

The Structure of Hydrous Zr(IV) Oxide-Polyacrylate Membranes: Poly(acrylic Acid) Deposition

G. B. TANNY and JAMES S. JOHNSON, JR., *Department of Plastics Research, The Weizmann Institute of Science, Rehovot, Israel, and The Chemistry Division, Oak Ridge National Laboratory,* Oak Ridge, Tennessee 37830*

Synopsis

The formation of hydrous Zr(IV) oxide-polyacrylate dynamic membranes was studied by the dependence of water flux decline and steady-state water flux on the concentration of poly(acrylic acid) in the feed. Analysis of the results indicates that the poly(acrylic acid) enters the pores of the hydrous Zr(IV) oxide layer, rather than forming a second layer. This configuration was consistent with scanning electron micrographs of the surface.

INTRODUCTION

Of dynamic membranes,¹ those composed of a hydrous oxide and a carboxylic organic polyelectrolyte^{2,3} have appeared most promising for brackish water desalination⁴⁻⁶ and for other applications requiring salt filtration, for example, in treatment of textile dyeing wastes⁷ and of kraft pulping wastes.⁸ The membranes are formed in a two-step process, in which a hydrous oxide layer is filtered at high circulation velocity onto a porous support from a dilute solution of a salt or a colloid of the metal ion, typically Zr(IV). The dynamic hydrous Zr(IV) oxide membrane usually has a high flux, perhaps 1000 gpd/ft², for the supports discussed here, and moderate salt rejection (~45% for a 0.05M NaCl solution at pH 4). In the second step, a dilute solution of poly(acrylic acid) (PAA) at pH 2 is contacted with the membrane, and the pH is gradually raised to 7.

The considerable information available concerning the effect of varying conditions during formation on final membrane properties^{2,3} indicates that the process is quite complex, and there is little known with certainty of the final structure. In this paper, which is part a general study of the mechanism of dynamic membrane formation,⁹ the effect of polyacrylate concentration in the formation of the second layer, particularly on flux decline during the process, is examined. Scanning electron micrographs of dual-layer membranes are also presented. The results are discussed in terms of two plausible mechanisms: formation of a gel layer through concentration polarization¹⁰ and a filling of pores or depressions in the hydrous oxide layer, as polyelectrolytes were found to do in the case of dynamic membranes formed on partially cured cellulose acetate supports.^{11,12}

* Research sponsored by the Energy Research and Development Administration under contract with Union Carbide Corporation.

EXPERIMENTAL

Flux Decline Experiments

A number of hydrous Zr(IV) oxide membranes were prepared simultaneously, in a hyperfiltration loop described previously,² on a 0.4- μ Acropor AN support (Gelman Inst. Corp.) using a $10^{-4}M$ ZrOCl₂ solution at pH 4 (adjusted from 3.6 with NaOH) in 0.05M NaCl at a formation velocity of 15 ft/sec and pressure of 950 psi. Acropor supports were wrapped around a porous stainless steel tube, and the pressurized membrane solution was circulated in the annulus. The various test sections were stored in water and individually subjected to polyacrylate layer formation at different concentrations of PAA. After exposure to a PAA solution at pH 2, the pH was gradually raised to 7. In a second set of experiments, a membrane was subjected to stepwise changes in the PAA concentration, with intervening cycles to pH 7.

Scanning Electron Micrographs

Dynamic membranes were simultaneously prepared on 0.025- μ Millipore supports in the manner already described. After completion of the hydrous Zr(IV) oxide layer, one sample was removed, while the other was subjected to polyacrylate layer formation with 50 ppm PAA. Both samples were freeze dried, coated with Pd-Au, and observed in a Jeol scanning electron microscope.

RESULTS

The fluxes and rejections of the hydrous Zr(IV) layer and of the dual-layer membranes at the end of their formation are summarized in Table I. The properties of all sublayers were roughly similar, and, except for the one formed

TABLE I
Flux and Rejection for Zr(IV)-PAA Dynamic Membranes Formed on 0.45- μ Acropor Support with Various Concentrations of PAA^a

Sample no.	PAA Acrysol A-3 concentration, ppm	Hydrous Zr(IV) oxide			Final result with polyacrylate		
		pH	Flux, gfd	Rej., ^b %	pH	Flux, gfd	Rej., ^b %
1	200	3.8	960	45	7.1	78	94
2	200	3.8	1000	47	7.1	74	94
3	100	3.8	850	43	7.0	71	83
4	50	3.8	820	43	7.2	82	91
5	25	3.8	890	43	7.0	74	88

^a $T = 25^{\circ}C$; pressure = 950 psi; feed = NaCl, $5 \times 10^{-2} N$.

^b Rejections are reported as $R_{obs} = 1 - [(C_{NaCl})_{\omega} / (C_{NaCl})_B]$, where ω indicates the filtrate and B is the turbulent core of the circulating solution. This rejection is lower than the rejection of salt at the membrane-feed interface, because of concentration polarization. Differences are substantial, particularly for the hydrous oxide membranes, because of their high flux.

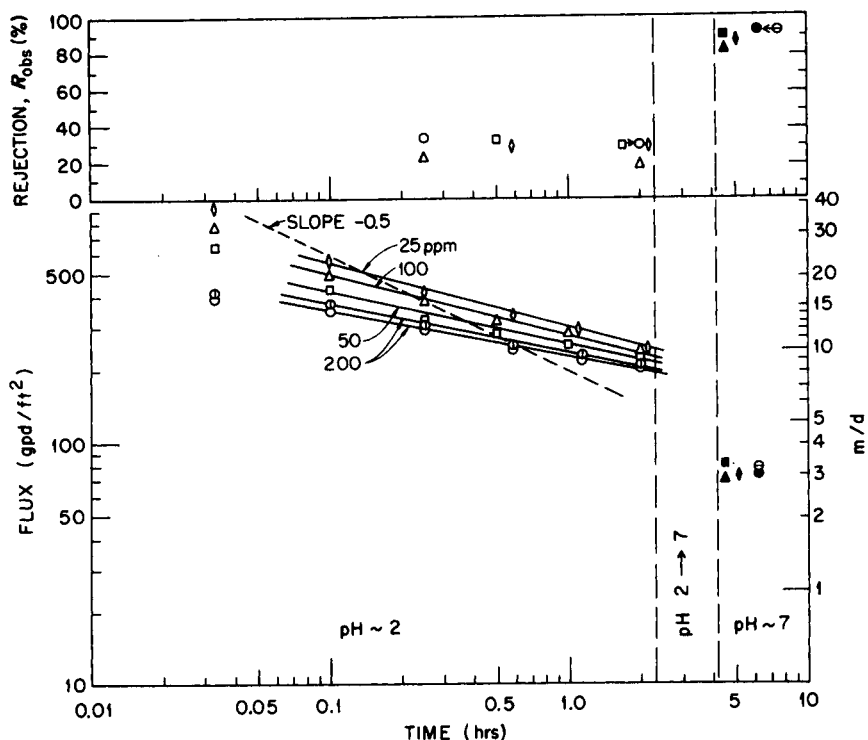


Fig. 1. Flux decline during formation of PAA layer on Hydrous Zr(IV) oxide membranes; 0.45- μ Acropor AN (950 psi; 15 ft/sec; 30°C; 0.05M NaCl):

pH 2	ppm PAA	pH 7
◇	25	◆
□	50	■
△	100	▲
○	200	●
○	200 ^a	⊖

^a Duplicate Wrap

from 100 ppm PAA, which had rejection appreciably lower than the others, the dual-layer membranes were not very different.

Flux decline and rejection during formation of polyacrylate layers for several concentrations of PAA are shown in Figure 1. Fluxes dropped sharply from the value for the hydrous oxide sublayer, particularly for the higher PAA concentrations. After a few minutes, an approximately linear decline of log flux versus log time set in. The slope was steeper for lower PAA concentrations, and the fluxes thus tended to approach one another. Rejections were lower at pH 2 than those of the sublayer. Raising pH to 7 resulted in a sharp rise in rejection and in a decline in flux by a factor of 3 or 4, fluxes for all PAA concentrations being within scatter of one another. (The changes induced by the treatment with PAA persist after the PAA is removed from the feed, and the final fluxes and rejections are measured with 0.05M NaCl alone.²)

Figure 2 summarizes a run in which the PAA concentration was initially 25 ppm. After the pH was raised to neutrality, the circulating solution was recycled

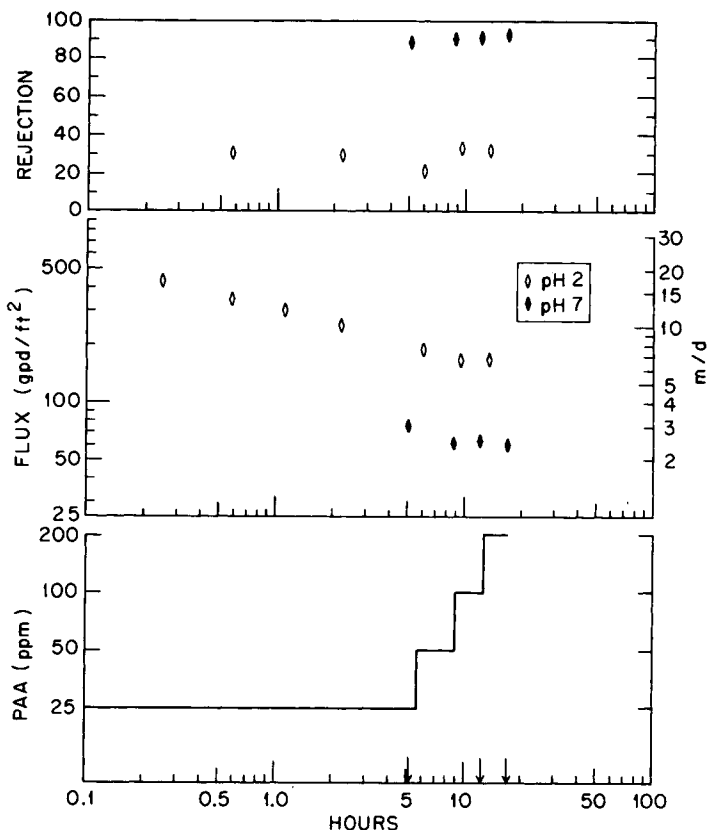


Fig. 2. Fluxes as a function of successive additions of Acrysol A-3 PAA. Cycles to neutral pH between polyacrylate additions (950 psi; 15 ft/sec; 30°C; ↓, shutdown; 0.45- μ Acropor AN; 0.05M NaCl).

to pH 2 and the PAA concentration raised; this cycle was repeated several times. Trends of flux and rejection with time did not appear to be influenced to any great degree by the change in PAA concentration, and the flux and rejection changes effected by pH were reversible.

Figures 3 and 4 present electron micrographs of a hydrous Zr(IV) membrane, and of a dual-layer membrane, respectively. The surface in both cases appears pitted, likely a reflection of exposure to the turbulent circulating fluid during membrane formation. There is relatively little difference between the appearance with and without polyacrylate, an observation which could be taken as indicating that there is no substantial gel layer. However, the expected high water content and the dehydration necessary in sample preparation might cause a thin layer to be overlooked by this method, and a conclusion on these grounds alone would not be warranted. A marked observed effect of PAA was a substantial decrease in susceptibility of the membrane to beam damage when it was present.

DISCUSSION

The fluxes and rejections of the membranes after pH was raised are in the range reported earlier. The increase in rejection on increase in pH has been

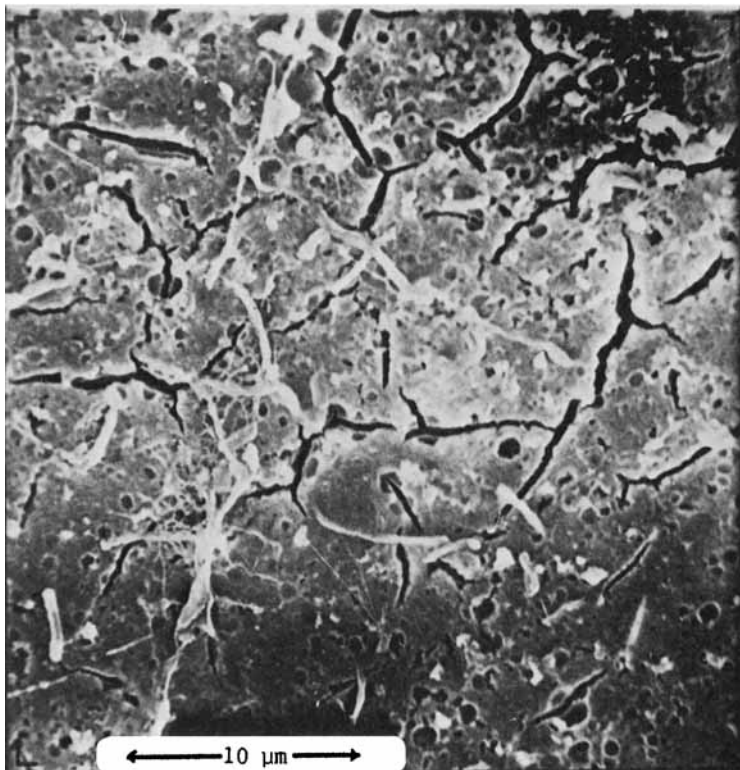


Fig. 3. Scanning electron micrograph of the surface of a Zr(IV) membrane formed on a 0.025- μ Millipore support at 15 ft/sec. Cracks in the surface are the result of beam damage during the focusing operation and were not present initially.

attributed to higher ion exchange capacity effected by neutralizing poly(acrylic acid), and the decrease in flux, to greater drag on the solution flowing through the ionized polyelectrolyte.^{2,3} The reversibility of these effects of pH are perhaps more strikingly documented in Figure 2 than in previous reports.

In this paper, our main interest is in the PAA component. Since hydrous Zr(IV) oxide is an anion exchanger at acidic pH, one possibility is that carboxylate groups attach themselves to positively charged sites in the sublayer. At least as a sole explanation of the formation of a PAA membrane, this picture seems unsatisfactory. Polyacrylate does not change properties to those expected of a polyacrylate membrane when introduced in NaCl solutions at pH values in the neutral range, even though the charge density of carboxylates is much higher under these conditions than at acidic pH, where conversion to polyacrylate properties does occur. It is possible that PAA adsorption occurs at low pH because the anion exchange capacity of the hydrous oxide sublayer is greater under these conditions,¹³ but it is not clear why the adsorption is not reversible on raising the pH; pH values above 10 are required to displace rapidly PAA from membranes stabilized by operation for some time.

Two other plausible structures for the PAA layer are (1) a gel deposit on top of the hydrous Zr(IV) oxide layer, or (2) filled pores in the hydrous oxide. We shall discuss the results in terms of idealized models of these possibilities.

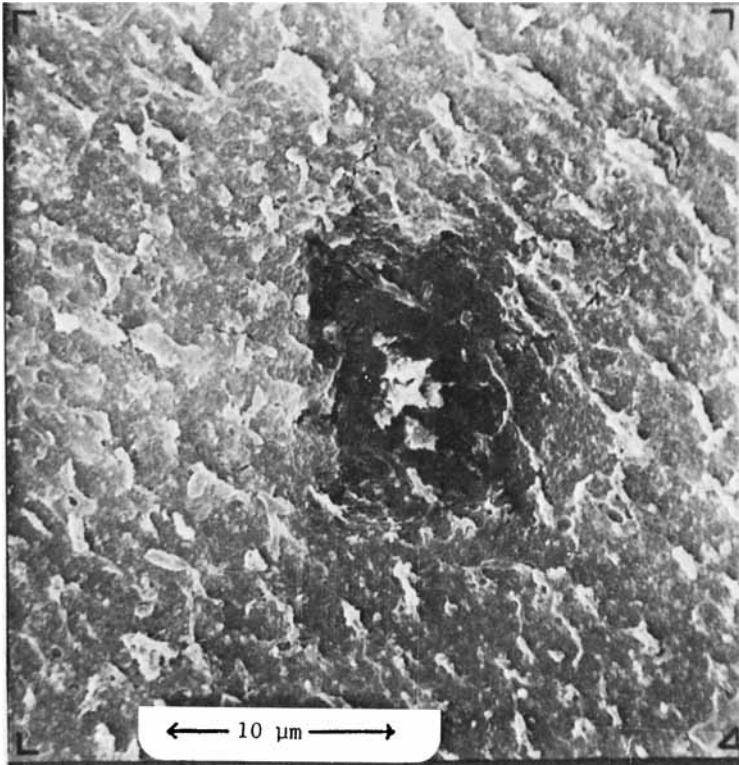


Fig. 4. Scanning electron micrograph of the surface of a poly(acrylic acid)-treated Zr(IV) membrane formed on 0.025- μ Millipore support at 15 ft/sec. Deformation in the center is due to beam damage. Surface debris indicate the direction of water flow over the surface.

In the model of Blatt et al.,¹⁰ polymer concentration (C) builds up from polarization at the interface until a gel precipitates (C_g). The gel thickens until flux is reduced to the point where the polymer carried up to the surface by volume flux J_v passing through the membrane is equal to polymer diffusing away from the interface. The steady state is described by

$$J_v C - D_p dC/dx = 0 \quad (1)$$

where x is distance in the direction normal to the membrane, and the diffusion coefficient D_p includes the effect of turbulent eddies, when appropriate.

Integration between the surface of the gel layer and a point in the solution where concentration is C_B , that of the bulk solution, gives

$$\ln(C_g/C_B) = J_v \delta / D_p \quad (2)$$

where δ is the thickness of the layer in which polymer concentration varies. In the simplest case, the filtered polymer does not affect osmotic pressure appreciably (a good approximation for PAA in acidic solutions), and there is no compaction of the gel layer. The last restriction implies that a step change in pressure will produce a transient increase in flux which falls to the original value as the gel layer thickens. Steady-state flux will be affected by hydrodynamics, however, and, more pertinent to the present case, where circulation velocity was kept constant, will depend linearly on $-\ln C_B$.

In the examples for which this model has been shown to be a good approximation, steady states are attained in the order of a minute.¹⁰ Flux declines continue to much longer times in Figure 1, but the concentration of PAA is much less than the 1%-and-up polymer solutions usually cited in illustrations. However, the fact that fluxes for all concentrations appear to be approaching one another with time, and are the same within scatter when pH is raised, does not follow predictions of the gel model. The insensitivity of flux trends to increments in PAA concentration in Figure 2 is confirmation. In addition, the fact that the membrane persists when PAA is removed from the pressurized solution, rather than diffusing away as one would expect for a reversible gel, argues against this picture.

The pore-filling model we shall use for discussion is highly idealized: an array of identical pores in the hydrous oxide layer is assumed, which are filled at a rate linearly dependent on PAA concentration. At the start, all pores are open; and at the end, all pores are filled. But the flux through a filled pore is smaller than that through an open pore, because of drag of the polyelectrolyte on water flow. The total number of pores/cm² is N , of which n are open and n' are filled. Volume flow/cm² will depend on the number of filled and unfilled pores:

$$J_v = k_2 n + k_3 n' \quad (3)$$

$$n = \frac{J_v - k_3 N}{k_2 - k_3} \quad (4)$$

and

$$\frac{dJ_v}{dt} = (k_2 - k_3) \frac{dn}{dt} \quad (5)$$

The rate of filling of the pores depends on the number of unfilled pores and the PAA concentration:

$$\frac{dn}{dt} = -k_1 [\text{PAA}] n \quad (6)$$

from which

$$n = N \exp \{-k_1 [\text{PAA}] t\} \quad (7)$$

$$\frac{dJ_v}{dt} = -(k_2 - k_3) k_1 [\text{PAA}] n = -(k_2 - k_3) k_1 [\text{PAA}] N \exp \{-k_1 [\text{PAA}] t\} \quad (8)$$

The initial value of J_v , $(J_v)_0$, is $k_2 N$; and the final value, $(J_v)_\infty$, is $k_3 N$. Integration of eq. (8) from 0 to t gives

$$\ln \left\{ \frac{J_v - (J_v)_\infty}{(J_v)_0 - (J_v)_\infty} \right\} = -k_1 [\text{PAA}] t \quad (9)$$

The pore filling model predicts (i) that the final flux is independent of PAA concentration, and (ii) that the rate of flux decline, as measured by the slope of $\ln \{[J_v - (J_v)_\infty] / [(J_v)_0 - (J_v)_\infty]\}$ versus t , should be directly proportional to the PAA concentration.

The observations, summarized in Figures 1 and 2 and Table I and discussed in the Results section, appear qualitatively more consistent with the pore-filling model than with the gel layer. The fact that fluxes at pH 2 appear to approach the same value for all PAA concentrations (they extrapolate to about 150 gpd/ft²

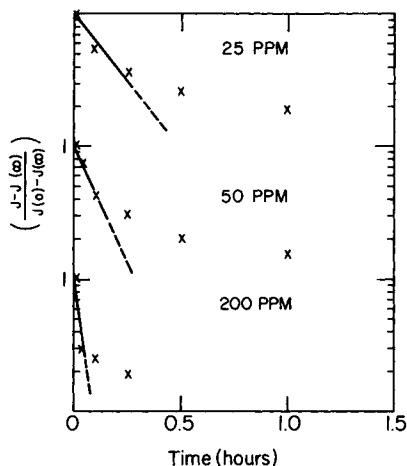


Fig. 5. Flux decline during formation of PAA layer on hydrous Zr(IV) oxide membrane (0.45- μ Acropor; 950 psi; 15 ft/sec; 30°C; 0.05M NaCl).

at 10 hr cf. Fig. 2) and that they are essentially the same at neutral pH (and the confirmation in Fig. 3, in which flux was insensitive to increases in PAA concentration) is the most obvious argument. A slope of -0.5 is indicated in Figure 1. This is the flux decline behavior which should be observed if all or a constant fraction of the material transported to the interface stays there¹⁴; we include it here for comparison with the mechanism of hydrous oxide sublayer formation, which is clearly different from that for the PAA layer. This will be discussed in a separate paper,⁹ but it is perhaps worth noting here that the equivalent pore radii calculated for the hydrous Zr(IV) oxide sublayer are of approximately the same magnitude as those suggested for cellulose acetate supports on which dynamic PAA membranes could be formed.¹²

A quantitative test of the pore-filling model is difficult even if the anomalous 100-ppm PAA results are ignored, as we shall do. Early fluxes are imprecise, since measurements required collections of samples over a period of time. In

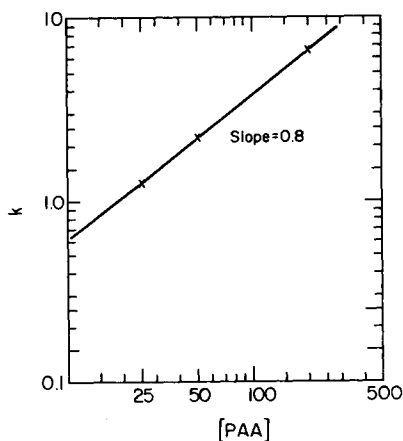


Fig. 6. Variation of initial slope of PAA flux decline plot as a function of PAA concentration.

addition, the assumption of linear dependence of dn/dt on PAA concentration implies a more uniform distribution of PAA sizes than is the case, and the assumption of monodisperse pore sizes is also an oversimplification. Estimation of $(J_v)_\infty$ is uncertain. These factors may be reflected in the nonlinearity of plots of eq. (9) (Fig. 5). We have estimated the initial slopes and plotted their logarithm against the logarithm of PAA concentration in Figure 6. Equation (9) predicts that this plot should be linear, with a slope of unity. In view of the approximations of the model, a slope of 0.8 is not a surprising deviation.

It thus appears that the results from membrane formation history and electron micrographs are inconsistent with a PAA gel layer and are at least consistent with a pore-filling model, even through they do not conclusively establish it. In this regard, the primary function of the acidic medium is to lower the charge density of the polyacrylate chains and thus cause them to coil into dimensions which can enter available pores. The maximum in rejection obtained with membranes formed from PAA of intermediate molecular weights^{2,3} can be taken as an indication of a necessity to match pore and polymer size and a further confirmation of this model.

This research was partially supported by a grant (to G.B.T) from the United States-Israel Binational Foundation, Jerusalem, Israel. The technical help of C. G. Westmoreland is gratefully acknowledged.

References

1. A. E. Marcinkowsky, K. A. Kraus, H. O. Phillips, J. S. Johnson, Jr., and A. J. Shor, *J. Am. Chem. Soc.*, **88**, 5744 (1966).
2. J. S. Johnson, Jr., R. E. Minturn, and P. H. Wadia, *J. Electroanal. Chem.* **37**, 267 (1972).
3. J. S. Johnson, Jr., in *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, Eds., Plenum Press, New York, 1972, p. 379.
4. D. G. Thomas and W. R. Mixon, *Desalination*, **15**, 287 (1974).
5. D. G. Thomas, P. H. Hayes, W. R. Mixon, and J. D. Sheppard, *Desalination*, **15**, 325 (1974).
6. D. G. Thomas, *Desalination*, **15**, 343 (1974).
7. C. Aurich, C. A. Brandon, J. S. Johnson, Jr., R. E. Minturn, K. Turner, and P. H. Wadia, *J. Water Pollution Control Federation*, **44**, 1545 (1972).
8. J. S. Johnson, Jr., E. Minturn, and G. E. Moore, *Tappi*, **57**, 134 (1974).
9. D. Freilich and G. B. Tanny, in preparation.
10. W. F. Blatt, A. Dravid, A. S. Michaels, and L. Nelsen, in *Membrane Science and Technology*, J. E. Flinn, Ed., Plenum Press, New York, 1970, 47-97.
11. G. B. Tanny and J. Jagur-Grodzinski, *Desalination*, **13**, 53 (1973).
12. Y. Ozari, G. B. Tanny, and J. Jagur-Grodzinski, *J. Appl. Polym. Sci.*, **21**, 555 (1977).
13. K. A. Kraus, H. O. Phillips, T. A. Carlson, and J. S. Johnson, Jr., in *Proc. 2nd Int. Conf. Peaceful Uses Atom. Energy, Geneva*, **28**, 3 (1958).
14. K. A. Kraus, *Proc. 29th Industrial Waste Conf.* 1974, Purdue Research Foundation, p. 1059.

Received July 28, 1976