Separation & Purification Reviews
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

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To cite this Article Tanny, G. B.(1978) 'Dynamic Membranes in Ultrafiltration and Reverse Osmosis', Separation & Purification Reviews, 7: 2, 183 — 220
To link to this Article: DOI: 10.1080/03602547808066063
URL: http://dx.doi.org/10.1080/03602547808066063

SEPARATION AND PURIFICATION METHODS, 7(2), 183-220 (1978)

DYNAMIC MEMBRANES IN ULTRAFILTRATION AND REVERSE OSMOSIS

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INTRODUCTION

In principle, the basis of the filtration process appears to be as clear as the filtrate one would sometimes like to achieve. One needs, (it would seem), only to select a porous matrix whose flow pathways are dimensionally compatible with the desired level of selectivity and to provide the necessary driving force in the form of a pressure gradient. Of course, even for classical microfiltration of particulates this concept is an oversimplification, since conventional filters often display significant selectivity toward species five to ten times smaller than their nominal pore size rating. Thus it comes as no surprise to find similar effects carrying over into the realm of ultrafiltration and reverse osmosis, and for identical reasons. The conditions at the filter/solution boundary and the interaction between the solute being filtered and the membrane barrier

often contain the key factors which determine the overall behavior of both volume flux and selectivity. When the solute is a particle of colloidal dimensions (whether organic or inorganic), these factors may create a relatively permanent change in the filtrative characteristics of the original membrane and one then speaks of "dynamic membrane" formation. Although the term "dynamically formed membrane" would be a more accurate description, the usage of "dynamic membrane" has become well established.

Due to the wide range of filtration conditions which can lead to dynamic membrane formation, it is possible to describe more than one class or type of membrane. To some, their existence is an undesirable by-product of the process, and a presence which one would prefer to minimize or eliminate [1-3].

Others have utilized dynamic membrane formation on microporous supports possessing no initial selectivity toward small molecules or ions to deliberately create barriers capable of desalting water[4]. Such systems constitute a distinct class within the family of reverse osmosis membranes and they are characterized by a high overall efficiency[5] due to their high water fluxes coupled with moderate salt rejections. For this reason they have been found particularly useful in wastewater treatment applications [6-8]. In addition, they offer the advantage of "in situ" formation and regeneration, thereby reducing "down time" on equipment.

Thus, whether we deal with dynamic membranes by choice or accident, it is important to consider the following questions about them, namely,

(a) what are the known types of "classes" of dynamic membranes and their usual constituents?

(b) what are the analytical tools available to distinguish these different classes?

and,

(c) how do the various operating parameters (e.g. pressure, concentration, etc.) effect the membrane water flux and rejection?

The contents of the following review of dynamic membranes will be structured toward providing some answers to questions (a) to (c). For additional background and detail the reader is referred to references 1,3 and 4.

CLASSIFICATION OF DYNAMIC MEMBRANES

In Table I, dynamic membranes have been divided into three distinct categories or "classes". The numerical assignment is based primarily on a set of simple geometrical considerations of the dynamic membrane forming solute radius, r_a, and the membrane pore radius, r_o. However, the Class I designation was also made because chronologically this dynamic membrane type was the first to be both identified and well modeled mathematically.

While each of the various columns in Table I will be examined in detail during the discussion of each membrane class, column four, relating to flux decline, deserves special attention. Flux decline data has often been reported, but the wealth of information which such data can provide has only rarely been tapped. What has been given insufficient recognition is the fact that the time dependence of the flux (or its integral the total volume of throughput) can constitute the key criterion by which dynamic membranes are classified.

CLASS I DYNAMIC MEMBRANES

A. Mechanism of Formation Effects of Concentration and Pressure:

When a solution gel forming macromolecular solute is ultrafiltered through a membrane whose pore size is sufficiently small to completely (or almost completely) retain the macromolecule, a phenomenon known as "concentration polarization - gelation 1,2" may produce a dynamic membrane on the surface

Table 1.

Dynamic Membrane Type	Relative Support Pore Size Necessary for Membrane Formation	Type of Dynamic Membrane Forming Additive and Porous Support
Class I	$r_o < r_a$ a)	gel-forming polymers and polyelectrolytes + ultrafilter
Class II	independent, will form for $r_o >> r_a$ and $r_o < r_a$	inorganic colloids non solute selective microporous filter medium
Class III	$r_o \approx r_a$	flexible polymers and polyeletrolytes + membrane which already demonstrates some salt rejection, usually 50-50% of 5×10^{-2} M NaCl

a) - r_o - support pore radius, r_a - radius of additive in solution.

of the ultrafilter. This class of dynamic membrane is probably the best known and, since the authors of that model have also thoroughly reviewed the subject, we shall include only its essential elements in order to compare and contrast its behavior with the two other classes of dynamic membranes.

The major features of the system may be summarized as

Characteristics of Dynamic Membrane Systems.

Flux Decline Law During Membrane Formation	Dependence of Final Flux on Additive Concentration	Flux Dependence on Pressure (in Presence of Additive)	Dependence of Secondary Solute Rejection on Support Pore Size
Steady-state achieved within seconds	- log C	independent	depends on separate solute σ's of dynamic membrane and support plus presence of other solutes
$\frac{1}{J} - \frac{1}{J_o} = k_1 t$ and/or $t/V - 1/J_o = k_1 t/2$ followed by $t/V = (V+2V_f)/K$ or $J_V(t) = (K/t)^{\frac{1}{2}}/2$	$C^{-\frac{1}{2}}$	$\Delta P^{\frac{1}{2}}$	independent
$\ln\{\frac{J-J_{(\infty)}}{J_{(o)} - J_{(\infty)}}\} = -k_2 t$ or $J_{(o)} - J_{(t)} = k^1 V$	independent	unknown b)	very sensitive

b) - the constant k_2, which determines the rate of approach in $J_{(\infty)}$, is directly dependent on C.

follows:

(a) the macrosolute is effectively retained by the UF filter;

(b) the system attains a steady state permeate flux, J_V, within a few seconds (and therefore the model does not consider the time dependence of the approach to steady-state);

(c) the system is in a state of well developed turbulent flow.

This situation is shown schematically in Fig. 1, in which a boundary layer of thickness, δ, exists next to the membrane wall. The concentration profile of the macrosolute within the layer δ is the result of the balance between the convective flow of macrosolute, $J_v C$, and the back diffusional processes,

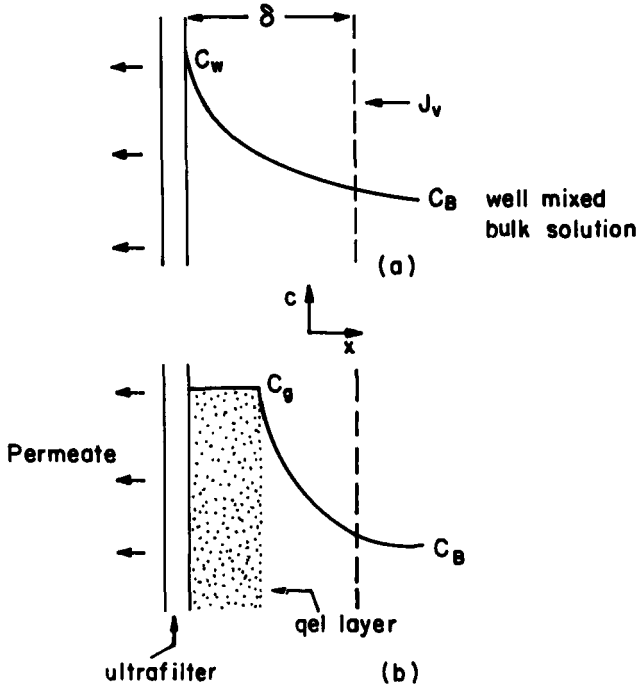


FIGURE 1

Schematic representation of concentration polarization (a) and the formation of a Class I dynamic membrane by concentration polarization-gelation (b).

The well mixed solution of bulk concentration, C_B, flows at the linear velocity, u, over the ultrafilter. The permeate flux, J_v, causes the wall concentration to increase to C_w within the polarization layer, δ.

including those due to stirring. Thus, within this layer, the concentration of the retained species drops from the maximum at the wall, C_W, to that of the bulk, C_B. If the concentration-polarization is such as to reach a gel concentration, C_g, a gel layer will form on the surface of the membrane. This layer acts as an additional membrane in series with the UF filter and it will grow until a point is reached at which $J_v C$ is again balanced by the back diffusion of macromolecules, so that the gel/liquid interface concentration drops below C_g. Since C_W is now a constant, equal to C_g, J_V becomes a dependent variable for a given C_B and the set of hydrodynamic conditions determining back diffusion.

This situation is expressed by the relation[1]

$$J_V = k_s \ln \frac{C_W}{C_B} \tag{1}$$

where k_s is the back diffusion mass transfer constant appropriate to the filtration conditions. Thus, in the case of Class I dynamic membranes, the flux is predicted to vary as $-\ln C_B$.

In the presence of the dynamic membrane - forming macrosolute, the water flux exhibits a two region behavior as a function of pressure (Fig. 2), which is typical of Class I dynamic membranes. The low pressure region characterized by a linear dependence of flux on the applied pressure, is sometimes termed the region of membrane control. The region of pressure in which the flux becomes <u>independent</u> of the applied pressure is the region of boundary layer control. This "saturation effect" dependence on pressure comes about in the following manner: The steady state flux is related to the pressure by

$$J_V = \frac{\Delta P}{R_m + R_p} \tag{2}$$

where $R_{m,p}$ are the hydraulic resistances of the membrane and the polarization layers, respectively. Equating equations (1) and

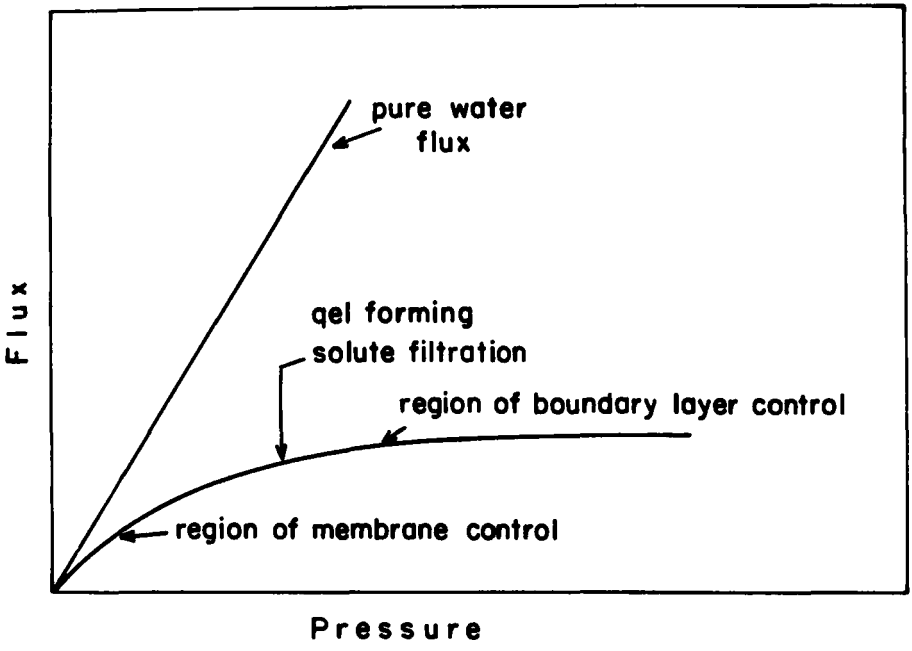


FIGURE 2

Flux versus pressure for a feed containing a solute which creates a gel polarization layer (pure water feed behavior is shown for reference).

(2) we obtain

$$\ell n \frac{C_W}{C_B} = \frac{\Delta P}{k_s (R_m + R_p)} \qquad (3)$$

For all applied pressures in which the hydrodynamic conditions maintain $C_W < C_g$, equation (3) will remain balanced by the fact that C_W will change with a change in ΔP. However, the moment $C_W = C_g$, the L.H.S. of equation (3) becomes constant and an increase in ΔP must be compensated for by an increase in R_p. Such an increase can come about either due to the compression of the gel

layer resulting in a partial loss of its fractional water content, thereby effecting the gel's intrinsic hydraulic permeability, or by a further growth in the thickness of the gel layer, δ. In principle, either or both of these processes can occur. For this reason the optimum operating condition is likely to be achieved at a low pressure and at as highly turbulent a flow regime as possible in order to minimize δ. It has usually been found that J_v varies as the 1/3 power of u, the linear velocity (over the membrane surface) of the solution being filtered[1].

B. Rejection, Stability and Uses of Class I Dynamic Membranes:

The presence of the gel layer also has an effect on the rejection of molecular weight solutes which are normally permeable to the ultrafilter. Hence, the separation of protein mixtures by ultrafiltration membranes of different molecular weight cut-off is often confounded by dynamic membrane formation. For example, the presence of γ-globulin in a protein mixture containing human serum albumin (HSA) can create a dynamic membrane whose rejection of HSA is proportional to the square root of the γ-globulin concentration[1]. Other examples may be found with respect to lower molecular weight solutes and even ionic species. Ultrafiltration membranes possessing a 10,000 M.W. cut-off do not usually display any significant rejection toward aqueous solutions of amino acids or mineral salts. However, in the ultrafiltraton of skim milk[9] or cheese whey[10] some rejection of such species is observed, and this phenomenon may be attributed to the polyelectrolyte nature of the proteinaceous dynamic membrane which is formed.

In principle, the Class I dynamic membrane should be unstable if the original macrosolute solution is replaced by another medium in which the macrosolute is soluble. However, if one could immobilize the gel layer, then the membrane would be stabilized and retain its useful properties. One example of such an approach was taken with enzymes which could then be used

for the continuous conversion of substrate[11,12]. These authors studied dynamic membranes prepared from β-glucosidase[11] and acid phosphatase[12] which were gelled on flat UF membranes and in a hollow fiber capillary reactor. They determined that the enzymes immobilized as gels not only retained their activity, but increased their stability. In addition, using a simple analytical model (Fig. 3) they were able to calculate fundamental kinetic constants of the enzyme reaction[12].

CLASS II DYNAMIC MEMBRANES

A. The Initial Formation Period

Class II dynamic membranes are first distinguished by the fact that they may be created by filtering dilute inorganic colloid solutions through porous substrates whose pore radius, r_o, may be as much as three orders of magnitude larger than the size of the particles being filtered[4]. The exact mechanism by which the membrane first begins to form has not been definitively established, although some qualitative ideas have been investigated.

Since the support clearly possesses little or no initial selectivity toward the colloid, it has been suggested[4b] that dust or bacteria present in the water could bridge the pore entrance and act as a very fine filter aid or adsorbent for active materials. This thesis was tested for hydrous Zr(IV)-oxide solutions in double distilled water (turbidity $\sim$ 0.2 NTU) through a 0.1μm Millipore support, in a small unstirred batch cell[13]. The flux decline behavior, plotted in Fig. 4, as the inverse of the flux versus time, was identical to that of solutions for which no special precautions were taken (turbidity 2-3 NTU). Furthermore, the mechanism of flux decline (cf. section B) corresponds to an internal pore clogging phenomenon, rather than a cake build-up on larger foreign particles retained

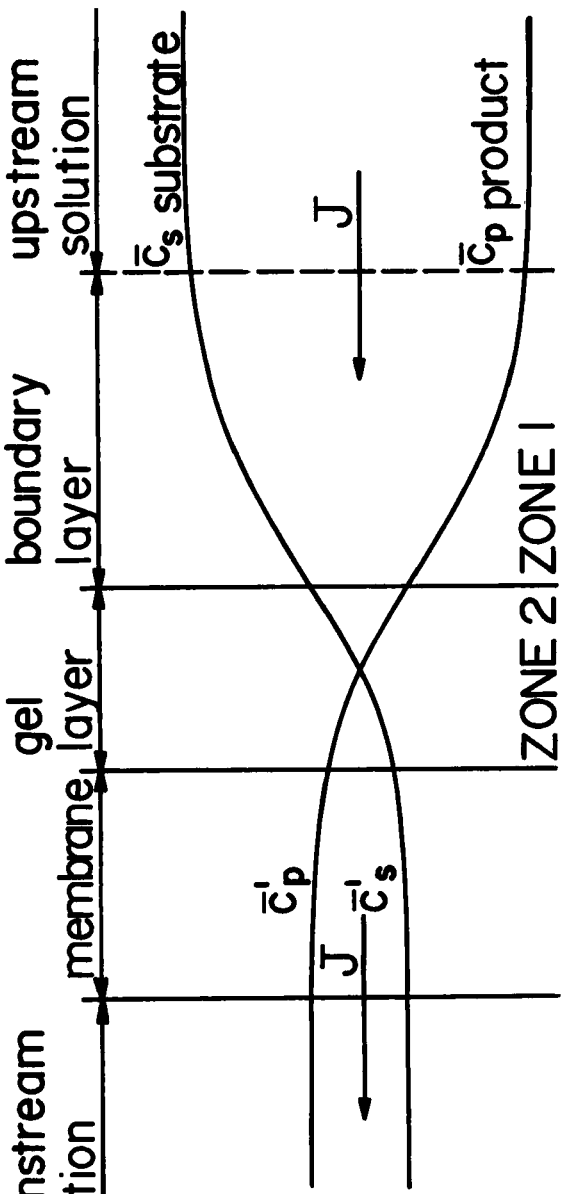


FIGURE 3. Operation of a model Class I Enzymatic Dynamic Membrane. a) qualitative concentration profiles. b) mass balance in the reservoir. Reproduced with permission from Ref. 12.

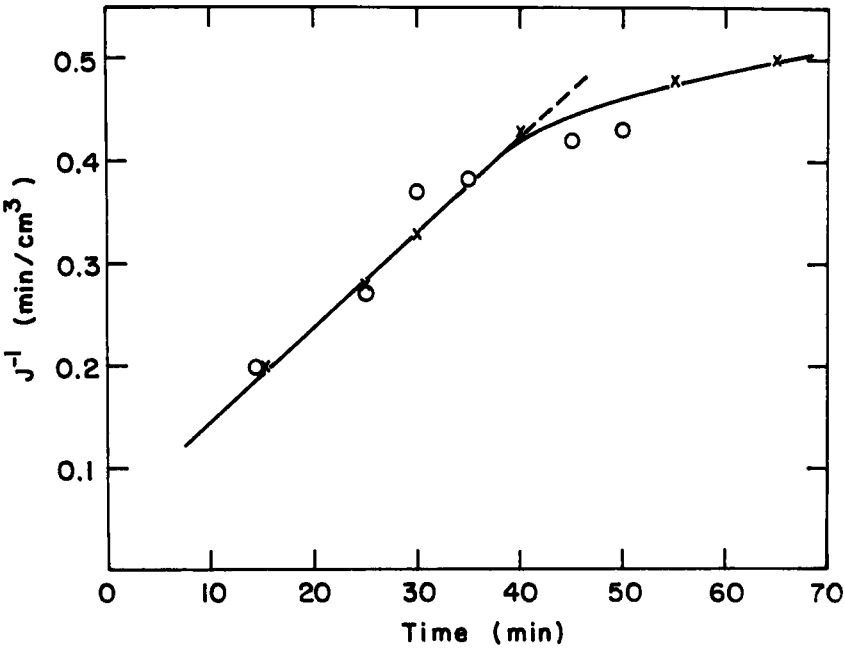


FIGURE 4

Initial flux decline of a 0.05%, pH=4, Zr(IV) solution made up with (o)-deionized water or (x)-double distilled water and filtered at 800 psi on 0.1μm Millipore support.

on the membrane surface. Thus, while the filter aid possibility can not be generally disregarded, this result is indicative of a more fundamental mechanism which is also operative.

B. Phenomenology of the Formation of Class II Dynamic Membranes

In contrast to the almost instantaneous formation of Class I dynamic membranes, Class II dynamic membranes possess a definite formation period which has been studied through observations of flux decline at constant pressure.[14]

These observations were made with dilute solutions of hydrous Zr(IV)-oxide and microporous support filters (pore diameter 0.05 - 1.0 μm) in unstirred batch cells.

At pressures < 7 atm., flux decline occurs via a mechanism of particle inception in the pore which decreases the flow rate due to a decrease in the pore volume (Fig. 5a,b). During this stage the rejection of colloid is considerably less than unity (Fig. 6), and the flux decline follows either the relation

$$\frac{1}{J_{(t)}} - \frac{1}{J_{(o)}} = k_1 t \qquad (4)$$

where $J_{(t)}$ is the volume flux (not normalized for the apparent membrane area)

or

$$\frac{t}{V_{(t)}} - \frac{1}{J_o} = \frac{k_1 t}{2} \qquad (5)$$

where $V_{(t)}$ is the total filtrate volume having passed the membrane up to time, t.

After some time, τ, (we may call it a "transition time") the colloid rejection approaches unity and the flux behavior becomes typical of that for classical "cake filtration"[15]. At this point, all (or a constant fraction) of the colloid particles brought up to the surface of the membrane are deposited as a "cake", and the flux follows the relation (Fig. 5c)

$$\frac{t}{V_{(t)}} = \frac{1}{K}\left(V_{(t)} - 2V_f\right) \qquad (6)$$

or

$$J_{(t)} = \frac{1}{2}\left(\frac{K}{t}\right)^{\frac{1}{2}} \qquad (7)$$

In equation (6), V_f is a volume of filtrate which produces a hydrodynamic resistance equal to that of the porous support and K is a "cake filtration constant" which may be expressed as

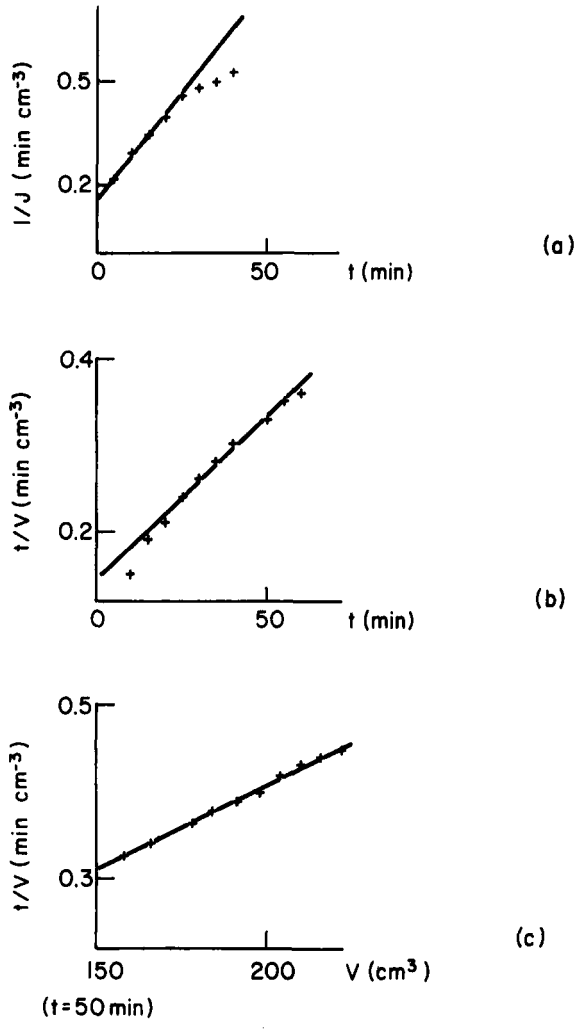


FIGURE 5

Filtration mechanisms during formation at 3.4 atm. (a) and (b) - pore clogging mechanisms. (c) - cake growth mechanism after 50 min. filtration. Feed: Zr(IV) 0.01%, 5 x 10^{-2}M NaCl, pH 3.8. 0.1μm Millipore support (reproduced with permission from Ref. 14).

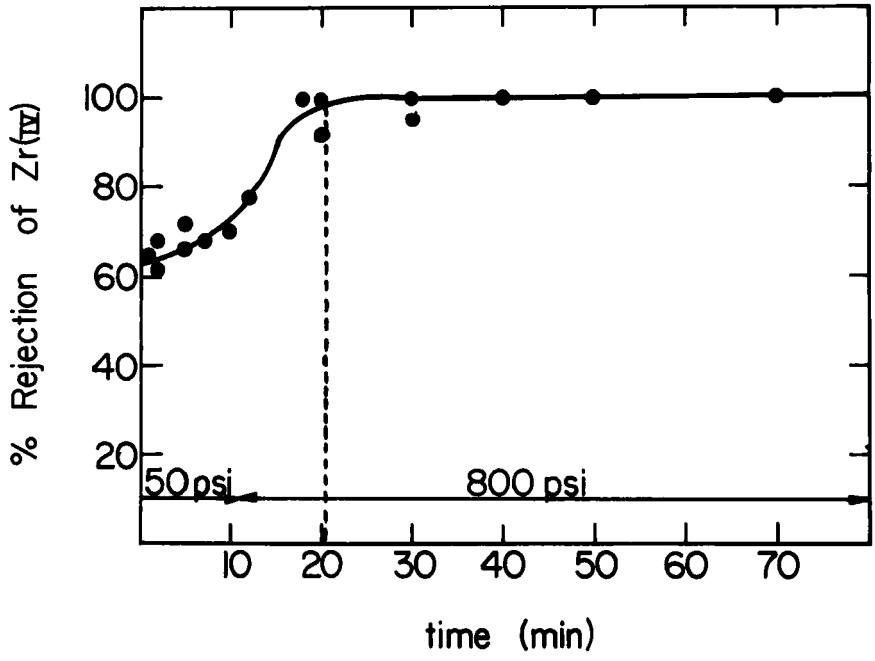


FIGURE 6

Zr(IV) rejection during dynamic membrane formation. Feed: 0.05% Zr(IV), 5 x 10^{-2}M NaCl, pH 4; 0.1μm Millipore support (reproduced with permission from Ref. 14).

$$K = \frac{2 A^2 \Delta P}{\eta c R_c} \qquad (8)$$

where A is the membrane filter area, η is the viscosity, c is the colloid concentration, ΔP is the applied pressure and R_c is the cake resistance.

Since these experimental observations were carried out at zero crossflow velocity (i.e., dead-ended filtration) it was necessary to establish their relevance to the tangential flow velocity conditions usual for Class II dynamic membrane formation. Equations (7) and (8) predict dependence of J_v on

$t^{-\frac{1}{2}}$ and also that J_v at some time, t, should depend on $c^{-\frac{1}{2}}$. Kraus[16] has shown that dynamic membranes formed from lead plating rinse water obey the relation of $J_v \propto t^{-\frac{1}{2}}$. Flux decline data for the formation of dynamic membranes from hydrous Fe_2O_3[17] can be replotted[14] and also proceed according to this same relation prior to attaining a steady state flux. In addition, for dynamic membranes of hydrous Zr(IV)-oxide the flux after sixty or thirty minutes of formation has been found to depend on $c^{-\frac{1}{2}}$, in the range of formation velocity from 0-35 ft/sec, [14,18] as may be seen in Figures 7a and 7b. Thus the tangential flow velocity does not seem to effect the basic phenomonology. However, it should be noted that equation (7) does not have the form necessary to predict the cake growth limiting mechanism observed in tangential flow dynamic membrane formation and this problem remains to be solved.

The effect of formation pressure on the Class II dynamic membrane is also predicted by equations (7) and (8). The flux, J_v, depends on $\Delta P^{\frac{1}{2}}$, a relation confirmed in batch scale trials[14]. In physical terms this represents the effect of pressure in creating a more tightly packed "cake" of colloid particles. Evidence for such an effect was obtained by Thomas and Mixon[19], who found that hydrous Zr(IV)-oxide membranes formed at low pressure (100-400 psi) had ultrafilter properties, while those formed above 600 psi had significant salt rejections and lower fluxes.

C. Effects of the Microporous Support:

Once formed, Zr(IV)-hydrous oxide dynamic membranes are inherently stable and do not require any fixation process to maintain them because the oxide is not soluble in water. Thus, the dynamic membrane and support may be "potted" in gelatin and fractured so as to measure the the hydrous Zr(IV)-oxide layer thickness (Fig. 8a). As may be seen from Table II, the series of dynamic membranes created on Millipore supports of different pore

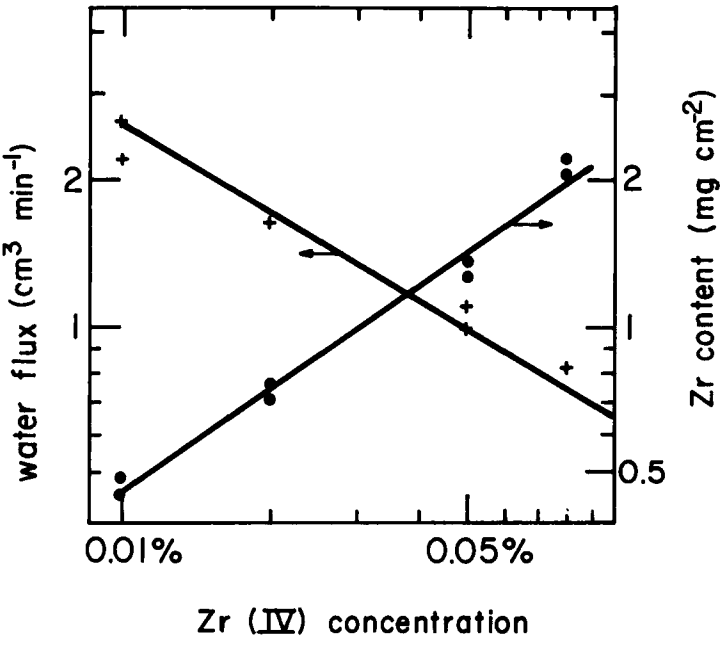


FIGURE 7a

Water flux and Zr contents after 50 minutes membrane formation as a function of the feed concentration. Supporting electrolyte 5 x 10^{-2}M NaCl, pH 4; 0.1μm Millipore support. (from Ref. 14 - zero circulation velocity).

sizes all have very similar membrane thicknesses[20]. However, considering their larger volume flux and rejection, the membranes are very thick by comparison to the 0.1-0.2μm asymmetric layer of conventional R.O. membranes. From electron micrographs, such as that in Fig. 8b, one learns that the dynamic layer almost does not enter the pores of the porous support, whose presence can be seen on the surface in a crack in the cake layer. It is therefore not surprising that the dynamic membrane salt rejection is essentially independent of the support pore size (Table II).

Although the support pore size does not play a definitive role in the formation of a dynamic membrane, this is

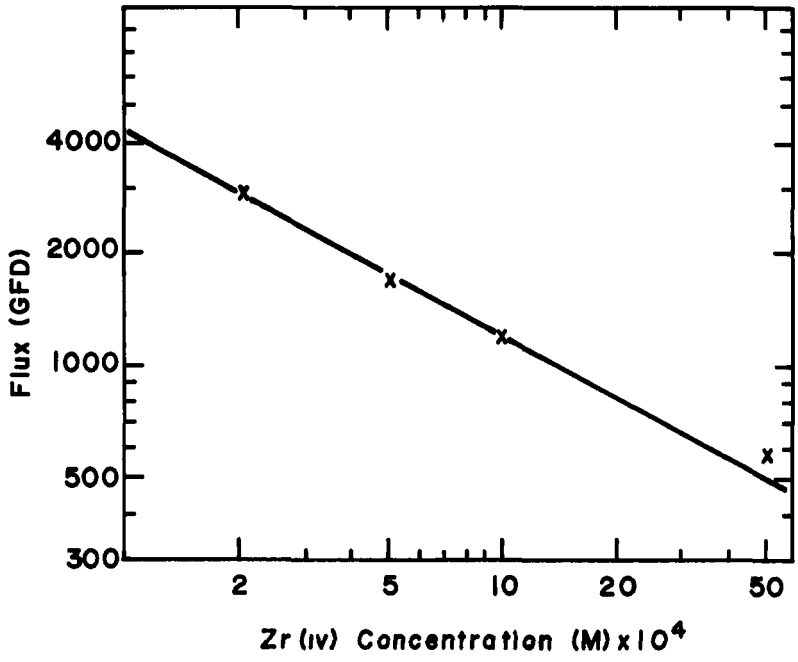


FIGURE 7b

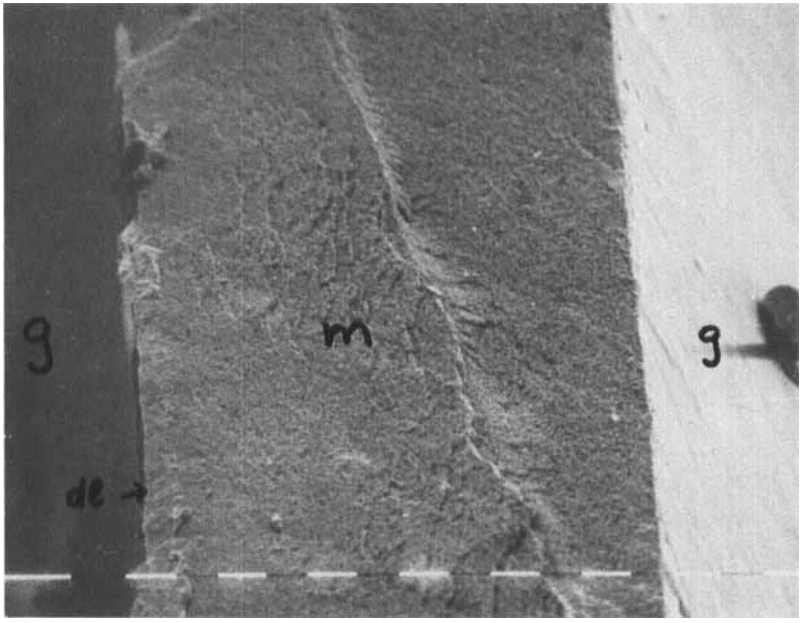
Effect of Zr(IV) concentration on the water flux of Zr(IV) layers formed at 25-35 ft/sec (at 950 psi after 30 minutes - data from Ref. 18).

not meant to imply that the process is completely independent of the nature of the support. Hydrous Zr(IV)-oxide membranes have been successfully formed on Selas porous ceramic tubes, carbon tubes, and microporous polymeric supports[4], with various resulting combinations of flux and rejection. Because of the possible variability between membranes formed on the same support but in different trials, it is difficult to absolutely assign a trend regarding the reason for efficacy of a given support. However, there is some evidence that the best dynamic membranes are formed when the crossflow velocity is sufficiently fast to interact with microroughness in the support surface[20]. This

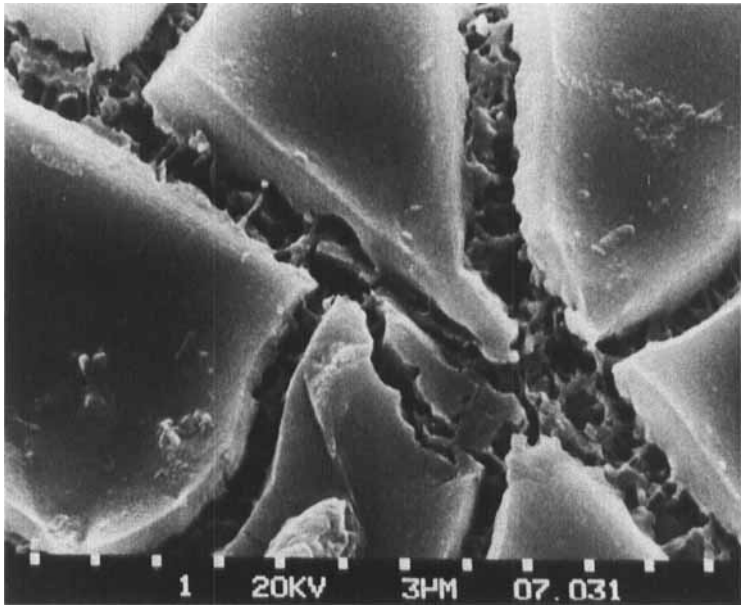
TABLE II.

The effect of support pore size on the average properties of Zr(IV)-hydrous oxide - polyacrylate dynamic membranes.
Pressure = 950 psi, Feed = 10^{-4}M $ZrOCl_2$ + $5x10^{-2}$M NaCl, circulation velocity = 25 ft/sec, T = 25°C. (Ref. 20)

Millipore support pore size (μ)	Zr(IV) hydrous-oxide sub-layer		Zr(IV) hydrous oxide polyacrylate layer		Dynamic membrane thickness (cm)x10^4	Sub-layer hydraulic permeability ($cm^4 dyne^{-1} sec^{-1}$) x 10^{13}	Zr content ($\mu g/cm^2$)	ϕ_w	r (Å)
	Flux (GFD)	Rejection (%)	Flux (GFD)	Rejection (%)					
0.05	337	37.5	53	94.7	10.4	2.51	224±3	0.88	15
0.10	293	45.5	64.5	95.8	18	3.78	388±3	0.88	18.5
0.22	359	39	77	95.2	15	3.86	608	0.78	19.9
0.45	337	44.5	75	95.9	14	3.39	601±21	0.77	18.8



(a)



(b)

evidence comes from two sets of experiments conducted as follows[20]: in the first trial set, two supports were run in the same experiment at crossflow velocities of 10 ft/sec and 25 ft/sec. The membranes were a 0.025μm Millipore support, which is very smooth, and a 0.45μm Acropor AN[1A], which is supported on a fabric and possesses a highly textured surface due to a different number of fibers in the fabric warp and weave. At a formation crossflow of 10 ft/sec the dynamic membranes were identical in flux and salt rejection, while at 25 ft/sec the 0.45μm Acropor AN membrane had more than twice the flux with the identical salt rejection. In the second experimental set, the orientation of the 0.45μm Acropor AN was varied such that in two samples the long axis of the fabric was perpendicular to the crossflow and in two other samples it was parallel. From the results in Table III it is clear that the interaction of the crossflow with the surface roughness creates local hydrodynamic conditions which determine the final membrane properties.

CLASS III DYNAMIC MEMBRANES

As one might expect, if the size of the pore, r_o, is very close to some solution dimension of a polymer or poly-

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FIGURE 8

(a) Cross-section of a hydrous Zr(IV)-oxide dynamic membrane formed at 950 psi, 10^{-4}M $ZrOCl_2$, and 25 ft/sec on a 0.05μm Millipore support. Membrane (m) was potted in gelatin (g). Dynamic layer (dl) may be seen at the interface. Each white bar represents 10μm.

(b) SEM of hydrous Zr(IV)-oxide dynamic membrane formed on a 0.45μm Acropor AN support. Cracks are due to handling and freeze drying. Note open pores of Acropor support between sections of broken membrane cake.

TABLE III.

Effect of 0.45μm Acropor Support Geometry on Zr(IV) - Hydrous Oxide Dynamic Membrane Properties.

pH = 3.8, Feed = 5 x 10^{-2} NaCl, Pressure = 950 psi.
(Ref. 20)

Sample	Feed Solution Flux Geometry Relative to	Flux (GFD)	R_{obs} (%)	With Polyacrylate Layer (pH = 7.0 - 7.2) Flux (GFD)	R_{obs} (%)
2B	|| to long dimension[2A]	850	43	71	83
2A	⊥ to long dimension	640	34	50	69
3B	|| to long dimension	820	43	82	91
3A	⊥ to long dimension	640	34	88	73

electrolyte molecule, r_a, the conditions may favor the formation of yet a third type of dynamic membrane. Polymer molecules of sufficient flexibility can diffuse, with or without the aid of a convective flow into the surface pores of a support membrane. Either as a result of restricted diffusion [21] or strong interactions between the polymer and the membrane, or both, the molecule will continue to reside in the pore. This presence of the polymer (or charged polyelectrolyte) within the surface pores causes a significant change in both the flux and rejection of the original support membrane, and we shall classify this phenomenon as Class III dynamic membrane formation. The conditions for generating such a system can be generalized from the behavior of the dynamic membrane formed by the contact or anionic or cationic polyelectrolytes with partially cured cellulose acetate membranes[22,23] as well as the further treatment of Zr(IV)-hydrous oxide membranes with polyacrylic acid[24].

A. Polyelectrolytes and Supports

The most successful Class III polyelectrolytes found to date have been characterized by a flexible C-C backbone carrying pendent charged groups such as quaternized 2-polyvinylpyridine[22], polyacrylic acid[23,24] and a block copolymer of polyacrylic acid with polystyrenesulphonic acid[23]. Since the "fit" between the pore and the molecule must be very close, the dimensions of the pores are usually quite small and thus the membrane support already demonstrates some salt rejection, usually between 40-50% of a 5×10^{-2} M NaCl solution. The salt rejection of the dynamic membrane is very sensitive to the initial salt rejection, which may be taken as a measure of the pore size. Examples of this effect are shown in Fig. 9a, b for quaternized 2-PVP-asymmetric cellulose acetate (CA) dynamic membranes, and 1:4:1 block copolymer PAA/PSSA/PAA - asymmetric CA dynamic membranes, respectively. Pores which are too large (low salt rejection) or too small (high salt rejection) do not form good Class III

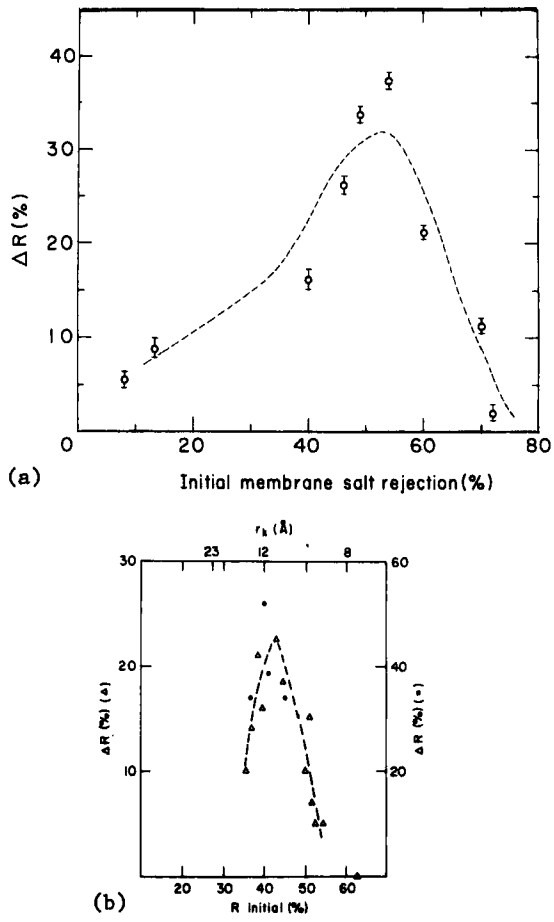

FIGURE 9

(a) Increment in membrane salt rejection due to quaternized 2-PVP treatment as a function of the initial salt rejection. Pressure 550 psi; 0.1N KCl, 0.1% quat. 2-PVP feed (reproduced with permission from Ref. 22).

(b) Increment in salt rejection due to dynamic membrane formation with 1:4:1 copolymer vs. initial salt rejection of the CA microporous support. Feed concentration 10^{-1}M NaCl, 0.1% copolymer; pressure 350 psi.

(Δ) results after 0.5 hr. filtration treatment (left hand ordinate); (o) results at plateau (cf. Fig. 10) (right hand ordinate) (reproduced with permission from Ref. 23).

dynamic membranes. A similar effect is found for Zr(IV)-hydrous oxide-polyacrylate dynamic membranes in which the optimum salt rejection is obtained when hydrous Zr(IV)-oxide membranes are treated with PAA of $5x10^4$ M.W.[4a].

B. Charge Effects

Class III dynamic membrane formation is quite sensitive to effects of pH and ionic strength, as these determine the ability of the polyelectrolyte to enter the pore. In some instances, as in Fig. 10, an increase in the ionic strength is sufficient to collapse the electrical double layer surrounding the polyelectrolyte and thus facilitate its entry[23]. For Zr(IV)-PAA dynamic membranes to form, the polyelectrolyte must first be brought to a neutral state in a coiled configuration

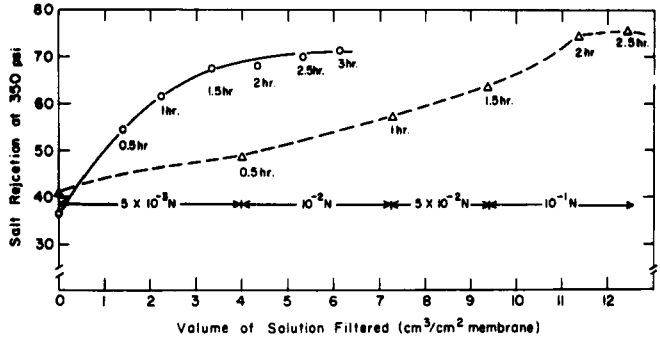

FIGURE 10

Effect of time and concentration of KCl on dynamic membrane formation: (o) 1:4:1 copolymer membrane formed at 0.1M KCl; (Δ) 1:4:1 copolymer membrane formed at various concentrations of KCl (reproduced with permission from Ref. 23).

either by adjusting to pH 2 or by the addition of CA^{2+} or Mg^{2+} at neutral pH[4a].

C. Convective coupling and flux decline

One of the major features which differentiate Class III systems from those of I and II is the fact that the dynamic membrane can form by a purely diffusional process, without the existence of a convective water flow due to the application of pressure. In Table IV, the salt rejection results are shown for CA membranes before and after the equilibration with a dilute solution of quaternized 2-PVP[22]. The increase in salt rejection observed is not due to simple adsorption on CA because trials at very large ratios of powdered CA to polyelectrolyte failed to show any adsorption of polymer, so the effect must be due to entry of the molecules into the surface pores of the membrane. Of course, in the absence of a convective flow, the formation time required undergoes a significant increase. Upon the application of pressure, we may consider the flux decline to result from the "reaction" of a surface "hole" with a polyelectrolyte molecule whose presence within the pore reduced the flux. Quantitatively this is expressed by the relation[24]

TABLE IV.

Hyperfiltration results for a dynamic membrane formed by adsorption from solution of quaternized 2-PVP.

0.1N KCl feed, pressure = 550 psi.[3A]

Membrane #	Prior to adsorption 2-PVP		After adsorption 2-PVP		After additional treatment with 2-PVP under pressure	
	R_o (%)	J_v (gfd)	R_t (%)	J_v (gfd)	R_t (%)	J_v (gfd)
10	54	66	73	36	77.5	34.5

$$\ln \frac{J_{(t)} - J_{(\infty)}}{J_{(o)} - J_{(\infty)}} = k_2 C_w t \qquad (9)$$

where k_2 is a constant, C_w is the concentration at the wall, $J_{(o)}$ is the initial flux and $J_{(\infty)}$ is the final steady state flux. One may note that the value $J_{(\infty)}$ in no way depends on the concentration of polyelectrolyte (in contrast to Class I and II membranes).

Alternatively, one may also derive the relation[13]

$$J = J_o - K^1 V(t) \qquad (10)$$

where V(t) is the volume of filtrate up to time, t.

D. A test case - the formation of Zr(IV)-polyacrylate dynamic membranes

Prior to the experiments, it was anticipated that PAA would create a Class I dynamic membrane on top of the Zr(IV)-hydrous oxide layer, as the reference to such membranes as "dual layer" suggests. However, the flux decline data of Fig. 11 rule out both Class I and II behavior. Furthermore, increasing the PAA concentration by a tenfold factor does not significantly change the flux which reaches a plateau, as shown in Fig 12. These facts fit the Class III type dynamic membrane quite well and the flux decline data from plots of both equations (9) and (10)(Fig. 13 and 14) and the concentration dependence of the flux decline slope (Figs. 15 and 16) are in reasonable agreement. The final proof that the PAA must enter the entire thickness of the Zr(IV) cake is shown in Fig. 17. It may be seen that a plot of Zr(IV)-polyacrylate membrane flux is a linear function of the inverse of the Zr(IV) membrane thickness[20].

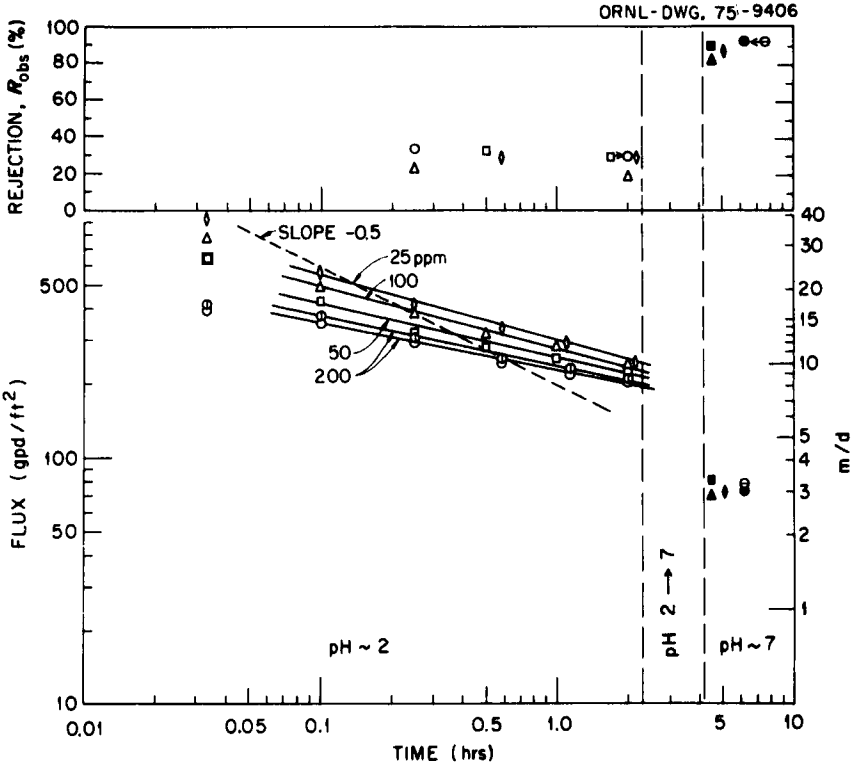

FIGURE 11

Flux decline during formation of PAA layer on hydrous Zr(IV) oxide membranes. 0.45μm Acropor AN support. (950 psi; 15 ft/sec; 30°C, 0.05M NaCl) (reproduced with permission from Ref 24).

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

* Duplicate wrap

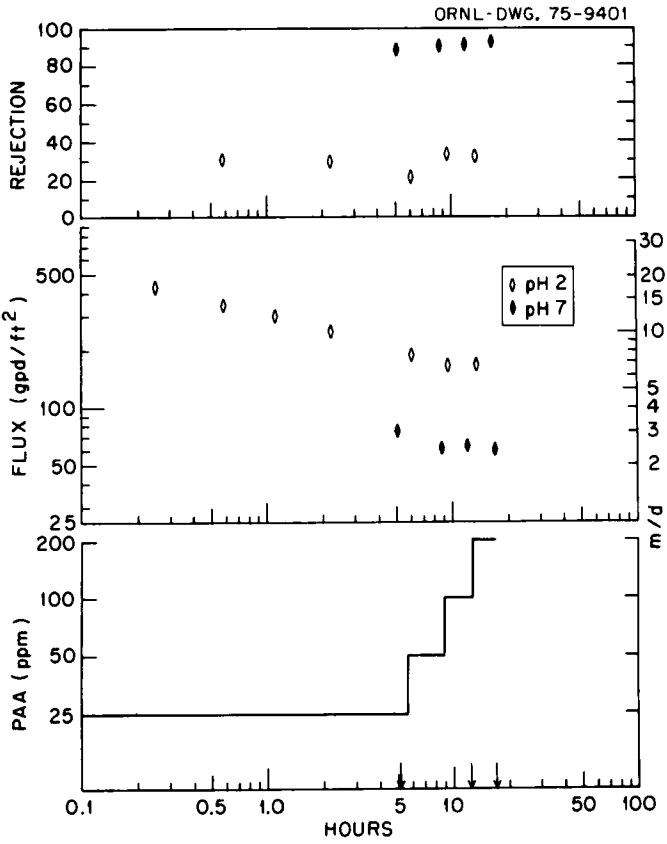

FIGURE 12

Fluxes as a function successive additions of acrysol A-3 PAA. Cycles to neutral pH between polyacrylate additions. (950 psi; 15 ft/sec; 30°C, Shutdown; 0.45μm Acropor 4N support; 0.05M NaCl (reproduced with permission from Ref. 24).

E. Stability of Class III Dynamic Membranes

Class III dynamic membranes formed on asymmetric cellulose acetate are initially quite stable and can maintain

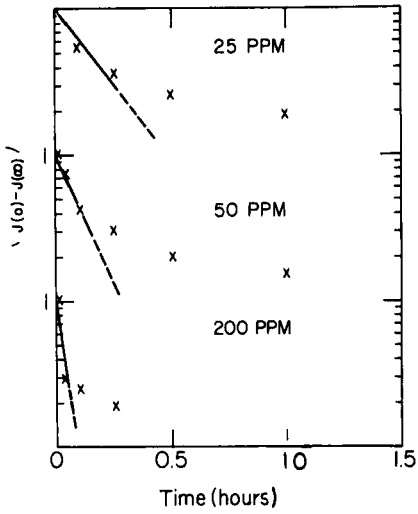

FIGURE 13

Flux decline during formation of PAA layer on hydrous Zr(IV) oxide membrane. (0.45μm Acropor AN: 950 psi, 15 ft/sec, 30°C: 0.05M NaCl (reproduced with permission from Ref. 24).

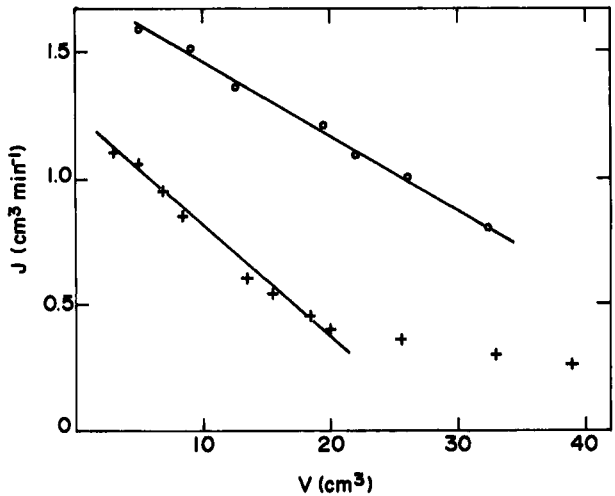

FIGURE 14

Water flux as a function of total permeate volume flow in the filtration of PAA through a hydrous Zr(IV)-oxide dynamic membrane. (+) - 0.04% PAA (o) - 0.02% PAA (Ref. 13).

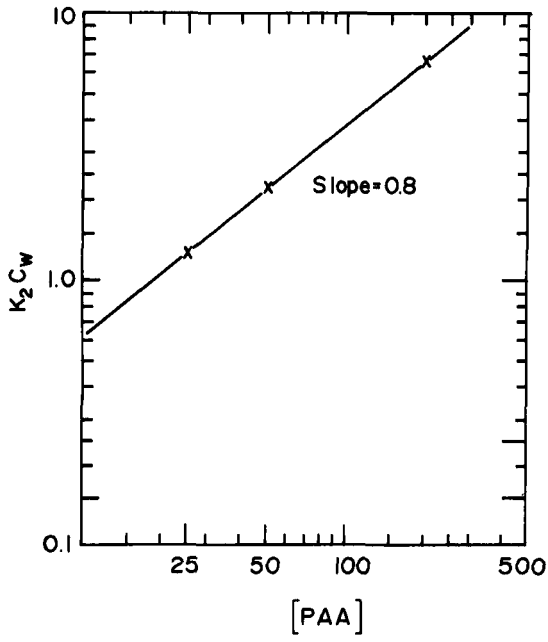

FIGURE 15

Variation of the initial slope of Fig. 13 as a function of PAA concentration (reproduced with permission from Ref. 24).

their properties during thirty to forty hours of continuous use. After this time a gradual increase in flux and decrease in the salt rejection is observed[22]. Electron micrographs[23] reveal that under the influence of the convective water flux, the polyelectrolyte gradually migrates through the thin asymmetric layer of the cellulose acetate membrane and enters the larger pore size regions.

Recently, copolymer Class III membranes of vinyl-acetate-crotonic acid formed on cellulose acetate have been stabilized by precipitation with zinc chloride[25]. These membranes showed stable flux and salt rejection for a period of

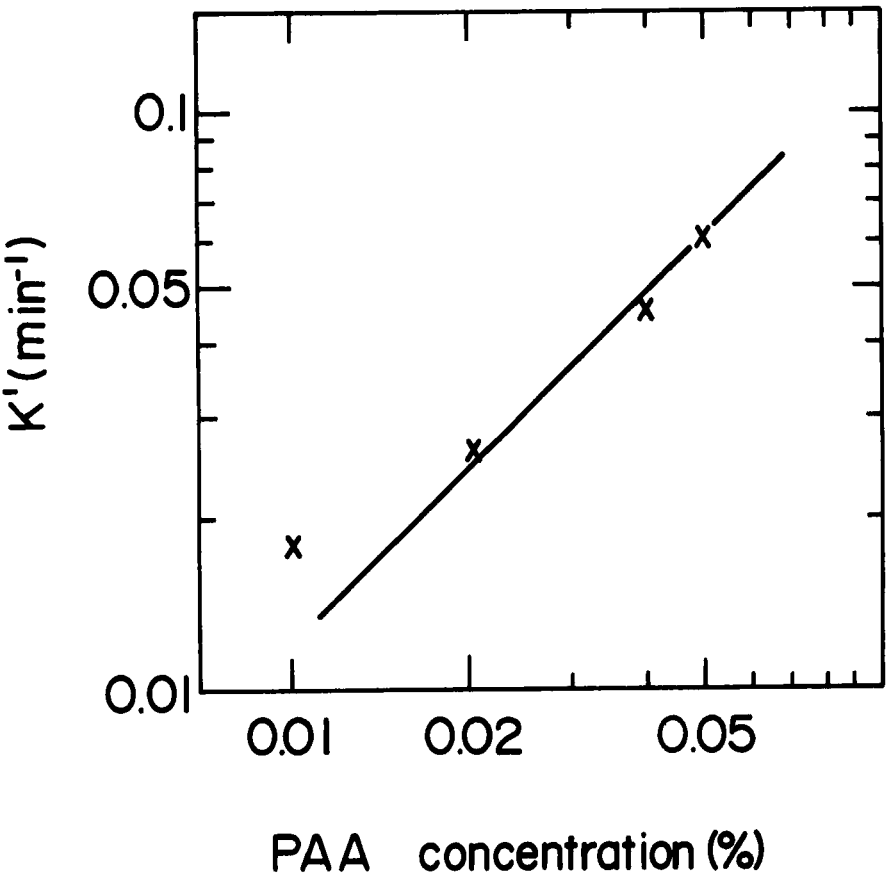

FIGURE 16

Constant K^1 (cf. equation 10) versus PAA feed concentration, for Class III dynamic membrane formation on Zr(IV) membranes (Ref. 13).

twenty-six days of operation on brackish water of 1500 ppm salt concentration. The zirconium oxide-polyacrylate membrane is also stable for hundreds of hours before it requires regeneration[4a,19]. This increased stability is most likely due to a combination of

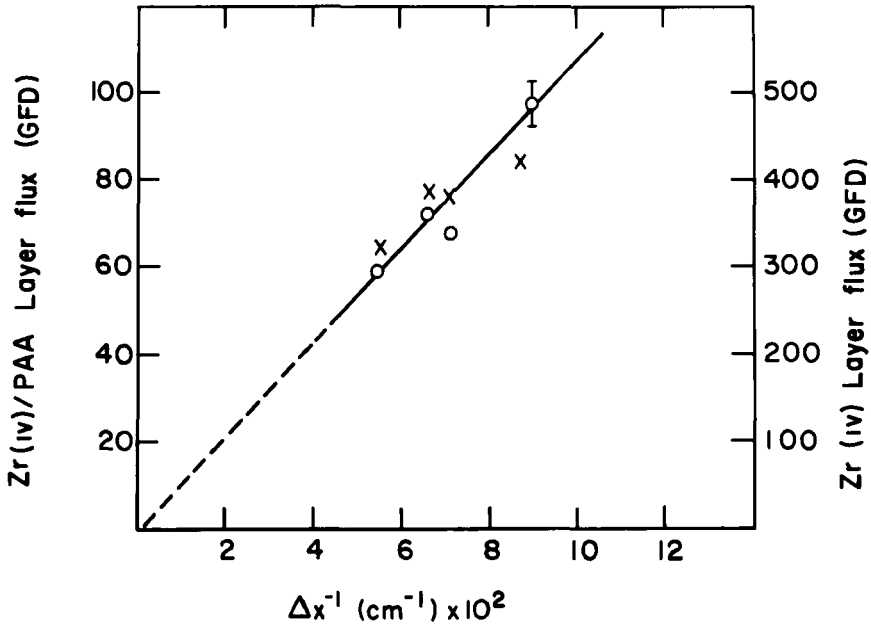

FIGURE 17

Flux of the Zr(IV)-polyacrylate membrane as a function of the inverse of the thickness of the hydrous Zr(IV)-oxide layer thickness. (o) - flux of hydrous Zr(IV)-oxide membrane (right hand ordinate); (x)-Zr(IV)-polyacrylate flux (left hand ordinate) (Ref. 20).

the much larger thickness of the hydrous zirconium oxide layer and a strong interaction between the polyelectrolyte and the porous matrix.

COMMERCIAL APPLICATIONS OF DYNAMIC MEMBRANES

Despite very encouraging results from small pilot plants for pulp bleach plant waste treatment and for textile

wastewater reuse[8], relatively little commercialization of dynamic membranes has taken place. The major application has come in the "Ucarsep" system, which utilizes a Class I membrane deposited in a porous carbon tube which is then fired at an elevated temperature to stabilize the dynamic layer and thereby produce a conventional asymmetric membrane constructed of inorganic materials. However, the possibility of "in situ" regeneration is lost. More recently, NASA has placed a small contract for the production of a hydrous Zr(IV) oxide-polyacrylate system to be used for on board regeneration of wastewater.

The future of dynamic membranes may be much brighter, since waste treatment constitutes a major market for membrane applications, an area in which conventional membranes have usually been outperformed by their dynamically formed counterparts. Furthermore, dynamic membranes are now better understood than they were previously, a fact which should stimulate additional experimentation. Finally, perhaps the most important stimulus to their commercialization may be the future availability of cartridges of polymeric microporous membrane support to replace the breakable ceramic and carbon tube units available to date.

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NOTES

1A. Gelman Instrument Co.

2A. Long dimension of the Acropor roll from which the samples of support are cut.

3A. Data from Ref. (22).

Symbols

A - membrane filter area (cm^2)

C - concentration of macromolecule

C_w - concentration of macromolecule at membrane interface

C_B - concentration of macromolecule in bulk solution

c - colloid concentration (g/cm^3)

J_v - steady state volume flux (cm/sec)

$J_{(t)}$ - total volume flux at time t (cm^3/sec)

k_1 - pore clogging flux decline constant $(cm^3)^{-1}$

k_2 - rate constant (cm^3/mole - sec)

k_s - back diffusion mass transfer constant (cm/sec)

K - cake filtration constant (cm^6/sec)

K^1 - rate constant (sec^{-1})

ΔP - Pressure ($dynes/cm^2$)

r_a - dynamic membrane forming solute radius

r_o - membrane pore radius

R_m - hydraulic resistance of membrane (cm^3/dyne-sec)

R_p - hydraulic resistance of polarization layer (cm^3/dyne-sec)

R_c - hydraulic resistance of the cake ($cm\ g^{-1}$)

u - solution circulation velocity parallel to membrane surface (cm/sec)

$V_{(t)}$ - total volume of filtrate to time t (cm^3)

S - thickness of the gel polarization layer (cm)

η - viscosity of the fluid (poise)

τ - transition time (min)