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Filtration of Organic Solutes by Dynamically Formed Membranes*

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Summary

Dynamically formed hydrous Zr(IV) oxide membranes partially filter neutral organic solutes from aqueous solutions in a hyperfiltration, or reverse osmosis, experiment. The degree of filtration depends primarily on the size of the solute and the history of the membrane.

We have reported elsewhere (*1*,*2*) that salt-filtering membranes can be dynamically deposited on bodies having pores in the micron range. Rejecting layers, apparently very thin, are formed when feeds containing certain additives are circulated under pressure past the porous supports. The most interesting films so far obtained are prepared with additives, such as organic polyelectrolytes (*2*) or colloidal hydrous oxides (*1*), which would be expected to form ion-exchange membranes. The salt rejection has been attributed (*1*,*2*) to an ion exclusion mechanism typical of ion exchangers (*3*). We have recently found that these membranes also reject nonelec-

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trolyte organic solutes, and in this article we report some observations of filtration of neutral organic materials.

Most of our studies have utilized membranes prepared from feeds containing ca. 10^{-3} M colloidal Zr(IV) hydrous oxide; the additive was from a 0.25 M $ZrOCl_2$ solution, which had been aggregated by boiling for several hours. A low concentration of additive [10^{-5} to 10^{-4} M Zr(IV)] was kept in the feeds to maintain the membrane. The porous substrates* were mounted in a test cell previously described (*4*); a pump operating at pressure (*1*) circulated the feed many times faster than in the equipment described in Ref. (*4*). Analysis for organic concentration was by refractive index.

We report filtration of solute in terms of "observed" rejections (given as per cent, or $\mathbf{R}_{\text{obs}} \times 100$):

$$\mathbf{R}_{\text{obs}} = 1 - \frac{c_\omega}{c_f}$$

where c indicates concentration in moles per liter or in grams per liter; f the feed solution, and ω the effluent, or product, solution. Observed rejections are less than those of which the membranes are capable if the circulation past the membrane is not fast enough to sweep away the filtered solute from the high-pressure interface (5). In the apparatus (*1,2*) used for this study, we have encountered appreciable concentration polarization, at least at fast permeation rates. In addition, even with procedures identical insofar as we can at present control them, the membranes we prepared have somewhat variable properties. In particular, properties of freshly prepared films tend to change with time, and rejection and permeabilities can be modified by exposure to high pressures. Figure 1 summarizes filtrations of a mono-, di-, and trisaccharide by a hydrous Zr(IV) oxide membrane, which rejected about 50% of salt from a 0.04 M NaCl solution. Rejections of the sugars were first measured at 400 psi (about 10-hr exposure); the rejections became higher, and permeabilities lower, on exposure to 1000 psi (5 hr). A repeat series at 400 psi (6½ hr) indicated that the effect of exposure of the membrane to higher pressure was only slowly, if at all, reversed by return to lower pressure. In each series, however,

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* Sources of porous supports (pore sizes are nominal values listed by the manufacturer or supplier): silver, Selas Flotronics Co.; carbon, Pure Carbon Co.; Vinyl Acropor VNW-450 [porous poly(vinyl chloride) with nylon substrate], Gelman.

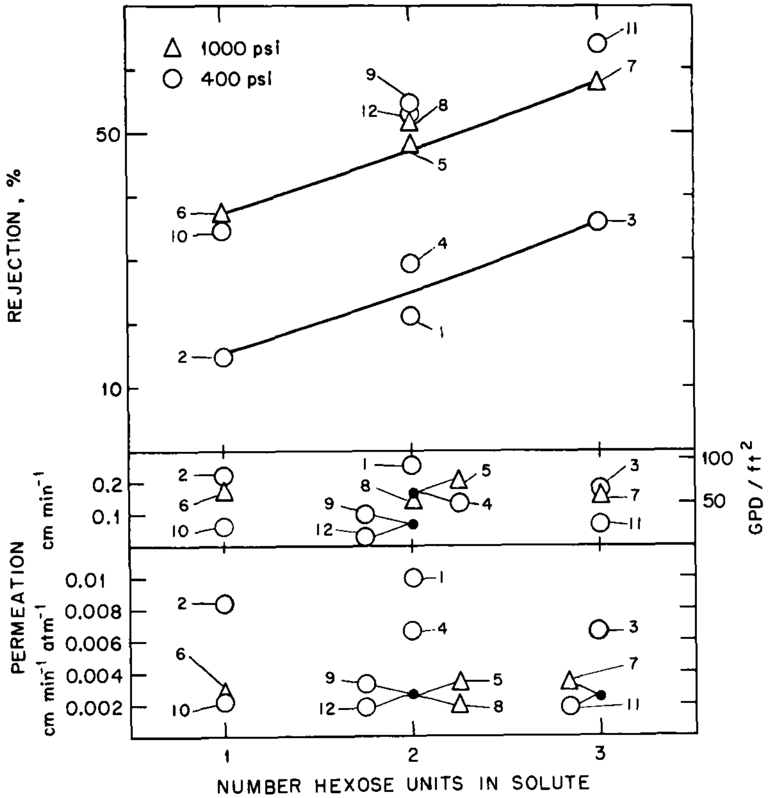
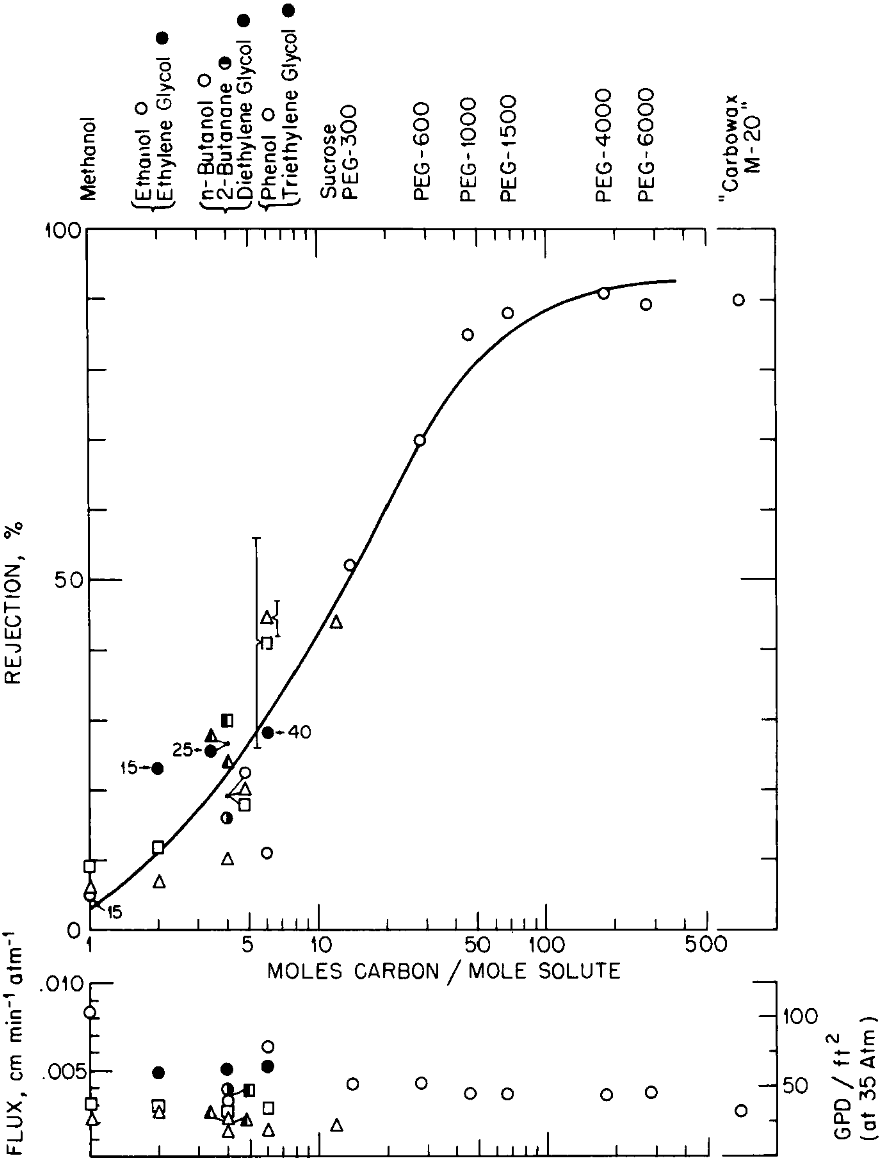


FIG. 1. Rejection of glucose, sucrose, and raffinose by hydrous Zr(IV) oxide membrane on 0.2-μ Ag filter. Solutions contain about 50 g/liter of sugar and are 10^{-5} M in Zr(IV). Numbers indicate order of experiments. Reprinted by permission of S. M. Fleming, Director of the Oak Ridge Station of the M.I.T. Practice school.

the filtration increased with increasing molecular weight of the organic solute.

Observations clearly depend to some extent on the history of the membrane. With this qualification, we present in Fig. 2 results of tests with a number of organic solutes as a function of moles of carbon per mole of solute, which should correspond roughly to molecular weight and molecular size. The numbers listed by the polyethylene glycols (PEG: actually polymeric ethers of ethylene glycol) are a supplier's (Wyandotte Chemicals) index of molecular



REJECTION OF ORGANIC SOLUTES FROM AQUEOUS SOLUTION BY DYNAMICALLY FORMED HYDROUS ZIRCONIUM OXIDE MEMBRANES.

35 ± 5 Atm ; Organic Concentration, 50 g/ℓ, Unless Noted by Numbers on Graph.

MEMBRANES

	SUPPORT	PORE SIZE, μ	FEED MOLARITY, Zr(IV)
○	SILVER	0.2	10^{-4}
□	PVC ON NYLON	0.45	10^{-5}
△	CARBON	0.3	10^{-5}

FIG. 2.

weights. We used these numbers to obtain the abscissa values for these solutes, although by equilibrium ultracentrifugation of PEG 6000, we found a molecular weight of only about half the nominal value. Carbowax M20 is also a polyethylene glycol, obtained from Union Carbide, Chemicals Division; rather crude turbidity measurements indicated a molecular weight of several hundred thousand.

The results in Fig. 2, in accordance with the trend in Fig. 1, indicate that the fraction of organic solute filtered is primarily a function of molecular size. There are considerable variations in rejection for a given solute; differences between rejections, measured at various times, occur both with membranes formed on the same support and on different supports. It thus appears that the scatter is not associated with differences between the support structures. With the poly(vinyl chloride) and carbon supports, sucrose rejections were remeasured from time to time over the course of the study and ranged between 40 and 47%.

Rejections of phenol were for some reason particularly erratic; there is considerable drift in values obtained in a given series. Average values are plotted and a range given for each series.

Rejection appears to be independent of concentration of the organic solute. In Table 1, results are given for a sequence of measurements with sucrose; agreement between the first and last values indicates that membrane properties did not change over the series. Lack of dependence on feed concentration contrasts with the highly concentration-dependent rejection of salt, one of the properties which suggests an ion-exclusion rejection mechanism with electrolytes (*1*).

TABLE 1

Effect of Feed Concentration on Rejection of Sucrose[a]

Sucrose, grams/liter	Permeation, centimeters/minute	Rejection, %
50	0.06	44
100	0.05	43
25	0.07	43
50	0.07	43

[a] Hydrous Zr(IV) oxide membrane on 0.3-μ carbon frit; 34 atm; 10^{-5} *M* Zr(IV) in feed.

At the high-molecular-weight end of the solutes studied, rejection leveled at less than 100% (Fig. 2). The unfiltered solute could have leaked through imperfections or could be a low-molecular-weight fraction of the PEG distribution. In an attempt to distinguish, we centrifuged to equilibrium (22,000 rpm, short radial columns) samples of effluent and feed, both diluted to about 5 g/liter of PEG, taken in a hyperfiltration experiment with PEG 6000 (membrane on carbon support; not included in Fig. 2). The molecular weight obtained for the effluent when rejection was 95% was about 1500, or less than half the values, 3600 ± 200, obtained for several bleed samples and for a feed sample to which no Zr(IV) had been added. There is clearly some fractionation when rejection is high, and we have confirmed this in other cases by comparing the light scattered by feed and effluent. From the results in Fig. 2, however, solutes having the molecular weight of the effluent should be highly rejected, and light scattering indicated that even higher-molecular-weight species came through the membrane with Carbowax feeds than with the Wyandotte PEG series. These observations argue that there is also substantial leakage through membrane imperfections, or that there is perhaps some lower limit on the permeability (relative to solvent) of organic solutes, not very sensitive to molecular weight.

Salt rejections (0.04 M NaCl, 10^{-4} M Zr(IV), feed pH 3), measured from time to time during the study summarized in Fig. 1, varied from 44 to 57% and did not correlate in any obvious way with the rejection of the sugars; exposure of the membrane to NaCl solution did increase permeabilities by 20–30% and temporarily lowered the rejection of a sugar below that observed immediately before exposure. In some cases during the measurement with silver frits summarized in Fig. 2, water–organic solute–salt solutions were tested. Results were erratic, but there appeared to be no major effect of presence of organic material on salt rejection, although at times introduction of salt seemed to decrease rejection of organic.

We have so far investigated filtration of organics by only a few other dynamically formed membranes. A membrane formed on a 0.8-μ silver frit by treatment with bentonite additive, followed by humic acid, rejected 77% of the sucrose from a 5 wt. % solution (permeation rate, 0.05 cm/min at 2000 psi). A membrane formed on 0.2-μ silver with the polyelectrolyte additive poly(vinylbenzyltrimethyl ammonium chloride) rejected 15% from a 5 wt. % sucrose solution with a transmission rate of 0.07 cm/min at 500 psi. Membranes that reject organic solutes have also been formed on other porous supports, for example, hydrous oxide membranes on porous carbon tubes.

The permeation rates are rather fast for conventional hyperfiltration membranes [although not for dynamically formed ones (*1*,*2*)]; most of them (unless tested at a low pressure after exposure to a high pressure) are 25–50 gal/day ft^2. It is too early, however, to say whether or not dynamically formed membranes will have practical applications, e.g., in separations or fractionations of organic solutes or in treatment of wastes.

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