

## **Semipermeable Membranes of Cellulose Acetate for Desalination in the Process of Reverse Osmosis.**

### **III. Bound Water Relationships\***

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#### **Synopsis**

The mechanism by which water and dissolved salts permeate selectively through membranes has been investigated. It has been demonstrated that the predominant mechanism of permeation involves the interaction of the various species with specific sites and their associated bound water molecules. The extent of the bound water held by the cellulosic membranes of interest has been determined. Correlation has been found between the permeation characteristics demonstrated by membranes at various steps in their preparation and its bound water content. The mechanism of rejection of salts has been shown to be related to the relative inability of their ions to become solvated by bound water. A model has been hypothesized which correctly describes the behavior of the desalination membrane with reference to water and soluble inorganic salts.

#### **I. INTRODUCTION**

The phenomenon known as "reverse osmosis" has in recent years received a great deal of attention because of its potential as a practical process for demineralization of saline waters. However, little progress has been made in understanding the mechanism of the process.

Reverse osmosis is the name given to the transport of a pure solvent across a semipermeable membrane caused by the application of pressure on solute-containing solution. Overwhelming evidence has been obtained in these laboratories with saline water systems which demonstrate that the gross mechanism of material transport through semipermeable cellulosic membranes must derive from interaction of the permeant species with the membrane.

It will be demonstrated that "bound" water in the membrane, by virtue of its interaction with the active sites (principally OH groups in the cellulosic structure), is unable to solvate salts appreciably, and consequently salt permeation is prevented. It will be also shown that the "bound" water does, however, retain the ability to form ligands with free water

\* This work was supported by the Office of Saline Water, U.S. Dept. of the Interior, Contract Nos. 14-01-0001-272 and 14-01-0001-378.

molecules and subsequently permit migration of the free water from site to site through the membrane. The studies described herein are concerned with the evidence for the existence of the bound water and its relationship to the ability of a membrane to permit the transport of pure water across its structure.

In order to explore the hypothesis the bound water is responsible for the selective permeation of various species through the membranes, three distinct experimental approaches were undertaken.

First, evidence of the existence of bound water was sought. It is to be expected that the bound water would demonstrate a greater tenacity for the membrane than would superficially held water. This was studied initially by carrying out an isothermal distillation of the water from the membrane by using high vacuum techniques. This approach was subsequently replaced by a demonstrably equivalent but markedly simpler and more rapid procedure of drying the membrane to a cobalt salt hydrate endpoint. The membranes were studied at different stages of their preparations with the use of varying amounts of membrane salt for which it has been established that a relation existed with the gross water content of the finished membrane.<sup>1</sup>

Second, a series of permeation studies was performed on the variously prepared membranes with the use of a saline-water solution in order to establish correlation between the selective permeation and the bound water content.

Third, the selection-rejection premise was further explored by performing a series of selective permeation studies on a given membrane with aqueous solutions of various combinations of cations and anions.

As a result of these studies, it has been concluded that some of the water is strongly bound to the membrane and is experimentally distinguishable from superficially held water. Further, the evidence clearly indicates that the greater the extent of bound water per site, the higher the flux rate of pure water through the membrane. The different permeations of specific ions strongly supports the premise that the rejection ability of the membranes of interest for the salts studied derives from the inability of these ions appreciably to solvate (form ligands) with the bound water. Finally, the small amount of salt transport which does occur through membranes whose surfaces are free of macroscopic imperfections is attributable to a diffusive permeation by participation of the salt ions with the membrane's bound water structure. From these results, it has been possible to develop a model for the membrane which is consistent with its behavior at the various stages of its preparation and with its ultimate performance in demineralizing saline solutions. This model *a priori* assumes the presence of specific permeation sites as responsible for selective permeation, and, for simplicity, presupposes a total permeation versus rejection with respect to the presence of the sites and their associated bound waters. In reality, of course, there are probably various degrees of permeability and rejection dependent upon the extent of the bonding of

"secondary" water molecules on the sites. These refinements will be considered in more detail later.

## II. EXPERIMENTAL

### Evidence for Bound Water

Initially the bound water was determined by an isothermal distillation. The vapor pressure of the water in the membrane was measured at a constant temperature as a function of the water content of the membrane. Because of its association, water bound to the polymer has a lower vapor pressure than that which is not bound, and a break appears in a curve of the vapor pressure as a function of the membrane water content. In practice this method was tedious because of the time required to establish equilibrium, especially in the lower vapor pressure ranges. With the long equilibration times, the system was prone to those difficulties that arise when a vacuum must be maintained for long periods of time.

A more expedient technique was adapted from the method of Hatschek<sup>2</sup> for determining the bound water in gelatin gels. It is based on the color difference of the various hydrates of cobaltous chloride and their degree of hydration by the water in the gel and consequently is directly related to the problem of ion hydration. The hexahydrate is red, the dihydrate is lavender, and the monohydrate and anhydrous forms are blue. Hatschek found that, upon drying, a gelatin film containing the pink cobaltous chloride hexahydrate turned blue before it lost all its water. Because it was not free to hydrate the cobaltous chloride, the water left in the gel after the color changed was termed bound water by Hatschek. Similarly, cellulosic membranes demonstrate this same behavior in that a membrane colored by immersing it in the pink cobaltous chloride solution changes color before it loses all its water in the same manner as the gelatin gel.

It was subsequently established that the results obtainable by the isothermal distillation techniques were also obtainable by the drying technique.

**Membrane Preparation.** The preparation of the cellulose acetate membranes which have been employed in this work has been described elsewhere.<sup>3</sup>

**Isothermal Distillation.** The isothermal distillation apparatus consisted of a sample flask connected through a standard high vacuum system to an expansion chamber, a mercury manometer, and a vacuum pump. The apparatus was immersed in a constant temperature water bath controlled to within 0.2°C. The mercury level in the manometer was read through the glass walls of the thermostat with a cathetometer. The water vapor was collected in a tared trap, cooled in a Dry Ice-acetone bath.

With the system thermostatted at  $25.0 \pm 0.1^\circ\text{C}$ ., the water vapor from the weighed membrane sample was expanded into the expansion chamber. Periodic vapor pressure measurements were taken while the system was equilibrating. Upon equilibration the vapor pressure was measured, and the membrane was isolated. The water vapor was col-

lected and weighed in the cold trap. This procedure was repeated until the vapor pressure approached zero. Prior to the measurements, the membrane sample was degassed at 0°C. to avoid freezing thereof and thus maintain the character of the membrane structure.

**Cobaltous Chloride Drying Method.** Membrane samples used in the cobaltous chloride bound water determination were immersed in a 20% cobaltous chloride hexahydrate solution for 2 hr. Those membranes that had been pressurized on the testing apparatus (and were therefore compressed) had to be immersed overnight in order to let the solution diffuse through the bulk of the membrane. The excess solution was blotted off. The blotting technique was patterned after that described by Neale.<sup>4</sup> The samples were supported above a white background to air-dry. After about 1 hr., the samples changed from the pink color of the cobaltous chloride solution to the lavender color of the dihydrate, at which time they were weighed in the lavender state and then dried in an oven for 1 hr. at 105°C. The bound water was driven off by the oven drying, and the dihydrate reduced to the bright blue monohydrate. The membrane was weighed in the blue state, after which it was leached in water overnight to remove the cobaltous chloride. The dried membrane was weighed again to obtain the weight of the polymer. The difference between the membrane weight in the lavender state and in the blue state constitutes the bound water in the membrane. A small correction for the water hydration was subtracted from the bound water by calculating, from the amount of cobaltous chloride leached out of the membrane, the difference in weight of the dihydrate and the monohydrate. These determinations were repeated with the membranes at various stages of their preparation, and/or utilization, i.e., before and after thermal conditioning and finally after being utilized at 102 atm. for permeation studies.

### Water Permeation

In order to explore correlation between bound water content and selective permeation, membranes whose bound water content was evaluated according to the procedures described in the previous section were utilized in controlled saline water permeation studies. By analysis of the feed and effluent streams, it was possible to evaluate the ability of a given membrane to pass water selectively (while rejecting the salt dissolved in the water) as a function of the bound water content.

A 0.6*M* aqueous solution of salt was fed at 102 atm. to the membranes being evaluated according to the procedure described in the previous paper.<sup>1</sup> The salt content was analyzed with the aid of a calibrated conductor bridge (Sol. Bridge RD-178, Industrial Instruments Inc.). The flux data are expressed as milliliters per square centimeter per day, and the permeation data as per cent retention, i.e., 100 (1 - conductivity of product solution/conductivity of feed solution).

### Salt Rejection

In order to explore the hypothesis that the ability of the cellulosic membranes to reject salt dissolved in water was related to the ability of the already solvated ions in solution to interact with the bound water in the membrane, a series of permeation experiments was performed with equivalent solutions of different salts. The salts were selected on the basis of the differences in their tendency to solvate with the water molecules. It was believed that the differences in the salt rejection behavior of the membrane would throw some light upon the controlling mechanisms. For this study, 0.6*M* solutions of the potassium and sodium halides were employed. The salt retentions were determined according to the previously described procedure.

## III. DISCUSSION AND RESULTS

### Bound Water Content

In the attempt to determine the bound water content of the membranes of interest it became apparent that the isothermal distillation procedure, although rigorously valid, was exceedingly tedious and time-consuming. Consequently the alternative and more easily consummated technique of drying to the cobalt chloride endpoint was explored. In order to justify the substitution, it was necessary to establish the equivalence of the two approaches. That this was true is substantiated by comparing the data in Figure 1 obtained by both techniques on equivalent membrane samples. Here it is clear that the endpoint in the drying procedure occurs at the point where essentially all of the superficially held water, which yields normal vapor pressure, has been removed but the bound water, which is

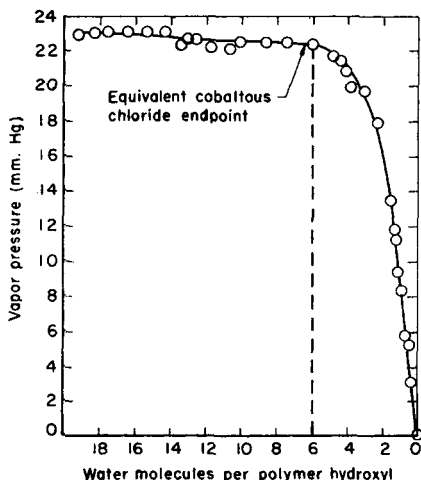


Fig. 1. Isothermal distillation.

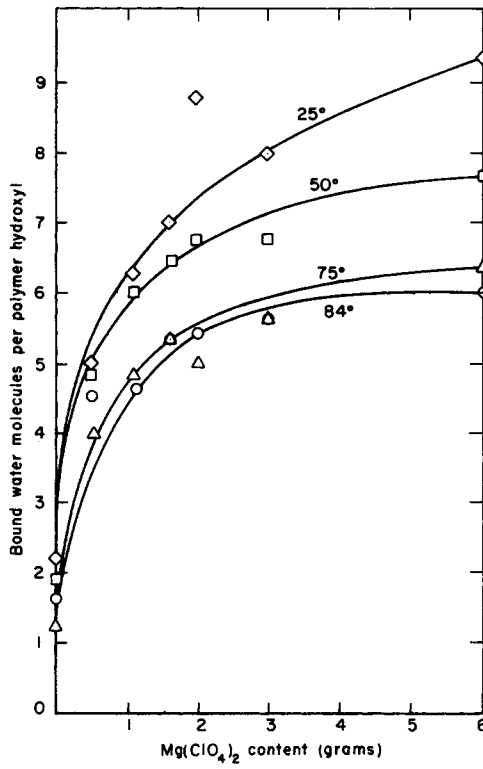


Fig. 2. Bound water vs. membrane salt content (unpressurized membranes).

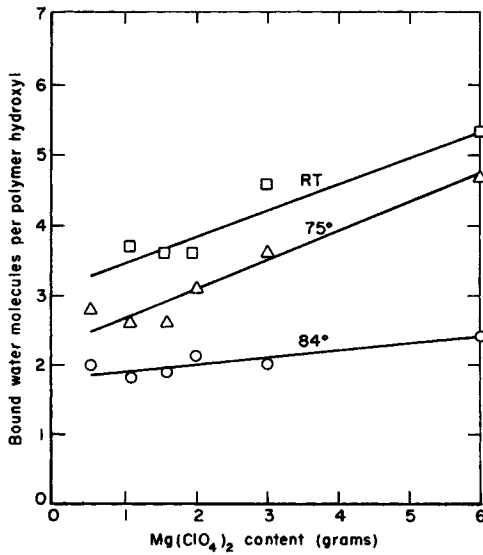


Fig. 3. Bound water vs. membrane salt content (pressurized membranes).

associated with the lower vapor pressure, still remains in the membrane. Subsequently the drying technique superseded the distillation technique in most of the bound water studies carried out. The bound water determinations are summarized in Tables I and II and in Figures 2 and 3. The data were determined with a precision of about 10%.

TABLE I

Bound Water Molecules per Cellulosic Hydroxyl Group on Unpressurized Cellulose Acetate (2.33 D.S.) Membranes Receiving Thermal Treatment at Various Temperatures

Mg(ClO <sub>4</sub> ) <sub>2</sub> content, g. <sup>a</sup>	Bound water molecules/hydroxyl			
	25°C.	50°C.	75°C.	84°C.
0.0	2.2	1.8	1.2	1.6
0.5	5.0	4.8	4.0	4.5
1.1	6.2	6.0	4.8	4.6
1.6	7.0	6.4	5.3	5.3
2.0	8.7	6.7	5.0	5.4
3.0	8.0	6.7	5.6	5.6
6.0	9.4	7.6	6.3	6.0

<sup>a</sup> Remainder of casting solution constant as follows: cellulose acetate, 22.2 g.; acetone, 66.7 g.; water, 10.0 g.; Mg(ClO<sub>4</sub>)<sub>2</sub>, variable.

TABLE II

Bound Water Molecules per Cellulosic Hydroxyl Group and Desalination Characteristics of Pressurized (102 Atm.) Cellulose Acetate (2.33 D.S.) Membranes

Mg(ClO <sub>4</sub> ) <sub>2</sub> content, g.	Treatment at 25°C.			Treatment at 75°C.			Treatment at 84°C.		
	H <sub>2</sub> O OH	Flux, ml./cm. <sup>-2</sup> day	Salt reten- tion, %	H <sub>2</sub> O OH	Flux, ml./cm. <sup>-2</sup> day	Salt reten- tion, %	H <sub>2</sub> O OH	Flux, ml./cm. <sup>-2</sup> day	Salt reten- tion, %
0.5	3.3	326	31	2.8	102	92	2.0	47	98.6
1.1	3.7	452	11	2.6	159	84	1.8	53	97.7
1.6	3.6	477	6	2.6	155	54	1.9	53	98.0
2.0	3.6	627	0	3.1	246	18	2.1	73	94.4
3.0	4.6	619	3	3.6	603	3	2.0	94	85.0
6.0	5.3	477	0	4.6	615	0	2.4	350	0.0

Since bound water is believed to associate primarily with hydroxyl groups, its concentration is expressed in terms of the number of bound water molecules per cellulosic hydroxyl groups and calculated according to the relationship

$$\frac{\text{H}_2\text{O}}{\text{OH}} = \frac{21.5 [(\text{lavender wt.}-\text{blue wt.}) - 0.122(\text{blue wt.}-\text{leached wt.})]}{\text{leached wt.}}$$

The number of hydroxyl groups is based on 2.30 acetyl degree of substitution cellulose acetate, corresponding to a molecular weight of 260 for a single acetylated glucose moiety. The second term in the numerator,

0.122(blue-leached), is the correction for the water of hydration that is removed along with the bound water in heating the membrane to 105°C.

From these data, it can be seen that the maximum number of water molecules per hydroxyl group was 9.4. This maximum occurs with an unheated membrane made from a casting solution containing 6.0 g. of  $\text{Mg}(\text{ClO}_4)_2$ , the amount that gives the swelling limit for this system.<sup>1</sup> The minimum quantity of bound water in a useful membrane (excluding membranes cast with solutions containing no membrane salt) was found to be 1.8  $\text{H}_2\text{O}/\text{OH}$ . This value was obtained with membranes fabricated from a solution containing 0.5 g.  $\text{Mg}(\text{ClO}_4)_2$  heated to 84°C. and pressurized to 102 atm. on the desalination testing apparatus. It may be noted that pressurizing decreased the bound water by 2-4 molecules/hydroxyl group. Increasing the thermal treatment temperature also reduced the bound water by 1-4 molecules/hydroxyl. By heating a membrane to 84°C. and pressurizing it to 102 atm., a limiting value of 2 molecules water/hydroxyl was reached. This value was found to be independent of the membrane salt concentration in the casting solution from which the membrane is fabricated. Because there seems to be a limiting value of 2 bound water molecules/hydroxyl, these two molecules might be termed primary bound waters. The additional molecules up to the maximum of nine may be termed secondary bound waters.

Because of their low water content, membranes made from solutions containing no membrane salt were difficult to dye with cobaltous chloride. The unpressurized membranes adsorbed a small amount of dye but not enough to permit the color changes to be detected. When drying they were included with the rest of the series, and the color change was determined by the color change of the others in the series. The pressurized membranes, having had the small amount of capillary water present removed through compression, would not take the dye at all, and consequently there are no results for this series. An attempt was made to determine the quantity of bound water in very thin membranes. Thin membranes are believed to consist entirely of active layer structure,<sup>3</sup> since attempts to dye them with the cobaltous chloride solutions were unsuccessful. A small amount of cobaltous chloride solution adhered to the surface, but was easily removed with a damp tissue. Consequently, any water present either in a very thin membrane or in the active surface of normal membranes then must be bound water, for it is not free to solvate the cobaltous chloride.

**Effects of Temperature.** The overall water content of semipermeable membranes of secondary cellulose acetate has been shown to diminish with increasing temperature owing to syneresis of the gel structure.<sup>3</sup> From Tables I and II it can be seen that the bound water content of the membrane decreases in a similar manner as the thermal treatment temperature is increased. A membrane has its bound water decreased by an average of 27% by increasing the thermal treatment temperature from 25 to 84°C. The reduction values ranged from 10 to 40%, representing a decrease of



2-4 water molecules/hydroxyl group. With these data, it is possible to interpret the irreversible nature of the thermal treatment step in the fabrication of useful selective permeation membranes as follows.

The mobility of the membrane-water system is increased by the additional thermal energy, and those bound water molecules which are loosely held overcome their binding forces and are set free. Because of their increased mobility, the polymer chains, and hence their polar crosslinking sites, are brought into closer proximity with each other. Additional stable crosslinks are formed, thereby irreversibly reducing the free volume in the polymer matrix. The water which is not bound to the polymer is squeezed out by this compaction. Because of the increased crosslink density and the subsequent reduction in volume and accessibility, the bound water content of the membrane cannot be restored to the level which was obtained prior to the heat treatment.

**Effect of Pressure.** Bound water is affected by pressure in a manner similar to temperature. Pressure reduced the bound water content of the unpressurized membrane by an average of 44% when it was subjected to pressures of 102 atm. The range of reduction was 22-65% or 1-5 water molecules/hydroxyl group. Compression of the membrane forces a large amount of the nonbonded (capillary) water and some of the bound water out of the gel structure.<sup>3</sup> The polymer chains are thus brought closer to each other, and additional crosslinks are formed. These crosslinks decrease the volume available to the bound water aggregates, and they therefore are reduced in size.

It is noteworthy that this effect is contrary to the conclusion of Reid and Koppers<sup>5</sup> that pressure increases the amount of bound water. This apparent inconsistency may be rationalized by realizing that they may have used a somewhat different system. Their compressive deformation studies were made on cellulose acetate (40% acetyl) films cast from an acetone solution and dried. Casting from an unmodified acetone solution and drying produces a highly crosslinked, inaccessible membrane. This type of membrane would be more highly crosslinked than the modified membrane used for the studies described in this paper. In the present study the semipermeable membranes have not been allowed to dry out, but have remained instead in their swollen condition prior to being subjected to pressure. Under such conditions the maximum accessibility of the hydroxyl groups will have been determined by such steric configurations as were prevalent in the primary gel structure.

Reid and Koppers compressed their membranes from 24 to 999 psi stepwise and then relaxed them stepwise back to 24 psi. This cycle was run several times. They found that when a membrane which was swollen with water at 24 psi for 24 hr. was in contact with excess moisture during the compression cycles, it started to swell after 2 cycles. Bound water then was being formed. This increase in bound water in this system is due to the rupturing of some of the crosslinks caused by the pressure cycling stresses and the increased accessibility of the membrane. These

ruptured crosslinks are then sites that are able to bind water. The new bound water is of the primary type and cannot be removed by further pressurizing cycles. But more crosslinks are ruptured by further pressurizing cycles, and more sites to bond water are produced. The difference in conclusions then is due to the difference in systems. The highly swollen membrane used for this study has some of its capillary water and some of its bound water forced out of it by the pressure. The highly crosslinked membrane with its limited degree of accessibility has some of its crosslinks broken down and hence its accessibility increased, and more bound water is formed.

The only circumstance under which the application of pressure to a swollen membrane could effect an increase in the amount of bound water would be one in which the volume of the complexes between bound water and the free cellulosic hydroxyl groups decreased below that of the sum of the partial molal volumes of the unassociated species. Although such a concept had previously been hypothesized on the basis of increased density observed for cellulose-bound water complexes,<sup>6</sup> more recent interpretations relate increases in density coincident to the application of pressure to decreases in the free volume in the polymer structure.<sup>7</sup>

Recall that when a membrane is subjected to both a thermal treatment at 84°C. and compression at 102 atm., the bound water content is nearly constant at 2 molecules water/hydroxyl, no matter what the membrane salt concentration was in the casting solution (Fig. 3). These two molecules are probably the primary bound waters and are hydrogen-bonded directly to the hydroxyl group of the cellulose acetate. Rowen and Plyler<sup>8</sup> have given infrared evidence for the formation of two hydrogen bonds per hydroxyl group of cellulose. The other bound waters (secondary) may be grouped about these primary bound waters. The primary bound waters are, of course, more tightly held than the secondary waters.

### Water Permeation and Bound Water Content

The determinations of the selective permeability of the salt solutions through the cellulosic membranes as a function of their bound water content are summarized in Table II. These data were derived from the permeation studies and from the "drying" procedures performed on the membranes used. The quantity of initial membrane salt required to prepare the various membranes are included for reference, since certain conclusions can be reached concerning their role in determining the extent of bound water content. The amount of water permeating the membrane by solution may be calculated by neglecting the permeation of salt which occurs by solution and assuming that all of the salt is accountable in terms of the original solution leaking through the membrane. This assumption is not valid, as will shortly become evident, but is permissible since only a small error in the estimation of the permeation of water by solution is thereby introduced. It can be seen from Table III that there is a correla-

TABLE III  
Bound Water and the Water Flux

Bound water $H_2O/OH^a$	Average calculated water flux by solution, ml./cm. <sup>-2</sup> -day	Average total water flux, ml./cm. <sup>-2</sup> -day
1.8	53	53
1.9	53	53
2.0	61	70
2.1	69	73
2.6	102	157
2.8	94	102
3.3	102	326

<sup>a</sup> Data were rejected for which the salt retention was less than 30% because of the excessive error introduced into the corresponding water fluxes owing to large contributions from viscous flow.

tion between the calculated number of bound water molecules per cellulosic hydroxyl group and the amount of water which permeates the membrane by solution. This may be interpreted as implying that the water in the feed solution permeates by virtue of its participation with the "bound" water complex. The beginning of divergence between the solution water flow and the total water flux which occurs at 2.1 bound waters/hydroxyl group indicates the point at which membranes are becoming porous enough to permit some viscous flow. Material transport by viscous flow permits the passage of capillary water together with hydrated salt ions and results in a substantial decrease of salt retention capacity.

Some consideration should be given to the reasons for the increase in bound water with increasing membrane salt concentration. The degree to which a membrane gel is swollen and the existence of a swelling limit have been found to be related to the concentration of the membrane salt in the casting solutions of these gels.<sup>1</sup> For those membrane salt concentrations below that which is necessary to produce the swelling limit, gel structures will be formed, some of whose hydroxyl groups will participate in crosslinking. Such crosslinked groups will possess a completely or partially diminished capacity for hydrogen bonding with water. As a consequence, both the total amount of water and the bound water contained in the gel structure will be determined by the available ligand-forming ability of the polymer hydroxyl groups.

A second factor which helps to account for the presence of increasing amounts of bound water as the swelling limit is approached is the fact that, since the volume contained by a gel increases with its degree of swelling, additional space is provided for the inclusion of secondary spheres of bound water (chiefly about the free polymer hydroxyl groups). As has been discussed in the second paper of this series, it appears probable that the water in cellulosic esters is associated to a much greater extent with hydroxyl than with ester groups.<sup>3</sup>

It has been stated that the water permeates the membranes by virtue of interaction with the bound water and that salt is prohibited from permeating by virtue of its inability to ligand with the bound water. Whereas the tightly held (or primary) bound waters appear to have no capacity to solvate salt ions, the less tightly held (or secondary) bound water molecules may retain some ability to solvate the salt. Consequently one anticipates some salt permeation by diffusion where the secondary bound waters are present. This is supported by the observation that the salt rejection behavior of a membrane is increased with increasing feed solution pressure and that the evidence clearly indicates the secondary but not the primary bound waters can be displaced from the membranes by increasing the pressure. In the overall view it is, therefore, valid to state that the salt is prohibited from permeating the membrane because of its inability to ligand with the bound water. However, closer scrutiny reveals that a small amount of salt does permeate by solution and that the degree of permeation is dependent on the nature of the salt. This subject is the topic of the next section.

### Salt Rejection and Bound Water Content

The permeations of a series of sodium and a series of potassium salts through membranes of secondary cellulose acetate have been employed for this study and the results are summarized in Table IV. Several considerations render it extremely unlikely that salt permeates the membrane by simple filtration. In the first place, the differences between the hydrated ionic radii of the halogens appear too slight (and are sometimes in the wrong direction) to account for the twentyfold difference in permeation which is observed (Table IV). Secondly, whereas the flux of water through porous membranes is affected by the nature of the salt in solution, no such effect is noticed when membranes possessing a truly semipermeable or nonporous surface is employed. This finding indicates that viscous flow of water is occurring through porous membranes.

It is an experimentally established fact that salt permeation occurs most readily in the case of salts in which both ions in the saline solution are relatively unsolvated by the water (Table IV). Since that portion of the membrane which is capable of desalination contains only bound water, part or all of whose capacity for solvation of ionic species is absent as a result of the hydrogen bonds formed between it and free cellulosic hydroxyl groups, it appears quite plausible that those ions which are most highly solvated, such as the  $F^-$  ion, will encounter the greatest amount of difficulty in diffusive permeation involving participation with the bound water held by the membrane. This is so because more energy is required to dislodge spheres of water held by a tightly hydrated ion than those held by a loosely hydrated ion. Existence in a relatively unsolvated condition is necessary before an ion can permeate the membrane by virtue of solvation by its bound water structure. This analysis is in agreement with Samoilov's theory of differential solvation spheres.<sup>9</sup> Whereas the mobilities of highly

TABLE IV  
Permeation of Various Salt Species

Salt species	Ionic radii, Å.				Water flux, ml./cm. <sup>2</sup> -day				Salt retention, % <sup>a</sup>	
	Cation		Anion		Solution membrane <sup>b</sup>		Viscous flow membrane <sup>c</sup>		Solution	Viscous flow
	Hydrated	Crystal	Hydrated	Crystal	H <sub>2</sub> O feed	Saline feed	H <sub>2</sub> O feed	Saline feed	Membrane <sup>b</sup>	Membrane <sup>c</sup>
NaF	3.58	0.95	3.52	1.36	120	76	—	—	99.5	—
NaCl	3.58	0.95	3.52	1.81	120	76	—	—	98.4	—
NaBr	3.58	0.95	3.30	1.95	120	76	—	—	95.5	—
NaI	3.58	0.95	3.31	2.16	120	76	—	—	93.6	—
KF	3.58	1.33	3.52	1.36	120	76	696	488	99.0	33.4
KCl	3.58	1.33	3.32	1.81	120	76	696	572	97.2	16.6
KBr	3.58	1.33	3.30	1.95	120	76	696	604	95.1	—
KI	3.58	1.33	3.31	2.16	120	76	696	648	89.9	14.0

<sup>a</sup> H<sub>2</sub>O feed = distilled water at 102 atm.; saline feed = 0.6M at 102 atm.

<sup>b</sup> Casting solution composition: cellulose acetate, 22.2; acetone, 66.7; water, 10.0; ZnCl<sub>2</sub>, 5.0. Immersed in water at 0°C. 3 min. after casting at -11°C. Heated at 86°C. for 5 min. No material transport by viscous flow.

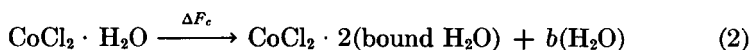
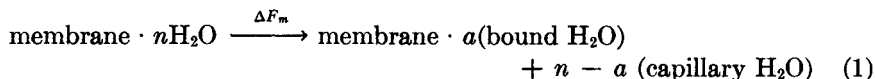
<sup>c</sup> Differs from solution membrane in that the cast film was unheated. A substantial amount of material transport by viscous flow.

hydrated ionic species are functions of their radii of hydration, the crystal radii tend to become limiting factors for weakly hydrated species (Table IV).

From what has been said, it is evident that an analysis on the basis of salt transport by solution appears to be far more consistent with the facts than an explanation on the basis of an ultrafiltrative separation by virtue of small differences in hydrated ionic radii. In the case of salt such as KF which is composed of two ions, one of which,  $K^+$ , is relatively unhydrated and the other,  $F^-$ , hydrated, the failure of the hydrated ion to become solvated by the bound water will prevent the permeation of its oppositely charged counterpart in order that electroneutrality may be maintained. The preceding discussions serve to explain the relative permeability of a series of inorganic salts through semipermeable membranes; it must be stressed, however, that even in the case of KI, a salt retention of almost 90% has been achieved. The detailed mechanism whereby water and other species capable of liganding permeate semipermeable membranes of cellulose acetate is the subject of the next paper in this series.

### Consideration of Energetics

It has been experimentally verified that the method of isothermal thermal distillation and cobaltous chloride techniques for the determination of bound water in the membrane yield equivalent results (Fig. 1). It follows, therefore, that the change of free energies (a measure of the escaping tendency of the water) of the two systems must be equivalent. Since, however, the values for the heats of absorption of water by cellulose acetate and by cobaltous chloride are of the order of 12 and 27 kcal./mole of water, respectively,<sup>10,11</sup> the change of entropies for the two systems at the temperature of interest must exactly compensate for the differences in the heats of absorption. One can thus equate the free energy changes for the two systems



as follows:

$$\Delta F_m = \Delta H_m - T\Delta S_m = \Delta H_c - T\Delta S_c = \Delta F_c \quad (3)$$

Although a measure of the  $\Delta H$ 's is available, the  $\Delta S$ 's of neither process have been studied. Consequently, it is not possible at the present time to estimate the relative degrees of ordering in the hydrated species. This brief treatment, however, does indicate that further studies of the cobalt or the membrane system might permit the development of a reasonably complete thermodynamic picture of the systems of interest. At this

point a model may be described which is consistent with the observed relationships involving bound water and permeation data.

### The Bound Water Model

The swollen polymer structure is a three-dimensional network of cellulose acetate chains which are linked together via dipole interactions between acetate groups, and to some extent via hydrogen bonding between acetate and hydroxyl groups of neighboring chains. Between the crosslinked sites are acetate groups, hydroxyl groups, and water. Although the acetate groups are largely unhydrated, each free hydroxyl group in the primary gel structure of the active layer of the membrane encompasses two molecules of primary and a maximum of seven molecules of secondary bound water within its solvation sphere. The primary gel permits salt permeation because it contains secondary bound water which is capable of solvating salt ions. The secondary gel, which is formed from the primary gel by the application of heat and pressure on the other hand contains only water of the primary bound type and, therefore, is much less capable of accommodating salt ions. Water and a limited small amount of salt, however, may still permeate the active layer of the membrane by a solution mechanism, involving participation with the bound water structure.

The authors would like to thank the Office of Saline Water, U.S. Department of the Interior for their support of this study. They would also like to express their gratitude to Dr. B. Keilin for his stimulating discussions and critical evaluations.

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### Résumé

Nous avons étudié le mécanisme par lequel l'eau et les sels dissous traversent sélectivement une membrane. Il est démontré que le mécanisme prédominant de la perméation, implique une réaction entre différents agents et entre des sites déterminés, associés avec des molécules d'eau liée. La quantité des molécules d'eau liée a été déterminée pour des membranes présentant un intérêt spécial. Une relation a été découverte entre le contenu en eau liée et les caractéristiques de perméabilité montrées par les membranes à diverses étapes de leur préparation. Le mécanisme de réjection des sels est en relation avec

l'impossibilité relative de leurs ions de passer en solution dans l'eau liée. Nous avons réalisé un modèle hypothétique qui décrit le comportement des membranes en relation avec l'eau et les sels inorganiques solubles.

### Zusammenfassung

Der Permeationsmechanismus für Wasser und gelöste Salze durch halbdurchlässige Membrane wurde untersucht. Es wird gezeigt, dass der Haupttransportmechanismus mit der Affinität gewisser Verbindungen für spezifische Polymergruppen und deren gebundene Wassermolekul zusammenhängt. Die Menge des an Zelluloseacetat gebundenen Wassers wurde bestimmt. Ein Zusammenhang zwischen den Transportphänomenen und dem Gehalt an gebundenem Wasser während der verschiedenen Operationen wurde gefunden. Der Mechanismus für die Salzabstossung hängt mit der Unlöslichkeit der Salze in gebundenem Wasser zusammen. Ein Modell, welches das Verhalten der Entsalzungsmembrane gegen Wasser und lösliche anorganische Salze korrekt beschreibt, wird diskutiert.

Received October 12, 1964