

## Hyperfiltration Studies. III. Effect of Certain Metal Ions on the Salt Filtration Properties of Cellophanes\*

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### Synopsis

The salt rejection properties of cellophanes are substantially increased, and permeation rates decreased, by pretreatment with certain metal ions or presence of these ions at low concentration in feed solutions. In a typical case, a cellophane which initially rejected about 20% of salt from a 0.05M NaCl solution rejected over 70% in presence of  $10^{-3}M$  ThCl<sub>4</sub>. Permeation rates were decreased, usually by a factor of 2 or 3. Additives found to have a marked effect were Fe(III), Th(IV), U(VI), Cu(II), Zr(IV), and hydrolyzed Pb(II). Mg(II), Ba(II), La(III), and unhydrolyzed Pb(II) had little effect. The mechanism by which the additives affect the cellophane is not clear.

Cellophane (regenerated cellulose) membranes have been known at least since the 1930's to filter low molecular weight solutes from solutions forced through them under pressure.<sup>2,3</sup> The fraction of salt rejected by cellophane, however, is low, except at low concentrations, below a few hundredths molar. The rejection has been attributed<sup>4</sup> to ion exclusion resulting from a small cation-exchange capacity of the cellophane, an explanation in qualitative agreement with the strong dependence of rejection on feed concentration, and the greater rejection of Na<sub>2</sub>SO<sub>4</sub> than of NaCl at a given (equivalent) concentration. Others have postulated a sieving<sup>5</sup> or somewhat similar process,<sup>6</sup> in which water migrates through the membrane by successive hydrogen bond formation, at a rate faster than that of salt.

Reid and Koppers<sup>6</sup> found that cellophane mercerized with NaOH solution and then treated with cupric acetate was far less compressible when wet than the original unmercerized wet cellophane, and further, that the copper-treated cellophane rejected substantially more salt than the untreated. Other investigators<sup>7</sup> report that treatment of cellophane with ZnCl<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and LiClO<sub>4</sub> raises salt rejection, sometimes to values as high as 99%, and depresses permeation rates, e.g., from 0.5 cm./hr. at 1000 psi to less than 0.1 cm./hr.

\* Previous paper see Kraus et al.<sup>1</sup>

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We report here an investigation of the effects of certain metal ions on the hyperfiltration properties of cellophane. We do not understand the mechanism of action of these additives, nor is their effect precisely reproducible. However, similar changes in properties occur with many different additives, and the effects are large. We believe these effects differ from those obtained by impregnation of cellophanes with insoluble salts,<sup>8</sup> such as AgCl or BaSO<sub>4</sub>.

## EXPERIMENTAL

### Equipment

Hyperfiltration measurements were made with equipment previously described.<sup>9</sup> A feed solution under pressure is circulated past a membrane, and the permeating solution is analyzed to determine the rejection  $R$

$$R = \frac{m_f - m_\omega}{m_f}$$

where  $m$  is concentration in moles/kg. H<sub>2</sub>O, the subscript  $\omega$  indicating the effluent or product solution, and  $f$ , the feed solution. The circulation past the membrane is kept fast enough essentially to eliminate concentration buildup of the solute at the high-pressure interface of the membrane (designated by subscript  $\alpha$ ) as salt is rejected, i.e., to keep  $m_\alpha = m_f$ .

### Cellophanes

The properties of the cellophanes used are summarized in Table I. We used Visking dialysis tubing in most experiments. The Schleicher and Schuell membranes were received wet from the supplier.

TABLE I  
Properties of Base Cellophanes

Cellophane	Thickness, $\mu$		Vol. fraction water, wet <sup>a</sup>	Nominal pore size, m $\mu$
	Dry	Wet <sup>a</sup>		
Visking dialysis tubing	16	45	0.67	
Schleicher and Schuell 08		73	0.70	5
Schleicher and Schuell 05		129	0.87	20-35
du Pont 300 HPT	20	49	0.71	
du Pont 300 APT	20	47	0.70	
Union Carbide wet gel <sup>b</sup>		77	0.80	
Union Carbide dry gel <sup>b</sup>	16	45	0.71	
Zenith Blanc <sup>c</sup>	20	38	—	

<sup>a</sup> Measurements at atmospheric pressure by H. O. Phillips, using technique described elsewhere.<sup>11</sup>

<sup>b</sup> Kindly supplied by W. F. Underwood of Union Carbide Food Products.

<sup>c</sup> Kindly supplied by SIDAC Division, Union Chimique, Ghent, Belgium.

### Analyses

Chloride analyses were by titration with silver nitrate. Most other solutes were determined by passage of aliquots through ion-exchange columns, in the hydrogen form for analysis of cations, or in the chloride form for analysis of anions. The effluents were then analyzed by titration. Thorium was estimated by titration with EDTA with xylenol orange indicator.<sup>10</sup>

### Procedure

In general, membranes were pretreated by exposure in the hyperfiltration apparatus to a feed solution containing the additive under investigation at a concentration of a few hundredths molar, sometimes with and sometimes without added NaCl; membrane rejection properties were then studied with salt solutions, usually containing a low concentration of additive. Usually such a pretreatment step, with an additive concentration higher than later used, hastened the attainment of steady-state behavior by the membrane with a given feed. Soaking the membrane in a solution of the additive before putting it into the hyperfiltration apparatus affected its properties very little; modification of properties was attained by forcing the solution through the membrane by pressure. Details of procedure varied from case to case, and where significant, variations will be cited in conjunction with individual results. In reporting permeation rates, we do not correct the applied pressure for the difference in osmotic pressure between feed and product. The difference between applied and effective pressure is small enough here to be neglected in comparison of rates.

## RESULTS

### Hyperfiltration Properties of Base Cellophanes

Hyperfiltration properties of the Visking dialysis tubing used for most of our studies are summarized in Figure 1. For NaCl, rejection increases with decrease in feed concentration. For Na<sub>2</sub>SO<sub>4</sub> and MgCl<sub>2</sub>, such a trend is not apparent. Permeation rates are in the range of 1–2 cm./hr. at 2500 psi. The scatter in rejection and transmission rate is rather great. It appears that different samples of the same cellophane (even when taken from the same roll, as these were) vary considerably. Rejections of MgCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> in general are higher than those of NaCl at a given feed concentration (expressed in equivalents/liter).

A few data are also given for other cellophanes. The two du Pont cellophanes have somewhat higher rejections and lower permeation rates than the others. Properties of a wet cellophane, which had never been dried, were similar to a sample whose manufacture had been carried through the drying state; these were obtained from Union Carbide Food Products.

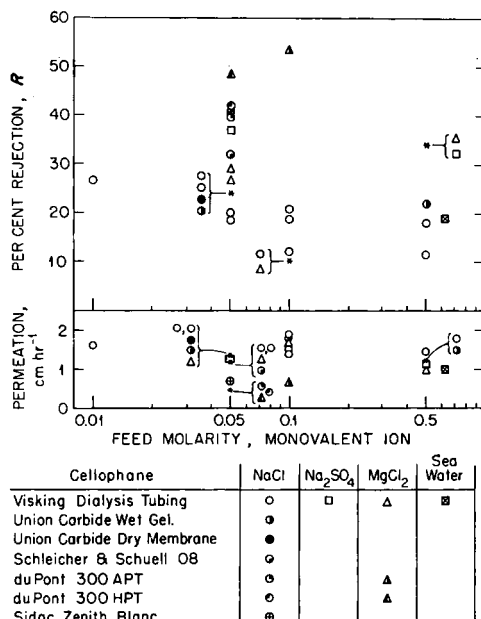


Fig. 1. Hyperfiltration properties of various cellophanes, 2500 psi, 25°C.

### Effect of Ions on the Hyperfiltration Properties of Cellophane

The observations reported here concern the effect of certain solutes on the salt filtration properties of cellophane. The effects are large, but not as yet closely reproducible; rejection and permeation rates of a given cellophane will depend somewhat on the past history of the sample, and perhaps on other as yet unidentified factors.

We shall illustrate the general nature of the effects and the spread in results by presenting chronologically the observations in a typical case, with Th(IV) as additive. For the other additives, we shall present data selected to demonstrate the general outlines of the behavior of cellophane in their presence, it being understood that the numbers listed are representative of values scattering roughly to the same extent as those obtained with feeds containing Th(IV).

**Hyperfiltration by Cellophane in Presence of Th(IV).** A series of measurements made over a period of 25 days is summarized in Figure 2. Salt rejections and permeation rates are reported for the end of a period of exposure to a given set of experimental conditions, when successive samples gave essentially the same results.

The base cellophane rejected about 24% of solute from 0.05M NaCl with a permeation rate of 1.25 cm./hr. at 2500 psi. Enough ThCl<sub>4</sub> was then added to the feed to make the solution 0.001M in Th(IV); salt rejection rose to 65% in a matter of hours, and the permeation rate fell to about 1 cm./hr. These values changed only slightly on dropping the ThCl<sub>4</sub> concentration by a factor of ten.

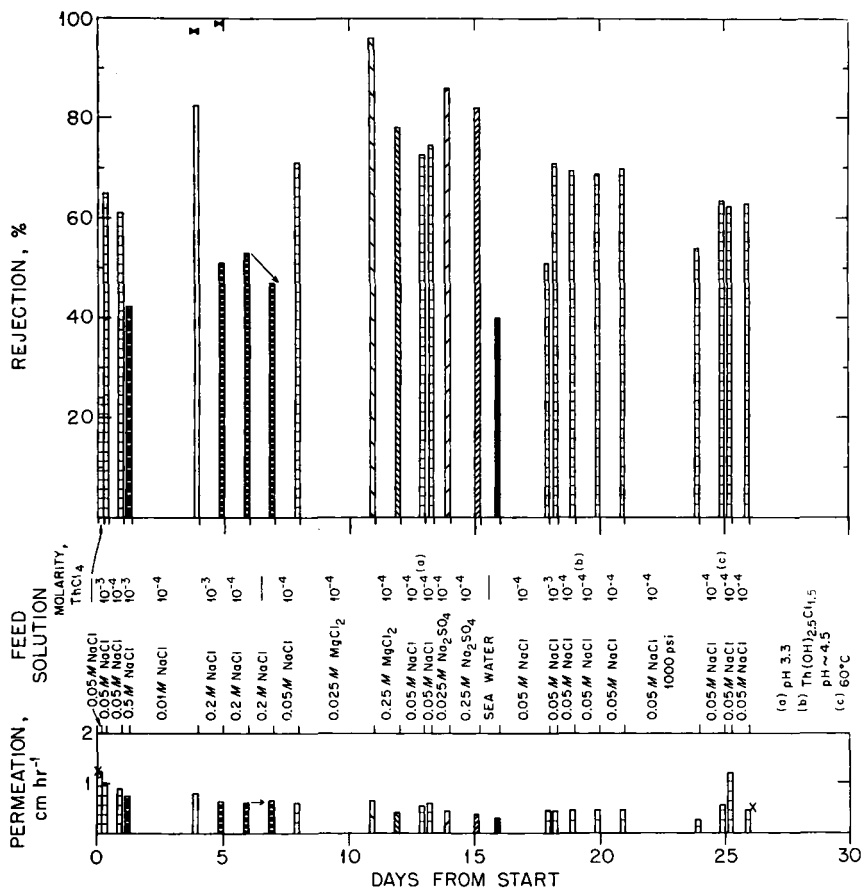


Fig. 2. Hyperfiltration properties of cellophane with Th(IV) additive, Visking dialysis tubing, 2500 psi, 25°C. unless indicated: (▶◀) rejection of Th(IV); (X) permeation rate, water.

Over the course of the run, the membrane was tested with  $0.05M$  NaCl- $10^{-4}M$  ThCl<sub>4</sub> several times, and usually rejections of 60% to slightly over 70% were observed. In one case (18 days) directly after exposure to sea water, the rejection was 50%, but a short period with a feed containing  $10^{-3}M$  ThCl<sub>4</sub> restored rejection to the neighborhood of 70% for the "standard" test solution. As for transmission rate, after an initial sharp decrease of a factor of two during the first two days, there appeared to be little change, or at most a very slow decrease, during the rest of the experiment, an average value being about 0.5 cm./hr. at 25°C. and 2500 psi.

After exposure to a feed containing thorium, the cellophane would continue to have enhanced rejection properties, but unless some Th(IV) additive was present in the feed, rejection would gradually decrease, at about the rate indicated by the arrow starting the 6th day (the point at the 7th day is not a steady state);  $0.0001M$  Th(IV) seemed adequate to

maintain good rejection, at least at the low NaCl concentration end of our study. In general, rejection of NaCl decreased with increasing NaCl concentration, from over 80% at 0.01M to about 40% at 0.5M NaCl. Increasing the temperature to 60°C. had little effect on rejection but increased permeation by a factor roughly to be expected from viscosity

TABLE II  
Hyperfiltration Properties of Cellophanes with Feeds Containing Various Additives  
(Visking Dialysis Tubing, 25°C., 2500 psi)

Initial pretreatment	Solute	Additive	Permeation rate, cm./hr.	Rejection, %
A. Fe(III)				
0.003-0.03M FeCl <sub>3</sub>				
	0.01M NaCl	0.00001M	0.5	80
	0.05M NaCl	0.0001-0.001M	0.2-0.3	60-80
	0.5M NaCl	0.003M	0.2	60
	0.025M MgCl <sub>2</sub>	0.001M	0.2	86
	0.025M Na <sub>2</sub> SO <sub>4</sub>	0.0001M	0.3	70
B. Cu(II)				
0.06M NaCl- 0.02M CuCl <sub>2</sub>				
	0.1M NaCl	—	0.7	50
	0.01M NaCl	—	0.8	69
	0.5M NaCl	—	0.6	32
	0.1M NaCl	—	0.7	42
C. Pb(II)				
0.1M Pb(ClO <sub>4</sub> ) <sub>2</sub>				
	0.05M NaClO <sub>4</sub>		1.5	19
	0.05M NaClO <sub>4</sub>	0.001M Pb(ClO <sub>4</sub> ) <sub>2</sub>	1.4	15
0.1M PbOHClO <sub>4</sub>				
	0.05M NaClO <sub>4</sub>	0.001M PbOH- ClO <sub>4</sub>	0.7-1.0	65-43
	0.05M NaClO <sub>4</sub>	—	1.3	22
D. Zr(IV)				
0.05M ZrOCl <sub>2</sub>				
	0.05M NaCl	0.001M ZrOCl <sub>2</sub>	0.95	53
	0.1M NaCl	—	1.3	27
E. U(VI)				
	0.05M NaCl	0.001M UO <sub>2</sub> Cl <sub>2</sub>	1.5	24
	0.05M NaCl	0.001M UO <sub>2</sub> OHCl	1	54
	0.5M NaCl	0.001M UO <sub>2</sub> OHCl	0.9	34

change. Decreasing pressure to 1000 psi (21-23 day) decreased rejection appreciably, but permeation rate did not decrease quite proportionately to the change in pressure. Moderate variations of pH by adding acid (13th day) or use of hydrolyzed Th(IV) additive (20th day) had little effect. At concentrations used here, ThCl<sub>4</sub> with no acid or base added is hydrolyzed to a small extent.<sup>12</sup>

Rejections of  $\text{Na}_2\text{SO}_4$  and  $\text{MgCl}_2$  were also greatly increased by presence of Th(IV), as one can see by comparing the results in Figure 2 between the 8th and 15th days with the results in Figure 1; with 0.025*M*  $\text{MgCl}_2$ , for example, rejection was 95%, compared to less than 30% for the base cellophane. The rejection of  $\text{MgCl}_2$  is greater than of NaCl at a given chloride concentration, and the rejection of  $\text{MgCl}_2$  also increases with decreasing concentration. The rejection of  $\text{Na}_2\text{SO}_4$  is relatively independent of concentration. The solute rejection of sea water (taken from the ocean at Pawleys Island, S. C.), to which  $\text{ThCl}_4$  had been added until precipitation occurred, was about 40%.

Thorium rejection was estimated in a few cases, and appeared to be 97% or greater.

**Ferric Additive.** The effect of presence of ferric chloride on salt rejection by cellophane is demonstrated in Table IIA. Rejections are comparable to those observed with Th(IV); permeation rates, however, were usually lower after a few days exposure than with thorium. No quantitative measurements of iron rejection were made, but since the effluent was colorless, most of the additive must have been filtered out. The membranes were strongly colored reddish-brown at the end of the runs.

**Cupric Additive.** The measurements in Table IIB, of hyperfiltration properties of cellophane pretreated with a solution containing  $\text{CuCl}_2$ , comprise a series covering several days, rather than a set of randomly selected results. It can be seen that hyperfiltration by the membrane was strongly enhanced by pretreatment with copper. The lower rejection of 0.1*M* NaCl observed at the end of the series presumably stems from gradual washing of copper from the membrane. Again no quantitative measurements of Cu(II) rejection were made, but the fact that the feed in pretreatment was strongly colored blue and the effluent was colorless to the eye indicates that the additive was efficiently filtered. The membrane was blue at the end of the experiment, in spite of the fact that it had been exposed to feeds containing no added copper for several days, and volumes of effluent thousands of times the membrane volume had passed through it.

**Lead (II).** With this additive, we could not use chloride solutions; in presence of chloride, effect of pretreatment with Pb(II) decayed rapidly, presumably because of strong complexing by chloride. We therefore used perchlorate solutes. Since Pb(II) is not very acidic, it was possible to investigate the effect on hyperfiltration of degree of hydrolysis, characterized by the hydroxyl number,  $n$ , the average number of hydroxyls bound per metal ion. We tried unhydrolyzed lead perchlorate,  $\text{Pb}(\text{ClO}_4)_2$ , and lead with  $n = 1$ ; the hydrolyzed Pb(II) is distributed in a number of species,<sup>13,14</sup> a tetramer of species hydroxyl number 1.0 and a hexamer of species hydroxyl number 1.33 being prominent.

The results, Table IIC, are for a series of measurements on a single membrane carried out over a period of about a week. The base cellophane rejected 19% of solute from a 0.05*M*  $\text{NaClO}_4$  solution (permeation rate,

1.5 cm./hr.) and 20% of the additive [0.1M Pb(ClO<sub>4</sub>)<sub>2</sub>] in the pretreatment step (permeation rate, 1.4 cm./hr.). Unhydrolyzed lead did little if anything to the hyperfiltration properties of the membrane. Hydrolyzed Pb(II) did however modify properties substantially. In pretreatment, rejection of 0.1M PbOHClO<sub>4</sub> rose to as high as 96% and permeation rate fell to 0.6 cm./hr. After pretreatment, the rejection of 0.05M NaClO<sub>4</sub> containing 0.001M additive was three times as great as before, but the concentration of additive used was apparently not sufficient to maintain rejection at this level. On exposure to 0.05M NaClO<sub>4</sub> without additive, rejection fell to essentially the initial value in a few hours.

**Zirconium(IV) and Uranium(VI).** Zirconium(IV), both when used in pretreatment and when present in the feed, affects the hyperfiltration properties of cellophane (Table IID). Under the conditions of these experiments, Zr(IV) is distributed in low molecular weight polymeric species.<sup>15</sup>

Unhydrolyzed U(VI) has little effect on hyperfiltration properties of cellophane, but hydrolyzed uranyl chloride raises rejection (Table IIE). In these experiments, about 1 mole of NaOH was added per mole of UO<sub>2</sub>Cl<sub>2</sub>, to give a degree of hydrolysis of one. A mixture of hydrolyzed uranium species will be present, a dimer of hydroxyl number 1.0 being prominent.<sup>16</sup>

**Other Additives.** A number of other additives were shown to have little effect on NaCl rejection by cellophane. Among these were MgCl<sub>2</sub>, BaCl<sub>2</sub>, and La(NO<sub>3</sub>)<sub>3</sub>. Pretreatment for 1 hr. with a negatively charged polymeric species also did not modify the membrane characteristics appreciably. The solution used was about 1M in Mo(VI) with 1.14 mole HCl added per mole of MoO<sub>4</sub><sup>=</sup>; under these conditions, the so-called paramolybdate, a heptameric species, is dominant.<sup>17</sup>

An attempt to duplicate a reported<sup>7</sup> effect of pretreatment of cellophane with LiClO<sub>4</sub> was unsuccessful. A sample of Visking dialysis tubing was soaked for 1 hr. at room temperature in 10% LiClO<sub>4</sub>. It was then tested with 0.05M NaCl feed at 25°C. under 1200 psi. Permeation rate was about 2.2 cm./hr. and rejection 14%, rather than the reported values, 0.05 cm./hr. and 98.6%. Details of procedure were not given in the original account,<sup>7</sup> nor was the concentration of salt in the test of rejection stated. Variations in our procedure or in the cellophane we used may therefore explain the discrepancy.

Since most of the ions active in modifying the cellophane properties are hydrolyzable, the possibility exists that free acid produced by reaction of additives with water is affecting the membrane. We tested this with a 0.09M NaCl-0.01M HCl solution; the rejection and permeation rates were not significantly different from those with 0.1M NaCl.

### Effects of Additives on Other Cellophanes

A few tests were carried out with other cellophanes. Rejection properties of cellophanes of comparable tightness (the term here signifying



membranes having 1–2 cm./hr. transmission rate for water at 2500 psi in the first hour of exposure to pressure) appeared to be similar after exposure to additives, even though the rejections by the untreated cellophanes were significantly different. For example, Schleicher and Schuell 08 (initial permeation rate of water, 1.5 cm./hr. at 25°C. and 2500 psi, the conditions of all the experiments in this section unless noted otherwise) rejected 30% of solute from a 0.05*M* NaCl solution. After pretreatment with 0.03*M* FeCl<sub>3</sub>, rejection was 60% for a 0.05*M* NaCl–10<sup>-3</sup>*M* FeCl<sub>3</sub> solution (permeation rate ~0.6 cm./hr.), a value in the range found for Visking dialysis cellophane (Table II). A wet gel obtained from Union Carbide Food Products (Table I) rejected 25% of solute from 0.05*M* NaCl, transmission being 1.4 cm./hr. After exposure to 0.03*M* FeCl<sub>3</sub>, rejection of 0.05*M* NaCl was 75%, and permeation 0.5 cm./hr. A cellophane similar to the wet gel, except that the manufacturing process had been carried through to a dry product, rejected 25% of 0.05*M* NaCl, permeation rate 1.4, and reached 65% rejection for a 0.05*M* NaCl–0.001*M* FeCl<sub>3</sub> solution, permeation rate being 0.65 cm./hr.

The tighter du Pont and Zenith Blanc cellophanes, whose rejection was considerably higher than the rejections of the others in absence of additives (Fig. 1), rejected about the same fraction of salt as the others in presence of additive. These were tested by first exposing them for 3–4 hr. to 0.03*M* FeCl<sub>3</sub> feed. After this, salt rejection with 0.05*M* NaCl–0.001*M* FeCl<sub>3</sub> feed was 68% for 300 APT (0.25 cm./hr.) and 71% for 300 HPT (0.25 cm./hr.). Zenith Blanc cellophane rejected 63% of salt from 0.05*M* NaCl–0.001*M* FeCl<sub>3</sub> feed (0.24 cm./hr.).

The behavior of a "porous" cellophane, Schleicher and Schuell 05 (Table I), was different. In this case, since permeation rates were high, the experiments were carried out on a different apparatus, which allows much faster circulation of feed past the membrane, in order to minimize possible interferences of concentration polarization. At 1900 psi, permeation rate was about 50 cm./hr. and rejection for a 0.05*M* NaCl solution essentially zero. The feed was changed to 0.05*M* NaCl–0.001*M* ThCl<sub>4</sub>; after 15 hr., the permeation rate had fallen to 13 cm./hr., with 12% rejection.

## DISCUSSION

There is clearly an increase in salt filtration by cellophane in the presence of certain metal ions, but the origin of the increase is obscure. With the exception of Cu(II), which is known to interact strongly with cellulosic material, ions are effective only in the pH range (or slightly below it) in which they are known to be hydrolyzed. The effect of Pb(II) is especially interesting in this connection. At pH values under which lead perchlorate is essentially unhydrolyzed, its presence has little effect on hyperfiltration by cellophane, but hydrolyzed Pb(II) has a strong effect on rejection. The behavior of U(VI) is similar. Nonacidic di- and trivalent metal ions, such as Mg<sup>+2</sup>, Ba<sup>+2</sup>, and La<sup>+3</sup>, had little effect on the membranes.

If the effective metal ions were adsorbed by cellophanes in the form of hydrous oxides or basic salts, the promotion of rejection properties might be ascribed to the resulting increase in ion-exchange capacity.<sup>18</sup> Under the conditions here, hydrous oxides of the metals in question [except U(VI)] should be anion exchangers (fixed positive charges). Increase in fixed charge on the cellophane would tend to exclude co-ions by a "Donnan" mechanism.<sup>4</sup> Some observations are consistent with ion exclusion. Rejection increases with decrease in feed salt concentration, and rejection of  $MgCl_2$ , a salt with divalent coions, is greater than rejection of  $NaCl$  at the same equivalent concentration. On the other hand, the increase of  $NaCl$  rejection with decrease in feed concentration is not nearly so great as one would predict from an ideal ion-exclusion mechanism; a tenfold decrease in feed concentration should result<sup>9</sup> in a tenfold decrease in  $(1 - R)$  for  $NaCl$ . In addition, the rejection of a salt with divalent counterion,  $Na_2SO_4$ , seems anomalously large. Although the organic ion exchangers also depart substantially from ideal behavior,<sup>9,19</sup> possible alternative models preclude a conclusion that the effect of the additives is by an ion-exchange mechanism. For example, the additives may tighten the cellophane network by introducing crosslinks [Cu(II), at least, very likely does something of the sort<sup>6</sup>], and in so doing decrease the preference of the membrane phase for solute relative to its preference for water.

From a practical point of view, rejections are not high enough at the permeation rates attained (about 3 gal./ft.<sup>2</sup>-day at 2500 psi) to be useful in desalination by the hyperfiltration or reverse osmosis process. However, the base cellophanes available are quite thick, and the intrinsic permeabilities high. If cellophanes thinner by a factor of ten could be obtained, they might begin to be of considerable interest for treatment of brackish waters, especially for natural waters which happen already to contain useful additives. The attempt to increase transmission rate by use of more porous base cellophanes was not successful; additives did not increase rejection to a useful level.

We are indebted to H. O. Phillips for permission to quote thicknesses of wet cellophanes.

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### References

1. K. A. Kraus, A. E. Marcinkowsky, J. S. Johnson, and A. J. Shor, *Science*, **151**, 194 (1966).
2. J. W. McBain and R. F. Stuewer, *J. Phys. Chem.*, **40**, 1157 (1936).
3. S. Trautmann and L. Ambard, *J. Chim. Phys.*, **49**, 220 (1952).
4. J. G. McKelvey, K. S. Spiegler, and M. J. R. Wyllie, *Chem. Eng. Prog. Symp. Series*, **55**, No. 24, 199 (1959).
5. L. Ambard and S. Trautmann, *Ultrafiltration*, Charles C Thomas, Springfield, Ill., 1960.
6. C. E. Reid and J. R. Koppers, *J. Appl. Polymer Sci.*, **2**, 264 (1959).

7. Monsanto Research Corp., Office of Saline Water Research and Development Progress Report 69, PB181, 467 (1962), p. 42.
8. P. Hirsch-Ayalon, *Rec. Trav. Chim.*, **80**, 376 (1961).
9. W. H. Baldwin, D. L. Holcomb, and J. S. Johnson, *J. Polymer Sci. A*, **3**, 833 (1965).
10. J. Körbl and R. Pribil, *Chemist Analyst*, **45**, 102 (1956); *ibid.*, **46**, 28 (1957).
11. H. O. Phillips, in preparation.
12. K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).
13. A. Olin, *Acta Chem. Scand.*, **14**, 126 (1960).
14. O. E. Esval and J. S. Johnson, *J. Phys. Chem.*, **69**, 959 (1965).
15. J. S. Johnson and K. A. Kraus, *J. Am. Chem. Soc.*, **78**, 3937 (1956).
16. R. M. Rush, J. S. Johnson, and K. A. Kraus, *Inorg. Chem.*, **1**, 378 (1962).
17. J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, **3**, 735 (1964).
18. K. A. Kraus, H. O. Phillips, T. A. Carlson, and J. S. Johnson, *Proc. 2nd U. N. Intern. Conf. Peaceful Uses Atomic Energy, Geneva*, **28**, 3 (1958).
19. E. Glueckauf and R. E. Watts, *Proc. Roy. Soc. (London)*, **A268**, 339 (1962).

### Résumé

Les propriétés de rejet de sel de cellophanes sont substantiellement augmentées et les vitesses de perméation diminuées par prétraitement avec certains ions métalliques ou en présence de ces ions à basse concentration dans les solutions de départ. Dans un cas typique, une cellophane qui initialement rejetait environ 20% de sel au départ d'une solution à 0.05M NaCl rejetait au del de 70% en présence de  $10^{-3}M$  de ThCl<sub>4</sub>. Les vitesses de perméation ont été diminuées utilisant habituellement un facteur de 2 à 3. Certains additifs ont un effet marqué tels le Fe(III), Th(IV), U(VI), Cu(II), Zr(IV), et le Pb(II) hydrolysée. Le Mg(II), Ba(II), La(III) et Pu(II) non-hydrolysé n'ont que peu d'effet. Le mécanisme suivant lequel ces additifs affectent la cellophane n'est pas clair.

### Zusammenfassung

Durch Vorbehandlung mit gewissen Ionen oder Anwesenheit dieser Ionen in niedriger Konzentration in der Ausgangslösung wird die Salzabweisung von Zellophan wesentlich erhöht und die Permeationsgeschwindigkeit herabgesetzt. In einem typischen Fall stieg die Salzabweisung von Zellophan von einem Anfangswert von 20% für eine 0,05M NaCl-Lösung in Gegenwart von  $10^{-3}M$  ThCl<sub>4</sub> auf über 70%. Die Permeationsgeschwindigkeit wurde üblicherweise um einen Faktor 2 oder 3 herabgesetzt. Additive mit merklichem Effekt waren Fe(III), Th(IV), U(VI), Cu(II), Zn(IV), und hydrolysiertes Pb(II). Mg(II), Ba(II), La(III), und nicht hydrolysiertes Pb(II) hatten wenig Effekt. Der Mechanismus des Additiveinflusses auf Cellophan ist nicht klar.

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