

Preparation, Morphologies, and Properties of Positively Charged Quaternized Poly(phthalazinone ether sulfone ketone) Nanofiltration Membranes

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ABSTRACT: Positively charged quaternized poly(phthalazinone ether sulfone ketone) (QAPPESK) nanofiltration (NF) membranes were prepared from chloromethylated poly(phthalazinone ether sulfone ketone) by the dye/wet phase inversion method with *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc) as solvents. The effects of the ratio of NMP to DMAc, the evaporation time, the evaporation temperature, and the coagulation temperature on membrane performance were evaluated by the orthogonal design method. The results showed that the optimal preparation conditions were an NMP/DMAc ratio of 2/8, an evaporation time of 5 min at 70°C,

and a coagulation temperature lower than 5°C. The effects of the additive type and concentration on the QAPPESK NF membrane cross-section morphology and performance were investigated in detail. Furthermore, QAPPESK NF membranes exhibited good thermal stability with stable membrane performance for 120 h at 60°C. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1389–1397, 2009

Key words: quaternized poly(phthalazinone ether sulfone ketone); nanofiltration; membrane performance and morphology; thermal stability

INTRODUCTION

Nanofiltration (NF) is a pressure-driven process with separation characteristics between ultrafiltration and reverse osmosis. The development of NF technology has given rise to worldwide interest because of its advantages, such as low operation pressures, high flux, high rejection of multivalent ion salts and organic molecules above 300 Da, relatively low investment costs, and low operation and maintenance costs.

So far, most commercially available NF membranes are generally neutral or negatively charged. Negatively charged NF membranes reject some organic substances and high-valence cations because of a sieving effect and static electrification, and they have been applied successfully in many fields, such as water softening, drinking-water purification, dye and antibiotic purification and concentration, color removal, and chemical oxygen demand reduction.^{1–5} However, positively charged NF membranes have

unique benefits and cannot be replaced by negatively charged NF membrane in some applications, such as the separation of biomacromolecules below the isoelectric point and the recovery of cathode electrophoresis lacquer.⁶ Recently, some studies have focused on positively charged NF membranes with good membrane performance.^{6–14} However, most of them are composite membranes, and their preparation technology is complex. Integrally skinned asymmetric membranes can be obtained relatively easily through phase inversion methods, in which a casting solution with multiple components is immersed in a coagulant bath.^{15,16} The desired membrane structures can be obtained by effective procedures, which include changing the compositions in the casting solution or in the coagulation bath and evaporating the casting solution.^{17–25} However, research on integrally skinned asymmetric membranes with positive charges is scarce because the materials for positively charged NF membranes are limited. Therefore, it is important and promising to select proper polymer materials to develop novel positively charged NF membranes with special performance.

Poly(phthalazinone ether sulfone ketone)s (PPESKs) are known as outstanding membrane materials with high glass-transition temperatures (263–305°C) and superior mechanical strength and chemical resistance.^{26–28} Chemical modification of PPESK, such as sulfonation and chloromethylation/

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quaternization, can lead to important functional membranes. Dai and coworkers^{29–31} synthesized sulfonated PPESKs and prepared negatively charged ultrafiltration and NF membranes. Su et al.⁷ successfully prepared positively charged quaternized poly(phthalazinone ether sulfone ketone) (QAPPESK) NF membranes with chloromethylated poly(phthalazinone ether sulfone ketone) (CMPPEK), and they showed good results in the separation of dyes and NaCl. They had good acid resistance and oxide resistance. However, the membranes had 20–80% rejection for 0.5 g/L MgCl₂. Therefore, the performance of QAPPESK NF membranes still needs to be further improved.

The purpose of this study was to further improve the properties of positively charged asymmetric QAPPESK NF membranes. The effects of preparation parameters on the cross-section morphology and performance of QAPPESK NF membranes were studied in more detail and optimized. In addition, the thermal stability of positively charged asymmetric QAPPESK NF membranes was investigated preliminarily.

EXPERIMENTAL

Materials and methods

CMPPEK with a degree of chloromethylation of 1.80 mmol/g was synthesized in our own laboratory according to the reported method,³² and it had a sulfone/ketone ratio of 8/2. *N*-Methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc) were used as solvents. Ethyl ether (EE), tetrahydrofuran (THF), 1,4-dioxane (DO), *n*-butanol, acetic acid (AA), ethylene glycol monomethyl ether (EGME), diethylene glycol (DEGC), and poly(ethylene glycol) 400 (PEG400) were selected as additives. The solvent NMP was industrial-grade and was purchased from Mitsubishi Corp. (Tokyo, Japan). A 33% trimethylamine aqueous solution was chemical-grade and was obtained from Shenyang Xinxin Reagent Factory (Shenyang City, China). Other chemicals were analytical-grade. Chemicals were obtained commercially and used without further purification.

The retention measurements were carried out in a stainless dead-end filtration setup, which had been designed and manufactured in our laboratory. It had a volume capacity of 850 mL and held an effective separation area of 41 cm². The concentrations of inorganic electrolytes were determined with a DDS-11A electrical conductivity instrument (Shanghai Leichi Instrument, Shanghai, China). The membrane samples for scanning electron microscopy (SEM) were immersed in liquid nitrogen, fractured, and then sputtered with metallic gold. The cross-section morphologies were observed with a scanning elec-

tron microscope (JSM-5600LV, Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan).

Membrane preparation

A positively charged QAPPESK NF membrane was obtained in two steps. First, an asymmetric CMPPEK membrane was prepared by a phase inversion method. CMPPEK and an additive were dissolved in a solvent at the ambient temperature until a homogeneous polymer solution was formed. The concentration of CMPPEK in the casting solution was 20 wt % in this study. After being filtered and degassed, the casting solution was cast onto a glass plate at a certain temperature for some time in air and then was precipitated by immersion into a water coagulation bath until the CMPPEK membrane formed and came off the glass plate. To replace the solvent completely with nonsolvent water, the membrane was moved into another water bath at the ambient temperature and kept for another 36 h. Second, a positively charged QAPPESK NF membrane was prepared from the CMPPEK membrane by quaternized modification. The CMPPEK membrane was immersed into a 5.0 mol/L trimethylamine solution for 5 h at 30°C, and the QAPPESK NF membrane was obtained with quaternary ammonium groups. Figure 1 shows the quaternization reaction of CMPPEK.

Membrane characterization

The membranes were characterized in the dead-end membrane module after they were pretreated under a pressure of 0.5 MPa for 30 min. The solution flux and rejection of a 1 g/L MgCl₂ solution were measured under a pressure of 0.4 MPa (the pressure was adopted for all the experiments except for the extra label) at the ambient temperature.

The permeation flux (F) can be calculated as follows:

$$F = \frac{W}{At} \quad (1)$$

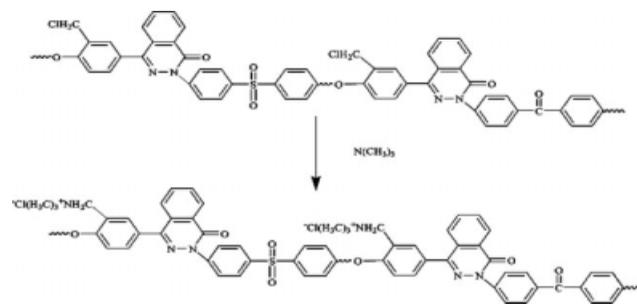


Figure 1 Quaternization reaction of CMPPEK.

TABLE I
Results of Orthogonal Experiments Concerning the Effect of the Membrane Preparation Method on the Membrane Performance

| | Factors | | | | | | | | Results | |
|---------------------------------|----------------|-----|------------------|-----|-------------------------|-----|-------------------------|-----|---------------|-----------------------------------|
| | NMP/DMAC | | Evaporation time | | Evaporation temperature | | Coagulation temperature | | | |
| | Level <i>i</i> | g/g | Level <i>i</i> | min | Level <i>i</i> | °C | Level <i>i</i> | °C | Rejection (%) | Aqueous flux (L/m ² h) |
| Membrane | | | | | | | | | | |
| M1 | 1 | 2/8 | 1 | 2 | 1 | 50 | 1 | 5 | 16 | 117 |
| M2 | 1 | 2/8 | 2 | 5 | 2 | 60 | 2 | 25 | 17 | 181 |
| M3 | 1 | 2/8 | 3 | 8 | 3 | 70 | 3 | 50 | 69 | 11 |
| M4 | 2 | 5/5 | 1 | 2 | 2 | 60 | 3 | 50 | 23 | 86 |
| M5 | 2 | 5/5 | 2 | 5 | 3 | 70 | 1 | 5 | 47 | 117 |
| M6 | 2 | 5/5 | 3 | 8 | 1 | 50 | 2 | 25 | 16 | 118 |
| M7 | 3 | 8/2 | 1 | 2 | 3 | 70 | 2 | 25 | 16 | 140 |
| M8 | 3 | 8/2 | 2 | 5 | 1 | 50 | 3 | 50 | 2 | 459 |
| M9 | 3 | 8/2 | 3 | 8 | 2 | 60 | 1 | 5 | 24 | 156 |
| R_1 | | 34 | | 18 | | 11 | | 29 | | |
| R_2 | | 29 | | 22 | | 21 | | 16 | | |
| R_3 | | 14 | | 36 | | 44 | | 31 | | |
| Maximum difference of rejection | | 20 | | 18 | | 33 | | 15 | | |
| F_1 | | 103 | | 114 | | 231 | | 130 | | |
| F_2 | | 107 | | 253 | | 141 | | 147 | | |
| F_3 | | 252 | | 95 | | 89 | | 185 | | |
| Maximum difference of flux | | 149 | | 158 | | 142 | | 55 | | |

R_i and F_i are the average MgCl_2 rejection and flux of level i ($i = 1, 2, \text{ or } 3$), respectively. The test condition was 14°C. The additive was 10 wt % EGME.

where W is the total permeate volume, A represents the membrane area, and t denotes the operation time. The rejection (R) can be expressed as follows:

$$R = 1 - \frac{C_p}{C_f} \quad (2)$$

where C_p and C_f are the concentrations of the permeate and feed, respectively.

RESULTS AND DISCUSSION

Orthogonal experiments for the preparation of QAPPESK NF membranes

Casting solvents, such as NMP and DMAc, have much larger effects on the performance of QAPPESK NF membranes. However, NMP and DMAc as casting solvents have their own deficiencies.³² To optimize the preparation conditions, the effects of the ratio of NMP to DMAc, the evaporation time, the evaporation temperature, and the coagulation temperature were characterized with orthogonal experiments. A three-level L9 standard array was selected. The experimental results are shown in Table I. The rejection and flux were measured for each membrane. The uncertainties of the rejection and flux are within 1% and 0.5%, respectively. The value of R_i

under each factor is the average of the three rejection values obtained from the three membranes made at the i th level of that factor. For example, R_1 under the factor of evaporation time, 18%, is the averaged value of 16, 23, and 16%. F_i is similar, its value under each factor being the average of the three flux values obtained from the three membranes made at the i th level of that factor. The maximum difference of rejection under each factor is the difference between the largest and smallest values of R_1 , R_2 , and R_3 . For example, the maximum difference of rejection under the evaporation temperature, 33%, is the difference between 11 and 44%. The maximum difference of flux is calculated similarly. The larger the maximum difference of rejection (or flux) is, the more important the factor is in affecting rejection (or flux).

Analyses of the data are shown in Table I. The order of the important factors tested in the orthogonal experiments for MgCl_2 rejection is as follows: evaporation temperature > ratio of NMP to DMAc > evaporation time > coagulation temperature. The order of the important factors for flux has been determined to be as follows: evaporation time > ratio of NMP to DMAc > evaporation temperature > coagulation temperature. It is found from the orders that the coagulation temperature is the least

TABLE II
Effect of the Additive Type on the QAPPESK NF Membrane Performance

| Additive | Rejection (%) | Flux (L/m ² h) |
|-------------------|---------------|---------------------------|
| EE | 79 | 80 |
| THF | 80 | 70 |
| DO | 76 | 72 |
| <i>n</i> -Butanol | 62 | 90 |
| AA | 39 | 88 |
| EGME | 64 | 69 |
| DEGC | 78 | 59 |
| PEG400 | 50 | 107 |

The test condition was 19°C.

important factor affecting rejection and flux. A lower coagulation temperature delays the speed of phase separation, resulting in a denser surface layer. Therefore, the coagulation temperature was selected to be lower than 5°C to maintain high rejection. The effects of the evaporation time, the ratio of NMP to DMAc, and the evaporation temperature on rejection were in contrast to their effects on flux. To maintain high rejection and flux at the same time, the optimum preparation parameters were determined by the orthogonal design method to be as follows: an NMP/DMAc ratio of 2/8, an evaporation time of 5 min at 70°C, and a coagulation temperature lower than 5°C.

Effect of the additive type on the performance of QAPPESK NF membranes

Additives play an important role in membrane preparation and can change the solubility and dissolution status of a polymer.^{15,33} In addition, the volatility and polarity of additives have much more important effects on the performance and morphology and NF membranes.

EE, THF, DO, *n*-butanol, AA, EGME, DEGC, and PEG400 were selected as additives in this study. The concentration of the additives was kept at 10 wt %. The QAPPESK NF membranes were prepared under the aforementioned optimum process conditions.

The effect of the additive type on the membrane performance was investigated, as shown in Table II. The membranes with EE, THF, DO, and DEGC as additives had better performance than those with *n*-butanol, AA, EGME, and PEG400 as additives. A possible reason involves the volatility and polarity of the additives. EE, THF, and DO were easier to volatilize in the evaporation period, and this led to a denser surface layer. Therefore, the MgCl₂ rejections of these membranes were much higher than those of the others. The volatility of *n*-butanol, AA, EGME, and PEG400 is lower, but their polarities are stronger. The additives of stronger polarity shared more solvent and thus formed more polymer aggregates in the casting solution. Thus, aggregate pores were formed

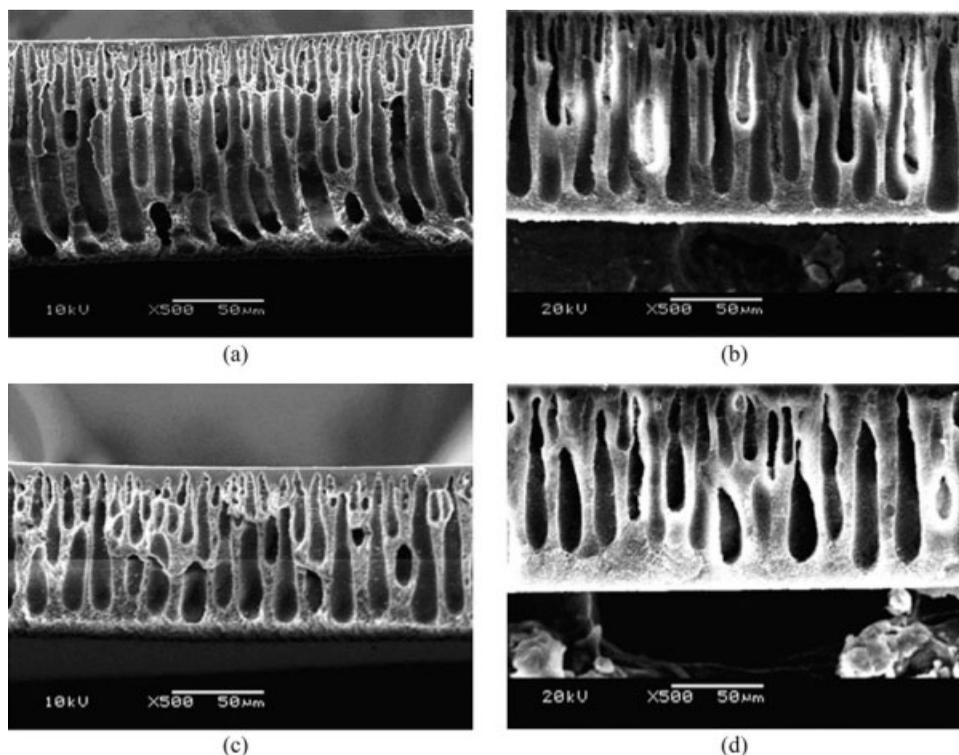


Figure 2 Effect of the EE concentration on the QAPPESK NF membrane cross-section morphology: (a) 5, (b) 10, (c) 15, and (d) 19 wt %.

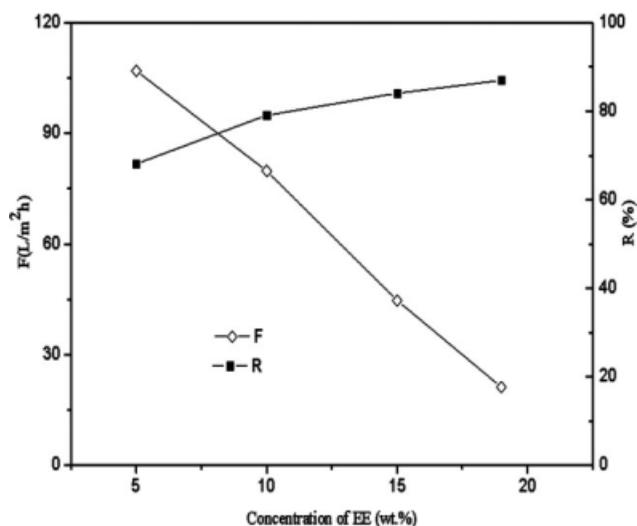


Figure 3 Effect of the EE concentration on the QAPPESK NF membrane performance (test condition: 20°C).

in the membrane surface layer. Therefore, the membrane with additives of higher polarity had higher flux and lower rejection. However, a QAPPESK NF membrane with DEGC as an additive had high rejection for MgCl₂. Although DEGC had lower volatility and stronger polarity, DEGC could make the casting solution become sticky. Thus, the exchange rate of the solvent into water became slower, and this delayed

the separation time. Therefore, the surface layer became denser, and this resulted in high rejection.

Effect of the additive content on the membrane performance and cross-section morphology of QAPPESK NF

Effect of the EE additive

EE (boiling point = 34°C) is a strong nonsolvent in a CMPPEK/solvent (8/2 NMP/DMAc)/EE system. When the concentration of EE in the casting solution was more than 19 wt %, the initial composition of the casting solution became very unstable and exhibited phase separation.

Figure 2 shows the cross-section morphologies of QAPPESK NF membranes fabricated from CMPPEK casting solutions with different EE concentrations. The fingerlike structures decreased in number and the top layer became thicker with increasing EE content.

The performance of QAPPESK NF membranes with different EE contents is shown in Figure 3. It appears that with an increase in the EE content in the casting solution, the MgCl₂ rejection increased from 68 to 87%, and the flux decreased from 107 to 21 L/m² h. EE was easy to volatilize in the evaporation period, and the volatilization became a dominant factor. Thus, the surface layer became denser

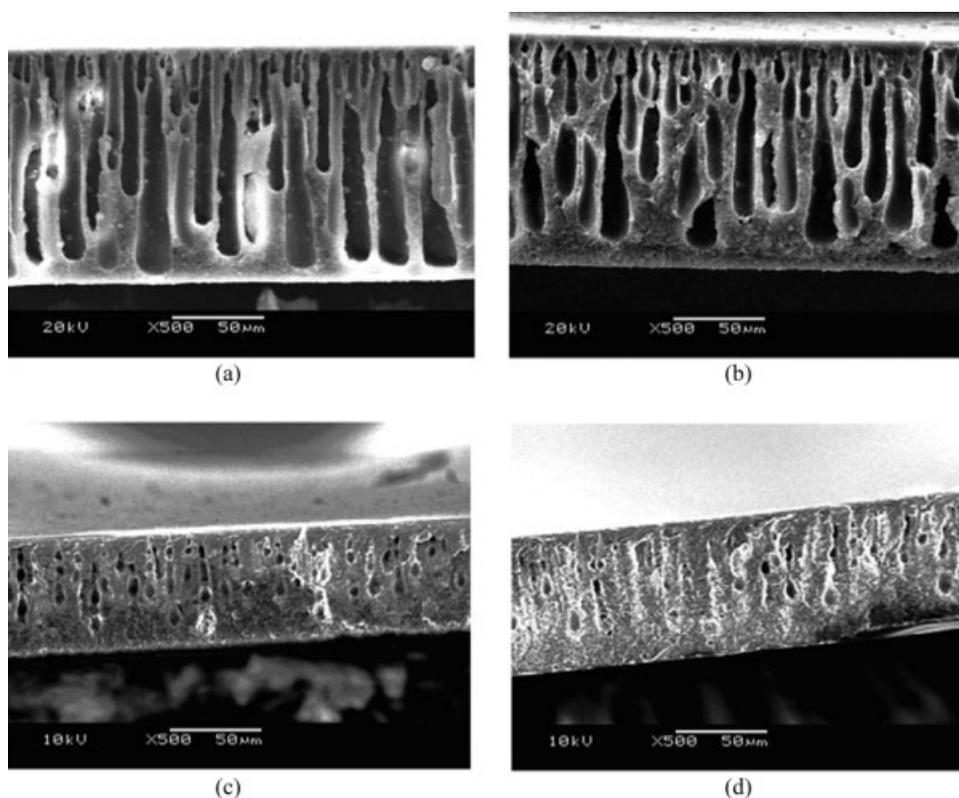


Figure 4 Effect of the THF concentration on the QAPPESK NF membrane cross-section morphology: (a) 10, (b) 20, (c) 30, and (d) 40 wt %.

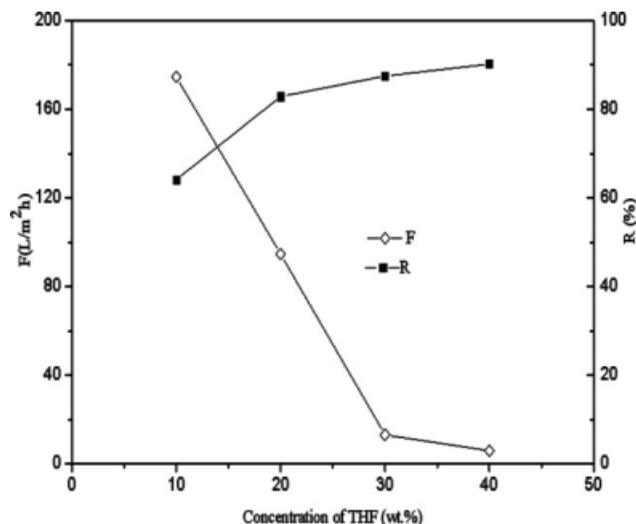


Figure 5 Effect of the THF content on the QAPPESK NF membrane performance (test conditions: 1.0 MPa and 23°C).

with increasing EE content. Therefore, the MgCl_2 rejection rose, whereas the flux decreased.

Effect of the THF additive

The SEM photographs in Figure 4 show the cross-section morphologies of QAPPESK NF membranes

with different THF contents. When the THF concentration increased from 10 to 20 wt %, the top layer became thicker. With the increase in the THF concentration from 20 to 30 wt %, the number and size of the fingerlike pores decreased, and they were replaced by a spongelike structure. As the THF concentration increased further, the change in the cross-section morphology was not obvious.

THF is a weak nonsolvent in a CMPPEK/solvent (8/2 NMP/DMAc)/THF system. The casting solution still remained stable when the concentration of THF was 40 wt %. THF (boiling point = 65.4°C) was easier to volatilize, and the volatilization also became a dominant factor. With the increase in volatilized THF, the surface layer became denser. Thus, the dense top layer increased the barrier, delayed the phase separation, and formed a thicker spongelike structure in the support layer. However, when the THF concentration was more than 30 wt %, the volatilization quantity of THF was almost invariable in the same evaporation period. Therefore, the degree of density of the surface layer changed slightly and took on a similar cross-section morphology.

The performance of QAPPESK NF membranes with different THF contents is shown in Figure 5. With an increase in the THF content in the casting solution, the MgCl_2 rejection increased from 64 to

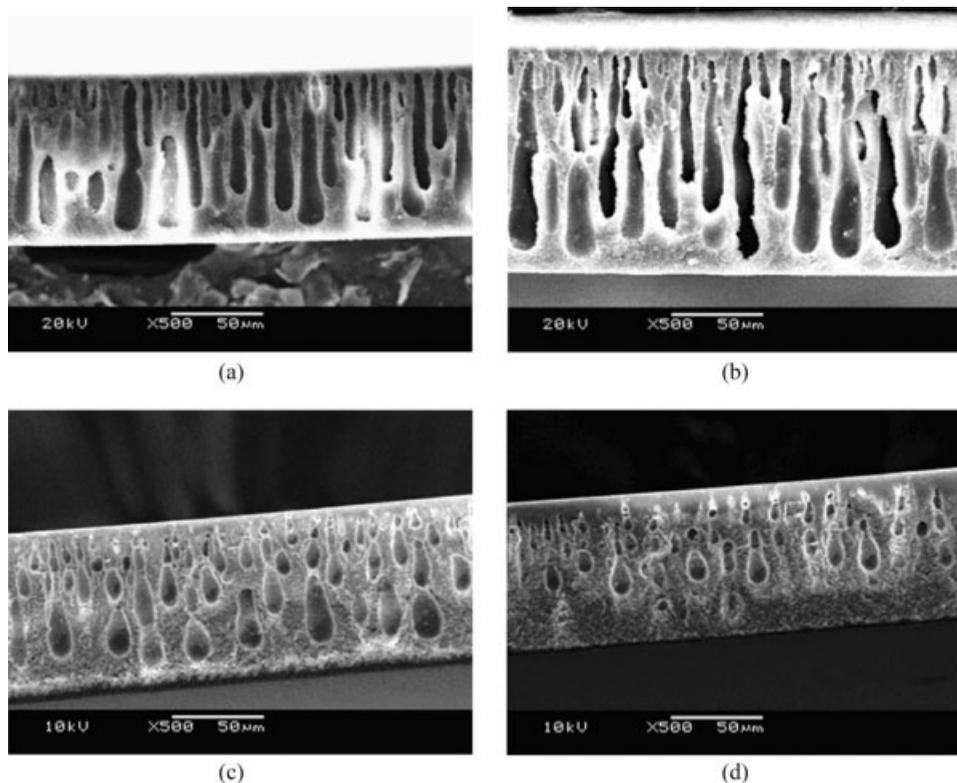


Figure 6 Effect of the DO concentration on the QAPPESK NF membrane cross-section morphology: (a) 10, (b) 20, (c) 30, and (d) 40 wt %.

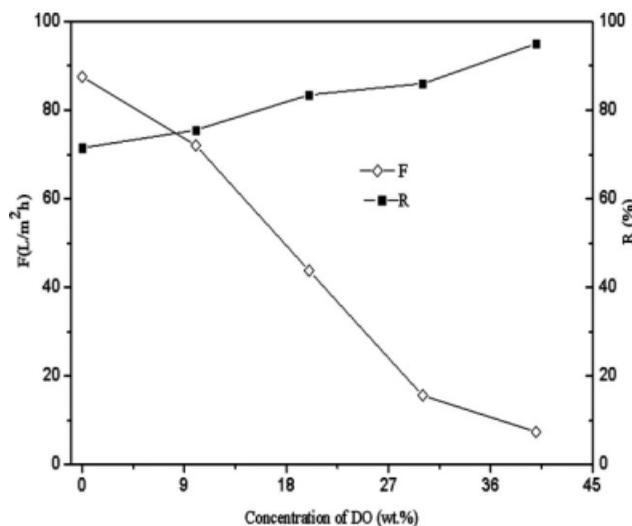


Figure 7 Effect of the DO concentration on the QAPPESK NF membrane performance (test condition: 20°C).

90%, and the flux decreased from 175 to 6 L/m² h. The performance of the membrane was decided by the structure of the membrane. With an increase in the THF concentration from 10 to 30 wt %, the surface layer of the membrane became denser, and the large, fingerlike macrovoids gradually disappeared. Instead, spongelike structure cross sections appeared, and the permeation resistance of the membrane

increased. Therefore, the rejection increased gradually, whereas the flux decreased dramatically. When the concentration of THF was more than 30 wt %, the decrease in the flux was not obvious.

Effect of the DO additive

The effects of the DO content on the cross-section morphologies of the membranes are shown in Figure 6. The cross sections of QAPPESK NF membranes changed from the fingerlike structure to the spongelike structure gradually with an increase in the DO content in the casting solution.

The explanation is also similar to that for THF. However, the volatility of DO is poorer than that of THF, and the volatilization quantity of DO increases with the content of DO. Thus, the surface layer of the membrane became denser and denser, and this increased the resistance of the surface layer and delayed the time of phase separation. Therefore, the fingerlike structures were replaced entirely by the spongelike structures when the concentration of DO was 40 wt %.

Figure 7 shows the effect of the DO content on the QAPPESK NF membrane performance. The MgCl₂ rejection increased from 72 to 95% and the flux decreased from 88 to 7 L/m² h with an increase in the DO content in the casting solution. The SEM photographs in Figure 7 provide a better explanation,

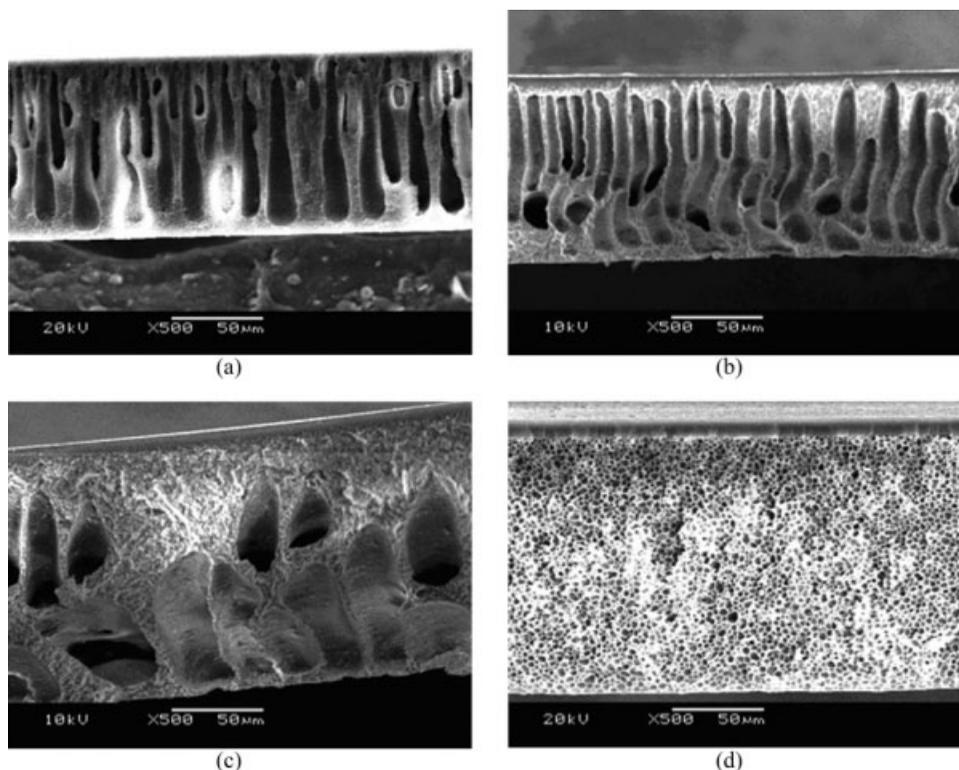


Figure 8 Effect of the DEG concentration on the QAPPESK NF membrane cross-section morphology: (a) 0, (b) 5, (c) 10, and (d) 15 wt %.

TABLE III
Effect of the DEGC Content on the QAPPESK NF Membrane Performance

| DEGC concentration (wt %) | Rejection (%) | Flux (L/m ² h) |
|---------------------------|---------------|---------------------------|
| 0 | 72 | 88 |
| 5 | 75 | 78 |
| 10 | 78 | 59 |
| 15 ^a | 93 | 11 |

The test conditions were 20°C and 0.4 MPa.

^a The operating pressure was 1.0 MPa.

showing that the changes in the morphology led to different membrane performances.

Effect of the DEGC additive

In this experiment, DEGC was also selected as an additive. As shown in Figure 8, the cross-section morphology of the membrane from DEGC exhibited a tendency similar to that of the membrane from DO. The cross-section morphology of the membrane was controlled not only by thermodynamic factors but also by kinetic factors. The casting solution became stickier with an increase in the DEGC concentration, and this limited the exchange rate of the solvent into water and surface solidification. Thus, the phase-separation time was delayed, and the surface layer became denser, forming the spongelike structure. However, the DEGC concentration could not be more than 15 wt % in a CMPPEK/solvent (8/2 NMP/DMAc)/DEGC system because the casting solution would be too sticky to form a smooth membrane.

Table III shows the effect of the DEGC content on the QAPPESK NF membrane performance. The MgCl₂ rejection increased gradually and the flux decreased significantly with increasing DEGC con-

centration. The results were decided by the different morphology of the membrane.

Thermal stability of the QAPPESK NF membrane

The thermal stability of the QAPPESK NF membrane was tested, as shown in Figures 9 and 10. Figure 9 shows the effect of the operating temperature on the QAPPESK NF membrane performance. Figure 10 shows that the MgCl₂ rejection increased from 83 to 88% when the solution temperature rose from 14 to 35°C and then declined from 88 to 75% when the temperature further increased to 85°C. In addition, the solution flux increased from 33 to 128 L/m² h as the operating temperature rose from 14 to 85°C. When the temperature decreased back to 14°C, the salt rejection and water flux changed slightly in comparison with the original value.

To examine the long-time thermal stability of the QAPPESK NF membranes, the membrane performance was tested at 60°C for 120 h, as shown in Figure 10. The QAPPESK NF membranes showed stable performance for 120 h. This indicated that the QAPPESK NF membranes had good thermostability.

CONCLUSIONS

Positively charged QAPPESK NF membranes were prepared successfully from CMPPEK (sulfone/ketone ratio = 8/2). The optimum preparation parameters were determined according to the orthogonal design method as follows: an NMP/DMAc ratio of 2/8, an evaporation time of 5 min at 70°C, and a coagulation temperature lower than 5°C. The membranes with EE, THF, DO, and DEGC as additives displayed better performance. The effects of different additive contents on the membrane morphology and

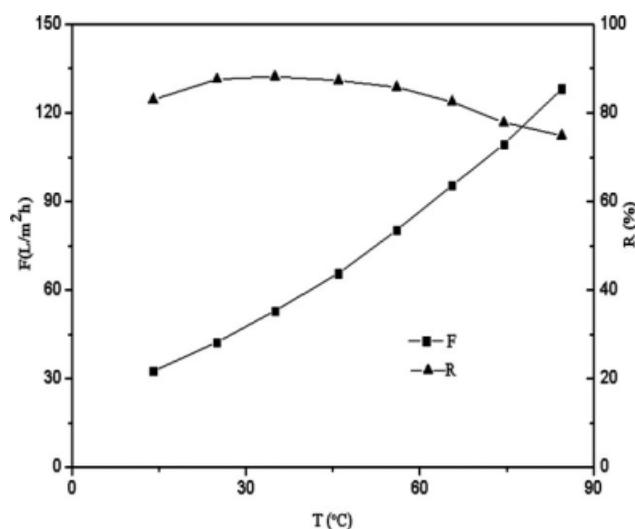


Figure 9 Effect of the operating temperature on the QAPPESK NF membrane performance.

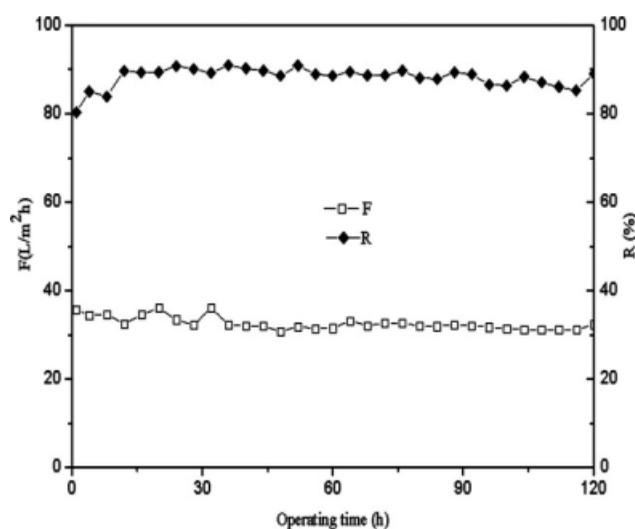


Figure 10 Effect of the operating time on the QAPPESK NF membrane performance (test condition: 60°C).

performance were examined. The results showed that the $MgCl_2$ rejection increased and the solution flux decreased with increasing contents of the additives. The SEM images illustrated that the membranes exhibited a spongelike structure when the additives were added beyond a certain content. Furthermore, QAPPESK NF membranes exhibited good thermal stability. When the operation temperature rose from 14 to 85°C, the flux increased by nearly 4 times with only a slight reduction of rejection. The QAPPESK NF membranes showed stable performance for 120 h at 60°C.

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