

# Synthesis and Transport Properties of Thin Film Composite Membranes. II. Preparation of Sulfonated Poly(phenylene Oxide) Thin Film Composite Membranes for the Purification of Alberta Tar Sands Waste Waters

R. Y. M. HUANG and J. J. KIM, *Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*

## Synopsis

Thin film composite membranes of sulfonated poly(phenylene oxide) (SPPO)-polysulfone (PS) (SPPO-PS) were prepared by coating the hydrogen or sodium form of SPPO onto various porous substrates such as polysulfone (PS). The effects of membrane preparation conditions and feed water variables on the salt rejection and production rates were investigated using reverse osmosis. Purification of the waste waters from the Alberta heavy oil fields for desalination and recycling use was carried out. Production rates and salt rejections for the various feeds were found to be in the range of 5–20 gfd (gallons/ft<sup>2</sup> day) and 80–99% respectively at 600 psig and 20°C, depending on the experimental conditions and membrane properties.

## INTRODUCTION

In Part I of this series, the synthesis of sulfonated poly(phenylene oxide) polymer and its kinetics was described in detail; this paper will describe the preparation of thin film composite membranes of sulfonated poly(phenylene oxide) (SPPO)-polysulfone (PS) (SPPO-PS) and its applications for the purification of Alberta tar sands waste waters.

Bitumen resources of Alberta oil sand fields are estimated to be 1350 billion barrels, and *in situ* recovery methods must be developed to exploit the 90% of reserves that are too deeply buried for surface mining.<sup>1</sup> Steam injection is one developing technology for the extraction of heavy oil/bitumen. However, this process generates a large volume of produced water. For economic and environmental reasons it is necessary to treat and recycle this water for the generation of injection steam. Reverse osmosis (RO) is now considered a technology for the reduction of total dissolved solids (TDS) and trace organic matter from produced water.<sup>2</sup>

Although success has been achieved in the past decade in reclaiming nonpotable waters by RO through various types of thin cellulosic ester membrane films, there exists the need for more stable longer life materials, and the membranes for use in treating organic chemicals are noncellulosic since the cellulosic membranes have strong membrane adsorption of non-ionic surfactants and they usually fail rapidly.<sup>2</sup> One of the most promising noncellulosic membrane systems for RO applications appears to be sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO).<sup>3</sup>

The advantage of using SPPO for RO application compared to other commercially available ion exchange membranes lies in its being readily cast into thin membranes having excellent chemical and physical stabilities with good flux and salt rejection characteristics. It is also found that, by applying the membrane to a suitable porous substrate in order to incorporate it into practical RO hardware and to reduce its thickness, improves it greatly since the flux is inversely proportional to the membrane thickness.<sup>4,5</sup>

This study is concerned with the preparation and transport properties of cation exchange thin film composite SPPO-PS RO membranes.

## EXPERIMENTAL

The synthesis of poly(phenylene oxide) and its subsequent sulfonation have been described in detail in Part I of this series.

### Preparation of Porous Polysulfone Substrate<sup>7</sup>

A solution containing 12.5 wt % PS and 12.5 wt % methyl cellosolve in dimethylformamide was cast onto a clean glass plate using a glass bar in the thickness of 0.3 mm. After the casting, the coated liquid film was immersed into 15 wt % NaCl quenching bath immediately. The film gelled very quickly, it was then washed with water, and cut into the required size with a membrane die. Finally it was put into deionized water for at least 24 h and thoroughly dried before SPPO polymer solution casting.

### Preparation of Sulfonated Poly(phenylene Oxide) Composite Membrane

The SPPO polymer was exhaustively dried for 200 h under vacuum at room temperature (hydrogen form) or 70°C (sodium form). The dry SPPO polymer was dissolved in 2:1 chloroform/methanol or pure methanol solvents, to form 4 wt % casting solution and cast onto 1.0 mil microporous polypropylene or polysulfone substrate stuck onto a glass plate to form a coating of SPPO polymer of 0.2 mil dried thickness, and the composite membrane formed was dried for a minimum of 2 h under cover and overnight without cover at ambient conditions. The dried membranes were removed from the glass plate immersing into 10 wt % NaCl aqueous solution to convert the hydrogen form into sodium form and stored wet in a 10 wt % NaCl aqueous solution container. Since polysulfone substrate was soluble in chloroform, the casting solvent was pure methanol (without chloroform).

### Transport Properties of Composite Membrane

The reverse osmosis test was conducted in six high pressure cells, which have been described in detail in many previous papers on reverse osmosis.<sup>8</sup> The effective membrane area was 18.1 cm<sup>2</sup> (4.8 cm in diameter). The experiments were conducted at pressures of 300–700 psig, at a room temperature of approximately 20°C, and with feed solution circulated during the experiment. Sodium chloride or other inorganic compound concentrations for single component solutions were determined using a Water Associates

TABLE I  
Dependence of Reverse Osmosis<sup>a</sup> Performance of Composite Membranes<sup>b</sup>  
on Different Substrates

Substrate <sup>c</sup>				
Material	Thickness (mil)	Pretreatment	Salt rejection (%)	Production rate (gfd)
PS-1M2P-W	3	—	87.7	3.45
PS-1M2P-SW	3	—	88.4	3.57
PS-DMF-MC-SW	3	—	86.9	16.52
PP (Celgard 2400)	1	—	83.3	0.50
PP (Celgard 2500)	1	—	90.1	1.32
PP (Celgard 2500)	1	Soap (20°C, 1 h)	74.9	3.70
PP (Celgard 2500)	1	Soap (45°C, 1 h)	72.9	9.95
PP (Celgard 2500)	1	Soap (95°C, 1 h)	12.1	169.2

<sup>a</sup> 600 psig, 20°C, 1000 ppm NaCl feed.

<sup>b</sup> Coated polymer; SPPO sodium form, IEC = 1.72 meq/g, thickness = 0.2 mil.

<sup>c</sup> PS-1M2P-W: 12.5 wt % PS in 1-methyl-2-pyrrolidone, water quenching.

PS-1M2P-SW; *ibid.*, 15 wt % NaCl aqueous solution quenching.

PS-DMF-MC-SW: 12.5 wt % PS in 75 wt % dimethylformamide and 12.5 wt % methyl cellosolve, 15 wt % NaCl aqueous solution quenching.

Differential Refractometer Model R403. Quantitative analyses of the mixed component solution in aqueous phases were carried out by standard methods.<sup>9</sup> Atomic absorption spectroscopy (Perkin-Elmer Model 303) was used for determination of dissolved sodium, calcium, and magnesium. Sulfate was determined by the turbidimetric method with BaCl<sub>2</sub> using a spectrophotometer (Bausch and Lomb Spectronic 20) at 420 nm. Chloride was determined by potentiometric titration with AgNO<sub>3</sub> solution using glass and silver-silver chloride electrodes (Potentiograph E576, Metrohm Herisaw Co., Switzerland). Heavy oil was determined by ultraviolet absorbance at 253.7 nm (Varian Techtron UV-VIS Spectrophotometer Model 635).<sup>10</sup>

## RESULTS AND DISCUSSION

### Reverse Osmosis Performance of Composite Membranes on the Various Porous Substrates

Some of the substrates, providing good mechanical strength to SPPO, were polysulfone (PS) and polypropylene (PP). PS substrates were made from various solvent and quenching solutions. PP substrate Celgard 2400 was obtained from Celanese Fibers Co. (Summit, NJ) and some of these SPPO-PP composite membranes were pretreated in aqueous soap solution (1 wt % Alconox).<sup>6</sup>

As shown in Table I, the best results were achieved with PS substrate from 12.5 wt % in 75 wt % dimethylformamide and 12.5 wt % methyl cellosolve with 15 wt % NaCl aqueous solution quenching. Other substrates were not bad, but their production rates were considerably lower. Though the pretreatment of composite membranes on microporous PP with soap solution showed increased production rate with increasing pretreatment temperature, their salt rejections were low. So, during this study, PS substrate (fabricating procedure described earlier in the experimental section) was used as the substrate of composite membrane.

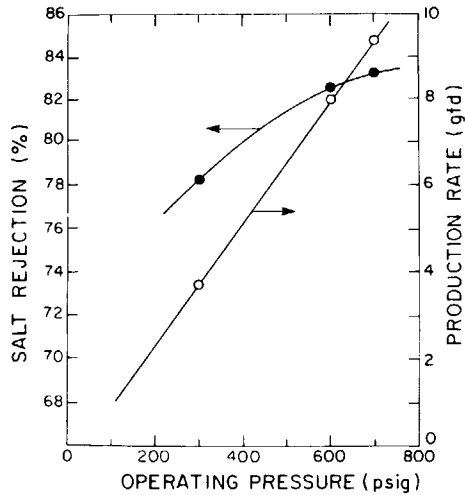


Fig. 1. Effect of operating pressure on reverse osmosis performance (membrane: SPPO-PS, 2-0118-5NM, IEC = 2.53 meq/g; feed: NaCl 1000 ppm, 20°C).

### Membrane Properties and Reverse Osmosis Performance

**Effect of Operating Pressure.** Figure 1 illustrates the effect of operating pressure on the separation and production rate characteristics of the SPPO-PS composite membrane. The production rate was linear with operating pressure to at least 700 psig, and the salt rejection also increased with increasing pressure. The former effect is understandable on the basis of increased driving pressure for fluid flow, and the latter effect might be due to a decrease in the average pore size on the membrane surface and/or increase in the preferential sorption mechanism of the membrane for pure water at a higher pressure.<sup>11</sup>

**Effect of Feed Concentration.** At a given operating pressure 600 psig, salt rejection was found to decrease and the production rate showed no

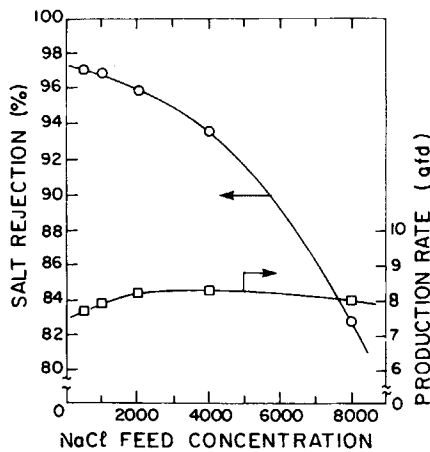


Fig. 2. Effect of NaCl feed concentration on reverse osmosis (membrane: SPPO-PS, 5-0224-12NM, IEC = 2.10 meq/g, 600 psig, 20°C).

great change with increase in feed concentration in the range of 500–8000 ppm NaCl, as shown in Figure 2. The former phenomenon is a typical characteristic of charged membrane and can be interpreted by the Donnan equilibrium.<sup>12</sup> The Donnan potential, and hence the ion exclusion, is highly dependent on the relationship between the membrane charge density and the solution ion concentration. It increases with increasing membrane charge density and decreasing solution counterion concentration.

**Membrane Ion Exchange Capacity (IEC).** The membrane properties that had the greatest effect on reverse osmosis performance were IEC, membrane water content, coated polymer thickness, and the substrate of composite membrane. The substrate effect was described previously in this discussion, and there were sufficient data to show that the production rate was inversely proportional to the membrane thickness.<sup>4,5</sup>

For membranes cast under identical conditions, the IEC (meq of  $\text{SO}_3^-$ /g dry polymer) affected water content, production rate, and salt rejection. The membrane water content increased with increasing IEC as shown in Figure 3, and increased water content of membrane made the porosity (volume of pore liquid/volume of wet membrane) and the production rate to be increased. The salt rejection showed the highest values between IEC value of 2.0 and 2.3 meq/g, and the production rate increased with increasing IEC and water content of membrane as shown in the same figure.

**Dependence of Feed Composition.** The production rate and salt rejections for water soluble single component feeds are shown in Table II. Salt rejections being consistent with Donnan mechanism rejection, increased with decreasing counterion (cation) valence and increasing coion (anion) valence. Sulfonated poly(phenylene oxide) membrane as a cation exchange membrane rejected different feed salts in the following order:

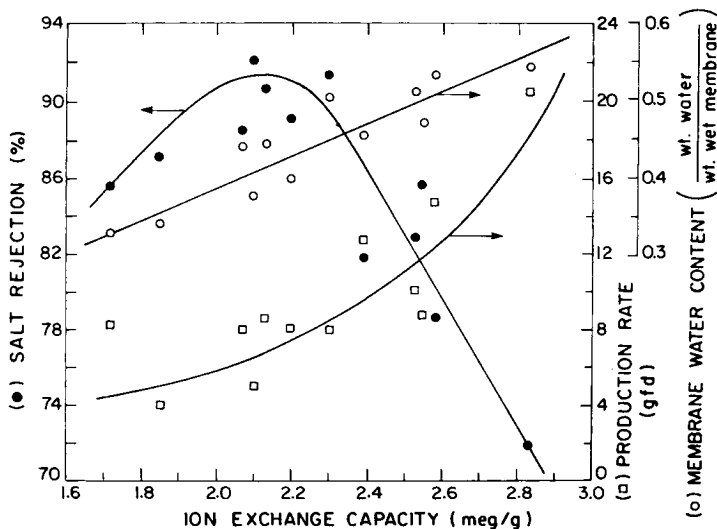
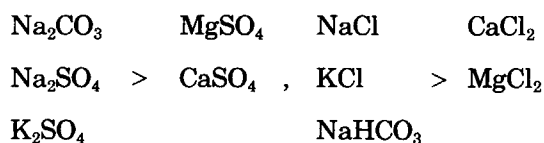


Fig. 3. Effect of membrane ion exchange capacity on the membrane water content and reverse osmosis performance (SPPO-PS composite membrane, 600 psig, 20°C, NaCl 1000 ppm feed).

TABLE II  
Dependence of Reverse Osmosis<sup>a</sup> Performance on Feed Composition

Feed composition	Production rate (gfd)	Salt rejection (%)
Na <sub>2</sub> CO <sub>3</sub>	7.24	99.8
Na <sub>2</sub> SO <sub>4</sub>	6.51	99.9
K <sub>2</sub> SO <sub>4</sub>	8.90	99.8
MgSO <sub>4</sub>	5.77	94.4
CaSO <sub>4</sub>	7.14	93.8
NaCl	6.65	92.9
KCl	5.96	93.9
NaHCO <sub>3</sub>	5.87	95.6
CaCl <sub>2</sub>	4.89	85.7
MgCl <sub>2</sub>	3.91	84.7

<sup>a</sup> 600 psig, 20°C, feed concentration 1000 ppm, SPPO-PS composite membrane 0222-12NM and 0224-12NM series, IEC = 2.10 meq/g.



### Purification of Waste Water from the Alberta Heavy Oil Fields

The produced waters from the Alberta oil sand operation contained 5000–15,000 ppm total dissolved solids (TDS) mainly Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and a certain amount of heavy oil.<sup>2</sup>

TABLE III  
Reverse Osmosis<sup>a</sup> Results for Waste Water from Heavy Oil Fields

Membrane IEC (meq/g)	Production rate (gfd)	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	TDS	Heavy oil
<i>Synthetic waste water</i>								
Feed (ppm)		3158	211	105	526	5160	9160	200
Product (ppm)	2.30	6.42	668	36.7	19.3	68.5	1622	2415
% rejection	2.10	5.30	588	25.2	9.3	27.3	1158	1807
	2.30	6.42	78.8	82.6	81.6	87.0	68.6	73.6
	2.10	5.30	81.4	88.1	91.1	94.8	77.6	80.3
								97.9
<i>Natural waste water (Texaco Athabasca emulsion)</i>								
Feed (ppm)		355	13.5	1.53		550	920	
Product (ppm)	2.10	9.15	26.0	0.11	0.011	43.0	69.1	
% rejection	2.10	9.15	92.7	99.2	99.3	92.2	92.5	

<sup>a</sup> 600 psig, 20°C, SPPO-PS composite membrane, 0317-2NM, 0322-12NM, and 0623-12NM series

Solvent-cast sulfonated PPO membranes of 0.2 mil thickness in SPPO-PS composite membrane with ion exchange capacity of 2.1–2.3 meq/g were prepared, and reverse osmosis tests were carried out on the synthetic and natural waste water from Alberta heavy oil fields at 600 psig and 20°C.

As shown in Table III, the rejection characteristics and production rate were excellent and considered sufficient for the application of purification of waste water from the heavy oil fields.

### CONCLUSIONS

SPPO-PS composite membrane was considered excellent for the application of purification of waste water from heavy oil field. Membranes with low IEC values about 2 exhibited higher rejection, but had lower flux while those with high IEC values resulted in higher flux, but had lower rejection. Product rate and salt rejections for various feeds were found to be in the range of 5–20 gfd and 99–80%, respectively, at 600 psig and 20°C, depending on reverse osmosis operating conditions and membrane properties.

The authors wish to thank the National Science and Engineering Research Council of Canada (NSERC) for their generous support of this research project. They also wish to thank Dean Wallace of the Alberta Research Council, Edmonton, Alberta, Canada, for kindly providing the samples of the Alberta tar sands waste waters.

### References

1. P. R. Tremaine, E. E. Isaacs, and J. A. Boon, *Chem. Can.*, **35**(4), 29 (1983).
2. B. H. Asano et al., "Review of Treatment and Recycling of Produced Water from Heavy Oil Fields," CH2M HILL Canada Ltd., Calgary, 1981.
3. A. B. LaConti, in *Reverse Osmosis and Synthetic Membranes*, S. Sourirajan, Ed., National Research Council of Canada, Ottawa, 1977, pp. 211–229.
4. C. W. Plummer, G. Kimura, and A. B. LaConti, "Development of Sulfonated Polyphenylene Oxide Membranes for Reverse Osmosis", Office of Saline Water Research and Development Progress Report No. 551, General Electric Co., Lynn, Mass., 1970.
5. P. J. Chludzinski, J. F. Austin, and J. F. Enos, "Development of Polyphenylene Oxide Membranes", Office of Saline Water Research and Development Progress Report No. 697, General Electric Co., Lynn, Mass., 1971.
6. R. M. Dempsey and A. B. LaConti, "Reclamation of Acid Rinse Water", National Technical Information Service AD784445, General Electric Co., Lynn, Mass., 1974.
7. C. E. Milsted and M. Tagami, "Polyacrylic Acid Composition Membranes", in *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, Eds., Plenum, New York, 1972, pp. 405–518.
8. S. Sourirajan and T. Matsuura, in *Reverse Osmosis and Synthetic Membranes*, S. Sourirajan, Ed., National Research Council of Canada, Ottawa, 1977, pp. 5–44.
9. *Standard Methods for the Examination of Water and Wastewater*, 15th ed., American Public Health Association, Washington, D.C., 1981.
10. R. A. Dobbs, R. H. Wise, and R. B. Dean, *Water Res.*, **6**, 1173 (1972).
11. S. Sourirajan, *Reverse Osmosis*, Logos, London, and Academic, New York, 1970, pp. 39–46.
12. O. Kedem, in *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, Eds., Plenum, New York, 1972, pp. 17–42.

Received March 7, 1984

Accepted April 16, 1984