

Low-Pressure Reverse Osmosis Desalination with Improved Cellulose Acetate Membranes

AJIT K. GHOSH* and KAMALESH K. SIRKAR,[†] *Department of Chemical Engineering, Indian Institute of Technology, Kanpur—208016, U.P., India*

Synopsis

The advantages of carrying out reverse osmosis desalination with improved membranes at low pressures have been pointed out. Cellulose acetate (CA) semipermeable membranes developed with low air-exposure periods by Sirkar et al. from novel Manjikian-type casting solutions having high CA content, partial replacement of acetone by dioxane, and small amounts of ZnCl₂ (or none) have been tested for the following combinations of operating pressure (lb/in.²)/feed brine concentration (in ppm): 250/5000; 300/7500; 400/10,000; 600/30,000; 700/40,000; 750/50,000; 800/60,000. In the pressure range of 250–600 lb/in.² (psig), the pure water permeability (PWP) constants of membranes for a given salt transport parameter are greater than those of similar membranes tested earlier by Sirkar et al. at 600 psig with a 5000-ppm brine feed. The PWP constants decrease faster with pressure as the casting solution CA concentration is reduced from 32% to 30% and the dioxane content of the solvent is raised from 40% to 60%. The intrinsic performances of membranes from a 32% CA casting solution with 40% dioxane improve as the pressure is increased from 250 to 600 psig. The solution structure-rate of evaporation concept along with the phenomenon of fingerlike cavities and protrusions in membranes from high dioxane casting solutions explain most of the observations of this work. The superior low-pressure performance of these CA membranes provide a basis for systematically lowering the operating pressure in reverse osmosis desalination.

INTRODUCTION

The development of improved polymeric semipermeable membranes for low-pressure reverse osmosis desalination is becoming increasingly attractive from various considerations. Besides the increase in membrane compaction slope with pressure for improved porous cellulose acetate (CA) membranes (Kunst and Sourirajan¹) and the loss under high-pressure operation of performance improvements obtained at lower pressures of 250 psig due to the closure of small-sized pores initially generated in the more productive CA membranes (Pilon et al.²), there are other factors disfavoring high-pressure operation. Brackish water desalination with improved CA membranes at higher pressures of around 600 psig yields a water flux of 35–60 gallons (U.S.)/ft² day (gfd) for salt rejection values of 96–90%. For a given feed-flow condition, this level of productivity leads to a much higher concentration polarization than that obtained with the water flux of 15–36 gfd (at 96–90% salt rejection) characteristic of the earlier generation of CA membranes.³ To achieve the full flux potential of the improved membranes at higher operating pressures, much higher feed velocity and pressure drop will therefore be needed, resulting in higher cost. Further-

* Present address: Chemical Engineering Department, Monash University, Clayton, Victoria, Australia—3168.

[†] To whom the correspondence should be addressed: Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030.

more, low-pressure operation reduces membrane fouling⁴ and allows brackish water desalination plants with improved membranes to be run with high-capacity multistage centrifugal pumps.

Kunst and Sourirajan¹ have studied the desalination of a 1500-ppm feed at 250 psig and lower pressures with improved porous flat CA membranes made from a type one casting solution⁵ of acetone, CA, water, and magnesium perchlorate. Desalination of a 3500-ppm feed at 250 psig with CA membranes from type one casting solutions have also been studied by Kunst and Sourirajan,⁶ Pageau and Sourirajan,⁷ and Thayer et al.⁸ With CA membranes from a type two⁵ (Manjikian-type) casting solution containing CA, acetone, and formamide, Pilon et al.² obtained better desalination performance than Kunst and Sourirajan.⁶ For a 3100-ppm feed, the 250-psig desalination performances of a new family of CA and cellulose triacetate (CTA) membranes are reported⁴ to be equivalent to or better than those of commercial membranes operating at 450 psig. While lower pressure operation is feasible with improved dry-reverse osmosis membranes of Kesting et al.⁹ from quaternized cellulose triesters, low-pressure desalination performances of improved thin-film composite membranes of polyurea NS-100, of poly(ether/amide) PA-100 and PA-300, and of poly(ether/urea) RC-100 are available in Channabasappa¹⁰ and Riley et al.¹¹ for sea water feeds.

Sirkar et al.⁵ have recently developed a series of highly productive CA membranes from novel Manjikian-type casting solutions with the following features: high CA concentration in the range of 29–32 wt %; composition close to the phase boundary; partial replacement (20%–80%) of acetone by dioxane; and the presence of small amounts of $ZnCl_2$. Membranes prepared from such casting compositions with very low air-evaporation times (0.05–2 sec) perform the desalination of 0.5 wt % NaCl feed at 600 psig as efficiently as the best known CA membranes in the literature.⁵ The objective of this study was therefore to find out the productivity of similar membranes under considerably lower pressures of operations for brine feeds encountered in the desalination of brackish and sea waters. Rangaiah¹² had tested a few of his membranes at 250 psig with a 5000-ppm feed. This paper analyzes the performances of these membranes for the desalination of feed brines of various concentrations between 5000 and 60,000 ppm at operating pressures varying between 250 and 800 psig, respectively. While this work is likely to open up new possibilities in systematic lowering of the operating pressure in reverse osmosis desalination with improved membranes, it will also enable us to know the effect of pressure on membranes prepared from various novel casting solutions at low evaporation times so that a rational choice can be attempted.

EXPERIMENTAL

Casting solutions were prepared from Eastman cellulose acetate (E-398-3), analytical reagent grade acetone, dioxane, formamide, and zinc chloride. Analytical grade sodium chloride was used for standardization of $AgNO_3$ solutions used for salt analysis of the feed and permeate. Laboratory grade sodium chloride and distilled water were used for preparing brackish and sea water feeds. The cellulose acetate powder was used in the as-received state without drying.¹²

The description of the vertical flat membrane casting apparatus capable of providing an air-exposure period of less than 1 sec is available in two theses.^{12,13} The evaporation time for this work was varied between 0.06 and 0.6 sec by varying the air gap between the casting knife and the ice-cold gelation bath at 0–1°C, as well as by variation of the speed of the glass casting plate. Room temperature varied between 17 and 35°C, but as Rangaiah¹² has shown, room temperature and humidity variation have a negligible effect on membranes cast with low air-evaporation time, since the enclosed local atmosphere is almost independent of the surrounding. Flat membranes were cast with a 0.008-in. gap between the knife edge and glass plates. Gelled membranes were kept in 0.5 wt. % formaldehyde solution¹⁴ to prevent undesirable bacterial growth.

Membrane Testing

The gelled membranes were heat treated in a thermostat for 5 min at any temperature between 70 and 92°C. Circular pieces of heat-treated membranes were tested in a high-pressure test loop¹² with a feed-flow rate of 600 cc/min. At this flow rate, the Reynolds number based on the channel gap at the outer diameter of the active membrane section was 112, and from Kimura-Sourirajan analysis¹⁵ the mass-transfer coefficient k was determined to be 40×10^{-4} cm/sec. The effective membrane desalination area was 1.225 in.² (7.88 cm²). Two identical test cells were used in series. All membranes were pressure treated for 1.5 hr with distilled water at a pressure 50 psig higher than that to be used in the subsequent desalination run with a given feed concentration. The pressure-treatment levels (psig) used are indicated below along with feed concentrations (wt. %): 300, 0.5; 350, 0.75; 450, 1.0; 650, 3.0; 750, 4.0; 800, 5.0; 850, 6.0. The corresponding operating pressures during the subsequent desalination runs were: 250, 300, 400, 600, 700, 750, and 800. The pure water permeability (PWP) was determined during the pressure-treatment stage as an average of the last two 0.5 hr of the 1.5 hr run. All desalination runs were conducted for 1.5 hr and the data reported for last 30 min are only for the water flux and the percent salt rejection. If a given membrane test piece has been evaluated with various feed concentrations, the order of the experiments was always from lower concentrations to higher concentrations, so that the membrane experiences increasingly higher pressure with time. The salt content of the permeate and the feed were determined by titration, as well as by means of a Direct Reading Conductivity Meter (DRCM) Type 303 of Systronics, Inc. The room temperature was recorded so as to obtain the correct permeate salt concentration from standard plots of conductivity vs concentration at different temperatures.³ The temperature of the feed to the test cell was also measured to obtain the water flux at 25°C from the following equation (recommended by Sourirajan¹⁶):

$$(\text{Water flux})_{25^\circ\text{C}} \times (\text{Viscosity of water})_{25^\circ\text{C}} = (\text{Water flux})_{t^\circ\text{C}} \times (\text{Viscosity of water})_{t^\circ\text{C}} \quad (1)$$

Only the water flux at 25°C is reported here.

RESULTS AND DISCUSSION

The low-pressure desalination performances of CA membranes cast with low evaporation times are presented and discussed under the following headings:

1. Low-pressure performance of various membranes,
2. effect of increasing pressure and feed concentration, and
3. comparison of membrane performance.

All the casting compositions reported are in weight percent.

Low-Pressure Performance of Various Membranes

Four different types of the novel casting solutions⁵ used in this study are shown in Table I. The desalination performances of CA membranes from these casting solutions in terms of water flux vs salt rejection are given in Figures 1-3. Since Sirkar et al.⁵ had observed that amongst nondioxane and non-ZnCl₂ compositions, a 30% CA casting solution (shown as S-1 in Table I) produced the most productive membranes, membranes produced from the same casting solution with low air exposure periods were tested at 250 psig with a 5000-ppm brine feed. Although the water fluxes of such membranes are considerably lower than those at 600 psig with an identical feed, the water flux of some of these membranes, namely, 15.6 gfd at 90.2% rejection are about half of that of a standard Eastman membrane RO-89¹⁷ at 600 psig with a 5000-ppm NaCl feed.

When dioxane replaces part of the acetone in S-1-type casting solutions, it is known from Sirkar et al.⁵ that the membrane performance improves significantly. It is also known that whereas the performances of membranes from 30% CA casting solutions with 20 and 40% dioxanes are about the same, membranes from 30% CA casting solutions with higher dioxane are somewhat inferior, especially at higher rejection levels. The performances of membranes from S-2 casting solutions are shown in Figure 2. For a 5000-ppm feed at 250 psig, 40% dioxane membranes perform significantly better than those obtained from casting solutions S-2 (60%), S-2 (80%), and S-2 (0%). As the pressure of operation and the feed brine concentration are increased, the membrane performances improve. In fact, the water flux at 600 psig with a 5000-ppm feed is only 1.5 times larger

TABLE I
Polymer Solution Composition for Casting with Low Evaporation Times

Solution constituents	Sample			
	S-1	S-2	S-3	S-4
Cellulose acetate	30	30	30	32
Solvent	45	45	45	46
(% D + % acetone) ^a	(0-100)	(40-60 ^b or 60-40 or 80-20)	(40-60 ^c or 60-40)	(40-60)
Formamide	25	25	25	22
ZnCl ₂	0	0	(1.33 g/100 g soln.)	(1.33 g/100 g soln.)

^a D refers to dioxane.

^b An S-2 casting solution with, say, 40% dioxane is designated as S-2 (40%).

^c An S-3 casting solution with, say, 60% dioxane will be designated by S-3 (60%).

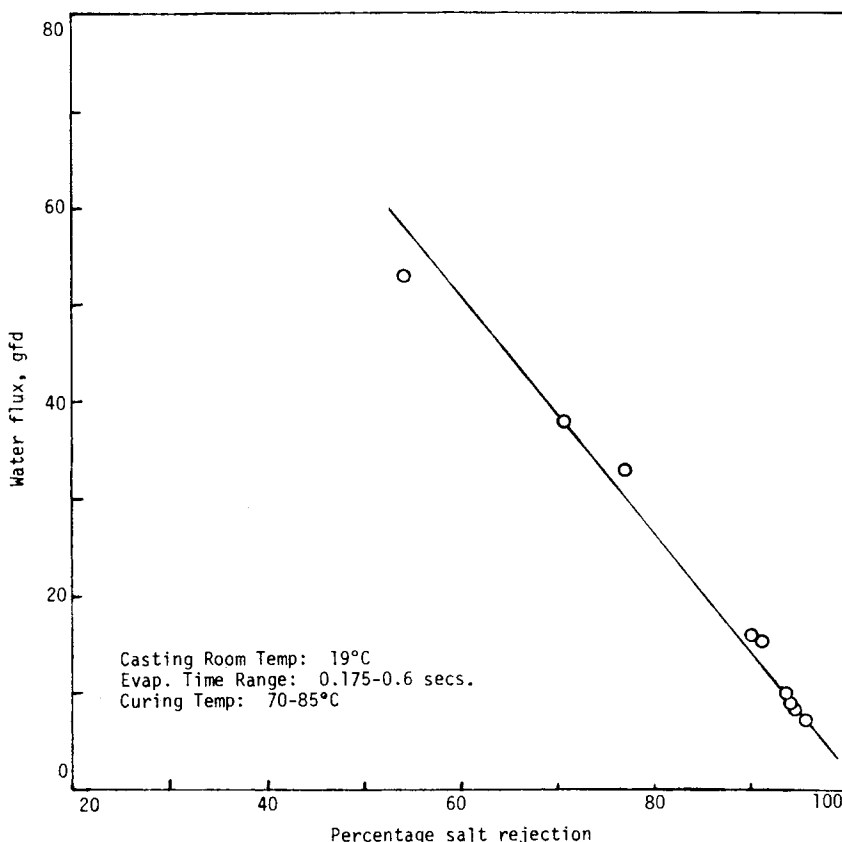


Fig. 1. Performance of membranes from S-1 casting solutions and low evaporation times at 250 psig with 5000-ppm feed.

than those at 600 psig with a 30,000-ppm feed at salt-rejection levels of 80% and lower. At higher rejection levels of 95%, however, the water flux at 600 psig with a 5000-ppm feed is about 2.8 times larger than those at 600 psig with a 30,000-ppm feed. The latter is still reasonable (about 10 gfd), so that concentration polarization will be much reduced for a given level of mixing.

In Figure 3 the performance of membranes from casting solutions S-3 (40%) and S-4 (40%) are shown for operation at three pressure levels: 250 psig (5000-ppm feed); 400 psig (10,000-ppm feed); and 600 psig (30,000-ppm feed). The behavior of these membranes are similar to those of the S-2 membranes vis-à-vis the membrane performances at 600 psig with a 5000-ppm feed. However, it would appear that at rejection levels of around 94%, the membrane water flux at 600 psig with a 5000-ppm feed is only about 1.7 times greater than the fluxes observed with 400- and 600-psig operation. Furthermore, 30% CA membranes appear to perform better at lower salt-rejection levels of around 82% compared to 32% CA membranes, which show an excellent performance at around 94% salt-rejection levels. This would indicate that 32% CA membranes have fewer small pores than 30% CA membranes, which have more small pores; however, these pores close up as higher heat-treatment temperatures and salt-rejection levels (as well as higher pressures) are encountered. An explanation for this based on the solution structure-rate of evaporation concept of Kunst and Sourirajan⁶ is offered in the next section.

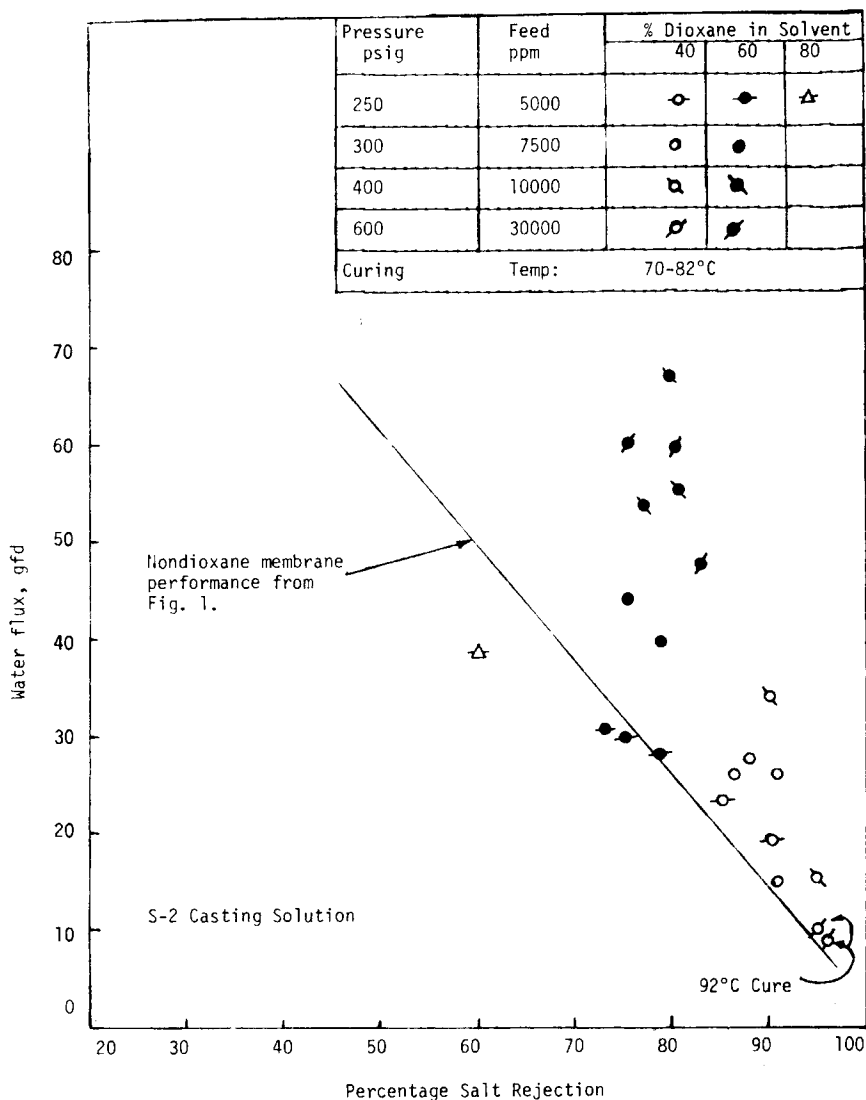


Fig. 2. Effect of partial replacement of acetone by dioxane on membrane performance.

Some of the representative membrane performance data for membranes from casting solutions S-4 (40%) and S-2 (40%) are reported in Table II for the following pressures: 250, 300, 400, and 600 psig. The data is presented for the various levels of pressure for each membrane sheet. In Table III the performance levels of individual membrane sheets from casting solutions S-2 (60%) are shown for a wider range of pressures, i.e., from 250 psig (5000-ppm feed) to 800 psig (60,000-ppm feed). The salt-rejection and flux levels of the membranes from Tables II and III suggest that these highly productive membranes for desalination of brackish as well as sea waters can be used with pressures much lower than usual. For example, for 50% water recovery with a brackish water feed of 5000 ppm, a pressure range of 250-350 psig is sufficient to produce an acceptable level of water flux. Similarly, a two-stage sea water conversion plant can operate its

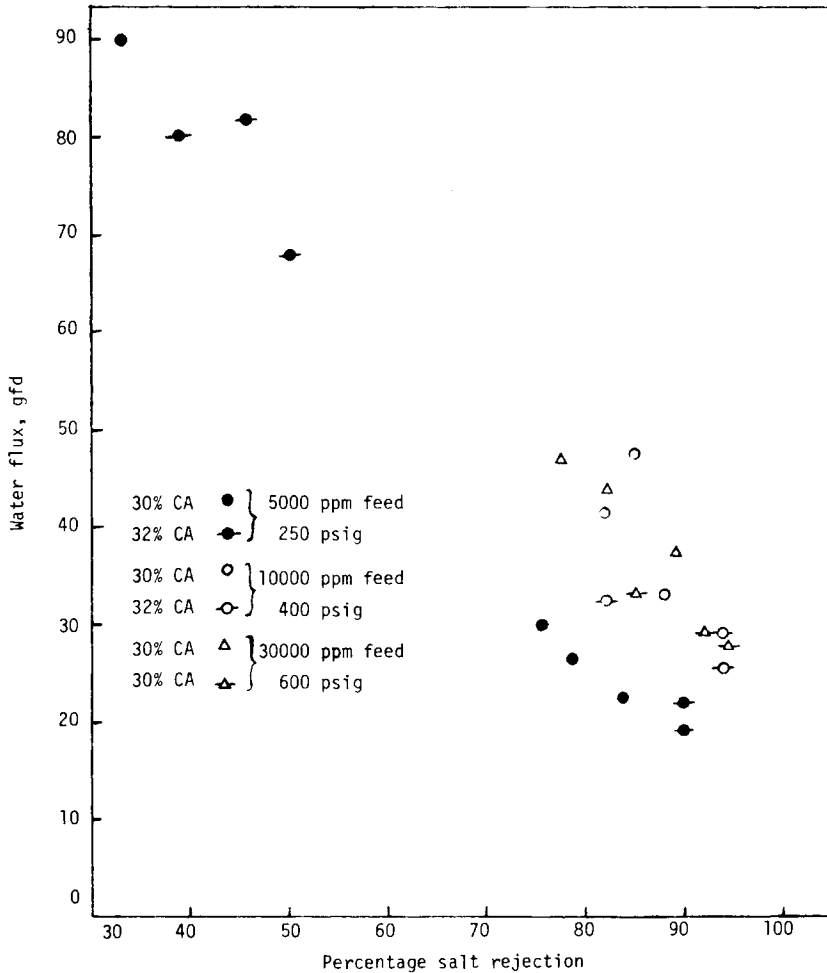


Fig. 3. Low-pressure performance of membranes with $ZnCl_2$.

first stage at 800 psig and the second stage at 300–350 psig if these improved CA membranes are used.

Effect of Increasing Pressure and Feed Concentration

The effect of pressure on the performance of reverse osmosis membranes is usually estimated by determining the dependence of PWP constant (A) and the solute transport parameter ($D_{AM}/K\delta$) on the pressure. Sourirajan¹⁶ has shown that at a given temperature for CA membranes used in a large number of studies, the PWP constant A at pressure P has been found to be related to that at zero pressure, A_0 , by

$$A = A_0 \exp(-BP) \quad (2)$$

where B is a constant to be determined from data. In the present investigation, it is of interest to know which set of membranes have comparatively lower values of B . The basic variations in the casting compositions⁵ are of two types: (1)

TABLE II
Low-Pressure Performance of Membranes from Different Casting Solutions with 40% Dioxane

Membrane identi- fication	Casting solution composition	Evaporation period, sec	Curing temp., °C	Desalination performance ^a			
				5000/250 Flux, gfd (% R) ^b	7500/300 Flux, gfd (% R)	10,000/400 Flux, gfd (% R)	30,000/600 Flux, gfd (% R)
M-11-51	32% CA	0.125	70.0	68.0 (50.0)	—	—	—
M-11-51	22% F	0.125	81.0	22.0 (90.0)	22.5 (91.5)	29.0 (94.0)	29.5 (92.0)
M-11-52	46% (40% D + 60% A)	0.125	81.0	19.6 (90.0)	22.5 (93.0)	29.0 (93.5)	29.5 (93.5)
M-11-53	ZnCl ₂ (1.33 g/100 g)	0.125	81.5	18.7 (87.8)	21.4 (94.0)	25.6 (94.0)	28.2 (94.5)
M-11-41		0.125	82.0	16.4 (82.6)	21.4 (95.0)	23.1 (94.0)	26.8 (91.5)
M-11-43		0.125	82.0	22.8 (77.5)	30.3 (82.0)	32.4 (82.0)	33.5 (85.0)
M-11-11		0.300	82.0	19.2 (90.0)	23.5 (92.0)	25.6 (92.0)	29.5 (93.5)
M-6-43	30% CA	0.250	82.0	23.4 (85.0)	27.5 (88.0)	32.0 (75.5)	—
M-6-43	25% F	0.250	92.0	—	—	5.8 (96.0)	6.0 (94.0)
M-6-31	45% (40% D + 60% A)	0.220	82.0	19.5 (90.0)	26.0 (91.0)	34.5 (90.0)	—
M-6-11		0.060	82.0	27.0 (81.0)	15.0 (91.0)	16.0 (94.5)	—
M-6-31		0.220	92.0	—	—	10.0 (96.0)	9.7 (95.0)

^a Desalination performance shown for combinations of feed concentration (ppm)/operating pressure (psig).

^b % R, salt rejection.

TABLE III
Low-Pressure Performance of Some Membranes from a High-Dioxane 30% CA Casting Solution^a

Feed concentration (ppm)	Membrane identification ^b							
	M-16-41		M-16-31		M-16-51		M-16-62	
	0.2 (81°C)	0.2 (86°C)	0.3 (81°C)	0.3 (86°C)	0.4 (81°C)	0.4 (86°C)	0.5 (81°C)	0.5 (86°C)
5,000/250								
flux ^c	32.4		29.7		31.0		28.4	
% R	70.0		75.5		73.0		78.5	
7,500/300								
flux	46.0		39.2		44.4		39.5	
% R	60.0		70.0		75.2		79.5	
10,000/400								
flux	49.5	25.2	54.0	27.0	67.5	34.2	55.5	29.0
% R	68.0	74.0	76.4	82.0	79.6	88.0	80.4	93.0
30,000/600								
flux	59.5		47.4		59.5		47.4	
% R	75.5		65.5		80.6		83.0	
40,000/700								
flux	41.8	26.5	48.6	31.0	47.4	29.5	40.5	25.0
% R	62.3	75.0	75.0	85.0	79.0	88.0	82.5	91.0
50,000/750								
flux		36.4		40.5		31.2		31.2
% R		86.0		83.0		90.0		88.0
60,000/800								
flux		36.0		34.4		30.0		28.8
% R		87.0		84.0		89.0		88.0

^a Casting solution composition (wt %): CA, 30; F, 25; solvent, 45 (60% dioxane, 40% acetone).

^b Data shown for two curing temperatures (in parentheses) at the specified evaporation periods (i.e., 0.2–0.5 sec).

^c In gfd.

increase in CA content between S-3 and S-4 and (2) variation of dioxane content in S-2. In Figure 4, the PWP constants (A) have been plotted against the pressures used during pressure treatments for membranes from casting solutions S-3 (40%) and S-4 (40%). One notices that over the pressure range of 300–650 psig, A values of membranes from S-4 containing 32% CA are relatively unaffected by pressure. On the other hand, the A values of membranes from S-3 containing 30% CA are decreasing somewhat, with pressure resulting in the following estimates of B for film numbers M-10-13, M-10-12, M-12-44, M-12-42: 0.0059, 0.0037, 0.0028, and 0.0025, respectively. For small evaporation times, a higher initial polymer concentration of 32% CA in the casting solution is very likely to generate a stronger skin with lower values of B than is possible with a casting solution having 30% CA. One may also use the solution structure-rate of evaporation concept developed by Sourirajan and coworkers to explain the above observation in the manner of Kunst and Sourirajan⁶ and Pageau and Sourirajan.⁷ Between the two casting solutions S-3 (40%) and S-4 (40%), the differences are that CA concentration increases from 30% to 32%, and formamide content decreases from 25% to 22%. This reduction in formamide content with increase in CA concentration will generate a lesser number of smaller droplets of nonsolvent in the interdispersed phase. Thus a smaller number of small pores are likely to have been created initially in S-4 (40%) membranes during casting.

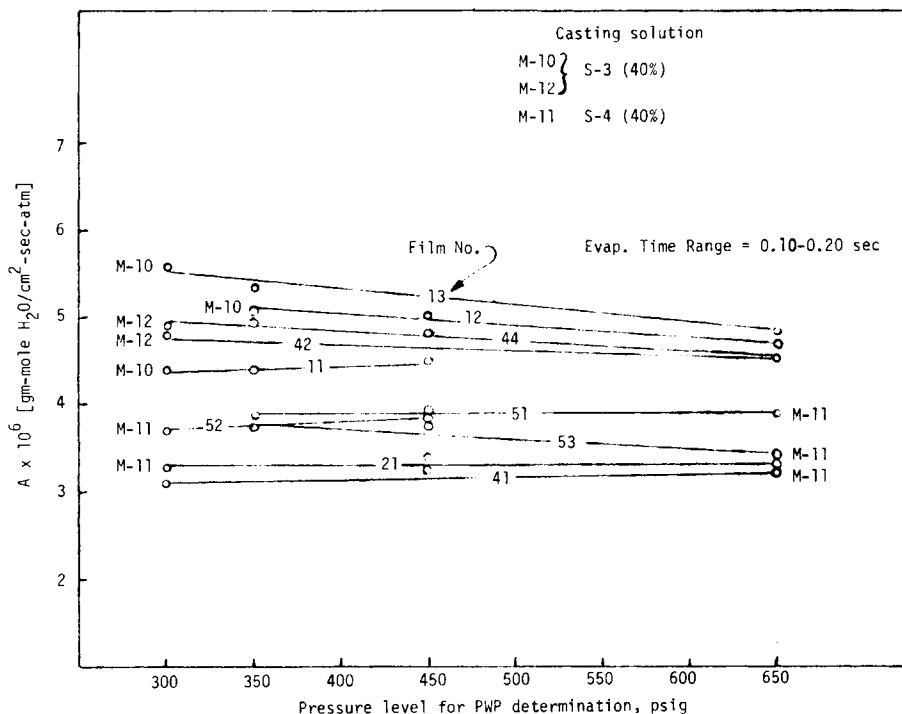


Fig. 4. Effect of pressure level on the pure water permeability constant of CA membranes cast from solutions with 40% dioxane.

Since higher operating pressures tend to close such pores² and reduce the advantages of improved membranes at higher pressures, membranes from S-4 (40%) casting solutions with fewer small pores are less likely to be affected by higher pressures of operation.

How increasing dioxane content in S-2-type casting solutions affects the pressure dependence of PWP constants is a matter of some importance too. In Figure 5, we have plotted the PWP constants (A) of various films from S-2 (60%) casting solutions as a function of pressure over a range of 300–850 psig. It is clear that the PWP constants decrease much more quickly with pressure in these membranes from a 30% CA solution with 60% dioxane than in the membranes from a 30% CA solution with 40% dioxane shown earlier in Figure 4. In fact, films M-16-51 and M-16-62 cured at 86°C have very high values of B , 0.02 and 0.023, respectively, whereas these very films cured at 81°C (earlier) have values of 0.004 and 0.007, respectively. An explanation for this behavior should be sought from two other observations about dioxane membranes in the literature. In a comprehensive study of CA-CTA blend membranes cast from a solution containing a mixture of dioxane and acetone besides nonsolvents, etc., King et al.¹⁴ have observed that the frequency of formation of voids per unit area in the dense skin of such membranes goes up drastically as the dioxane:acetone ratio increases beyond 1. Such voids related to casting solution compositions (as opposed to voids related to casting surface) weaken the modulus of the skin layer considerably and would create high values of the constant B in eq. (2). The observations of Frommer et al.¹⁸ with regard to the membranes from CA-dioxane casting

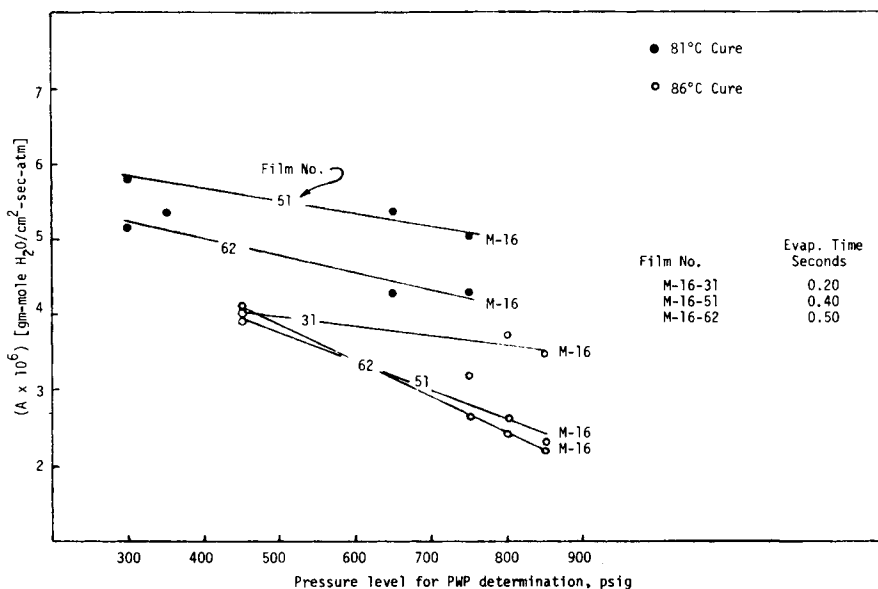


Fig. 5. Effect of pressure level on the pure water permeability constant of CA membranes from S-2 casting solution with 60% dioxane.

solutions provide additional evidence. They have observed in these membranes the existence of a large number of fingerlike cavities and protrusions extending right up to the top of the membrane skin, which appears more like a fractured polymer layer with channels. With acetone-dioxane mixtures the likelihood of development of these features increases with an increasing proportion of dioxane in the solvent. Though the cavities and protrusions reduce the skin resistance to water transport, leading to improved water flux, they are also likely to be the cause of a sharper compression of the skin as the pressure increases, leading to increased values of B . The much higher values of B for the high curing temperature of 86°C (compared to those at 81°C) are due to the considerable reduction in the pore sizes at higher curing temperatures, since the number of pores smaller than a given size will increase with curing temperature. A given increase in operating pressure will tend to close a larger number of small-size pores at a higher curing temperature, thus leading to a higher value of B .

The dependence of the solute transport parameter ($D_{AM}/K\delta$) on the applied pressure has not been shown explicitly here. Rather, plots of ($D_{AM}/K\delta$) vs PWP constant A have been prepared for a membrane sheet subjected to successively higher pressures of operation with increasing feed concentration. In Figure 6, performances of membranes from casting solutions of composition S-4 (40%) have been shown for brine feed concentrations 7500, 10,000, and 30,000 ppm used with pressures of 300, 400, and 600 psig, respectively. These membranes are such that over this pressure range the A values are essentially constant, whereas the ($D_{AM}/K\delta$) values decrease as the feed concentration and therefore the operating pressure are increased. The approximate constancy of the A values for membranes from this 32% CA composition (with 40% dioxane) are already evident from Fig. 4. The observed decrease of solute transport parameter of a film with increasing pressure (and therefore feed concentration in the present case) has been documented earlier by Sourirajan (Ref. 16, pp. 194, 195) for CA mem-

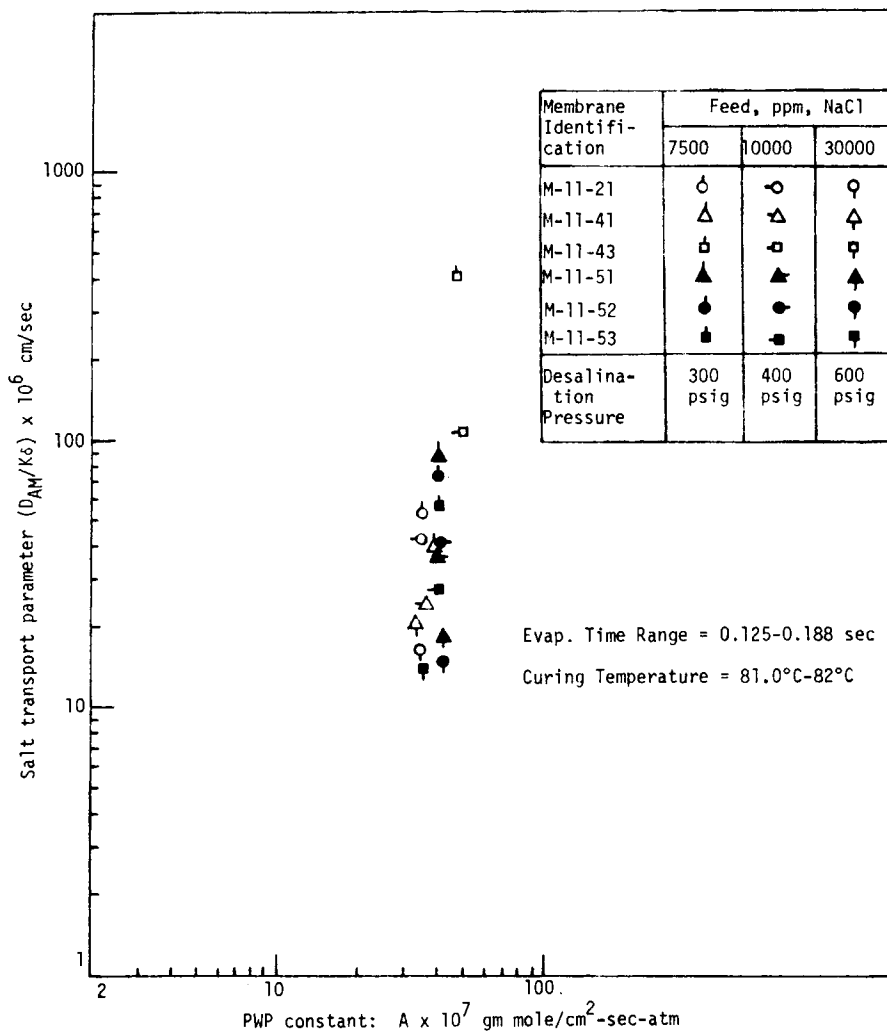


Fig. 6. Effect of operating pressure on intrinsic membrane performance from a 32% CA (40% dioxane) S-4 casting solution.

branes. It would appear therefore that significant improvements are possible by operating these CA membranes with much higher feed compositions at operating pressures characteristic of brackish water compositions, provided the B values are very small. The latter condition is likely to be satisfied if the operating pressures are in the range of 500–700 psig, beyond which severe compression of the skin layer is likely.

The effect of a large value of B as the operating pressure is increased is shown in the plot of $(D_{AM}/K\delta)$ vs A in Figure 7 for a series of membranes from casting solutions S-2 (60%). It is known from Figure 5 that the PWP constants for these membranes decrease rapidly with increasing pressure. Thus, as Figure 7 shows, even if $(D_{AM}/K\delta)$ values for a particular membrane sheet decrease with increasing pressure, the decreases in the corresponding A values are substantial, so that no particular performance improvement is obtained by increasing feed concentration at a given operating pressure used currently for less concentrated

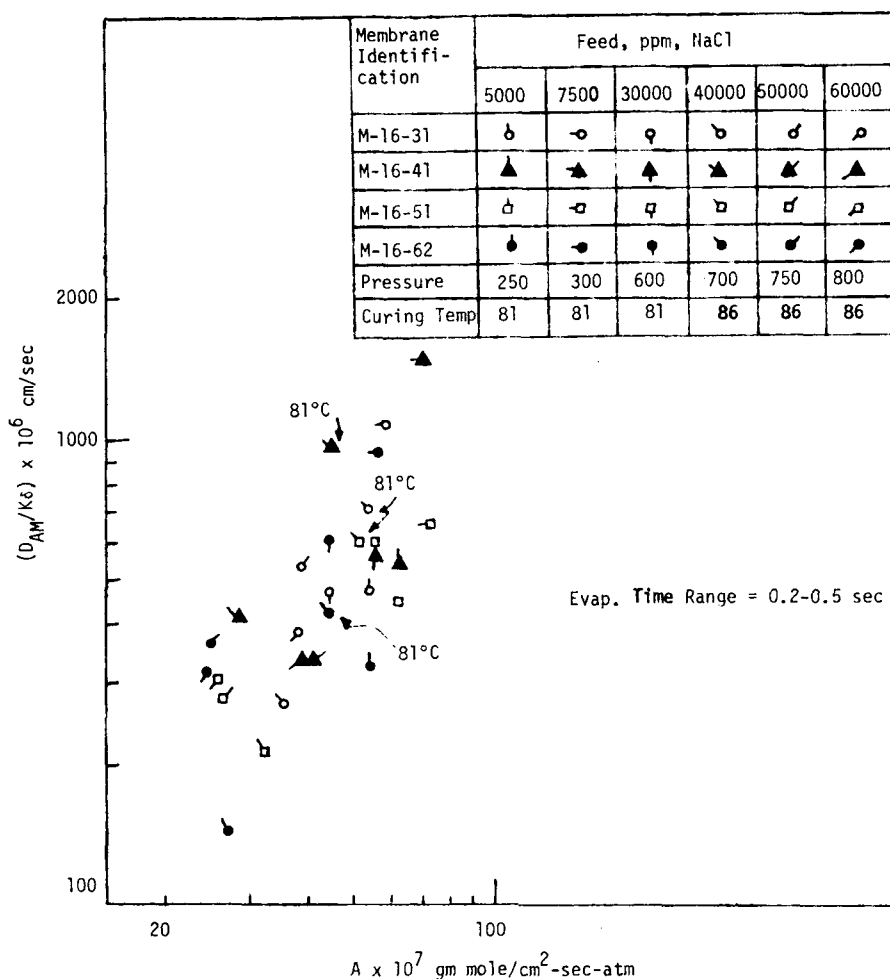


Fig. 7. Effect of operating pressure on intrinsic membrane performance from a 30% CA (60% dioxane) S-2 casting solution.

feeds. Thus a rapid increase in dioxane content over acetone in this particular mixed solvent system for CA membranes is not beneficial for making productive membranes with acceptable compression resistance.

Comparison of Membrane Performance

It is worthwhile to compare the low-pressure desalination performances of the CA membranes of this work with those of membranes used in other studies. There are two ways of comparing membrane performances. In the first method, the water flux vs percent solute rejection relationships are compared for different membranes under apparently identical test conditions. The effects of concentration polarization on membrane performance are not taken care of in this method. In Tables IV and V such a comparison is shown between some of the best membranes of this work and the membranes from other published sources for brackish and sea water feeds, respectively. Another difficulty in carrying out this comparison is the lack of data in literature for low-pressure operations

TABLE IV
Comparison of Membrane Performances at Low Pressures for Brackish Water Feeds

Membrane	Reference	Feed, ppm	Pressure, psig	Flux, gfd	Salt rejection, %
Batch 400	2	3500	250	22.1	90.0
Batch 401		3500	250	23.2	88.0
CA-NRC-18	6	3500	250	9.3	92.0
Batch 316	8	3500	250	9.5	90.7
Batch 316	8	3500	250	6.3	95.4
M-27-2	12	5000	250	14.0	94.9
M-30-6	12	5000	250	18.6	91.0
CA-spiral (under development)	4	3100 (70% product recovery)	250	20.0	88.0
PA-300 spiral	10	3300	200	12.0	95.5
	11	4580 (50% H ₂ O recovery)	450	18.9	98.6
Dry-RO membranes of QCTES	9	5000	400	30.0	90.0
M-11-51 ^a	This work	5000	250	22.0	90.0
M-11-52	work	5000	250	19.6	90.0
M-11-41		7500	300	21.4	95.0
M-11-53		7500	300	21.4	94.0
M-11-51		10,000	400	29.0	94.0
M-11-52		10,000	400	29.0	93.5
CA blend	14	10,000	800	30.0	94.7
CA blend	14	10,000	800	43.0	92.2
CA tubular	19	10,200	800	22.9	97.2

^a See Table II for this group of membranes.

TABLE V
Comparison of Membrane Performances at Low Pressures for Sea Water Feeds

Membrane	Reference	Feed, ppm	Pressure, psig	Flux, gfd	Salt rejection, %
NS-200 thin-film composite	10	35,000	1000	18-20	99.0
Dry-RO QCTE	10	35,000	1000	10.0	99.0
PA-300	10	35,000	800	19.0	98.5
PA-300	11	32,000	600	8.9	97.4
		36,000			
RC-100	11	31,000	650	9.4	98.7
M-11-53 ^a	This work	30,000	600	28.2	94.5
M-11-52 ^a	This work	30,000	600	29.5	93.5
M-16-62 ^b	This work	40,000	700	25.5	91.0
M-16-51 ^b	This work	50,000	750	31.2	90.0
M-16-51 ^b	This work	60,000	800	30.0	89.0
PA-300	11	32,000	800	8.3	98.1
		36,000 (40% H ₂ O recovery)			

^a See Table II.

^b See Table III.

under feed and pressure conditions identical with the present. However, the data in Table IV demonstrate that the membranes developed from casting solutions of Sirkar et al.⁵ under low air-exposure conditions and tested at low

pressures perform brackish water desalination as well as any other cellulosic or noncellulosic membrane. Furthermore, highly reduced pressures of operation around 300–350 psig yield excellent desalination performance on concentrated brackish water feeds. Table V illustrates the possibilities for a considerable reduction in the pressures of operation for sea water conversion with two stages if the improved membranes of this work are used. It would appear further that the productivities of these membranes at 600 psig with 30,000 ppm brine feed are almost comparable with those of the thin-film composites developed by Riley et al.¹¹ from noncellulosic polymers.

The second method of comparing membrane performance follows from Kimura–Sourirajan analysis,¹⁵ wherein a plot of membrane PWP constant (A) vs the solute transport parameter ($D_{AM}/K\delta$) is prepared for a given operating pressure. This plot is usually accompanied by the value of the mass-transfer coefficient, k , characterizing the feed-flow conditions on the high-pressure side of the membrane. Such a plot is shown in Figure 8 for two pressure levels: 600

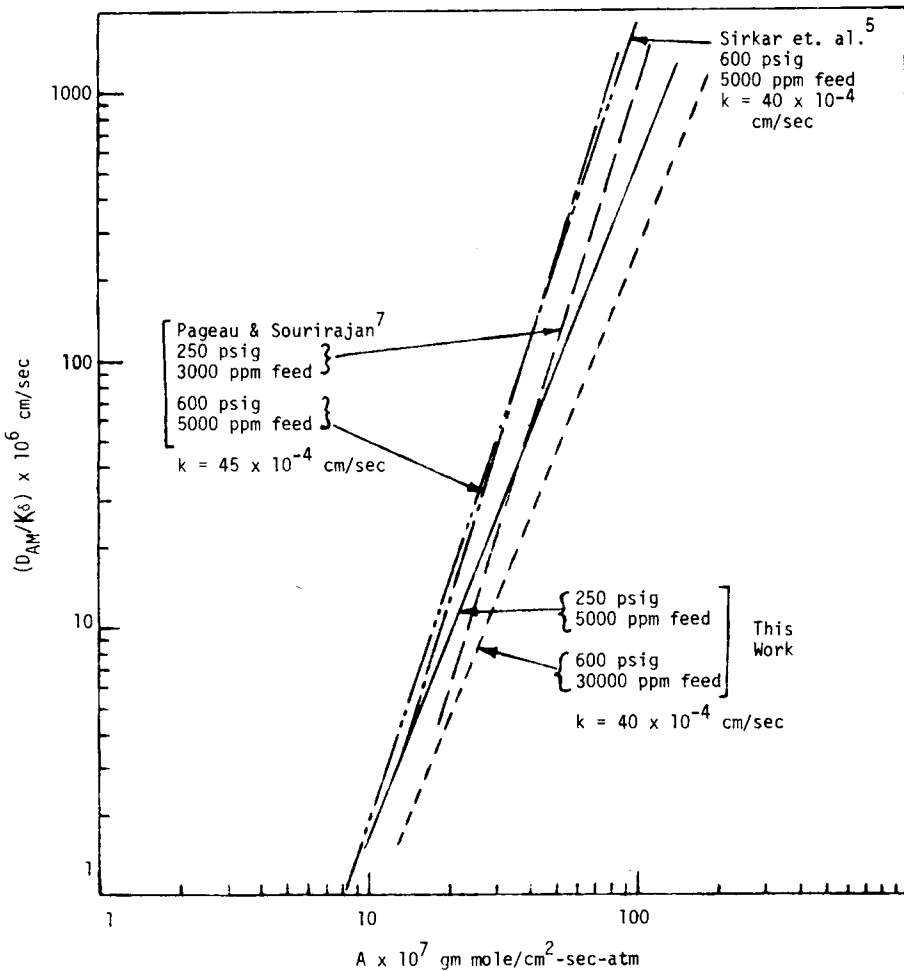


Fig. 8. Comparison of salt transport parameter for given PWP constants for various CA membranes at different pressures.

psig (30,000 ppm feed) and 250 psig (5000 ppm feed). For the sake of comparison, the performances of the highly productive membranes of Pageau and Sourirajan⁷ at two pressures, 250 psig (3500 ppm feed) and 600 psig (5000 ppm feed) are also included in Figure 8. It may be noted that even though the CA membranes of this work are as productive as those of Pageau and Sourirajan⁷ at 250 psig, their performances at 600 psig with 30,000 ppm feed are quite superior to those of all other CA membranes known in literature.⁵

CONCLUSIONS

Low-pressure reverse osmosis desalination performances for various brackish and sea water feeds have been carried out with improved CA membranes cast with low air-exposure periods from casting solutions of CA-acetone (with or without dioxane)-formamide-ZnCl₂, which are close to the phase boundary and have a high CA content. Industrially acceptable levels of water flux and salt rejection have been obtained for the following operating pressure (psig)/feed composition combinations (ppm): 250/5000; 300/7500; 400/10,000; 600/30,000; 700/40,000; 750/50,000; 800/60,000. Brackish and sea water conversion plants may be run with such membranes at 250-350 and 750-800 psig (first stage), respectively.

The replacement of acetone by dioxane to the extent of 40% by weight improves the performance of membranes over nondioxane membranes. Dioxane content higher than 40% leads to somewhat inferior performance, as reported earlier.⁵ The PWP constants of membranes from 32% CA solution S-4 with 40% dioxane undergo smaller reductions with increasing pressure than those from similar casting solutions with 30% CA. The PWP constants of membranes from casting solutions with 60% dioxane decrease faster with increasing pressure than those of membranes from identical casting solutions with 40% dioxane. The solution structure-rate of evaporation concept is capable of explaining these later observations as well.⁵ Kimura-Sourirajan analysis of the intrinsic performance parameters of these highly productive CA membranes indicates that reduction in operating pressure for a given feed concentration leads to considerable improvement in membrane performance, so that operating pressures considerably lower than currently used are possible in reverse osmosis desalination plants.

References

1. B. Kunst and S. Sourirajan, *Desalination*, **8**, 139 (1970).
2. R. Pilon, B. Kunst, and S. Sourirajan, *J. Appl. Polym. Sci.*, **15**, 1317 (1971).
3. A. K. Ghosh, Low Pressure Reverse Osmosis Desalination of Brackish Water and Sea Water with Improved Cellulose Acetate Semipermeable Membranes, M. Tech. Thesis, Department of Chemical Engineering, Indian Institute of Technology, Kanpur, August 1976.
4. K. C. Channabasappa, *Desalination*, **18**, 15 (1976).
5. K. K. Sirkar, N. K. Agarwal, and G. Pandu Rangaiah, *J. Appl. Polym. Sci.*, **22**, 1919 (1978).
6. B. Kunst and S. Sourirajan, *J. Appl. Polym. Sci.*, **14**, 723 (1970).
7. L. Pageau and S. Sourirajan, *J. Appl. Polym. Sci.*, **16**, 3185 (1972).
8. W. L. Thayer, L. Pageau, and S. Sourirajan, *J. Appl. Polym. Sci.*, **18**, 1891 (1974).
9. R. E. Kesting, K. F. Jackson, and J. M. Newman, Proceedings of the Fifth International Symposium on Fresh Water from the Sea, ALGHERO, Vol. 4, 1976, pp. 73-78.
10. K. C. Channabasappa, *Desalination*, **17**, 31 (1975).
11. R. W. Riley, C. E. Milstead, A. L. Lloyd, M. W. Seroy, and M. Tagami, Preprint of "Spiral

Wound Thin-film Composite Membrane Systems for Brackish and Sea Water Desalination by Reverse Osmosis"—Presented at International Congress on Desalination and Water Re-use at Tokyo, JAPAN, November 27–December 3, 1977.

12. G. Pandu Rangaiah, A Study of Casting Solution Compositions at Low Evaporation Times for Improving Cellulose Acetate Membranes, M. Tech. Thesis, Department of Chemical Engineering, Indian Institute of Technology, Kanpur, January 1976.

13. N. K. Agarwal, The Effect of Casting Conditions and Casting Solution Composition on Cellulose Acetate Desalination Membranes, M. Tech. Thesis, Department of Chemical Engineering, Indian Institute of Technology, Kanpur, May 1974.

14. W. M. King, D. L. Hoernschemeyer, and C. W. Saltonstall, Jr., in *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, Eds., Plenum, New York, 1972, pp. 131–161.

15. S. Kimura and S. Sourirajan, *A.I.Ch.E.J.*, 13, 497 (1967).

16. S. Sourirajan, *Reverse Osmosis*, Logos Press, London, 1970, pp. 175–184.

17. Eastman Membrane for Reverse Osmosis and Other Membrane Processes, Technical Bulletin, Publication TBM-1A, Eastman Kodak Company, U.S.A.

18. M. A. Frommer and D. Lancet, in *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, Eds., Plenum, New York, 1972, pp. 85–110.

19. J. L. Richardson, G. Segovia, W. H. Bachr, and H. A. Parker-Jones, in *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, Eds., Plenum, New York, 1972, pp. 205–240.

Received December 14, 1977

Revised February 20, 1978