

Preparation of Ultrathin Reverse Osmosis Membranes and the Attainment of Theoretical Salt Rejection

R. L. RILEY, H. K. LONSDALE,
C. R. LYONS, and U. MERTEN,

*John Jay Hopkins Laboratory for Pure and Applied Science,
General Atomic Division, General Dynamics Corporation,
San Diego, California*

Synopsis

Cellulose acetate reverse osmosis membranes, 600–2800 Å thick, have been prepared on glass surfaces by dipping a clean glass plate into a dilute solution of cellulose acetate. After drying, the membranes are floated off onto a water surface and placed on molecular filter supports. Theoretical salt rejections, as calculated from the solution-diffusion model of membrane transport for cellulose acetate, were obtained with imperfection-free membranes.

INTRODUCTION

The reverse osmosis process of water desalination has been under intensive study for a number of years. In this process high-pressure saline water is placed in contact with a membrane that is permeable to water but relatively impermeable to salt. The desalinated water passes through the membrane, while the brine is concentrated and eventually discarded.

The work of Reid and Breton¹ in the 1950's showed that fully dense cellulose acetate films act as highly selective membranes in the separation of water from salt solutions by reverse osmosis. More recently, Loeb and Sourirajan,² by employing a suitable casting technique, were able to prepare cellulose acetate membranes, referred to hereafter as modified membranes, which pass much greater quantities of water than the membranes used by Reid and Breton without destroying the desalination characteristics of the membrane.

An understanding of the properties and osmotic behavior of the modified cellulose acetate membranes as first prepared by Loeb and Sourirajan was aided by an electron microscope study of the structure of the membranes and measurements of the intrinsic permeability properties of cellulose acetate films. The existence of a dense layer of cellulose acetate about 0.2 μ in thickness on the air-dried surface of the modified membranes was demonstrated in the electron microscope,³ and a correlation was attained between the thickness of this layer, the measured water permeability of cellulose acetate,⁴ and the water fluxes observed in reverse osmosis tests.

The modified membrane can therefore be viewed to good approximation as a very thin membrane with an integral porous support. This paper describes the preparation of ultrathin cellulose acetate films by an alternative method as well as the performance in reverse osmosis of composite membranes consisting of the ultrathin film and a porous support.

Transport Phenomenology

In previous studies⁴ it has been shown that the transport of water and simple salts in cellulose acetate membranes can be described by a solution-diffusion model. Thus, the water flux is given by

$$J_1 = \frac{D_1 C_1 \bar{V}_1}{RT} \left(\frac{\Delta P - \Delta \pi}{\Delta X} \right) \equiv A(\Delta P - \Delta \pi) \quad (1)$$

where J_1 = water flux, (in grams per square centimeter-second); D_1 = diffusion coefficient for water in the membrane (in square centimeters per second); C_1 = dissolved water concentration in the membrane (in grams per cubic centimeter); \bar{V}_1 = the partial molar volume of water in the external phase; $\Delta P = P' - P''$, and $\Delta \pi = \pi' - \pi''$ are the applied pressure difference and osmotic pressure difference, respectively, across the membrane (in atmospheres); and ΔX = membrane thickness (in centimeters). Here, the prime and double prime refer to the feed and permeate, respectively. The other terms have their usual significance. The quantity A , defined by eq. (1), is a measure of the water flux per unit net pressure; it is a characteristic of the membrane, having dimensions in grams per square centimeter-second-atmosphere, and has been referred to as the membrane constant. Similarly, the salt flux through an imperfection-free membrane in the case of large concentration differences can be described by

$$J_2 = D_2 K \Delta \rho_2 / \Delta X \quad (2)$$

where J_2 = salt flux (in grams per square centimeter-second), D_2 = diffusion coefficient for salt in the membrane (in square centimeters per second); K = distribution coefficient for salt (in grams sodium chloride per cubic centimeter membrane/grams sodium chloride per centimeter solution), and $\Delta \rho_2 = \rho'_2 - \rho''_2$ = difference in salt concentration in the solutions on the two sides of the membrane (in grams per cubic centimeter). The salt rejections in reverse osmosis are usually defined as

$$S = (\rho'_2 - \rho''_2) / \rho'_2 \quad (3)$$

In reverse osmosis, the concentration of salt in the permeate is determined only by the relative fluxes of water and salt; thus, $\rho''_2 = J_2 \rho''_1 / J_1$, where ρ''_1 is the water concentration of the permeate. It follows that

$$S = 1 - \frac{J_2 \rho''_1}{J_1 \rho'_2} = \left[1 + \frac{D_2 K R T \rho''_1}{D_1 C_1 \bar{V}_1 (\Delta P - \Delta \pi)} \right]^{-1} \quad (4)$$

The values of water permeability, $D_1 C_1$, and salt permeability, $D_2 K$, found previously⁴ for 39.8% acetyl cellulose acetate at 25°C. are $D_1 C_2 = 2.6$

$\times 10^{-7}$ g./cm.-sec. and $D_2K = 3.2 \times 10^{-11}$ cm.²/sec. With these values one can use eq. (4) to predict the salt rejection as a function of the applied pressure and the salt concentration of the feed. Some typical values for a 1% NaCl brine at 25°C. are: at 500 psi (34 atm.), $S = 99.37\%$; at 1000 psi (68 atm.), $S = 99.72\%$; and at 1500 psi (102 atm.), $S = 99.82\%$. The temperature dependence of the water and of the salt permeabilities appear to be similar, and the predicted salt rejections are not strongly temperature dependent.

In practice, the salt rejections observed experimentally have not been as great as those calculated from eq. (4). [The term "theoretical rejection" will be used to indicate that the rejection has been calculated by using eq. (4) and the permeability values cited above.] Furthermore, the observed results cover a considerable range, generally 96–98.5% for the most selective membranes. The discrepancy between observed and predicted values has been assumed to be the result of membrane imperfections; observations of a pressure-dependent component of salt flow^{4,5} along with the random nature of the results lend support to this assumption. Improving the attainable salt rejection from a nominal range of 96–98.5% to greater than 99% has great practical application. In present engineering design studies, a two-stage system must be assumed for sea-water conversion because 98% salt rejection is not sufficient to produce potable water in a single pass.

A linear relationship between water flux and net pressure is predicted from simple diffusion theory and is, in fact, obtained in dense membranes and in short-term experiments with modified membranes. After longer periods at high pressure, however, the water flux through modified membranes declines significantly in contrast to the behavior of dense membranes, which is relatively independent of time. This decline is believed to be the result of compaction of the porous substructure in the modified membrane or of a greater effective thickness of the surface layer. The decrease in water flux with time is a serious problem, since as the water flux declines the membrane area required for a plant of a given output capacity increases proportionately.

There are several disadvantages to preparing membranes by the Loeb-Sourirajan procedure. First, it is difficult to control and reproducibly vary the effective membrane thickness. Second, the salt rejections actually observed are less than desirable from the practical point of view. Third, the compaction effect has proved to be quite difficult to control. It seemed desirable, then, to seek alternative ways to prepare ultrathin reverse osmosis membranes. One alternative technique has been reported by Francis.⁶ Another alternative method for preparing very thin membranes, reported in recent publications by Carnell and Cassidy,^{7,8} was used in the present work. The Carnell-Cassidy method consists basically of slowly drawing a clean glass plate out of a dilute solution of a polymer in a suitable solvent. The film dries on the plate as the plate is drawn from the dilute solution and is subsequently floated off in water. In this way,

films as thin as 300 Å. were prepared from several polymers. Although they did not work with cellulose acetates, they give a number of details of technique and other observations that are applicable to cellulose acetate.

EXPERIMENTAL

The ultrathin films investigated in this study were prepared from cellulose acetates of varying acetyl contents and molecular weights supplied by Celanese Corporation of America and Eastman Chemical Products, Inc.

The following solvents of varying grades of purity were used to prepare the dilute solutions from which ultrathin membranes were drawn: acetone (Mallinckrodt, AR, and Matheson, Coleman and Bell, spectroquality reagent); methyl ethyl ketone (Mallinckrodt, AR); methyl acetate, (Matheson, Coleman and Bell, chromatoquality reagent); pyridine (Mallinckrodt, AR).

Dilute acetone solutions of 0.0063, 0.0125, 0.0250, 0.0312, 0.0440, and 0.0525 g. of cellulose acetate per cubic centimeter of solvent were prepared by rolling the solutions on a mill for several hours. The solutions were stable for several months, as indicated by their ability continually to produce membranes with stable water and salt permeabilities; the viscosity of the solutions was checked periodically during 1 month and found to be stable. Many of the solutions were filtered through fritted glass filters of 4–5.5 μ pore size and smaller before use; several solutions were centrifuged for 1 hr. at 17,000 rpm (35,000 relative centrifugal force) in an International Model HT centrifuge.

A glass plate, 140 mm. long, 37 mm. wide, and 5 mm. thick, was used for the film-forming surface. Carnell and Cassidy have noted that it is essential that the plate glass surfaces upon which the membrane is deposited be free of imperfections. The surfaces of several kinds of plate glass from different suppliers were found to be quite adequate in this respect. Plate glass manufactured by the "tin float" process was examined with the electron microscope and found to be relatively free of surface features. The membranes reported in this paper were drawn on glass of either the standard or tin float type.

The plate glass was cleaned by vigorous scrubbing of the surfaces with Aquet liquid laboratory detergent. Large volumes of tap water followed by several rinses of distilled water were used to rinse the detergent from the plate. After being rinsed with distilled water, the plate was rinsed with reagent-grade acetone. The glass plates were conditioned in spectroquality acetone, reagent-grade methyl ethyl ketone, or in some instances with methyl ethyl ketone plus 0.1% tridodecylamine, for $\frac{1}{2}$ hr. prior to dipping them into the dilute polymer solution. The tridodecylamine was added to the methyl ethyl ketone to assist in the dissipation of any static charge that might have been produced on the glass plate by the rubbing during the cleaning step.

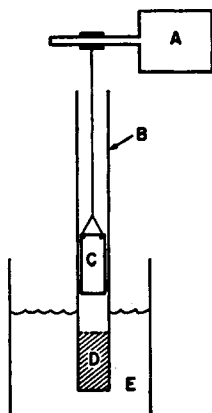


Fig. 1. Apparatus for preparing thin membranes.

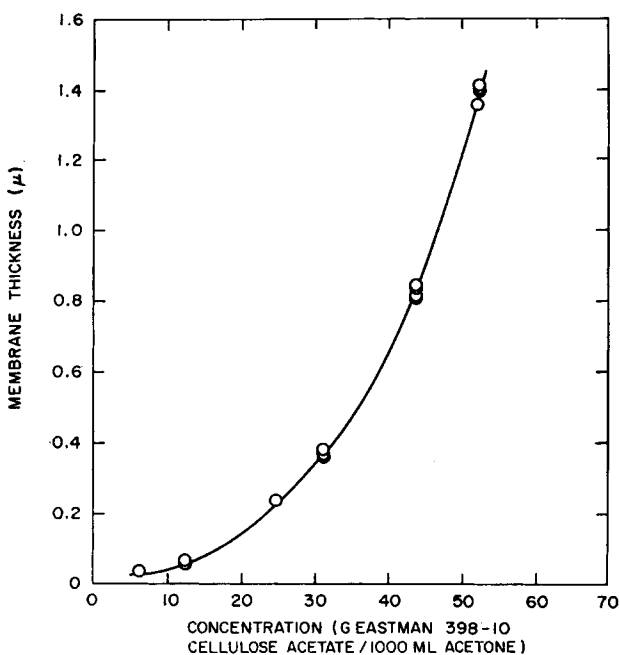


Fig. 2. Thickness of cellulose acetate membranes vs. concentration in acetone.

Figure 1 is a diagram of the apparatus used for drawing the thin membranes. The dilute cellulose acetate solution (D) was placed in a Pyrex tube (B) (460 mm. long, 42 mm. I.D.), to a depth of 80 mm., requiring approximately 225 ml. of solution. The tube was then immersed in a 30°C. water bath (E) to maintain constant temperature of the dilute polymer solution during the film formation. The glass plate (C) was rapidly taken from the acetone conditioning vessel to prevent drying and immersed into the dilute polymer solution while supported by a fine wire from a variable-

speed motor (A) that was supported above the Pyrex tube. The glass plate remained in the dilute polymer solution for 5 min. The glass plate was then withdrawn from the dilute polymer solution and raised to within 60 mm. of the top of the open tube, where it was allowed to dry for 20 min. At that time the plate was removed from the tube, the membrane edges were cut with a sharp blade, the plate was immersed in a clean water trough, and the membranes were floated off each surface of the glass plate onto the surface of the water.

The first step in this study was to establish a relationship between the polymer concentration in a given solvent and the thickness of the resulting membrane. The membrane thickness was determined by dimensioning a rectangular membrane section approximately 1 in. \times 3 in., weighing the dried membrane with a Cahn microbalance, and using the bulk density (1.3 g./cm.³ for cellulose acetate) to calculate the thickness. In this way, the relation shown in Figure 2 was obtained. The results in this figure apply only to acetone solutions and to the temperature (30°C.) and membrane withdrawal rate (22 cm./sec.) used in these studies. Useful membranes as thin as 600 A. have been reproducibly prepared. Thinner membranes were difficult to handle and possessed many more imperfections. The membranes are fragile, but no unusual difficulties were encountered in handling them. They were removed from the water trough by floating them onto Millipore filters, which were then used to support the thin membranes. The finest grades of Millipore filters were used as membrane supports: types VF and VM with mean pore sizes of 100 and 500 A., respectively. Several cellulose triacetate filters of 500 A. pore size, manufactured by the Gelman Company were also used. By themselves, these filters have very high water permeability and no measurable selectivity to sodium chloride.

A "modified" membrane was prepared by a procedure essentially similar to that described by Loeb and Sourirajan.² In this case, the casting solution consisted of 22.2 wt.-% cellulose acetate (39.8 wt.-% acetyl, Eastman No. 398-3), 1.1 wt.-% Baker anhydrous Mg(ClO₄)₂, 66.7 wt.-% reagent-grade acetone, and the balance distilled water. The solution was cooled to -5°C. and cast on cold glass plates in a deep freeze maintained at this temperature. The membranes were allowed to dry for 4 min. after casting and were then immersed in ice water and kept there for at least 1 hr. Finally, the membranes were annealed in water at 81°C. for 30 min.

The modified membranes were tested alone and with thin membrane overlays in a reverse osmosis apparatus. The composites were supported on a piece of filter paper supported in turn on porous stainless steel. A salt solution of known concentration and under pressures ranging from 40 to 110 atm. was circulated across the membrane, and the throughput water was collected from the porous plate. The brine was circulated over the surface of the membrane under conditions such that the boundary layer effect is not significant, as had been previously shown.⁹ Membrane con-

stants, as defined by eq. (1), were calculated from the water throughput rate and the salt rejection from the salt content of the feed and permeate in accordance with eq. (3).

Ethyl violet dye was added to the reverse osmosis system. This intense dye stains the supporting white Millipore filter only where an imperfection appears.

A Hitachi HU-11 electron microscope was used to examine both ultrathin films in transmission and replicas of ultrathin films. By using a previously developed replication method,¹⁰ the dried membrane was shadowed with palladium metal at an angle of 20° in a vacuum evaporator, and a thin (~200 Å.) carbon film was deposited over the palladium. The membrane was then placed on a 200-mesh copper grid and the cellulose acetate membrane dissolved away with acetone in a reflux column, leaving a palladium-carbon replica.

RESULTS AND DISCUSSION

Results obtained with 2400, 1500, and 620 Å. thick membranes drawn from unfiltered dilute cellulose acetate solutions are presented in Table I. These reverse osmosis tests were carried out with 1.2% NaCl brine at 30–31°C.

TABLE I
Reverse Osmosis Data for Six Thin Membranes
(Eastman 398-10 Cellulose Acetate)*

Membrane thickness, Å.	Applied pressure, psi	Water flux, gal./ft. ² -day	Salt rejection, %	Membrane constant, 10 ⁻⁵ g./cm. ² -sec.-atm.
2400	1500	17.0	95.2	0.96
2400	1500	15.4	96.5	0.92
1500	1500	25.4	97.0	1.5
1500	1500	23.9	97.0	1.4
620	800	33.8	92.1	4.1
620	800	33.4	92.0	4.1

* Conditions: temperature, 30–31°C.; 1.2% NaCl brine; membranes supported on Millipore VF filters.

The thin membranes generally perform as well as modified reverse osmosis membranes. Membrane thickness and therefore water flux can be reproducibly controlled and varied. The 600 Å. membranes had quite high water flow rates with reasonable salt rejection.

Imperfections were present in each of these ultrathin membranes. These imperfections were readily seen by observing the ethyl violet dye pattern in the membrane support after the experiment was terminated.

A precipitate was deposited by placing a dilute aqueous solution of Cu(NO₃)₂ on one side of the 2400 Å. membrane and a dilute K₄Fe(CN)₆ solution on the opposite side. The submicron holes, or imperfections,

TABLE II
Reverse Osmosis Data for Thin Membrane Overlays
(Eastman 398-10 Cellulose Acetate)^a

Symbol ^b	Membrane	Applied pressure, psi	Duration, hr.	Water flux, gal./ft. ² -day	Membrane constant, 10 ⁻⁵ g./cm. ² -sec.-atm.	Salt rejection, %
●	Modified	400	0.1	4.2	1.23	94.4
○	Modified, plus overlay ^c			2.8	0.63	96.6
△	Modified, plus overlay ^c			2.8	0.63	96.6
□	Modified, plus overlay ^c			1.9	0.61	97.2
●	Modified	820	24	9.7	1.21	96.9
○	Modified, plus overlay ^c			4.7	0.58	98.3
△	Modified, plus overlay ^c			4.8	0.61	97.4
□	Modified, plus overlay ^c			4.3	0.54	98.4
●	Modified	1520	30	15.6	0.94	97.9
○	Modified, plus overlay ^c			8.0	0.48	99.0
△	Modified, plus overlay ^c			8.0	0.48	97.6
□	Modified, plus overlay ^c			7.4	0.45	98.9

^a Conditions: temperature, 30°C.; 1.5% NaCl brine.

^b The symbols refer to the graphic data shown in Fig. 3.

^c This is a modified membrane plus a 2400-A. thick membrane overlay.

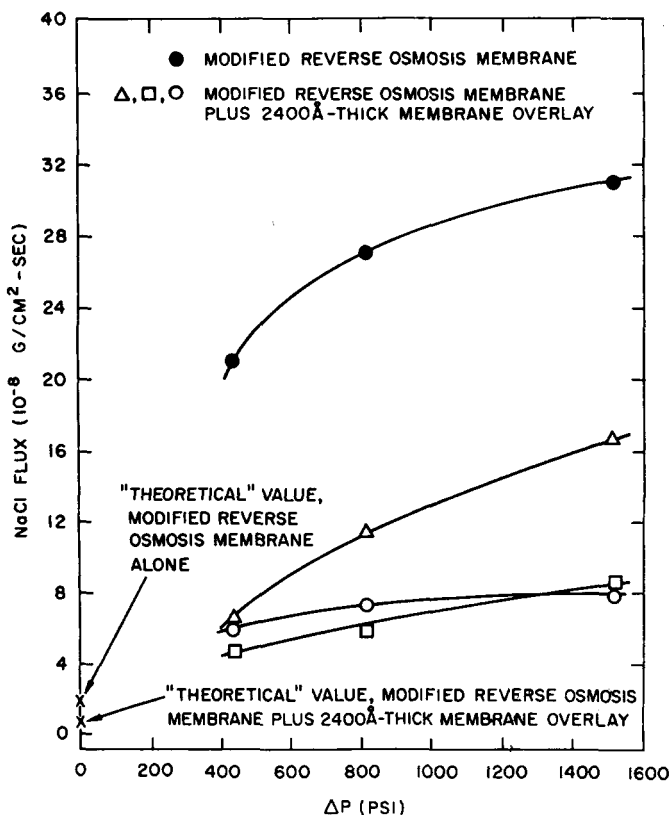


Fig. 3. Salt flux vs. applied pressure.

were seen with the electron microscope as very dark, electron-opaque regions within the thin membrane when the thin membranes were viewed directly in transmission.

Assuming that the pressure-dependent salt flow that has been reported^{4,5} occurs through imperfections, it would be expected that if the imperfections are relatively widely spaced, overlapping two films would effectively seal off nearly all the imperfections. If this were the case, salt rejection should approach the theoretical value based on salt permeability measured by "immersion" experiments.⁴ Three nominally identical overlaying-type experiments were performed; the results are summarized in Table II.

Salt rejection did improve significantly when modified membranes were overlaid with thin membranes of cellulose acetate; however, the salt rejection still did not reach the "theoretical" value. Figure 3 shows the salt flux through these membranes as a function of applied pressure, along with the theoretical (pressure-independent) salt flux as calculated from eq. (2). Even with the overlay membrane, salt flux is still a function of pressure, indicating that a significant fraction of the salt flow is strongly

coupled to the water flow or, alternatively, that the imperfections have not been sealed off. If salt flow is via imperfections, it must be concluded that the seal between the two membranes is imperfect and permits communication between imperfections in the two films.

Reverse osmosis experiments were also conducted with membrane overlays 600 A. thick and with a 1500 A. membrane laid over a second 600 A. membrane. Again, "theoretical" salt rejection was not attained.

A series of ultrathin membranes was prepared under immaculate preparation conditions. Spectroquality acetone was used both as the solvent for the cellulose acetate and as the glass-conditioning agent. The dilute cellulose acetate solution was also filtered through a fritted glass filter of 0.9–1.4 μ pore size. Reverse osmosis results for two membranes prepared in this way are summarized in Table III. The membranes rejected 99.81%

TABLE III
Reverse Osmosis Data for Six Thin Membranes^a
(Eastman 398-10 Cellulose Acetate)

Membrane thickness, A.	Applied pressure, psi	Water flux, gal./ft. ² -day	Salt rejection, %	Membrane constant, 10 ⁻⁵ g./cm. ² -sec.-atm.
Acetone solvent, acetone glass conditioner				
2800	1560	9.0	99.81	0.44
2800	1560	9.7	99.81	0.46
Methyl acetate solvent, methyl ethyl ketone-0.1% tridodecylamine glass conditioner				
3000	840	4.5	99.47	0.39
3000	840	4.8	99.10	0.42
3000	840	4.5	99.35	0.39
3000	840	4.3	99.10	0.37

^a Conditions: temperature, 24°C.; 0.9% NaCl brine; membranes supported on Millipore VF filters.

of the salt, which is very close to the value (99.83%) calculated from eq. (4) for the experimental conditions. These membranes showed no ethyl violet dye spots when they were removed from the reverse osmosis cells after the experiment was terminated, indicating that no imperfections were present in the membrane. The membrane constant *A* for the thin membranes was somewhat lower than that calculated on the basis of the thickness of the thin membrane and eq. (1). The deviation of the observed membrane constants from the calculated values is attributed to the Millipore filter supports.

The improved cleanliness of the entire process of making thin films appear responsible for the attainment of theoretical salt rejection. In a number of other membranes the number of imperfections noted with the aid of the ethyl violet dye qualitatively correlated with the given salt rejections. The fact that the dye was visible to the unaided eye does not, of course,

TABLE IV. Reverse Osmosis Data for Six Thin Membranes* (Eastman 398-10 Cellulose Acetate)

Thin membrane	Applied pressure, psi	Duration, hr.	Membrane constant, 10^{-3} g./cm. ² . sec.-atm.	Water flux, gal./ft. ² -day	Salt rejection, %
Supported on Millipore molecular filter of 100 A. pore size	A	0.33	1.09	21.2	98.2
		15.5	0.79	20.8	99.4
		24.0	0.74	19.4	99.1
		39.5	0.74	19.4	99.2
	B	0.33	1.26	24.6	97.2
		15.5	0.77	20.4	99.0
Supported on Millipore molecular filter of 500 A. pore size		24.0	0.70	18.2	98.9
		39.5	0.71	18.6	99.0
	A	0.33	1.24	24.2	98.4
		15.5	0.97	25.4	99.3
		24.0	0.87	22.5	99.1
		39.5	0.91	23.4	99.2
Supported on cellulose triacetate Gelman Metrice molecular filter of 500 A. pore size	B	0.33	1.20	23.4	97.5
		15.5	0.84	22.4	99.4
		24.0	0.75	19.7	99.2
		39.5	0.78	20.4	99.2
	A	0.33	1.32	25.6	97.2
		15.5	0.81	21.6	99.0
Supported on cellulose triacetate Gelman Metrice molecular filter of 500 A. pore size		24.0	0.74	19.4	99.0
		39.5	0.75	19.7	—
	B	0.33	1.41	27.5	97.2
		15.5	0.81	21.6	99.0
		24.0	0.74	19.4	99.0
		39.5	0.74	19.4	99.0

* Conditions: temperature, 22°C.; 1.5% NaCl brine; thin membrane thickness, 1250 A.

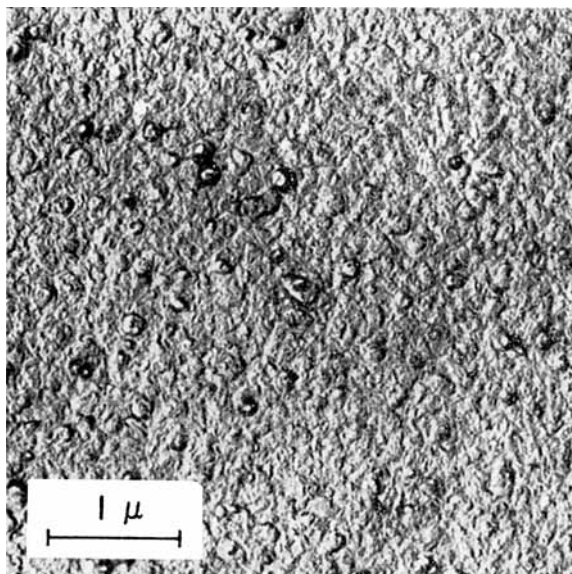


Fig. 4. Electron micrograph of a preshadowed carbon replica of the glossy surface of a Millipore filter of 100 A. pore size.

imply that the imperfections themselves were large. In fact, the imperfections must have been quite small, as one can show from the observed high salt rejections with the assumption that the flow through imperfections obeys Poiseuille's law. The dye was so prominent because it was retained in the relatively large pores of the membrane support.

From an inspection of the data from a large number of reverse osmosis experiments on thin membranes, it was concluded that both the standard and tin-float type plate glasses are equally satisfactory. Under identical conditions, thin membranes drawn from solution on the same glass surface gave salt rejections ranging from 96.0 to better than 99.0% at 800 psi with 1% NaCl feed solution. It was therefore concluded that the glass plate surfaces were not the principal cause of membrane imperfections.

Table III also shows that imperfection-free thin membranes can be drawn from methyl acetate solutions of cellulose acetate and that the nature of the glass conditioning agent is not a critical parameter, provided that immaculate preparation conditions are used. The physical properties and the surface smoothness of the supporting material for the thin membranes are critical factors for successfully making the composite membranes.

Table IV summarizes the reverse osmosis data for membranes supported on Millipore filters of different pore sizes and on Gelman cellulose triacetate filters. The thin membranes, 1250 A. thick, were placed on the non-glossy or dull surface of the Millipore filters. There was no pronounced difference in the rate of water flux decline between any of the composite membranes described in Table IV, indicating that within the scatter of the experimental results Millipore filters having 100 or 500 A. diameter pores

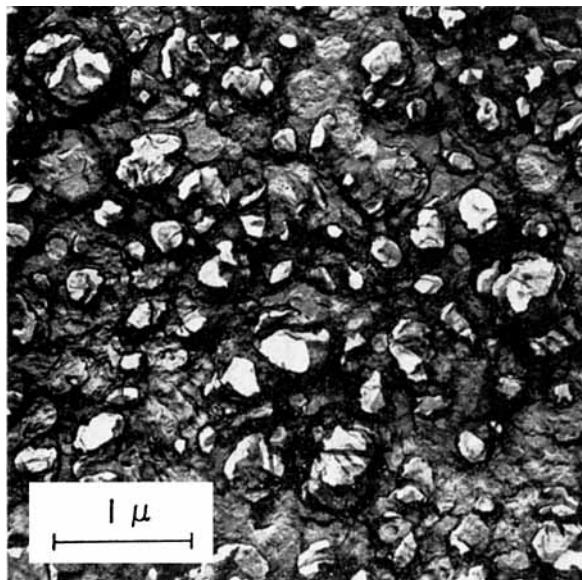


Fig. 5. Electron micrograph of a preshadowed carbon replica of the dull surface of a Millipore filter of 100 A. pore size.

and the Gelman cellulose triacetate filters all compact about equally under these conditions. The rates of water flux declines of the composite membranes at 1500 psi were generally a factor of two lower than those observed for modified membranes. Membrane compaction is thus a serious problem in these composite membranes but not as severe as observed with modified membranes.

The appearance of the surfaces of Millipore filters suggested that the performance of the composite membrane may be dependent on the orientation of the Millipore filter. One surface of the Millipore filter is very glossy while the other surface is quite dull; all thin membranes referred to thus far were supported on the dull surface. Figures 4 and 5 are electron micrographs of the glossy and dull surfaces, respectively, of Millipore filters of 100 A. pore size. The photographs were taken of preshadowed carbon replicas. The pore size on the dull surface appears to be a factor of three or four larger than the pore size on the glossy surface. These pores, however, actually appear to be about 4000 and 1000 A., respectively, in these photographs, indicating that the 100 A. restrictions must occur in the interior of these filters.

Table V summarizes reverse osmosis data obtained for composite membranes with the thin membranes supported on either the glossy or dull surface of the Millipore filter. When the thin membranes are placed on the glossy surface of the Millipore filter, the initial membrane constants are much lower than when the dull surface is used to support the membrane, indicating significant resistance to flow in the Millipore filter in at least

TABLE V
Reverse Osmosis Data for Three Thin Membranes* (Eastman 398-10 Cellulose Acetate)

Thin membrane	Applied pressure, psi	Duration, hr.	Membrane constant, 10^{-5} g./cm. ² sec.-atm.	Water flux, gal./ft. ² -day	Salt rejection, %
Supported on dull surface of 100 A. Millipore filter	A	0.5	1.01	19.7	98.0
		1.3	0.94	18.4	98.6
		16.5	0.83	16.2	98.7
		41.5	0.75	14.7	98.8
		48.5	0.76	14.9	98.8
Supported on glossy surface of 100 A. Millipore filter	A	0.5	0.33	6.5	93.6
		1.3	0.26	5.0	95.4
		16.5	0.17	3.3	93.3
		41.5	0.15	3.0	93.0
		48.5	0.14	2.8	92.5
B		0.5	0.16	1.3	93.4
		1.3	—	—	—
		16.5	0.08	0.9	90.0
	41.5	0.08	0.9	89.6	
	48.5	0.08	0.9	89.7	

* Conditions: temperature, 23°C.; 1.2% NaCl brine; thin membrane thickness 2400 A.

one orientation. Apparently, the smoothness of the glossy Millipore filter surface results in a large amount of surface contact with the thin membrane; this effectively decreases the area of the thin membrane, thereby reducing the membrane constant. The compaction is also severe in view of the low initial membrane constant. When the thin membrane was supported on the dull surface of the Millipore filter, however, the initial membrane constant was more consistent with predictions based on the thin membrane thickness. In this case the thin membrane is in physical contact with much less of the supporting surface of the Millipore filter, minimizing the decrease in effective membrane area. The membrane constant-membrane thickness correlation was much more consistent when the Millipore filters were cut from the same piece rather than from different pieces of the same lot or different lots. In either case, compaction is a significant effect, and it is worth noting that Millipore filters undergo a nonrecoverable decrease in thickness of one third or more of the initial thickness when used as supports at high pressures.

Thin membranes prepared from 39.8% acetyl cellulose acetate of varying molecular weights did not show any observable difference in salt rejection or membrane constant. The fact that molecular weight has no significant effect on transport properties was expected from previous experience with modified reverse osmosis membranes.⁴

Thin membranes drawn from dilute solutions of cellulose triacetate had salt rejections which were more erratic, suggesting that these membranes tend to contain more imperfections than membranes with a lower degree of substitution.

Membranes prepared from cellulose acetates supplied by the Celanese Corporation of America performed equally well in reverse osmosis experiments as membranes prepared from cellulose acetates of the same degree of acetylation supplied by Eastman Chemical Products Inc. The differences noted by others^{11,12} between modified membranes cast from cellulose acetates from different sources have not been noted in thin membrane experiments.

A thin membrane-Millipore composite was dried and heat-treated in an air oven at 180°C. for 20 min. There was only a slight change in membrane properties. Similarly, heat treatment of the thin membranes in water at 70°C. for 1 hr. did not significantly alter the performance of the membrane composite in reverse osmosis tests. This supports and extends the conclusion previously presented⁴ that heat treatment of fully dense cellulose acetate membranes does not significantly alter the transport properties.

CONCLUSIONS

Ultrathin reverse osmosis membrane composites have been prepared by drawing thin films from dilute cellulose acetate solutions and supporting them on molecular filters. These composite membranes have performed at least as well in reverse osmosis tests as have typical modified membranes

prepared according to the Loeb-Sourirajan technique. It has been found possible by using immaculate techniques to prepare thin films that are apparently free of imperfections and with which "theoretical" salt rejection has been achieved, apparently for the first time. The composite membranes have demonstrated lower rates of flux decline than modified membranes, suggesting that they are more resistant to compaction.

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Résumé

Des membranes à base d'acétate de cellulose servant à l'osmose inverse, de 600 à 2800 Å d'épaisseur, ont été préparées sur des surfaces de verre en plongeant une plaque de verre nettoyée dans une solution diluée d'acétate de cellulose. Après séchage, des membranes flottent à la surface de l'eau et sont placées sur des supports de filtres moléculaires. Les réjections théoriques de sel, tel qu'on le calculé au départ du modèle solution-diffusion pour le transport à travers une membrane pour l'acétate de cellulose, ont été obtenus pour des membranes dépourvues de toute imperfection.

Zusammenfassung

Celluloseacetatmembrane für umgekehrte Osmose mit einer Dicke von 600 bis 2800 Å wurden auf Glasoberflächen durch Eintauchen einer reinen Glasplatte in eine verdünnte Celluloseacetatlösung hergestellt. Nach dem Trocknen werden die Membranen auf einen Wasseroberfläche abgehoben und auf einen Molekularfilterträger aufgebracht. Mit fehlerfreien Membranen wurde die theoretische, für das Lösungs-Diffusionsmodell des Membrantransportes berechnete Salzabseisung erhalten.

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