

directional in character, the stereochemistry of the ion is probably determined by the configuration minimizing the energy of the $(\text{CH}_3)_2\text{M}$ moiety.¹⁷

The fact that $(\text{CH}_3)_2\text{Au}^+$ seems to exist exclusively

as the *cis* ion may indicate a strong *trans* effect associated with the methyl groups. Similarly, synthesis of dimethylplatinum(II) compounds always seems to give the *cis* isomer.

Hyperfiltration Studies. IV. Salt Rejection by Dynamically Formed Hydrous Oxide Membranes¹

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Received August 8, 1966

Abstract: Salt-filtering layers can be formed on porous bodies (pore diameters as large as 5μ) by circulating by them under pressure solutions containing colloidal dispersions of hydrous oxides or solutions of hydrolyzable salts. These films reject substantial fractions of solute from dilute solutions, frequently with transmission rates through the membranes as high as 1 cm/min (35 atm).

In a canvass of materials for possible usefulness as salt filters in the hyperfiltration, or reverse osmosis, process for desalination, hydrous oxides and basic salts deserve consideration. These materials are known to have ion-exchange properties,³ and ion-exchange membranes and porous bodies are known to reject salt from solutions⁴⁻⁵ forced through them by pressure. It is not obvious, however, how to prepare a hydrous oxide layer suitable for hyperfiltration. In order to reject, it must be compact enough for intimate contact with feed;⁵ at the same time, it must be thin enough to allow fast permeation (as the "active layer" of presently prepared cellulose acetate membranes does).⁹

We have found that "membranes" can be dynamically created by exposing a porous body mounted in a hyperfiltration apparatus to a solution containing a colloidal dispersion of a hydrous oxide. A hyperfiltration apparatus consists of a membrane and support in contact with a pressurized feed solution; the solution is circulated past the membrane to decrease the salt buildup resulting from rejection of solute from the solution permeating the membrane.¹⁰ The

equipment used in this study differed from that previously described⁶ in that a large volume of solution was pressurized, and circulation was effected with a separate pump operating at pressure.

In a typical example, enough of a 0.1 *M* FeCl_3 solution, which had been aggregated by having been brought to a boil, was added to a 0.02 *M* NaCl solution to make it 0.0005 *M* in Fe(III) ; the sodium chloride solution was circulating in the hyperfiltration apparatus past a silver frit of 0.8- μ average pore size.¹¹ The initially fast permeation rate rapidly dropped to 0.2 cm min^{-1} (1 $\text{cm/min} = 354 \text{ U. S. gal day}^{-1} \text{ ft}^{-2}$) at 35 atm, and salt rejection, $R_{\text{obsd}} = (c_f - c_w)/c_f$, based on total chloride, rose to 0.6. The symbol *c* refers to concentration in moles/liter, subscript *f* refers to the feed solution, and ω refers to the solution effluent from the membrane.

Results of a more extended experiment are given in Table I. A 0.25 *M* ZrOCl_2 solution was boiled for several hours, until formation of a suspension was barely perceptible, and enough of this solution was added to the feed to bring it to the additive concentrations shown in the table. The initial exposure of the 0.8- μ silver frit to a solution 0.02 *M* in NaCl containing 0.001 *M* Zr(IV) additive resulted in formation of a rejecting layer; the rejection properties of the membrane decayed only slowly when the experiment was continued without the presence of Zr(IV) . The slow decrease could be arrested or reversed by addition of 10^{-4} *M* Zr(IV) to the feed. Even with the high circulation rates possible with our present apparatus (residence time of solution in contact with membrane about 0.01 sec), concentration polarization is not eliminated at these high permeation rates (around 350 $\text{gal day}^{-1} \text{ ft}^{-2}$); lower rejections were obtained when the circulation was decreased from the maximum. The rejections given are thus not the maximum possible

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Table I. Hyperfiltration Properties of a Zr(IV) Rejecting Layer^a

Cumulative operating time, hr	Feed, M		Permeation, cm/min	R_{obsd}
	NaCl	Zr(IV)		
4.7	0.02	0.001	1.1	0.60
6.7	0.01	...	1.1	0.61
7.7	0.02	...	1.0	0.58
8.3	0.1	...	1.0	0.28
9.3	0.06	...	1.3	0.22
10.5	0.01	...	1.1	0.48
11	0.01	0.0001	1.1	0.69
12	0.1	0.0001	0.8	0.44
14	0.06	0.0001	0.8	0.38
15	0.02	0.0001	0.8	0.67
16	0.01	0.0001	0.8	0.80
18	0.02	...	0.9	0.60
18.2	0.02	...	0.9	0.40 ^b
18.3	0.02	...	0.9	0.20 ^c
19	0.02	0.001	0.8	0.69

^a 0.8- μ Ag frit; 35 atm pressure; maximum circulation rate possible with apparatus unless specified; rejection based on total chloride. ^b Same as previous experiment, but circulation rate one-half maximum. ^c Same as previous experiment, but circulation rate one-fourth maximum.

for the films in question. In general, although results are not closely reproducible, higher fractions of solute are filtered at lower feed concentrations, in qualitative agreement with an ion-exchange rejection mechanism.

Rejections of multivalent ions also indicate an ion-exchange mechanism. As used in these experiments, the Zr(IV) additive makes the solutions acidic, and the hydrous oxide layer should be in the anion-exchange form.³ The simple ion-exclusion model (activity coefficient ratios in the membrane to solution phase taken as unity) would predict that salts having divalent co-ions (here anions) should be better rejected than 1:1 electrolytes at the same equivalent concentration. We list the results of such a test in Table II; a membrane

Table II. Rejection of Various Solutes by a Dynamically Created Hydrous Zr(IV) Oxide Membrane^a

Solute	Permeation, cm/min	R_{obsd}
0.02 M NaCl	0.7	0.68
0.01 M MgCl ₂	0.7	0.90
0.01 M Na ₂ SO ₄	0.8	0

^a 0.8- μ silver frit, 34 atm.

previously formed with a solution containing Zr(IV) additive rejected 68% of solute from a 0.02 M NaCl solution, and 90% of 0.01 M MgCl₂. With 0.01 M Na₂SO₄, which contains a divalent counterion, rejection is destroyed. Apparently strong interaction of sulfate with the charged sites greatly decreases the effective charge density of the matrix. The rejecting properties of this membrane were restored by further exposure to solutions containing Zr(IV) additive without sulfate. The presence of additive in sulfate solutions does not bring about sulfate rejection, however; a series similar to that given in Table II, carried out with 10⁻⁴ M Zr(IV) present in all solutions, gave similar results.

The chemical nature of the porous body does not seem to be critical; we have been able to form rejecting membranes on porous carbon, ceramic, and sintered

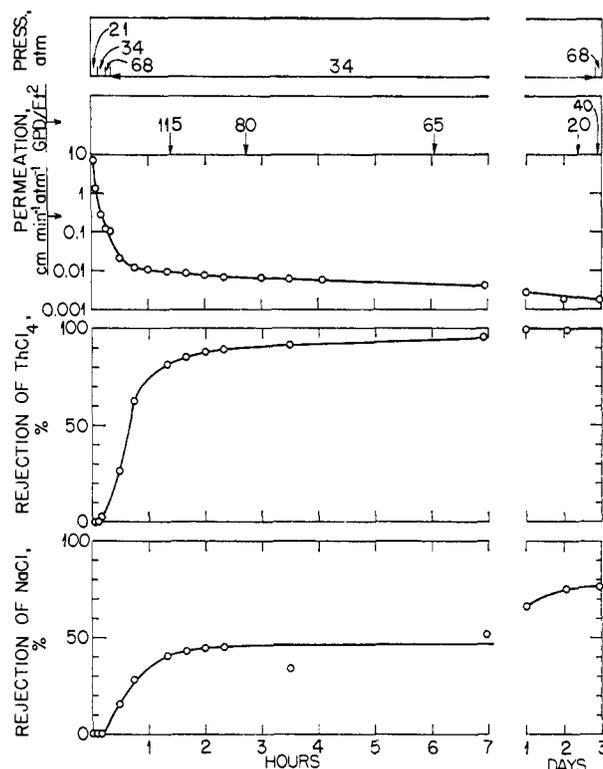


Figure 1. Hyperfiltration with silver frit: Th(IV) additive; nominal pore size, 0.2 μ ; feed, 0.018 to 0.026 M NaCl-0.0014 to 0.0026 M ThCl₄.

glass, as well as on porous metals and Millipore filters. Nominal pore sizes have been as high as 5 μ . It is not clear that the actual plugging, as distinguished from the imparting of rejecting properties, is done by the colloidal additives. Variable results have been obtained with solutions prepared to have identical composition, and it may well be that dust, corrosion products from the apparatus, or other extraneous impurities actually form a film on which the additives collect and activate for rejection. Plugging with no colloidal additive intentionally present has sometimes occurred, though usually in such cases there was little or no rejection. From the high permeation rates frequently obtained with rejecting membranes, the rejecting layer must be much thinner than the porous substrate and must be located near the frit-feed interface; otherwise, concentration polarization would quickly mask rejection.

A further indication that the additive is more important as activator than in the formation of the film is the fact that rejecting membranes can be dynamically created with hydrolyzable ions, under conditions where the aggregation of the additive is known to be low. For example, with a 0.2- μ Ag frit and a 0.02 M NaCl-0.002 M ZrOCl₂ solution, 85% rejection of chloride was observed, with 0.9 cm min⁻¹ permeation rate at 140 atm; the Zr(IV) polymers in this case should be much smaller than the pore size of the frit.¹²

In Figure 1, the course of an extended run with ThCl₄ is outlined. Under the conditions of this experiment, Th(IV) is only slightly hydrolyzed,¹³ and the polymers,

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at least with unaged solutions,¹⁴ are small. Both rejection of total chloride and of Th(IV) were measured and rejection of NaCl estimated by difference. As the permeation rate falls (Figure 1), rejection of NaCl and of ThCl₄ increases sharply, then more gradually. After several days, thorium rejection has become virtually complete. In general, in cases where we have measured it, rejection of additives is high.

We have seen behavior similar to that of Figure 1 in the presence of low molecular weight hydrolytic polymers many times, though the observations are not always quantitatively reproducible. As with membranes formed with more highly polymerized additives, the presence of sulfate or other polyvalent anions in appreciable concentration decreases rejection dramatically, and with membranes freshly prepared from low molecular weight solutes, a sharp increase in permeation rate sometimes indicates that the film is essentially destroyed.

As we have stated, the mechanism appears to involve formation of a thin rejecting layer at the feed-frit interface. The α counting rate obtained from this side of 40- μ -thick silver frits treated with thorium chloride was an order of magnitude higher than that from the other side. In addition, the films can sometimes be destroyed by brushing the feed interface and reconstituted on further exposure to additive-containing solutions. We believe the mechanism is different from that in-

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involved in the promotion by Th(IV) additive⁷ of rejection by unfired Vycor glass, where we believe the thorium adsorbs on the walls of the uniform pores and increases the charge density. We also believe the mechanism is different from the effect of Th(IV) and other hydrolyzable ions on the hyperfiltration properties of tight cellophanes,^{1b} where the additive appears to impregnate the whole thickness of the membrane.

The fact that membranes of substantial rejection properties can be created with permeation rates sometimes of several hundred gal day⁻¹ ft⁻² is of considerable interest, at least for treatment of waters containing a low concentration of solute; even with the loose cellulose acetate membranes, prepared specifically for brackish water, permeation rates are usually less than 50 gal day⁻¹ ft⁻². Since most natural waters contain polyvalent anions, some way to ameliorate their effect will have to be found before dynamically created membranes are useful in desalination. These filters may, however, be useful for processing waste waters of more restricted composition.

It is interesting to speculate that similar mechanisms may be of importance in geological processes involving porous formations, since ground and surface waters frequently contain colloidal hydrous oxides, as well as other natural ion exchangers.

Acknowledgment. We are indebted to Warren Sisson and Neva Harrison for technical assistance.