

Preparation and Properties of Poly(acrylic Acid) Composite Membranes*

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Synopsis

A new type of membrane has been prepared for hyperfiltration (reverse osmosis) desalination that is essentially a very thin polyelectrolyte membrane. It is prepared by casting an aqueous solution of a polyelectrolyte, specifically poly(acrylic acid) (PAA), directly on one surface of a finely porous support membrane. In hyperfiltration tests, these composite membranes exhibit desalination performance comparable in dilute solutions to that observed with cellulose acetate membranes of the Loeb-Sourirajan type. The water flux through these membranes is linear in the pressure up to 100 atm. Salt rejection is a function of pressure; it is also a function of the concentration of the feed solution and the charge of the counterion, in qualitative agreement with the Donnan ion-exclusion mechanism. Typical long-term results range from water fluxes of 2×10^{-3} g/cm²-sec (50 gal/ft²-day) and 80% salt rejection to 0.2×10^{-3} g/cm²-sec (5 gal/ft²-day) and >99.5% salt rejection at 1500 psi with 0.3 wt-% NaCl. These membranes appear to be useful for brackish water desalination.

INTRODUCTION

Because of their ability to exclude coions, membranes containing fixed charge groups have been considered for water desalination applications for many years. It was observed in some of the early ultrafiltration research that some salt removal occurs when dilute solutions are forced through cellophane membranes under pressure.¹ More recently, McKelvey, Spiegler, and Wyllie² carried out a thorough study of the use of commercial ion-exchange membranes for desalination by means of a pressure-driven process. Their results were at least qualitatively consistent with the Donnan ion-exclusion mechanism³: salt rejection was a decreasing function of concentration, and divalent coions were rejected better than univalent coions which, in turn, were rejected better than divalent counterions. The water flux was approximately linear in the applied pressure difference; but even at the highest pressures studied, the fluxes were very low (generally less than 10^{-5} g/cm²-sec) because the membranes possessed a low water permeability and also because they were relatively thick, generally

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being more than $100\ \mu$ thick. (Multiply flux in $\text{g}/\text{cm}^2\text{-sec}$ by 2.1×10^4 to convert to $\text{gal}/\text{ft}^2\text{-day}$.) Baldwin, Holcomb, and Johnson⁴ succeeded in improving the selectivity properties of cellophane by grafting acrylate groups to the base cellophane, thereby considerably increasing the small intrinsic ion-exchange capacity of the cellophane. In hyperfiltration tests, these membranes exhibited water permeabilities about one half that of the untreated cellophane with considerably improved rejection of several salts. However, the water flux was still relatively low ($<3 \times 10^{-4}\ \text{g}/\text{cm}^2\text{-sec}$), and the rejection of $0.5M$ NaCl was generally less than 50% even at 170 atm applied pressure. By way of comparison, desalination membranes of the Loeb-Sourirajan type^{5,6} (referred to in this paper as modified cellulose acetate membranes) typically exhibit water fluxes of $10^{-3}\ \text{g}/\text{cm}^2\text{-sec}$ and $>95\%$ rejection of $0.5M$ NaCl at an applied pressure of 100 atm. Another approach to polyelectrolyte desalination membranes was taken by Sachs, Hoffer, and Kedem⁷ who prepared both polyglutamic acid and collodion-albumin membranes. Some of these exhibited water fluxes of $5 \times 10^{-4}\ \text{g}/\text{cm}^2\text{-sec}$ and 40% to 50% rejection of $0.025M$ NaCl at 10 atm applied pressure.

Some of the dynamically formed membranes described by Marcinkowsky and co-workers at Oak Ridge National Laboratory⁸⁻¹⁰ appear to be effectively very thin polyelectrolyte membranes. The dependence of salt rejection on concentration and ionic charge indicate a Donnan exclusion mechanism when these membranes are prepared from colloidal metal oxides or from naturally occurring or synthetic polyelectrolytes. One of the most efficient of the dynamically formed membranes was formed from poly(acrylic acid) (PAA) on ceramic and Millipore VFWP filter supports as described by Sachs, Baldwin, and Johnson.¹¹ In addition, these investigators prepared diamine-crosslinked, cast PAA membranes. Both types of PAA membrane exhibited water fluxes in the range 1 to $4 \times 10^{-3}\ \text{g}/\text{cm}^2\text{-sec}$ and rejections of $0.05M$ NaCl in the range 50% to 80% at pressures of 68 to 100 atm.

In the present paper, we describe a distinct route to preparing high-flux polyelectrolyte membranes. These membranes are prepared by casting or dip coating an aqueous solution of a polyelectrolyte directly on the surface of a finely porous support membrane. The polyelectrolyte membrane is tested in hyperfiltration equipment without further treatment. Most of the polyelectrolyte is rapidly dissolved on exposure to water, but a thin layer remains on the surface and in the pores. When prepared on suitable porous supports, these composite membranes exhibit desalination performance similar in most respects to that of Loeb-Sourirajan membranes.

EXPERIMENTAL

Preparation of Membranes

The composite membranes were prepared by casting or dip coating an aqueous solution of poly(acrylic acid) (PAA) on one surface of a finely

porous membrane which served as a support. The porous membranes were cast from a solution consisting of mixed cellulose esters (cellulose nitrate and cellulose acetate, CN-CA), a good solvent (acetone), and certain nonsolvents (alcohol and water). The solutions were cast by doctoring onto a glass plate, and the solvent was allowed to evaporate under conditions in which the humidity and the temperature were controlled. The dried membranes were opaque and highly porous (60% to 70%), but the porosity of the air-dried surface was less than 20% and on a very fine scale. From electron photomicrographs, the pores in this surface were estimated to be $<1000 \text{ \AA}$ in diameter. In the as-prepared state, these membranes are highly permeable to water and exhibit no selectivity with respect to low molecular weight solutes. The "membrane constant" (defined as water flux divided by $\Delta p - \Delta\pi$, where Δp and $\Delta\pi$ are, respectively, the applied pressure difference and osmotic pressure difference across the membrane) was measured with distilled water at 2.7 atm applied pressure and 25°C. Values fell in the range $100 \text{ to } 1500 \times 10^{-5} \text{ g/cm}^2\text{-sec-atm}$.

The PAA film was cast on the finely porous surface from a 25 wt-% solution of Rohm and Haas Acrysol A-5 (molecular weight stated by the manufacturer to be less than 300,000) in water. The membrane was allowed to dry (under ambient conditions) for one day, after which it was ready for use. The dry thickness of the PAA layer was typically 40 μ . The PAA adhered tightly to the support membrane and could be removed only with difficulty. During the hyperfiltration experiments, much of the PAA dissolved from the membrane surface. Following one such run, the composite membrane was put into acetone, which dissolved the support membrane and left behind a tenuous layer of PAA. By drying and weighing this layer and using a density of 1.1 g/cm³, the thickness of the layer was estimated to be 4 to 5 μ .

PAA membranes were also prepared by dip coating the CN-CA support. One side of the support membrane was masked by taping the support to a glass plate for the dipping operation. The time of immersion in the PAA solution was varied from a few seconds to 5 min. The PAA solution concentration was 2.5 wt-%. The membranes were allowed to dry in air, after which they were ready for use. Some of these membranes were subsequently annealed in air at 110°C for 3 hr. The thickness of the PAA layer deposited by dip coating could not be accurately measured; however, it was substantially less than that of the PAA layer deposited by casting.

Modified cellulose acetate membranes were prepared essentially according to the procedure of Loeb and Sourirajan.⁵ The transport properties were varied by annealing in water at temperatures in the range 60° to 90°C.

Hyperfiltration Tests

The equipment used has been described previously.^{12,13} Unless otherwise noted, the experiments were performed at 25° \pm 1°C and pH 7.

Intentional changes in pH were made by addition of NaOH or HCl. The concentration of feed and product solutions was determined by conductivity when only one salt was present or by atomic absorption for Na^+ and Ca^{2+} and Mohr titration for chloride when mixtures were used. Organic solutes such as urea and PAA were determined by means of a Beckman Carbonaceous Analyzer. With cast membranes, the PAA dissolved from the membrane surface, bringing the feed concentration to about 5 ppm; however, the system was flushed with distilled water until the PAA content was less than 0.1 ppm before any of the reported data were taken. On the other hand, in tests performed with dip-coated PAA membranes, no PAA was detected in the feed solution or added to it.

In some experiments, PAA membranes were dynamically formed on nominally identical pieces of CN-CA support membranes using the methods described by Marcinkowsky and co-workers.⁸⁻¹¹ The PAA content of the feed solution was adjusted to 6 ppm during these tests, and the PAA was neutralized by titrating with NaOH to a pH of 7.5. Early in the test, the flux and rejection properties of both cast and dynamically formed membranes changed with time, but the sampling interval was kept short relative to the time scale of these changes so that flux and rejection were virtually constant over this interval.

The experiments were all performed at a constant feed velocity over the surface of the membrane of 150 cm/sec. This was the maximum velocity that could be achieved in our apparatus, and it is recognized that in some experiments concentration polarization effects at the feed-membrane interface were significant. The importance of feed velocity on water flux and salt rejection in our apparatus has been described.¹² Under conditions where the water flux through the membrane was about 5×10^{-4} g/cm²-sec, it was shown that above a linear velocity of about 50 cm/sec the effect of feed velocity on flux and rejection was not detectable with sodium chloride feed. In some of the present experiments, however, water fluxes were greater than 5×10^{-3} g/cm²-sec, so that polarization effects must be reconsidered. It is convenient to discuss these effects in terms of a polarization modulus, c_s'/c_s^0 , where c_s is the salt concentration in the feed solution and the superscripts ' and 0 refer to values at the solution-membrane interface and in the bulk solution, respectively. Brian¹⁴ has discussed polarization effects in hyperfiltration in detail, including the method for calculating the polarization modulus in turbulent flow as a function of feed velocity, membrane flux, feed channel dimensions, and solution properties. Unfortunately, this theoretical treatment is not directly applicable to the small test cell used in this work because of entrance and exit effects and the lack of fully developed turbulent flow. Consequently, we have used the form of the polarization equation and moduli previously measured in our equipment with NaCl and lower flux membranes to estimate the modulus in the present experiments. For the conditions used here, an empirical equation useful for estimating the modulus in terms of water flux for all the salts studied is

$$\log \frac{c_s'}{c_s^0} = 30J_v$$

when J_v is expressed in $\text{g}/\text{cm}^2\text{-sec}$. For example, at fluxes of 0.5, 1.0, and 5.0×10^{-3} $\text{g}/\text{cm}^2\text{-sec}$, the moduli are approximately 1.03, 1.07, and 1.4, respectively. All the reported rejections are the observed values and have not been corrected for the polarization effect. Because dilute salt solutions were used in general, the effect of polarization on water flux (through $\Delta\pi$) is small in all cases.

RESULTS AND DISCUSSION

Cast and Dynamically Formed PAA Membranes

Time Dependence of Rejection and Flux

Figure 1 summarizes the dependence of the rejection of 0.3 wt-% NaCl and the water flux on time. Two PAA membranes were tested simultaneously, one prepared by casting and one prepared dynamically in the general manner described by Marcinkowsky and co-workers.⁸⁻¹¹ The porous CN-CA support used for both membranes exhibited the same membrane constant at 2.7 atm, namely; 150×10^{-5} $\text{g}/\text{cm}^2\text{-sec-atm}$. The dynamic membrane was prepared with approximately 5 ppm PPA in the feed solution and the pH was adjusted to 9; after about 1 hr, the pH was reduced to the range 7 to 8, where it was maintained for the remainder of the test. The test

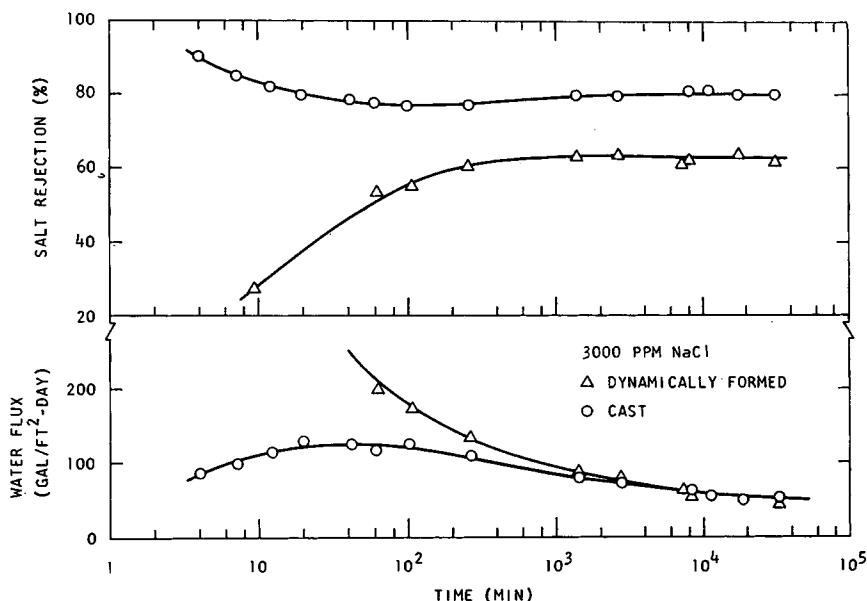


Fig. 1. NaCl rejection and water flux as functions of time for a dynamically formed and a cast PAA membrane.

was performed at 102 atm. For the dynamic PAA membrane, rejection increased at the beginning of the run while the flow rate decreased due to the buildup of the PAA film on the surface of the CN-CA support. On the other hand, the NaCl rejection for the cast PAA membrane decreased early in the run and the water flux increased, apparently due to partial dissolution of PAA from the surface of the cast membrane. For both membranes, the salt rejection leveled off much before the water flux, a fact which may be attributed to a kind of compaction phenomenon occurring in the PAA-CN-CA composites. Comparison of the NaCl rejection results achieved with the cast and the dynamically formed PAA membranes shows the importance of the way the membrane is prepared: at 3000 ppm and 50 gal/ft²-day water flux, NaCl rejection was 80% and 62% for the cast and dynamically formed membranes, respectively. Because of boundary layer effects, which are significant at these water fluxes and brine velocities, the observed salt rejections in both cases are predictably less than the intrinsic membrane properties would permit. The product water was tested for PAA content by means of total organic carbon (TOC) measurements. Even at feed concentrations as high as 800 ppm, the TOC content of the product remained at essentially the background level, from which it was concluded that the PAA rejection was at least 99.8%.

Concentration Dependence of Rejection and Flux

The dependence of rejection on feed concentration for NaCl, Na₂SO₄, and CaCl₂ for one membrane out of six tested is summarized in Figure 2. In this figure, rejection results with a dynamically formed PAA membrane measured at ORNL¹¹ are also given for comparison. In the experiments performed in our laboratory, water flux decreased with time throughout the run, falling from ≥ 100 gal/ft²-day after 30 min to 25-45 gal/ft²-day after one day. The data presented in Figure 2 were recorded over the time period during which the water flux and salt rejection, at a fixed feed concentration, did not change markedly (36 to 98 days). In each case, the rejection-versus-concentration data were collected over a relatively short time period, during which the rejection at a fixed concentration was constant. The data points indicated by 1 and 2 in the figure were taken at the beginning and end, respectively, of each series. Rejection increased with decreasing concentration qualitatively in agreement with the ion-exclusion mechanism expected for an ion-exchange membrane. For an ideal solution, the coion distribution coefficient K for a uniunivalent electrolyte is given by

$$K = \frac{\bar{c}_s'}{c_s'} = \frac{-X + \sqrt{X^2 + 4(c_s')^2}}{2c_s'}$$

where \bar{c}_s' is the coion concentration within the pore fluid of the membrane and X is the fixed charge capacity. At low solution concentrations, $X \gg c_s'$ and $K \rightarrow c_s'/X$ and $\bar{c}_s' \rightarrow (c_s')^2/X$. Thus, having the distribution

coefficient allows one to estimate the effective fixed charge capacity of the membrane. Further, in the high-flux limit, the product water concentration c_s'' approaches \bar{c}_s' and the salt rejection R (defined as $1 - c_s''/c_s'$) approaches $1 - c_s'/X$. Therefore, in this limit, a plot of $\log(1 - R)$ versus $\log c_s'$ should be linear, with unit slope for a univalent coion. By a similar argument, it can be shown that the slope should be 2 for a divalent coion and $\frac{1}{2}$ for a divalent counterion. These slopes are clearly not

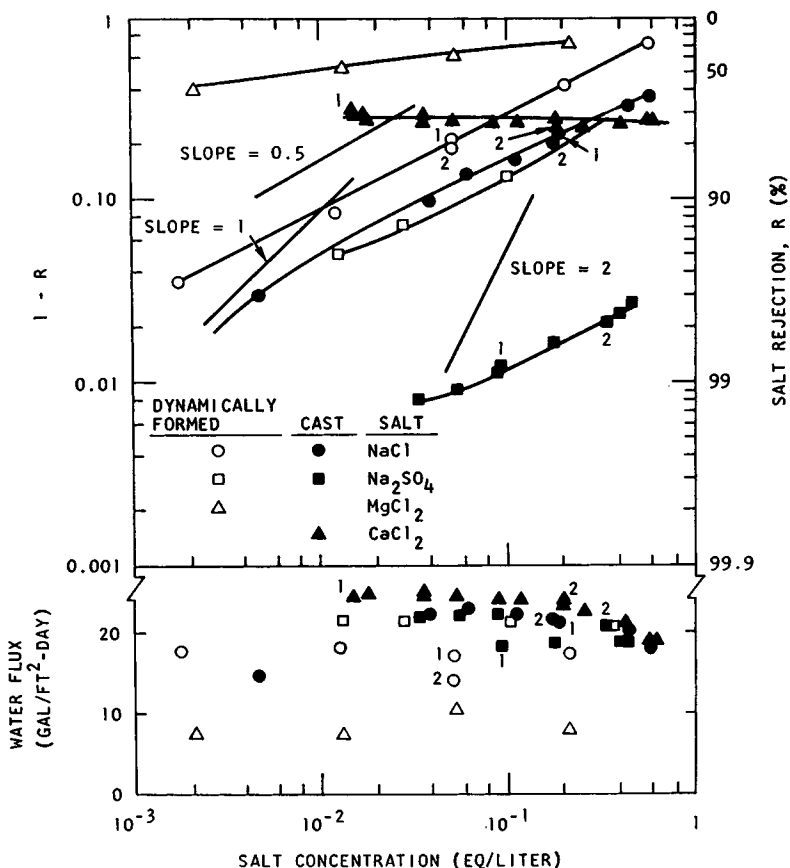


Fig. 2. Concentration dependence of rejection and flux by a dynamically formed and a cast PAA membrane. Open symbols: 0.3 μ ceramic tube support, 68 atm, pH \sim 7, 1 ppm PAA¹¹; closed symbols: CN-CA support membrane, 102 atm, pH \sim 7.

reached for either type of membrane in this test. Salt rejection values for the three different salts with the cast PAA membrane are markedly higher over the whole concentration range than with the dynamically formed PAA membrane.

Figure 3 illustrates the increase in the rejection of NaCl (12,000 ppm) and the water flux with net pressure difference, $\Delta p - \Delta\pi$. The membrane

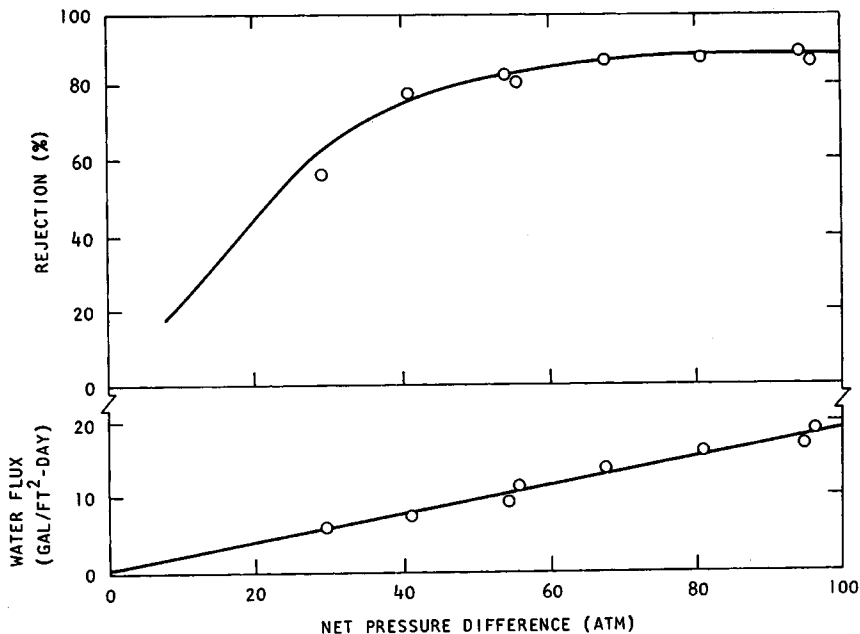


Fig. 3. Pressure dependence of rejection and flux for a cast PAA membrane; pH ~ 7 , feed concentration $\sim 12,000$ ppm NaCl.

constant calculated from the slope of the flux-pressure plot is 1.0×10^{-5} g/cm²-sec-atm.

pH Dependence of Rejection and Flux

Plots of salt rejection and water flux versus pH are presented in Figure 4. With CaCl₂, the flux and rejection clearly improved with decreasing pH below 6, similar to what was observed by Sachs and co-workers for MgCl₂ rejection by dynamically formed PAA membranes.¹¹ The trends became less pronounced above pH 7, where the carboxylic acid groups are highly dissociated.¹⁵

With 10,000 ppm NaCl feed solution at 102 atm, membrane properties were virtually independent of pH above about 6. With decreasing pH, the rejection decreased, passing through a minimum at about pH 5, and returned to the high value obtained above pH 6 at about pH 3.

Although the pH dependence of membrane properties is not entirely clear, it appears that for NaCl the PAA membrane is effective in both the regions of complete dissociation and negligible dissociation. With the divalent counterion Ca²⁺, performance is superior when the PAA is in the undissociated form.

A Low-Flux, Cast PAA Membrane

A PAA film cast on a CN-CA support of very low permeability (membrane constant $< 100 \times 10^{-5}$ g/cm²-sec-atm at 2.7 atm) initially gave

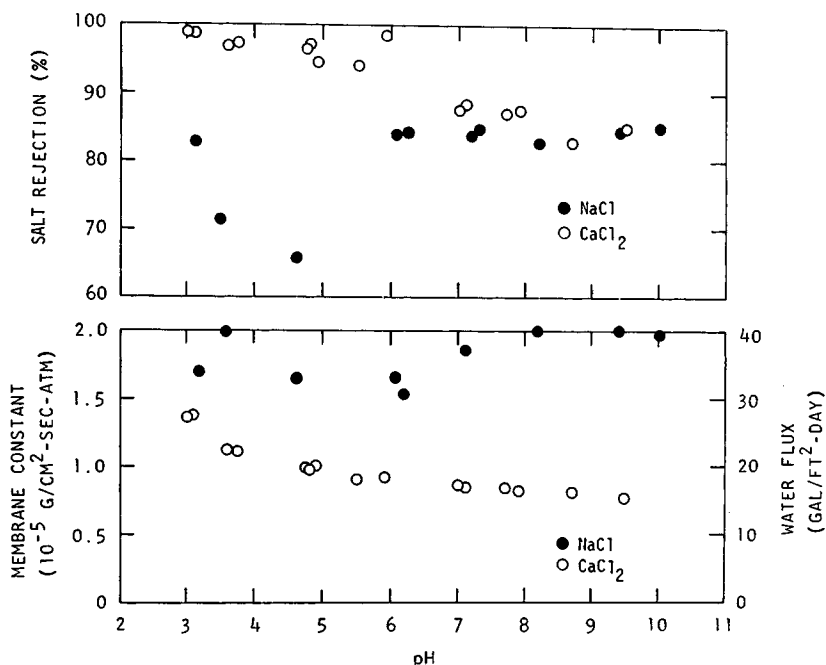


Fig. 4. Performance of PAA membrane vs. pH; 10,000 ppm NaCl or CaCl₂, 1500 psi.

98.6% rejection of 8700 ppm NaCl with water flux between 3 and 4 gal/ft²-day at 102 atm. This is, of course, comparable to the rejection observed with modified cellulose acetate membranes, although the flux here was somewhat lower. In order to examine the rejection of a nonelectrolyte by this membrane (relative to cellulose acetate), a small amount of urea was added to the feed. Addition of urea to the system did not substantially influence the salt rejection or the water flux. The concentration dependence of the rejection of NaCl and urea, while both were present in the same feed solution, is summarized in Figure 5. In each case the rejection-versus-concentration data were collected over a relatively short time period, during which the rejection at a fixed concentration was constant. The numbers next to the data points in the figure indicate the order in which the data were taken and also indicate the concentrations of urea and NaCl present simultaneously.

In this test, rejection of NaCl increased strongly with decreasing concentration, qualitatively in agreement with the ion-exclusion mechanism expected for a charged membrane. At low concentration, the plot of $\log(1 - R)$ versus the logarithm of concentration seems to approach a slope of 1. At the lowest concentration (~ 3000 ppm NaCl), NaCl rejection was 99.8%. Urea rejection was observed to be relatively concentration independent, as one would expect for a nonelectrolyte. At the highest urea concentration, urea rejection fell slightly, but this is presumably due to the reduced water flow caused by a decrease in $\Delta p - \Delta \pi$. The low NaCl

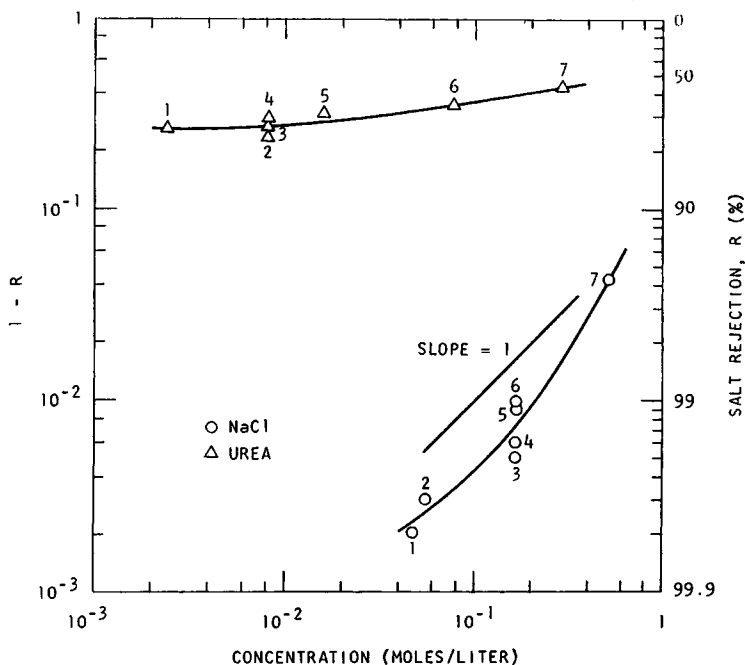


Fig. 5. Dependence of the rejection of NaCl and urea on feed concentration for a cast PAA membrane.

rejection for point 7 is partly attributable to the same cause. The rejection of both urea and NaCl was exceptionally high; in dilute NaCl solution, this membrane exhibited even higher rejection of both salt and urea than is exhibited by modified cellulose acetate membranes.¹⁶

Dip-Coated PAA-CN-CA Membranes

Rejection of Mixed Solutes

One source of concern in the use of polyelectrolyte membranes for desalination is the effect of divalent counterions on membrane performance. This effect was studied on dynamically formed PAA membranes by Sachs, Baldwin, and Johnson.¹¹ They found that, at constant coion concentration (0.055M Cl⁻), the rejection of Na⁺ was lowered as the ratio of Mg²⁺ to Na⁺ concentration was increased.

A similar experiment was carried out with dip-coated PAA-CN-CA membranes using CaCl₂-NaCl solutions with a fixed total electrolyte concentration of 0.17N (about 6000 ppm Cl⁻). The experiments were performed at 102 atm, 25°C, and pH 7.

The results are presented in Figure 6. The Ca²⁺-to-Na⁺ ratio was increased during the test so that the time of the run generally increases from

left to right in the figure; the final data, obtained with pure NaCl, are shown as solid circles. There was essentially no change in water flux during the 18-day test and no loss in NaCl rejection. The results with three other membranes were similar. Compared with the results obtained with the dynamically formed PAA membranes, the present membranes exhibited higher rejection of both sodium and the divalent cation over the entire range of concentration ratio, even though the total ion concentration in the present test was about three times as large. With the dynamically formed membrane,¹¹ the water flux decreased from about 20 to 8 gal/ft²-day (at approximately constant net pressure) as the Mg²⁺-to-Na⁺ ratio was increased. In both tests, rejection of all ions decreased with increasing divalent ion concentration. However, in a typical brackish water, the mole ratio of Ca²⁺ to Na⁺ is on the order of 0.1 to 0.5, where the salt rejection of the present membranes was still reasonably high.

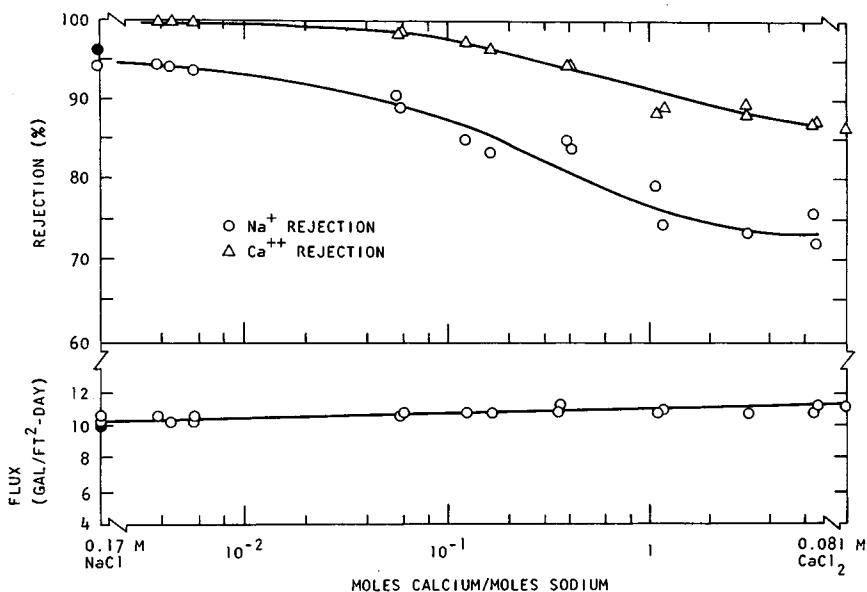


Fig. 6. Hyperfiltration results with mixed NaCl-CaCl₂ solutions with a PAA-CN-CA membrane.

A possible explanation for the improved rejection exhibited by the cast or dip-coated PAA membranes as opposed to the dynamically formed membranes is that the PAA layer on the former has fewer "imperfections" because of the high concentration of the solution from which it is applied. When membranes are dynamically formed from dilute solution, impurities in the test system can also deposit in the pores of the support medium in competition with the PAA, and these impurities may be less efficient in rejecting salt. If this explanation is correct, it suggests that the rejection of

dynamically formed membranes would increase with the concentration of the feed additive during membrane formation.

Comparison with Modified Membranes

While it is difficult at present to reproducibly prepare PAA-CN-CA membranes of prescribed performance, a general relationship between flux and salt rejection appears to exist. As with modified cellulose acetate membranes, higher fluxes are associated with lower rejections. In addition, rejection is concentration dependent for the PAA membranes. The relationship between flux and rejection for modified membranes is usually

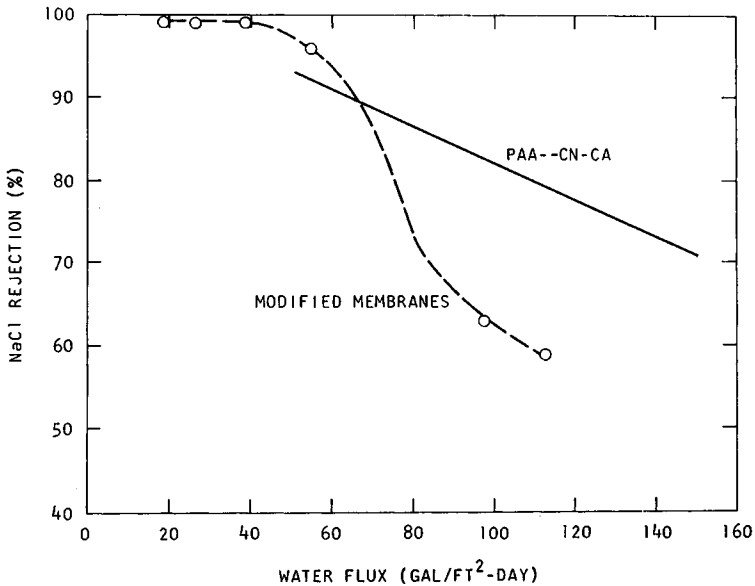


Fig. 7. Water flux vs. NaCl rejection for modified CA membranes and PAA-CN-CA membranes.

fixed by the aqueous annealing temperature, whereas with PAA membranes it depends on the porosity and pore size distribution of the support membrane. A rough comparison between the two types of membranes operated at 102 atm with 3000 ppm NaCl feed is presented in Figure 7. The solid line describing the behavior of the PAA membranes is a trend line that is indicative of the range of performance observed with one membrane set. It appears that the PAA membranes compare most favorably in the low-rejection high-flux region.

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