

Preparation of Reverse Osmosis Composite Membrane with High Flux by Interfacial Polymerization of MPD and TMC

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ABSTRACT: In this study, reverse osmosis (RO) composite membrane with extra-thin separation layer was prepared by the interfacial polymerization (IP) of metaphenylene diamine (MPD) with trimesoyl chloride (TMC) on the surface of polysulfone (PS) support membrane. The properties and structures of skin layer of RO composite membranes were characterized by FTIR and SEM, it was found that IP had occurred and the separation layer was formed. The effects of the monomer concentration on membrane flux and salt rejection were investigated, and the optimum concentration of MPD and TMC were 2 and 0.3% (w/v), respectively. To improve flux, the phase-transfer catalyst was added to the

water phase, and the effects were remarkable when the concentration of MPD was low, in which both salt rejection and flux increased by 20% than initial results. When some of the hydrophilic additives such as alcohols and phenols were added into water phase, the flux of the prepared membrane increased from 13.03 to 33.42 L/(m² h) without loss in salt rejection. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2066–2072, 2009

Key words: reverse osmosis; composite membrane; interfacial polymerization; metaphenylene diamine; trimesoyl chloride

INTRODUCTION

The composite membranes are extensively used in reverse osmosis (RO) desalination processes.^{1–4} These membranes have a thin and dense active layer that controls membrane permeability and rejection, and a much thicker porous substrate provides mechanical support to the active layer. To achieve high permeability and selectivity, the active layer should be ultra-thin and hydrophilic. Much previous research revealed that polyamide (PA) membrane prepared via interfacial polymerization (IP) was the most effective for RO processes. The ultra-thin PA membranes synthesized via IP exhibit a range of physicochemical properties based on the polymerization conditions including the monomer concentration and the additives.⁵ These properties play a vital role in the membrane performance. Since Morgan⁶ first put forward the conception of IP in 1965, the IP

has become an important method of RO membrane formation. The NS-100 membrane prepared by North Star Research Institute was the first successful interfacial-formed membrane, which achieved high salt rejection.⁷ After the development of the NS-100 membrane, many commercial composite membranes had been developed,^{8,9} such as the NF series made by Filmtec Corporation, NTR series by the Nitto Denko Company, UTC series by Toray Industries, ATF series by Advanced Membrane Technology, etc. These commercial membranes all exhibited high salt rejection.

Most of the researches^{10–13} to improve membrane performance have attempted to improve the salt rejection at the expense of the product water flux. Less work has been done to improve the flux simultaneously or to study the effect of such parameters on membrane flux while maintaining the salt rejection. Recently, Zhou et al.¹⁴ has prepared high-performance (both flux and rejection) RO membrane via synthesizing different functional monomers, such as *m*-phenylenediamine-5-sulfonic acid and 5-chloroformoxy-isophthaloyl chloride. However, it was complicated to obtain these monomers, which seriously confined its application. Another simple method was developed by some researchers.¹⁵ They found that permeability could be remarkably improved by adding some additives such as phenols

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and alcohols to monomers, and separation performances of the membrane prepared were much better than some commercial membranes.^{8,9}

In this study, PA composite RO membranes were prepared by the IP method. Polysulfone (PS) UF membranes were used as the support membrane. Trimesoylchloride (TMC) and metaphenylene diamine (MPD) were used as monomers of the IP reaction. The properties and structures of PA RO composite membranes were characterized by FTIR and SEM. After that, the effects of the monomers concentration on membrane performance were investigated. Phase-transfer catalyst and some of the hydrophilic additives were added into water phase to improve membrane flux.

EXPERIMENTAL

Materials and reagents

The PS support membrane whose molecular weight cutoff was about 30,000 was supplied by the Development Center for Water Treatment Technology, Hangzhou, China. MPD was purchased from Annuo Chemical Reagent Company, Shanghai, China. Analytical-grade TMC was obtained from Sanli Technology Company, Qingdao, China. Analytical-grade *n*-hexane and cetyltrimethylammonium bromide were purchased from Sinopharm Chemical Reagent, Shanghai, China. Sodium chloride (NaCl) was purchased from Chemical Reagent Company, Ningbo, China.

Preparation of composite RO membranes

For the preparation of PA membrane from MPD and TMC, the support PS membrane was immersed in aqueous solution of MPD for 30 s and pulled up slowly. Excess of the diamine solution was removed from the surface of the PS support membrane. The PS substrate was then covered with a solution of TMC in *n*-hexane phase for 10 s to deposit the polymeric thin layer on the substrate by the interfacial reaction. The resulting composite membrane was dried at room temperature for 24 h.

Characterization of separation performance

The membrane performances were evaluated in a RO test system as Figure 1 at 25°C and 1.6 MPa. The membrane sample was supported in the cell by a porous stainless steel disk. The active area of the membrane was determined as 38.5 cm². The aqueous solution containing 3.28 wt % NaCl was used as the feed. The conductivities of the feed and the permeate water were measured by DDS-11A conductivity meter (Model DDS-11A) from Shanghai Neici Instrument, China.

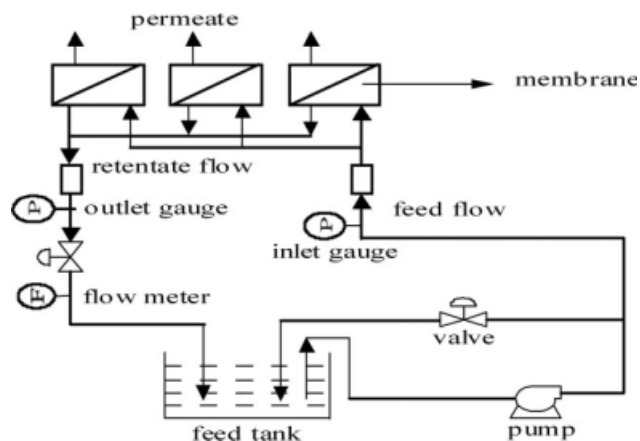


Figure 1 Schematic diagram of device for the permeation tests.

The RO performance was reported in terms of permeation flux (F) and solute rejection (R).

Permeation fluxes of membranes were obtained as follows:

$$F = \frac{V}{S \times t} \quad (1)$$

where, F is the permeation flux of membrane [L/(m² h)], V is the volumetric flow rate of permeate (L), S is the active area of membrane (m²), and t is the operation time (h).

Salt rejection of membrane was defined as:

$$R = \left(1 - \frac{c_2}{c_1}\right) \times 100\% \quad (2)$$

where R is the salt rejection of membrane, and c_1 and c_2 represent feed and permeate salt concentrations, respectively.

Characterization of membrane structure

The surface and cross-section morphology of membrane were observed by SEM (SIRION-100), and the chemical structure of separation layer and support membrane were observed by FTIR (Nexus-670, Nicolet Company).

RESULTS AND DISCUSSION

Characterization of membrane structure

SEM

The surface and cross-section morphology of membrane are shown in Figure 2. It is observed that a new dense layer is produced at the external surface because of an IP reaction process, the thickness of PA active layer is less than 3 μm, and it was found that the membrane surface was dense enough and porous structure disappeared. The SEM images of

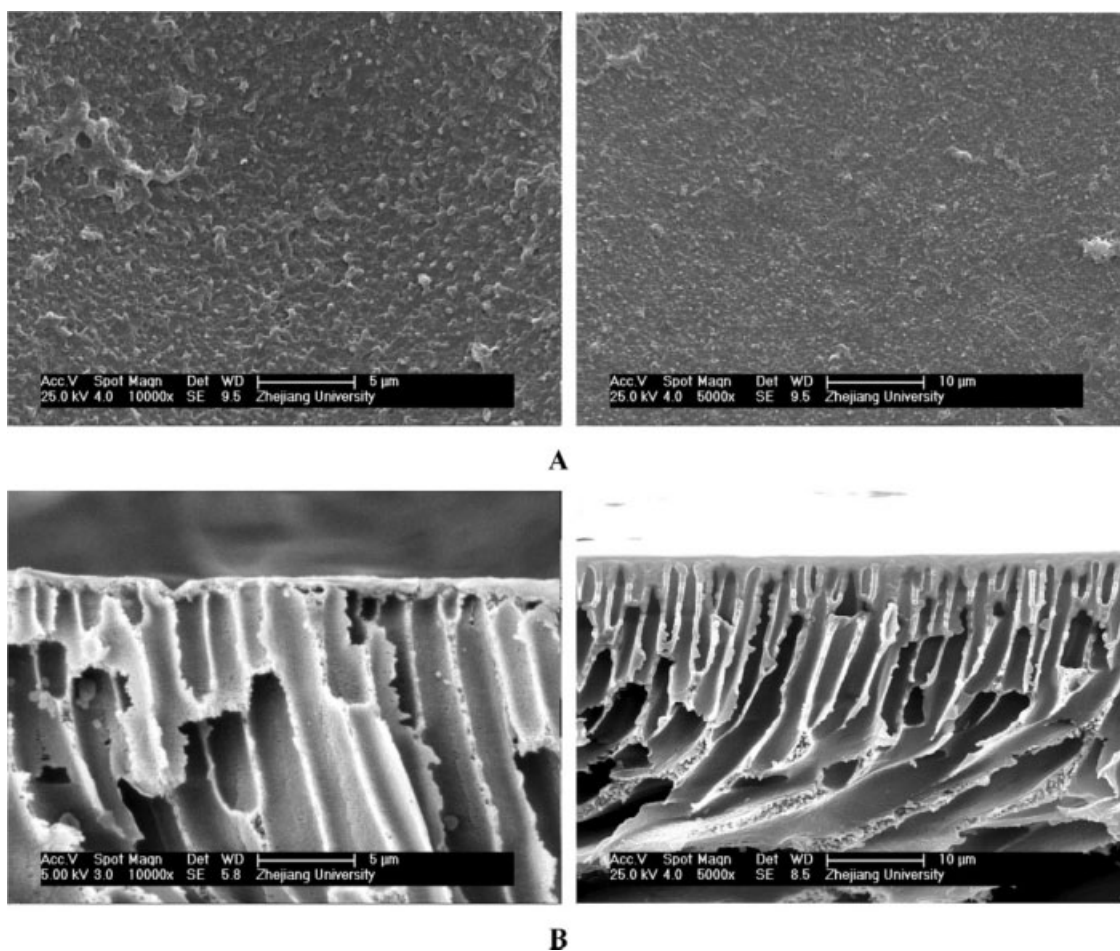


Figure 2 SEM images of membrane made from TMC/MPD. (A) Top surface; (B) cross-section; left: PS membrane, right: PS composite membrane.

cross-section show that the porous composite membrane is produced on the dense surface layer of support membrane.

FTIR

Figure 3 presents the typical FTIR spectrum of PS supporting film, RO composite membrane TMC/MPD, and improved RO composite membrane TMC/MPD by isopropyl alcohol. The skin layer is so thin that the underlying PS also contributes to the spectrum. The acyl chloride band at 1763 cm^{-1} is absent, and the band at 1653 cm^{-1} (amide I) is present, which is characteristic of C=O band of an amide group. Especially, C=O band of an ester group that is different from other two spectrums at 1735 cm^{-1} is obviously present in the spectrum of improved RO composite membrane TMC/MPD. In addition, other bands characteristic of PA are also seen at 1544 cm^{-1} (amide II, C–N stretch) and 1611 cm^{-1} (aromatic ring breathing). The detailed IR spectral data of TMC and TMC/MPD membrane are

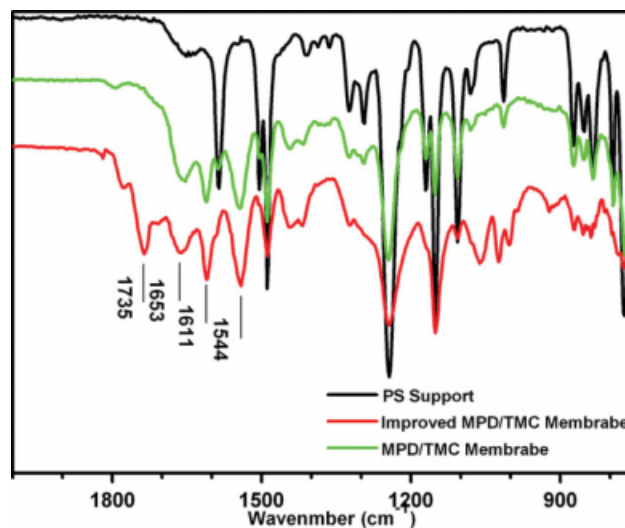


Figure 3 FTIR spectrum of a porous PS membrane and TMC/MPD membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

TABLE I
FTIR Spectral Data for Monomer and
RO Membrane Barrier

Sample	IR (cm ⁻¹)
TMC	1763 (acyl chloride $\nu_{C=O}$)
TMC/MPD	1653 (acylamide I serial $\nu_{C=O}$), 1611, 1544 (acylamide II serial δ_{NH})

shown in Table I. All of these characteristics indicate that the IP has occurred.

Effects of TMC and MPD concentration on membrane performance

The effects of concentration of TMC and MPD on flux and rejection were investigated, which are shown in Figures 4 and 5. Overall, the water flux and the salt rejection were more sensitive to change in the MPD concentration than that of the TMC concentration. From Figure 4, the water flux evidenced a decrease of 20% over TMC concentrations from 0.05 to 0.4% w/v, but remained almost constant at higher TMC concentrations. Similarly, the salt rejection increased slightly (7%) as the TMC concentration increased from 0.05 to 0.4% w/v, but remained essentially unchanged at higher TMC concentrations. Figure 5 demonstrates that the water flux decreased by 34% as the MPD concentration was increased from 0.8 to 2.4% w/v. The flux decrease was more modest (8%) at higher MPD concentrations, and the flux did not reach an asymptotic value at the maximum MPD concentration tested (2.4% w/v). The salt rejections were sensitive to low MPD concentration, increasing by 40% as the MPD concentration increased from 0.8 to 2.4% w/v, but reaching a

constant value for greater MPD concentrations. Overall, these results suggest that the permeability and rejection greatly depend upon the monomer concentrations.

Effects of additives on membrane performance

Phase-transfer catalyst

The collision of reagent molecular is basic conditions of chemical reactions. If two molecules could not get together, no matter what high energy one molecule has, the chemical reaction could still not occur. MPD and TMC were dissolved in water phase and organic phase, respectively, so the monomers did not contact with each other directly, and they should diffuse to the phase interface so that the chemical reaction could proceed. In view of this, the reaction rate can be increased through the method of phase-transfer catalysis. The mechanism of phase-transfer catalysis is that the complex compound of one monomer with phase-transfer catalyst can be easily transferred to the other phase in which other monomer dissolved, so the monomers can collide with each other in same phase.

Cetyltrimethylammonium bromide is a sort of quaternary ammonium salts, and it first formed an ion pair with MPD, and the ion pair was rapidly extracted in the organic phase so as to increase the probability of collision of molecular, and then the ions could easily form crosslinking condensation polymerization with TMC. The whole course is shown in Figure 6.

In Figures 4 and 5, the best rejection (0.952) is seen when the concentration of MPD and TMC were 2% (w/v) and 0.3% (w/v), respectively. In this condition, the phase-transfer catalyst, cetyltrimethylammonium

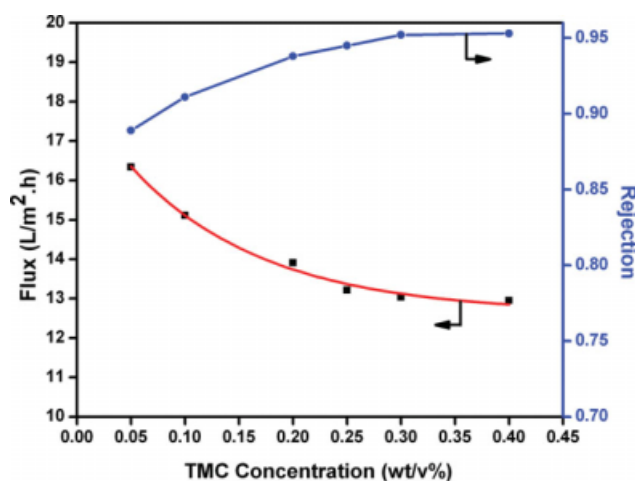


Figure 4 Effect of the concentration of TMC on the flux and rejection when MPD was 2% w/v. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

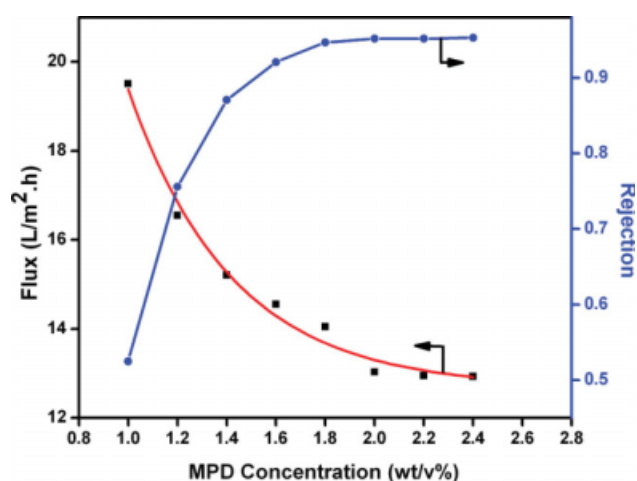


Figure 5 Effect of the concentration of MPD on the flux and rejection when TMC was 0.3% w/v. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

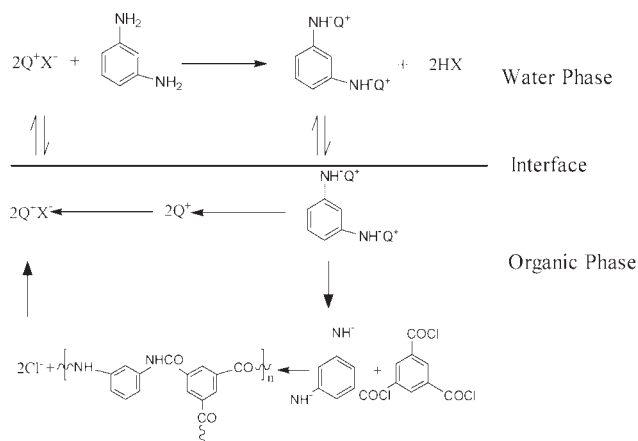


Figure 6 Schematic diagram of the mechanism of phase-transfer catalyst, Q^+X^- represent cetyltrimethylammonium bromide.

bromide was added to water phase, and then the effects of mass fraction of catalyst to MPD on flux and rejection were investigated, which is shown in Figure 7, when the concentrations of MPD and TMC were 2.0 and 0.3% (w/v), respectively. Meanwhile, the effects of mass fraction of catalyst to MPD on flux and rejection were investigated, which is shown in Figure 8, when the concentrations of MPD and TMC were 1.2 and 0.3% (w/v), respectively.

Figure 7 depicts that salt rejection changed very slightly, which revealed that the phase-transfer catalyst had no significant effect on the salt rejection when MPD concentration was high. However, the flux had increased from 13.03 to 19.13 $L/(m^2 h)$. Figure 8 indicated that when the concentration of MPD was lower, the phase-transfer catalyst had remarkable effects on both salt rejection and flux. The salt rejection increased to 21% as the mass fraction of

catalyst to MPD increased from 0 to 0.5% (w/v), and the flux increased to 36% as the mass fraction of catalyst to MPD increased from 0 to 1.5% (w/v). The reason was that the reaction rate of IP was already high when the concentration of MPD was higher, so the phase-transfer catalyst had less effect on the separation performance, but with decreasing the concentration of MPD, the reaction rate decreased rapidly, and then the phase-transfer catalyst played an important role. Therefore, the phase-transfer catalyst could effectively improve IP yield. Why phase-transfer catalyst could improve the property of membrane was described by three reasons. First, the hydrophilic functional group was introduced by phase-transfer catalyst, which served as one kind of ionic surfactant. Second, the effect of electrostatic exclusion was helpful to the salt rejection. Third, when ionic surfactant was introduced, the binding energy between support-layer and top-layer was changed, which also influenced the property of membrane.

Alcohols and phenols

Both alcohols and phenols are hydrophilic reagents. When they are added to the monomer in water phase, the hydroxyl rapidly reacts with acyl chloride of TMC, and the physicochemical properties of composite membrane changed so that the flux would improve. In view of this, isopropyl alcohol and phenol were added to the MPD aqueous solution before the IP, respectively. The experiment results coincided with the anticipation that the flux was obviously improved; the results are shown in Figures 9 and 10.

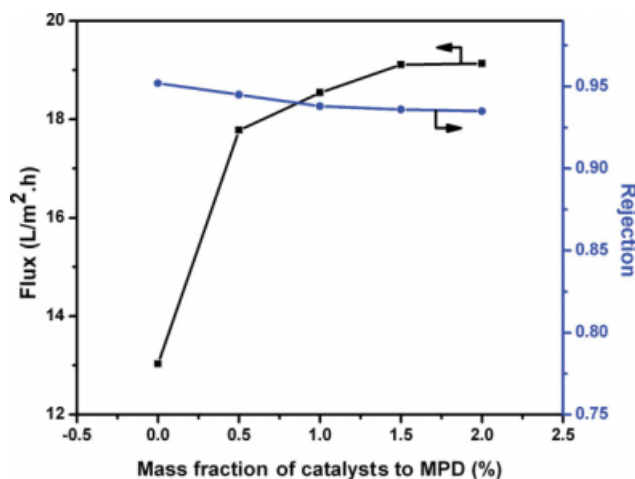


Figure 7 Effects of mass fraction of the catalysts to MPD on the flux and rejection when concentration of MPD was 2% (w/v). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

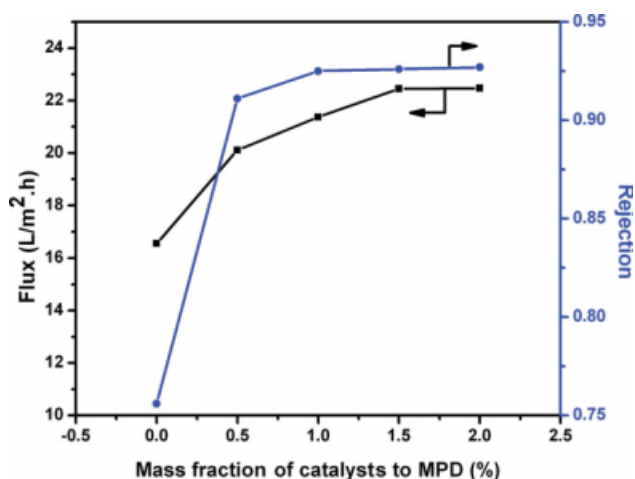


Figure 8 Effects of mass fraction of the catalysts to MPD on the flux and rejection when concentration of MPD was 1.2% (w/v). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

As shown in Figures 9 and 10, the effects of isopropyl alcohol and phenol on flux were very obvious, and the optimum was nearly up to 36 L/(m² h), which was two and a half times than initial results. Especially for isopropyl alcohol, the rejection was fairly constant while the flux was increasing, even for phenol, the rejection only decreased 1% but the flux increased from 13.03 to 33.42 L/(m² h). The composition of top layer was also varied that the structures of ester were formed, which was caused by the hydroxyl rapidly reacting with acyl chloride, and it was characterized by FTIR shown in Figure 3. The increase of flux treated with isopropyl alcohol and phenol may be attributed to both alcohol–water and phenol–water system, which could change the property of interface between porous support-layer and dense top-layer by two ways: swelling and polarity. The effect of swelling expanded the distance of the molecular chains of both support-layer and top-layer. The increase in polarity enhanced the interaction between membrane and water molecules. Both factors caused the improvement of water flux. In addition, there was less effect with salt rejection while the mobility of solute did not change seriously. Another reason is that isopropyl alcohol and phenol are mild solvent with respect to PAs. Hildebrand solubility parameters are good indicators of the ability of certain solutions to act as solvents or swelling agents for membranes.¹⁶ The solubility parameter of aromatic PA networks was about 23–24 MPa^{1/2}, which were obtained by Aharoni¹⁷ by using various solvents, nonsolvents, and solvent mixtures, whereas the value of the solubility parameter of isopropyl alcohol and phenol are 23.6 and 24.1 MPa^{1/2}. The approximate solubility parameters of isopropyl

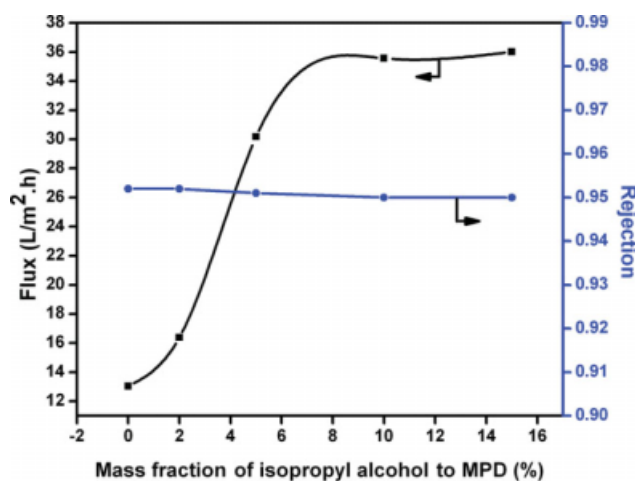


Figure 9 Effects of mass fraction of isopropyl alcohol to MPD on the flux and rejection when MPD was 2 wt % and TMC was 0.3 wt %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

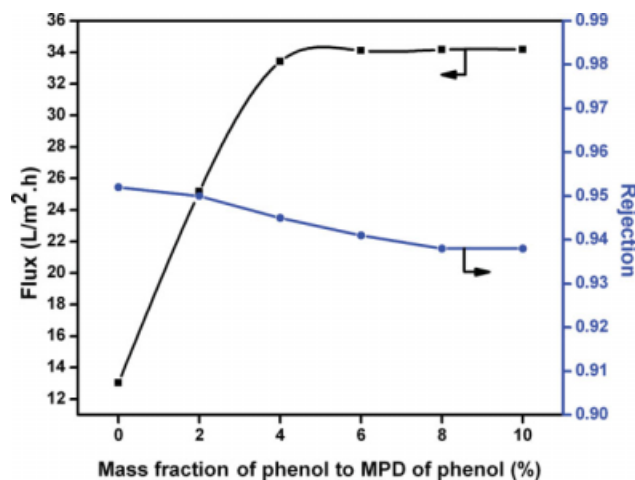


Figure 10 Effects of mass fraction of phenol to MPD on the flux and rejection when MPD was 2 wt % and TMC was 0.3 wt %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

alcohol, phenol, and aromatic PA networks suggest that isopropyl alcohol and phenol are swelling agents.¹⁸

CONCLUSIONS

The PA thin film RO composite membranes were prepared by using the IP of MPD and TMC on the surfaces of porous PS membranes. These experiments demonstrated that variation in the acid chloride concentration had a more pronounced effect on the thin film material properties than corresponding variations in the amine concentration. In addition, a simple method for improving the flux of thin film composite RO membranes has been demonstrated here. Flux enhanced up to two and a half times with this type of treatment. Isopropyl alcohol improved the flux nearly with no loss in rejection. The other additives made the flux increase with some loss in salt rejection properties. From the results of our experiments, we may predict that a series of alcohols or hydrophilic reagents or ionic surfactants, which were directly or indirectly able to vary physicochemical properties of membrane, could also attain the objective of enhancing flux. The treatment method demonstrated here can be applied easily for improving the flux for many applications including desalination and waste treatment. Indeed, the large flux increases obtained would reduce the surface area needed and the size of the units that would make RO systems significantly more effective.

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