

# Composite Reverse Osmosis Membranes Prepared by Plasma Polymerization of Allylamine. Evaluation of Membrane Performance for the Treatment of Washwater and Its Components

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## Synopsis

Reverse osmosis membranes prepared by plasma polymerization of allylamine-nitrogen mixtures over a porous substrate were evaluated for the rejection of components present in washwater. The membranes exhibited high rejections for sodium chloride, potassium chloride, detergent, and dextrose. High rejections of urea could be achieved, but only at a sacrifice of water flux. Lactic acid could also be rejected but caused a degradation of the plasma-deposited layer.

## INTRODUCTION

Recent publications by Bell et al.<sup>1</sup> and Peric et al.<sup>2</sup> have demonstrated that high performance reverse osmosis membranes could be prepared by plasma polymerization of allylamine over a porous substrate. These studies showed that the rejection of sodium chloride and the water flux through the membrane were strongly dependent on the nature of the substrate and the conditions used to prepare the plasma-polymerized rejecting layer. The present studies were undertaken to characterize membrane performance for the rejection of urea, dextrose, potassium chloride, lactic acid, and detergent (sodium *n*-dodecylbenzene sulfonate) in addition to sodium chloride. These solutes were selected because they are characteristic of used washwater, and it was desired to establish the suitability of plasma-prepared membranes for the recovery of fresh water from used washwater in closed environmental systems, such as those found in manned spacecraft.

## EXPERIMENTAL

The apparatus used to plasma deposit the rejecting layer was identical to that described by Peric et al.<sup>2</sup> It consisted of a pair of parallel plate electrodes enclosed within a glass bell jar. The lower electrode was water cooled and was surrounded by an annular cup into which monomer vapor was fed. Product gases were evacuated to a mechanical vacuum pump through a hole in the base plate supporting the bell jar. Power for the discharge was supplied by a 13.56-MHz generator (Tracerlab) coupled to the electrodes through an impedance matching network.

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An asymmetrical cellulose acetate-cellulose nitrate film (Gulf Environmental Systems) was used as the substrate for all of the membranes prepared in this study. The supply of this film was kept in a sealed polyethylene bag in a refrigerator to minimize the loss of plasticizer. Allylamine (Aldrich Chemical Co.), the monomer used to prepare the rejecting layer, was distilled and then degassed by repeated freezing and thawing under vacuum.

Membranes were prepared by depositing a layer of plasma-polymerized allylamine on a 4-in. disk of the substrate. Deposition was carried out at a pressure of 0.25 Torr, a power of 25 W, and a monomer flow rate of 4.4 cm<sup>3</sup> (S.T.P.)/min. These conditions had been established previously by Peric et al.<sup>2</sup> to be optimal for the preparation of high-quality membranes. The length of the deposition process was set at 650 sec in order to yield a plasma-deposited film 3800 Å thick. After deposition the 4-in. disk was immersed in distilled water at 80°C for 30 min to swell the plasma-deposited layer and thereby enhance the ability of the membrane to reject solute. The 4-in. disk was then dried and a 2-in. disk was cut from its center to be used for evaluation of the membrane.

The membranes were tested in a high-pressure recirculation loop nearly identical to that described previously.<sup>2</sup> The only modification made to this unit was the addition of a second test cell (Universal Water Corp.) in parallel with the first, so that two membranes could be characterized simultaneously. In all of the experiments reported here, the pressure of the recirculating feed solution was held at 1500 psi. Each membrane was allowed to operate for a minimum of 20 hr before the first sample of effluent was collected for determination of flux and rejection. The flux was determined by measuring the effluent volume collected over a fixed period of time. Rejection was determined from measurements of solute concentration in the feed and effluent using the following techniques.

#### *Sodium Chloride*

When present by itself or with other, nonionic species in the feed solution, the concentration of sodium chloride was determined from measurements of the feed and permeate conductivities. If more than one cation was present in solution, the concentration of sodium ions was determined by atomic absorption spectroscopy. In the latter case, chloride ion was determined by concentrating the permeate and titrating it with silver nitrate.

#### *Potassium Chloride*

Potassium chloride concentrations were determined by the same methods used for sodium chloride.

#### *Lactic Acid*

Lactic acid concentrations were determined by measurements of conductivity or pH.

*Urea*

The spectrophotometric method of Watt and Chrisp<sup>3</sup> was used for urea analysis.

*Dextrose*

Dextrose concentrations were determined by measuring the solution absorbance at 195 nm. In the presence of interfering solutes the indole method for carbohydrates was used.<sup>4</sup>

*Detergent (Sodium n-Dodecylbenzene Sulfonate)*

Detergent concentration was determined by the ASTM D2330-68 standard method for alkylbenzene sulfonate in water.

**RESULTS AND DISCUSSION**

Table I compares the performance of membranes prepared using allylamine as the monomer with those prepared using mixtures of allylamine and nitrogen. The addition of nitrogen to the monomer was motivated by the work of Yasuda et al.<sup>5,6</sup> For a given level of sodium chloride rejection, a wide variation in water fluxes is observed. This feature prevailed throughout these studies and made it difficult to establish unambiguously the effects of reaction conditions on membrane performance. Nevertheless, it appears that membranes prepared using allylamine-nitrogen mixtures exhibit higher water fluxes than membranes prepared using allylamine alone. A comparison of urea and sodium chloride rejections shows that there is little correlation between these two performance characteristics. On the other hand, urea rejection does appear to correlate fairly well with water flux. Figure 1 shows that while sodium chloride rejection is relatively insensitive to water flux, urea rejection falls off as the water flux increases. This suggests that the flow of urea through the membrane may be

TABLE I  
Effect of Monomer Composition and Flow Rate on Membrane Performance for Rejection of Sodium Chloride and Urea<sup>a</sup>

Membrane no.	Allylamine flow rate, cm <sup>3</sup> /min	Nitrogen flow rate, cm <sup>3</sup> /min	Sodium chloride rejection, % <sup>b</sup>	Urea rejection, % <sup>b</sup>	Flux, gfd <sup>b</sup>
594	4.4	—	97.9	83	1.5
600	4.4	—	93.9	80	2.7
601	4.4	—	98.3	66	6.5
604	4.4	—	99.1	64	7.4
633	4.4	4.4	99.1	—	12.9
637	4.4	4.4	99.1	62	7.0
640	4.4	4.4	98.7	—	1.4
635	2.2	6.6	95.1	—	21.6
638	2.2	6.6	95.4	34	18.5
641	2.2	6.6	98.9	—	7.4

<sup>a</sup> Membrane preparation conditions: pressure, 0.25 Torr; power, 25 W; allylamine and nitrogen flow rates, see table.

<sup>b</sup> Feed concentration, 1% NaCl plus 1% urea; feed temperature, 20°C; applied pressure, 1500 psi.

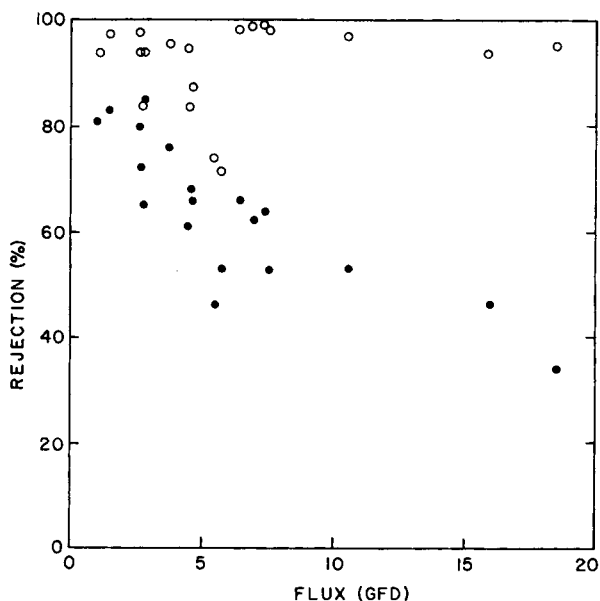


Fig. 1. Sodium chloride and urea rejections as function of water flux: (●) urea; (○) NaCl; feed, 1% NaCl and 1% urea; pressure, 1500 psi.

coupled to the water flow but that the flow of sodium chloride is not. An interpretation of this phenomenon on the basis of the structure of the rejecting layer cannot be offered at present.

Membrane characteristics for the rejection of dextrose are listed in Table II. Only one of the four membranes exhibited a rejection below 90%. The presence or absence of sodium chloride in the feed solution does not appear to influence either the rejection of glucose or the flux of water.

Tests for the rejection of lactic acid were conducted in the following fashion. Each membrane was first evaluated using a feed containing sodium chloride alone. Then the sodium chloride solution was replaced by one containing lactic acid. After the lactic acid rejection and water flux had been determined, the lactic acid solution was replaced by the sodium chloride solution, and the membrane performance for sodium chloride rejection was established again. The results of these experiments are summarized in Table III. For each membrane it is observed that the lactic acid rejection is significantly lower than the sodium

TABLE II  
Membrane Performance for Rejection of Dextrose<sup>a</sup>

Membrane no.	Dextrose rejection, % <sup>b</sup>	Flux, gfd <sup>b</sup>	Feed composition, % dextrose/% NaCl
613	98	7.3	1/1
614	77	5.1	1/1
618	94	5.1	1/0
619	91	3.5	1/0

<sup>a</sup> Membrane preparation conditions: pressure, 0.25 Torr; power, 25 W; allylamine flow rate, 4.4 cm<sup>3</sup>/min.

<sup>b</sup> Feed composition, see table; feed temperature, 20°C; applied pressure, 1500 psi.

TABLE III  
Effect of Monomer Composition and Flow Rate on Membrane Performance for Rejection of Lactic Acid and Sodium Chloride<sup>a</sup>

Membrane no.	Monomer flow rate allylamine/N <sub>2</sub> , (cm <sup>3</sup> /min)/(cm <sup>3</sup> /min)	NaCl rejection before acid exposure, % <sup>b</sup>	NaCl rejection after acid exposure, % <sup>b</sup>	Flux before acid exposure, gfd <sup>b</sup>	Lactic acid rejection, % <sup>c</sup>	Flux, gfd <sup>c</sup>
611	4.4/0.0	97.5	59.7	2.6	25	28.7
612	4.4/0.0	93.8	50.0	4.3	21	25.2
618	4.4/0.0	98.9	83.2	5.8	47	12.5
619	4.4/0.0	96.2	93.3	4.9	60	6.8
632	2.2/2.2	97.0	72.0	6.0	48	7.1
633	4.4/4.4	99.1	60.4	12.9	37	31.1
634	2.2/6.6	79.5	73.3	6.5	25	17.2
635	6.6/2.2	95.1	78.0	21.6	33	33.6

<sup>a</sup> Membrane preparation conditions: pressure, 0.25 Torr; power, 25 W; monomer flow rate, see table.

<sup>b</sup> Feed composition, 1% NaCl; feed temperature, 20°C; applied pressure, 1500 psi.

<sup>c</sup> Feed composition, 0.2% lactic acid; feed temperature, 20°C; applied pressure, 1500 psi.

chloride rejection measured prior to testing with lactic acid and that the water flux is considerably higher when a lactic acid feed solution is used. All of the membranes show a noticeable decline in sodium chloride rejection after testing with a lactic acid solution, and the extent of deterioration in sodium chloride rejection is higher for the solution containing the higher concentration of acid. These observations suggest that lactic acid promotes a degradation of the rejecting layer, causing the observed increase in water flux and decrease in sodium chloride rejection. While the mechanism of degradation has not been studied, it is quite likely that lactic acid catalyzes the hydrolysis of imine-type nitrogen-nitrogen bonds present in the plasma-polymerized film.<sup>1,2</sup>

Two membranes were tested with a synthetic washwater containing detergent (sodium *n*-dodecylbenzene sulfonate), urea, dextrose, sodium chloride, and potassium chloride. Lactic acid, while known to be present in washwater,<sup>7</sup> was excluded from the synthetic washwater because of its tendency to degrade membrane performance. Before beginning the washwater tests, the membranes were run for four days with a 1% sodium chloride solution. The rejection and flux at the end of this initial test period are noted in Table I (membranes 640 and 641). Upon switching to the washwater feed, the water flux decreased substantially, possibly because of an occlusion of the membrane micropores by detergent. The flux and rejection data given in Table IV were obtained about 24 hr after starting the feed of washwater. It is observed that the rejection of all components in the feed is very high. We also note that, consistent with previous observations, the rejection of urea is higher for the membrane exhibiting the lower water flux.

## CONCLUSIONS

In summary, composite reverse osmosis membranes exhibiting high rejections of detergent, dextrose, sodium chloride, and potassium chloride can be prepared by plasma polymerization of allylamine or allylamine-nitrogen mixtures. High rejections of urea can be achieved, but at a sacrifice of water flux. Lactic acid

TABLE IV  
Membrane Performance for Rejection of Components of Synthetic Washwater<sup>a</sup>

Component	Feed concn., ppm	Membrane 640		Membrane 641	
		Rejection, % <sup>b</sup>	Flux, gfd <sup>b</sup>	Rejection, % <sup>b</sup>	Flux, gfd <sup>b</sup>
—	—	—	0.5	—	2.8
Detergent	2000	98.0		99.9 <sub>8</sub>	
Urea	455	95.2		87.7	
Sodium	575	99.4		99.7	
Potassium	316	99.6		99.8	
Chloride	1230	94.7		98.4	
Dextrose	410	98.0		99.8	

<sup>a</sup> Membrane preparation conditions: pressure, 0.25 Torr; power, 25 W; allylamine flow rate, 4.4 cm<sup>3</sup>/min; nitrogen flow rate, 4.4 cm<sup>3</sup>/min.

<sup>b</sup> Feed concentration, see table; feed temperature, 20°C; applied pressure, 1500 psi.

can also be rejected but appears to bring about a degradation of the plasma-deposited layer.

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