

# Preparation and Separation Properties of Polyamide Nanofiltration Membrane

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**ABSTRACT:** Utilizing an interfacial polymerization technique for the preparation of a polymeric composite nanofiltration membrane, both high permeation flux of water and high salt rejection can be achieved. Synthesis conditions, such as concentration of monomer, reaction time, and swelling agent, significantly affected the separation performance of composite membranes. The composite polyamide membrane had a permeation rate of  $\sim 2\text{--}5$  gallon/ft<sup>2</sup>/day (gfd) and a salt rejection rate of  $\sim 94\text{--}99\%$  when 2000 ppm aqueous salt solution was fed at 200 psi and 25°C. Also, a higher performance nanofiltration membrane could be prepared by suitably swelling the support matrix in the period of polymerization. The results of various feed concentrations showed that permeate flux decreased with increasing salt concentration in the feed solution. This result may be due to concentration polarization on the surface of polyamide membranes. The separation performance of polyamide membranes showed an almost independent relationship with operation pressure until it was up to 200 psi. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1112–1118, 2002

**Key words:** composite membrane; interfacial polymerization; nanofiltration; polyamide

## INTRODUCTION

Nanofiltration membranes reject some salts and exhibit organic compound molecular weight cut-offs in the 200–500 Da range. The term nanofiltration is derived from the fact that these molecular weight cutoff values correspond to hypothetical pores of  $\sim 10$  Å (i.e., 1 nm).<sup>1</sup>

To achieve higher separation performance, the composite membrane is a way to achieve both high water permeability and high salt rejection. Polyamide and cellulose acetate currently dominate the field of commercial reverse osmosis membrane. The cellulose membrane was gener-

ally prepared as an asymmetric membrane, which had only modest application in the overall commercial market. The polyamide membrane was generally prepared by interfacial polymerization method, which was usually applied for nanofiltration and reverse osmosis.

In the last few years, the application of the membrane separation process for wastewater treatment has received much attention.<sup>2–10</sup> Many synthetic membranes for separation of metal ions from wastewater have been prepared in recent years.<sup>11–14</sup> The NF 70 membrane, which was prepared by interfacial polymerization method, has practical application for softening the water.<sup>1</sup> It was also found that NF 70 rejected divalent cations very well and that the fluoride level in permeates was reduced to acceptable levels.

An interfacial polymerization composite membrane is defined as a bilayer film formed by a

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two-step process. Generally, a composite membrane consists of a porous support nonselective layer with a surface of another ultrathin selective barrier layer.<sup>15–19</sup> The separation performance of composite polyamide membranes prepared by interfacial polymerization method is dependent on several variables, such as concentration of reactant, solubility of nascent polymer in the solution phase, reaction time, and partition coefficients of the reactant.<sup>20</sup> It was found that the improvement of solvent resistance, salt rejection, permeation flux, and fouling resistance of polyamide membranes still require further investigation.<sup>21–24</sup>

Because of the significant effect of membrane formation on separation performance of thin film composite membranes, formation of the polyamide composite membrane by the interfacial polymerization method was chosen to prepare the higher performance membranes. The purpose of this study was to understand and control the reaction conditions of the interfacial polymerization method, thereby creating a high-performance nanofiltration polyamide membrane. Salt rejection and flux values of polyamide membrane were reported for various synthetic conditions, such as concentration of reactant, swelling agent, and reaction time. The effects of operating conditions on separation performance of composite membranes were also discussed.

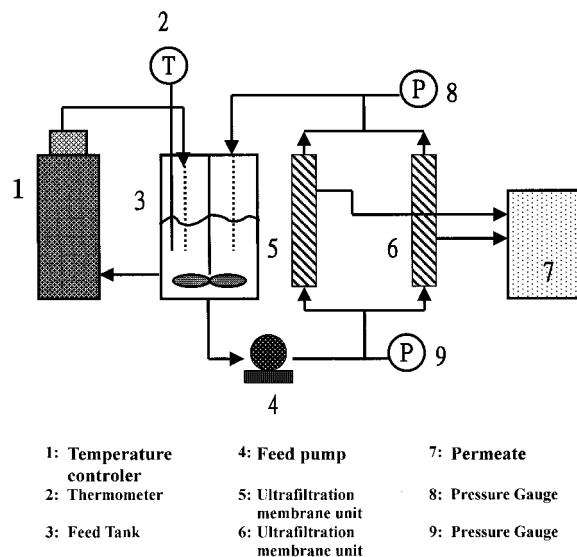
## METHODS

### Material

The microporous polysulfone membrane (molecular cutoff = 10,000 Da), was a product of Millipore Company. Diethylene triamine, poly(ethylene glycol) (MW = 10,000), terephthaloyl dichloride, and dimethyl formamide were supplied by Merck Company. NaCl, MgCl<sub>2</sub>, AlCl<sub>3</sub>, FeCl<sub>3</sub>, MnCl<sub>2</sub>, and CoCl<sub>2</sub> were also obtained from Merck Company.

### Composite Membrane Synthesis

The microporous polysulfone membrane (molecular cutoff = 10,000 Da, a product of Millipore) was used as a support layer for composite membrane. Polyamide was prepared by interfacial polymerization method.<sup>25</sup> The water-saturated microporous polysulfone membrane was immersed into an aqueous solution of diethylene triamine for a period of time (0–800 s) and was positioned ver-



**Figure 1** The experimental nanofiltration membrane apparatus.

tically to drain for 2 min. Then it was immersed in a hexane solution containing a certain amount of terephthaloyl dichloride for 120 s. The hexane solution was drained off and dried in a vacuum oven at room temperature for at least 12 h.

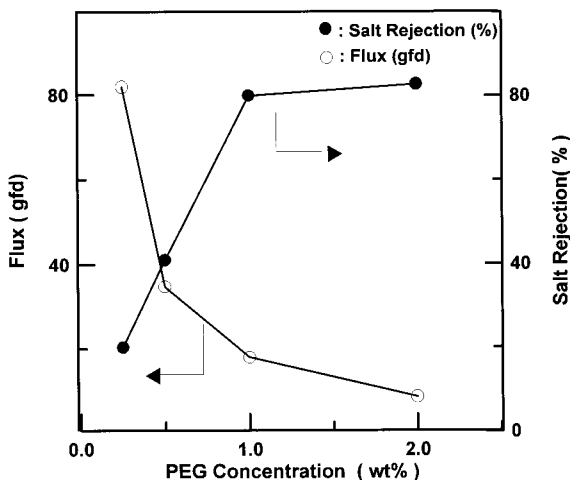
### Nanofiltration Test

The salt concentration in the feed was 2000 ppm. The tested membrane was immersed in distilled water overnight to accomplish complete swelling before the nanofiltration test. The operating pressure of 200 psi was applied at 25 °C, using a crossflow cell. The product concentration was determined by electric conductance measurement. Salt rejection,  $R$ , and hydraulic water permeability,  $P$ , were obtained by the following equations, respectively:

$$R = 100(c - c')/c \quad (1)$$

$$J_v = P(\Delta P - \Delta\pi)/\Delta x \quad (2)$$

where  $c$  and  $c'$  are feed and product concentrations, respectively;  $J_v$  is the permeation rate;  $\Delta P$  represents pressure difference;  $\Delta\pi$  is the operating pressure between feed and product solution;  $\Delta x$  is the membrane thickness; and  $P$  is the permeate permeability. Five or six samples of the permeation data were tested with 90% confidence. The experimental apparatus is shown schematically in Figure 1.



**Figure 2** Effect of PEG concentration on the membrane performance (0.5 wt % terephthaloyl dichloride/*n*-hexane and 1 wt % diethylene triamine/water reacted at 25 °C for 2 min; operating pressure, 200 psi; and NaCl in feed solution, 2000 ppm).

## RESULTS AND DISCUSSION

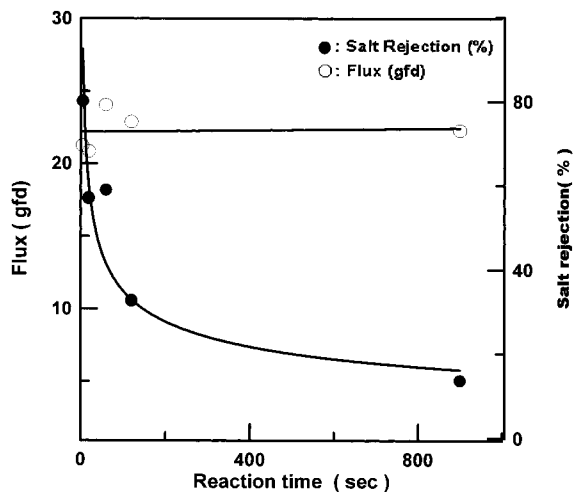
### Effect of PEG Concentration on the Transport Property of Polyamide Membrane

The relationship between the performance of polyamide membranes and synthesizing conditions was studied. The nanofiltration test was conducted with an operating pressure of 200 psi and an NaCl concentration of 2000 ppm in the feed solution. Because of the poor hydrophilicity of the polysulfone support membrane, poor composite membrane formation was found in the interfacial polymerization step. To improve the membrane formation, it was necessary to change the hydrophilicity of the support membrane. Therefore, poly(ethylene glycol) (PEG) was added to the aqueous solution as a wetting agent when the *n*-hexane solution contained 0.5 wt % terephthaloyl dichloride and the aqueous solution contained 1 wt % diethylene triamine. Interfacial polymerization was conducted in the organic phase at 25 °C for 2 min. The effect of PEG concentration on the membrane performance is shown in Figure 2. The permeation flux decreased and salt rejection increased with increasing PEG concentration in aqueous solution. The salt rejection increased from 30 to 80% as the PEG concentration increasing to 2 wt %. Also, the permeate flux decreased from 80 to 10 gfd. This result indicates that the concentrations of PEG in aqueous solution improved the thin layer formation on the

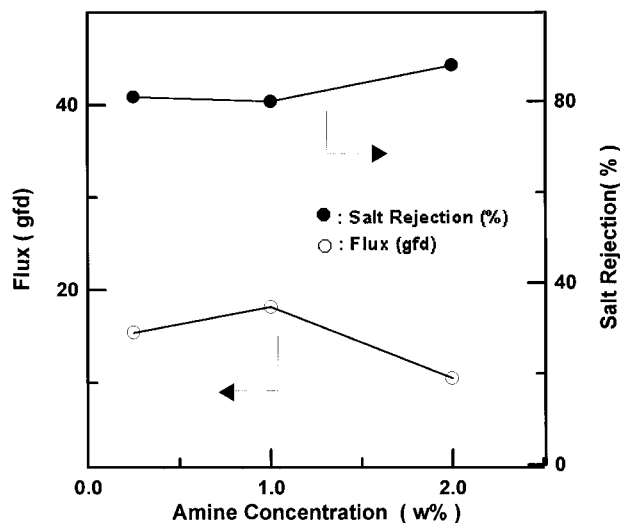
porous support. This result also shows that the salt rejection leveled off after PEG concentration was >1 wt % in aqueous solution. Therefore, the PEG concentration in aqueous solution is suggested to be no higher than 1 wt % in a polymerization reaction when high performance membranes are prepared.

### Effect of the Reaction Time on Transport Properties

The thickness of the top layer of the composite membrane depended on the reaction time and the diffusion rate of monomer through the interface between water phase and organic phase in interfacial polymerization. Generally, the top layer thickness of composite membrane increased with increasing polymerization time. When the thickness of the thin layer was enough to prevent the monomer from diffusing into the other phase, the top layer thickness will stop growing and then the separation performance of composite membrane would be almost constant. The effect of reaction time on membrane separation performance is shown in Figure 3. The salt rejection was almost independent of the reaction time in range 20–900 s. The permeate flux significantly decreased with increasing reaction time when the reaction time was up to 180 s and then decreased slightly. A decrease in permeation flux indicates an increase of barrier. Therefore, it could be con-



**Figure 3** Effect of reaction time on membrane separation performance. (0.5 wt % terephthaloyl dichloride/*n*-hexane and 1 wt % diethylene triamine/water reacted at 25 °C; operating pressure, 200 psi; and NaCl in feed solution, 2000 ppm).



**Figure 4** Effect of diethylene triamine concentration on the separation performance of membrane (0.5 wt % terephthaloyl dichloride/*n*-hexane and 1 wt % diethylene triamine/ water reacted at 25°C; operating pressure, 200 psi; and NaCl in feed solution, 2000ppm).

cluded that the thickness of the thin layer increased with reaction time. However, the salt rejection was still <85% in all ranges of reaction time. This low salt rejection may be due to the poor morphology on top of the surface of this composite membrane.

#### Effect of Monomer Concentration On Transport Properties

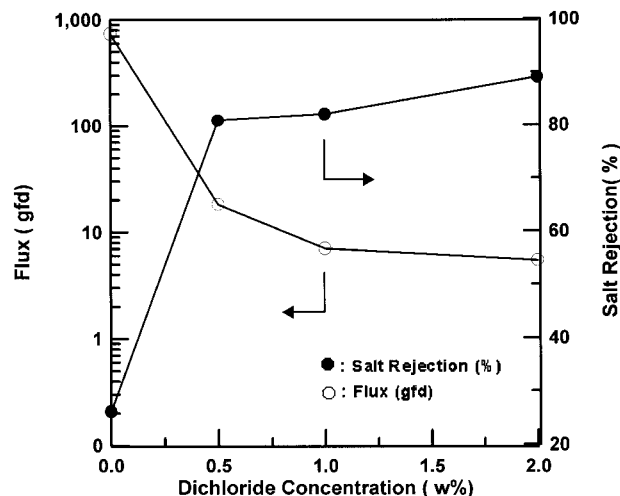
To further increase the separation performance of composite membranes, other factors to enhance the top layer morphology were considered. One such factor, which affected the top layer formation, was monomer concentration in polymerization. The effect of diethylene triamine concentration on the separation performance of the membrane is shown in Figure 4 with 1 wt % dichloride in hexane solution. The permeate flux and salt rejection hardly changed with increasing diethylene triamine concentration in the range 0.25–2 wt %. It can be concluded that the triamine concentration in the aqueous phase was not the dominant factor for polymerization.

The effect of dichloride concentration on separation performance is shown in Figure 5. The aqueous solution contained 1 wt % PEG and 1 wt % diethylene triamine. By increasing the dichloride concentration, the permeate flux was significantly decreased and the salt rejection rate was

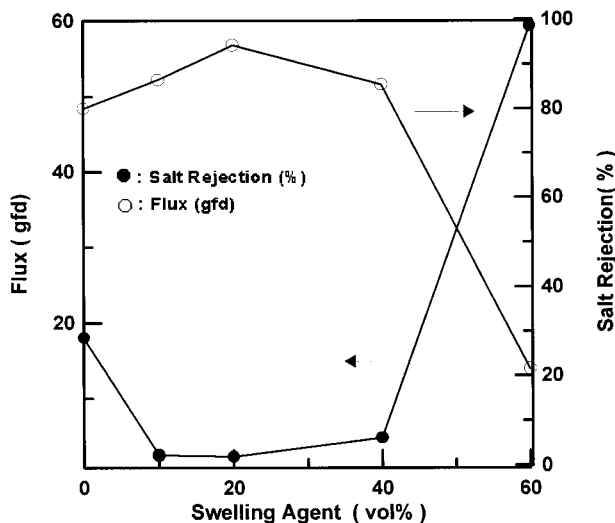
increased. The dichloride concentration in the organic phase significantly decreased the permeation flux of composite membrane. This result indicates that the increase of thickness of the polyamide membrane was due to the increase of dichloride concentration in the organic phase. It is supposed that the separation performance of composite membranes was mainly due to the change of monomer composite in organic phase rather than in aqueous phase. A similar result was previously obtained by Sundet.<sup>26</sup>

#### Effect of Swelling Agent on Transport Properties

To further improve the separation performance of polyamide membrane, we added a swelling agent to the aqueous solution to enhance the adhesion between polyamide membrane and support membrane. The swelling agent, dimethyl formamide (DMF), was chosen for addition to the aqueous solution to improve the separation performance of the composite membrane. The effect of the swelling agent in aqueous solution on separation performance of the membrane is shown in Figure 6. The permeation flux decreased with increasing swelling agent up to 20 vol % in aqueous solution, and then increased with increasing DMF. On the other hand, the salt rejection rate increased with increasing amount of swelling agent in aqueous solution up to 20 vol %. When the DMF concentration was >20 vol % in aqueous solution, the



**Figure 5** Effect of dichloride concentration on separation performance (1 wtpercent; diethylene triamine and 1 wt % PEG/water reacted at 25 °C; operating pressure, 200 psi; and NaCl in feed solution, 2000 ppm).



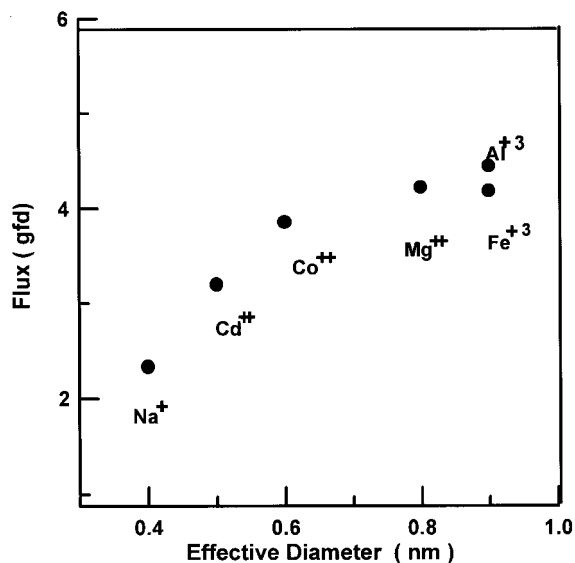
**Figure 6** Effect of swelling agent in aqueous solution on separation performance (1 wt % terephthaloyl dichloride/*n*-hexane and 1 wt % diethylene triamine and 1 wt % PEG/water reacted at 25 °C; operating pressure, 2000 psi; and NaCl in feed solution, 2000 ppm).

salt rejection rate decreased with increasing concentration of DMF in solution. This result indicates that the optimum composition of swelling agent was 20 vol % in aqueous solution because higher concentrations of swelling agent added to the solution would not improve the thin layer formation. It is suggested that an optimum amount of swelling agent could enhance the performance of the polyamide membrane.

#### Effect of Ion Diameter on Separation Performance

The effects of ion diameter on separation performance of composite membrane when the ion concentration in feed was 2000 ppm at 25 °C are shown in Figures 7 and 8. Permeate flux decreased and the salt rejection increased with an increase of effective ion diameter of metal ion in the feed. It is concluded that the salt rejection rate was strongly dependent on the effective diameter rather than on the molecular weight of the metal ion.

For the chloride salts tested in this study, the salt rejection rate of composite membrane increased in the order  $\text{Al}^{3+} > \text{Mn}^{2+}, \text{Fe}^{3+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Na}^+$ . This trend is similar to the order of effective diameter of those metal ions. The lowest rejection rate is for a salt with monovalent cation (sodium), but there are high rejection rates for salts with divalent and trivalent cations

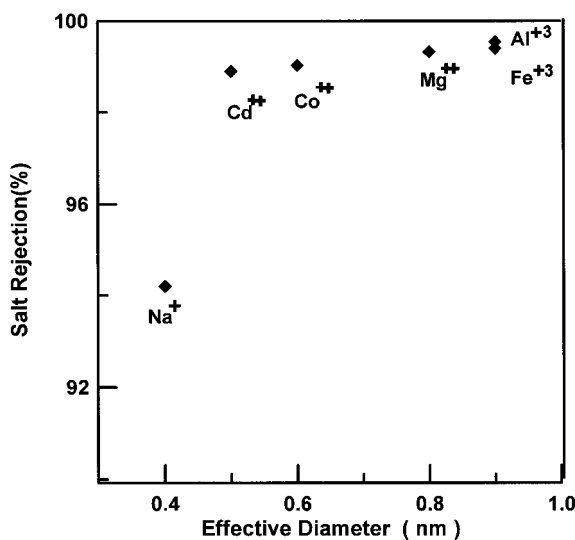


**Figure 7** Effect of ion diameter on permeation flux of composite membrane.

( $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ ). This result indicates that the thin layer may form an ionic barrier on the membrane surface, which could come about through partial hydrolysis of the amide group. The Danan ion repulsion effect led to high salt rejection for divalent and trivalent ions, and a similar result can also be seen with a reverse osmosis membrane.<sup>27</sup>

#### Effect of Feed Concentration and Operating Pressure on Membrane Performance

The effects of salt concentration in feed on permeation flux and salt rejection of composite mem-



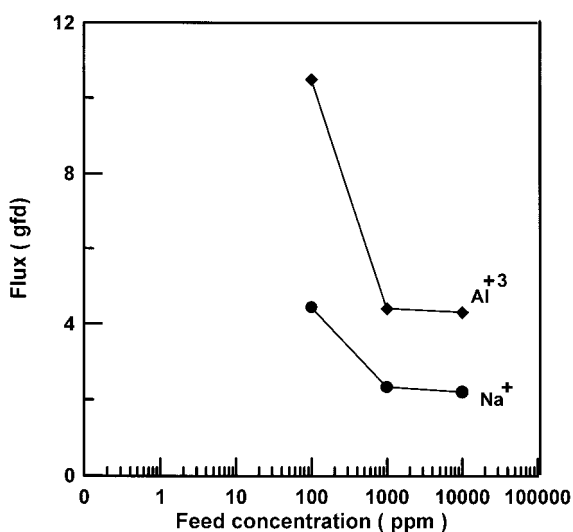
**Figure 8** Effect of ion diameter on salt rejection of composite membrane.



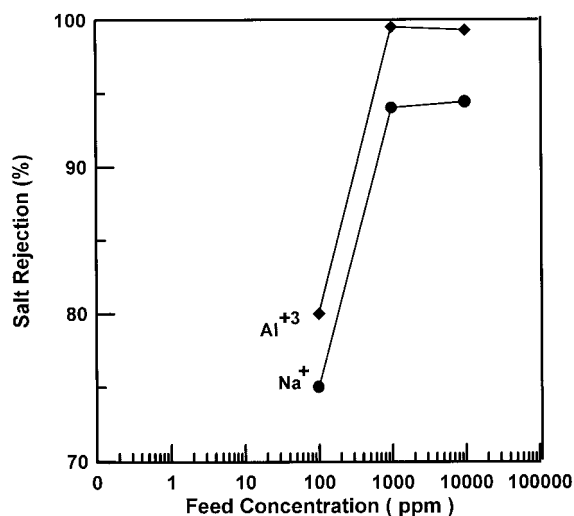
branes are shown in Figures 9 and 10. The permeation flux decreases with increasing salt concentration, whereas the salt rejection rate decreased with increasing salt concentration. This result indicates that the salt concentration significantly affected the separation performance of composite membranes. On the other hand, the operating pressure was almost independent of separation performance as the operating pressure ranged up to 200 psi.

## CONCLUSION

Polyamide nanofiltration membranes can successfully separate metal ions, and the following conclusions are offered based on this study. The high-performance membranes could be prepared by adding  $\leq 1$  wt % PEG in the polymerization reaction. The effect of reaction time on membrane separation performance showed that the thickness of the thin layer increased with reaction time and the permeation flux decreased with increasing reaction time. With various monomer concentrations in interface polymerization, the dichloride concentration in the organic phase significantly decreased the permeation flux of composite membrane. This result also indicates that superior interfacial polymerization occurred in the organic phase than in the aqueous phase. With increasing valence of the metal ion, the Danner ion repulsion effect increased. The permeation flux decreases and salts rejection increases with in-



**Figure 9** Effect of salt concentration in feed on permeation flux of composite membranes.



**Figure 10** Effect of salt concentration in feed on salt rejection of composite membranes.

creasing effective diameter of ion. Because of the concentration polarization effect, a lower concentration of metal ion in the feed would yield higher permeation flux and salt rejection. The operating pressure was almost independent of separation performance in the range up to 200 psi.

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