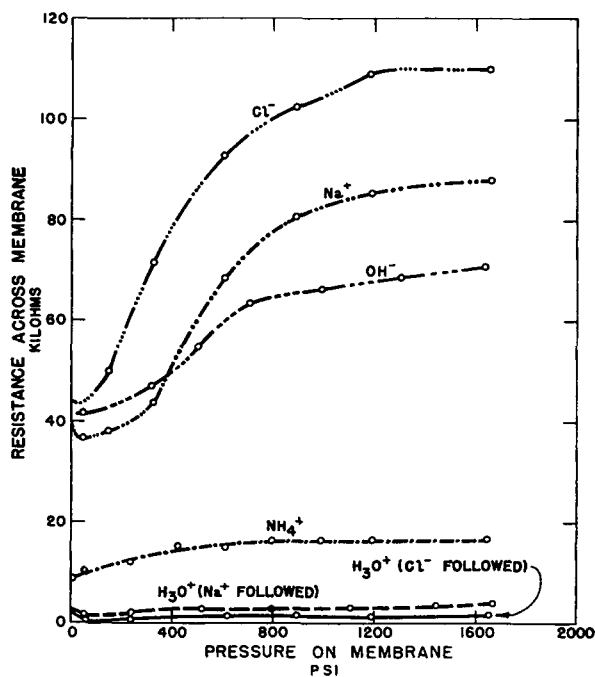

Fig. 6. Resistance versus pressure across 40% cellulose acetate membranes.

measurements were made as the pressure was reduced. Two to three minutes were allowed at each pressure before measuring the resistance. A weighted lever was used to apply pressures up to 1600 psi. For pressures up to 8000 psi, a hydraulic press was used.

With the use of the appropriate solutions and the ion exchange membranes, the membrane resistances of Na^+, NH_4^+, H_3O^+, and OH^- were determined. For example, carborundum blocks saturated with a 0.018 N NH_4Cl solution and an Amberplex cation exchange membrane in the NH_4^+ form were used in determining the membrane resistances of the

ammonium ion. For all determinations 0.018 N solutions were employed.

The electrical resistances for Na^+, NH_4^+, Cl^-, and OH^- across cellulose acetate as functions of pressure are plotted in Figure 6. As expected, the membrane resistances of Na^+ and Cl^-, which cannot enter into hydrogen bonding, was high in contrast to the low membrane resistances of H_3O^+ and NH_4^+, which can enter into hydrogen bonding with cellulose acetate. Furthermore, the membrane resistances of Na^+ and Cl^- were much more sensitive to pressure than the resistance of H_3O^+ and, to a lesser extent, NH_4^+.
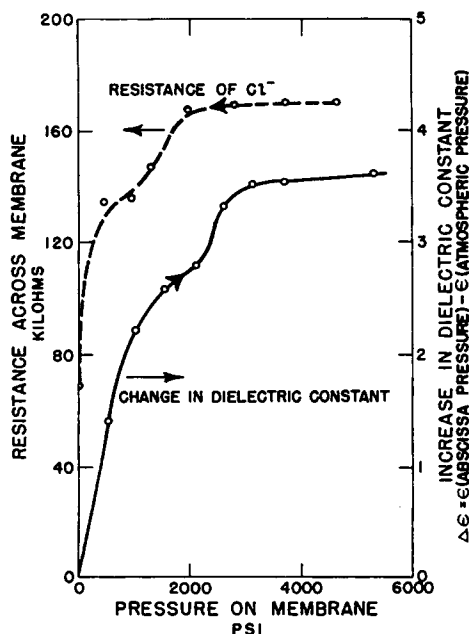
mechanism than those ions that cannot. Furthermore, the resemblance between the resistance versus pressure curves for Cl^- and the salt rejection versus pressure curve suggests that the semipermeability of cellulose acetate is an outgrowth of these two diffusion mechanisms.

Effect of Bound Water on Hole-Type Diffusion

In a previous section, dielectric constants were used to show that compression of cellulose acetate sets up regions of bound water. In the preceding section, membrane resistances were used to show that compression of cellulose acetate causes the rate
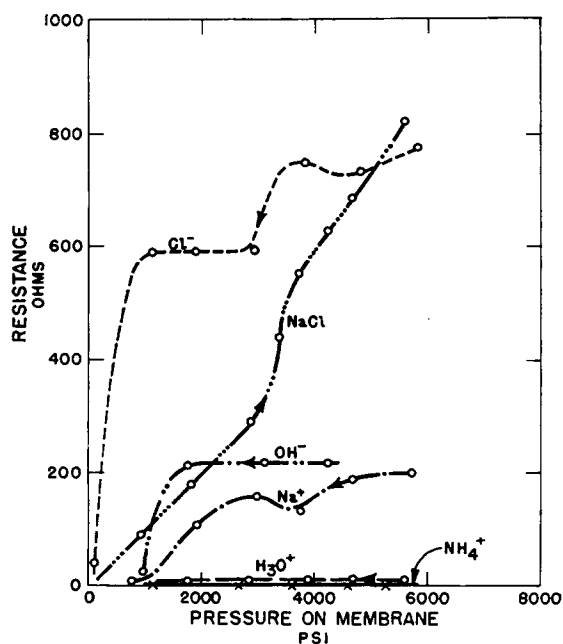

Fig. 7. Comparison of semipermeability and dielectric constant of cellulose acetate membranes.

Fig. 8. Resistance vs. pressure for cellophane (du Pont PT-300).

The high membrane resistance of the hydroxyl ion may be due to its relatively low tendency to form hydrogen bonds with the carboxyl groups in cellulose acetate. In this type of membrane the carboxyl groups are the principal sites for hydrogen bonding. An alternative explanation is that hydroxide ions may cause ionization of the free hydroxyl groups in cellulose acetate. This would make the film act as a cation exchange membrane with consequent high resistance to anions. The tendency of OH^- to associate with the membrane was definitely greater than that of Cl^-, as indicated by the resistance measurements at higher pressures.

These results shown in Figure 6 indicate that those ions that can associate with cellulose acetate through hydrogen bonding diffuse by a different

of hole-type diffusion to decrease. A comparison of dielectric constants and membrane resistances as a function of pressure should indicate whether or not the formation of bound water regions restricts hole-type diffusion. Such a comparison is made in Figure 7. The lower curve in Figure 8 represents the increase in hydrogen bonding with pressure. The close resemblance of the dielectric constant curve to the resistance curve of Cl^- does indicate that the bound water regions in cellulose acetate structure are responsible for the high membrane resistance or low diffusion rate of strong electrolytes.

The shift of the resistance-versus-pressure curve to the left was probably the result of hysteresis effects as the pressure was reduced.

Semipermeability of Cellophane

It was mentioned earlier that the low degree of semipermeability of cellophane is attributable to its low degree of crystallinity. A certain amount of force is required to overcome the Brownian motion of the cellulose polymers and to compress the system so that a cross linked water-cellulose structure can be set up. Crystallinity supplies force required for the formation of the desired structure. Cellulose acetate has a high degree of crystallinity, so only little additional pressure is needed to set up the bound water structure. With cellophane, however, much additional pressure is needed to accomplish the same result.

To learn whether or not the semipermeability of cellophane increases at higher pressures, the membrane resistances of H^+, Na^+, Cl^-, and NaCl were determined up to 5500 psi. These results are presented in Figure 8. The membrane resistance of H_3O^+ remained relatively constant as the membrane was compressed. In contrast, the resistance of Cl^- increased rapidly. Therefore, the semipermeability of cellophane should increase with pressure.

The semipermeability of cellophane has been determined up to 1500 psi. The salt rejection of cellophane did increase from about 8% at 600 psi. to 14% at 1500 psi.

Also included in Figure 8 are the membrane resistances of NH_4^+ and OH^- across cellophane. Whereas the passage of ions through cellulose acetate was influenced predominately by hydrogen bonding, the passage of ions through cellophane is influenced by the ion exchange properties of cellulose in addition to hydrogen bonding. Neale and Standing[13] have shown that the hydroxyl groups of cellulose may be regarded as weak monobasic acids thereby imparting cation permeable properties to cellophane. In cellulose acetate, however, most of the hydroxyl groups have been esterified so it behaves only slightly as an ion exchange membrane. The relatively low resistance of the cations across cellophane at higher pressures is attributed to the ion exchange properties of this film.

Since cellophane is more permeable to cations than anions, the effect of hydrogen bonding on membrane resistance can best be illustrated by comparing the resistances of those cations that can enter into hydrogen bonding with those that cannot. From Figure 8 it is seen that the resistances of NH_4^+ and H_3O^+ which can enter into hydrogen bonding are very low compared to that of Na^+.

Also the resistance of OH^-, which can associate with cellulose, is much lower than that of Cl^-, which cannot associate with cellulose.

On the basis of hydrogen bonding, the resistance of OH^- should be less than the resistance of Na^+ in cellophane, which is not the case. In a basic solution, the active hydrogens in cellulose are more highly ionized, which makes cellophane more highly resistant to the passage of anions. It is apparently for this reason that OH^- has a higher membrane resistance than does Na^+.

Since transference numbers are related to the relative resistances of individual ions in a system, the membrane resistance of a specific ion should serve as an index for the transference number of that ion in the membrane. For example, in cellophane above 1500 psi, the resistance of Cl^- is very high, yet the resistance of NH_4^+ is almost zero. Therefore, in a NH_4Cl solution, the transference number of NH_4^+ in cellophane should approach one above 1500 psi.

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Synopsis

The primary objective of this investigation has been to explain why cellulose acetate behaves as a semipermeable

membrane in saline water. To explain this phenomenon, two different mechanisms for the transfer to water and ions through cellulose acetate membranes were formulated. 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 polymers to form bound water regions is favored 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 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. Cellulose acetate begins to behave as an effective semipermeable membrane in saline water when it is compressed sufficiently to retard greatly the diffusion of NaCl. Several types of experiments were conducted to support these hypotheses. The most important evidence was obtained from resistance experiments. The electrical resistances of specific ions was measured across cellulose acetate at various pressures by using permselective membranes to prevent migration of the ion of opposite charge. It was observed that the rate of diffusion of those ions that cannot combine with the membrane actually does decrease as the membrane is compressed. The rate of diffusion of H_3O^+, which can enter into hydrogen bonding with cellulose acetate, is much higher and is not appreciably reduced as the membrane is compressed. These resistance-pressure relationships are correlated with the semipermeability of the cellulose acetate.

Résumé

Le principal objectif de cette étude a été d'expliquer pourquoi l'acétate de cellulose se comporte comme une membrane semiperméable dans l'eau salée. Pour expliquer ce phénomène, on a formulé deux mécanismes différents pour le transfert de l'eau et des ions à travers des membranes d'acétate de cellulose. Ces ions et molécules qui ne peuvent pénétrer par l'intermédiaire de liaison hydrogène au sein la membrane, sont transférés par des trous de diffusion. Il apparait que la vitesse de diffusion est gouvernée par une structure eau-acétate de cellulose. La réaction entre l'eau et les polymères cellulosiques, pour former des régions d'eau liée, est favorisée par compression de la membrane. Lorsqu'on applique une certaine pression sur la membrane, il y a beaucoup plus d'eau liée qui se produit et qui est la cause d'une diminution de la vitesse de diffusion. D'autre part, ces ions et molécules peuvent s'associer avec la membrane et être transportés à travers celle-ci par diffusion l'un derrière l'autre. La formation de la structure eau-acétate de cellulose ne diminue pas appréciablement la vitesse de diffusion de l'eau à travers la membrane. L'acétate de cellulose commence à se comporter comme une membrane semiperméable réelle dans l'eau salée quand elle est suffisamment comprimée que pour retarder la diffusion du NaCl. Plusieurs types d'expériences ont été réalisées pour étayer ces hypothèses. L'élément le plus important fut obtenu par des expériences de résistance. Les résistances électriques d'ions spécifiques ont été mesurées à travers de l'acétate de cellulose à diverses pressions en employant des membranes sélectivement perméables pour prévenir la migration d'ion de charges opposées. On a observé que la vitesse de diffusion de ces ions qui ne peuvent pas se combiner avec la membrane est diminuée quand la membrane est comprimée. La vitesse de diffusion de H_3O^+, qui peut former une liaison hydrogène avec l'acétate de cellulose, est beaucoup plus grande et n'est pas réduite appréciablement lorsque la membrane est comprimée. Ces rapports entre la résistance et la pression sont réliés avec la semiperméabilité de l'acétate de cellulose.

Zusammenfassung

Das ursprüngliche Ziel der vorliegenden Untersuchung war es, eine Erklärung dafür zu finden, warum sich Celluloseacetat in Salzlösungen als semipermeable Membran verhält. Zur Erklärung dieser Erscheinung wurden zwei verschiedene Mechanismen für den Durchgang von Wasser und von Ionen durch Celluloseacetatmembranen formuliert. Diejenigen Ionen und Moleküle, die keine Wasserstoffbindung mit der Membrane eingehen können, werden nach dem Typ einer Diffusion durch Löcher übertragen. Die Diffusionsgeschwindigkeit scheint durch eine Wasser-Celluloseacetatstruktur bestimmt zu werden. Die Reaktion zwischen Wasser und den Cellulosepolymeren, die zur Bildung von Bereichen mit gebundenem Wasser führt, wird durch Zusammenpressen der Membrane begünstigt. Wenn Druck auf die Membrane ausgeübt wird, wird mehr gebundenes Wasser erzeugt, was zur Herabsetzung der Diffusion vom Loch-Typus führt. Andrerseits werden diejenigen Ionen und Moleküle, die sich mit der Membrane assoziieren können, durch dieselbe mittels einer Diffusion vom gerichteten Typus transportiert. Die Bildung der Wasser-Celluloseacetatstruktur ruft keine merkliche Herabsetzung der Diffusionsgeschwindigkeit des Wassers durch die Membrane hervor. Sobald Celluloseacetat genügend zusammengepresst wird, um die Diffusion von NaCl stark zu verzögern, beginnt es sich in Salzlösungen als eine wirksame semipermeable Membrane zu verhalten. Zur Stütze dieser Hypothese wurde eine Reihe von Versuchen ausgeführt. Die wichtigsten Belege wurden aus Versuchen über den elektrischen Widerstand erhalten. Der elektrische Widerstand spezifischer Ionen wurde bei verschiedenen Drucken quer durch das Celluloseacetat unter Benützung permselektiver Membranen zur Verhinderung der Wanderung des Ions entgegengesetzter Ladung gemessen. Es wurde beobachtet, dass die Diffusionsgeschwindigkeit derjenigen Ionen, die sich nicht mit der Membrane verbinden können, tatsächlich abnimmt, sobald die Membrane zusammengepresst wird. Die Diffusionsgeschwindigkeit von H_3O^+, das mit Cellulose acetat Wasserstoffbindungen eingehen kann, ist viel höher und wird durch Zusammenpressen der Membrane nicht merklich verringert. Diese Widerstand-Druckbeziehungen werden mit der Semipermeabilität des Celluloseacetats in Beziehung gebracht.