Influence of hexamethyl phosphoramide on polyamide composite reverse osmosis membrane performance

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ABSTRACT

In order to improve the performance of polyamide thin-film-composite (TFC) reverse osmosis membranes, hexamethyl phosphoramide (HMPA) was used as an additive in the aqueous polyamine solution during the interfacial polymerization. The addition of HMPA facilitated the diffusion rate of MPD from the aqueous phase to the organic phase resulting in a thicker reaction zone. HMPA could also increase the reaction rate between m-phenylenediamine (MPD) and trimesoyl chloride (TMC). X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy revealed that both the thickness and the cross-linking extent of the polyamide skin layer increased when more HMPA was added. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) revealed that membrane surface morphology changed with increasing HMPA concentration. The contact angle measurement results revealed that the membrane surface became more hydrophilic due to the addition of HMPA. The flux and salt rejection of MH-3 membrane (3 wt% HMPA addition) reached 51.67 L/m² h and 98.27%, respectively, for 2000 mg/L NaCl under 1.55 MPa. The flux increased by 73% and the salt rejection loss was less than 0.21% compared with the non-additive membrane. Colloidal silica fouling experiments suggested that the average peak-valley distance and average peak spacing width on the membrane surface could be used as important parameters to explain fouling behavior.

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ARTICLE INFO

Article history:
Received 6 February 2010
Received in revised form 29 July 2010
Accepted 9 August 2010

Keywords:
Thin-film-composite membrane
Reverse osmosis
Morphology
Hexamethyl phosphoramide
Colloidal fouling

1. Introduction

Since Cadotte developed the thin-film-composite (TFC) reverse osmosis (RO) membrane, FT-30, for seawater desalination in 1980 [1], TFC membranes have been extensively used in many fields such as desalination of seawater and brackish water, ultrapure water production, wastewater treatment and separation of organics from aqueous streams [2–10]. A great variety of TFC membranes have been successfully developed from polymer materials such as polyurea, polyamide, polyether, polyurea-amide, but the most commercially successful one is the aromatic polyamide TFC membrane fabricated through interfacial polymerization of m-phenylenediamine (MPD) in the aqueous phase with trimesoyl chloride (TMC) in the organic phase on the top surface of a microporous polysulfone support that provides mechanical support to the skin layer [11–13]. The performance of TFC membranes, including permeability, selectivity and antifouling performance mainly depends on the ultra-thin skin layer.

Over the years, many efforts have been made to improve TFC membrane permeate flux or/salt rejection. In general, the strategies include the following: the first is to develop new skin layer materials [13–16]; the second is modification by post treatment with various chemicals such as acids, alcohol, oxidants and alcohol amines [17–20]; the third is to modify the polymer chains by using additives in the aqueous solution or/and in the organic solution during the interfacial polymerization [21–23]. Among the three strategies, developing new materials for skin layer is the hardest work. By contrast, the remaining two strategies are much easier to achieve.

Previous studies have revealed that using polar aprotic solvents in the aqueous solution could enhance flux of TFC membranes [24,25]. Polar aprotic solvents are those solvents whose dipole moments are larger than 2.5 D but lack acidic hydrogen. Generally, this sort of solvent contains electronegative oxygen atom (\(\text{O}^{-}\), \(\text{S}^{-}\), \(\text{P}^{-}\)) and has high polarity. The typical polar aprotic solvents are N-methylpyrrolidone (NMP), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and hexamethyl phosphoramide (HMPA). In the structure of the polar aprotic solvent, electronegative oxygen atom can combine with a reagent molecule to form a highly active anion, but its electropositive part hides inside the molecule with big steric hindrance which makes it dif-
difficult to solvate the anion. As a result, bimolecular nucleophilic substitution (SN2) reaction can be greatly accelerated in polar aprotic solvents. The reaction between MPD and TMC is a representative SN2 reaction, and thus using polar aprotic solvents in the aqueous solution during the interfacial polymerization reaction can accelerate the film-forming rate. It was reported that using polar aprotic solvents in the aqueous solution could enhance membrane permeate flux without a considerable loss of salt rejection as well as change the membrane surface morphology. Chau [24] reported that the membrane surface with NMP or DMF in the aqueous phase was smoother than those membranes made without using polar aprotic solvents. Kwak and his colleagues [25] found that the adhesion of DMSO in the aqueous solution could increase membrane surface roughness. However, using HMPA as an additive has not been reported in the literature. HMPA has the greatest polarity among these polar aprotic solvents, which means that it has the strongest effect on accelerating the film-forming rate.

Membrane fouling is an inevitable phenomenon during the application of RO technology and it always results in decreased product quantity and deteriorated product quality. Colloidal fouling is considered as one of the most common fouling problems, because small colloidal particles are ubiquitous in natural waters [26]. Many studies have shown that membrane surface morphology and hydrophilicity play a significant role in colloidal fouling [26–29]. Elimelech et al. [26,27] reported that colloidal fouling of RO and NF membranes were nearly perfectly correlated with membrane surface roughness, regardless of physical and chemical operating conditions. Boussu et al. [28] suggested that the most pronounced colloidal fouling was observed for the hydrophobic membranes and that membrane roughness also plays a secondary role during the filtration of small colloids. Hoek et al. [29] found that both the resistance of colloidal deposit and the cake-enhanced osmosis pressure contributed significantly to the flux decline in colloidal fouling of RO and NF membranes. Although numerous studies have been carried out for several decades, the fouling mechanism has not been entirely understood due to its complexity.

To mitigate fouling, pretreatment of the feed water and periodic cleaning of fouled membranes are frequently implemented. However, these measures cannot solve the fouling problem completely. As a result, developing antifouling RO membrane is attractive. So far, surface modification is considered as the most effective way to prepare fouling-resistant membranes by changing membrane surface morphology or improving membrane surface hydrophilicity. Water-permeable polymers such as polyether–polyamide block copolymer and cross-linked poly(ethylene glycol)-based hydrogels have been successfully used as coatings to fabricate antifouling RO membranes with smooth membrane surfaces [30,31]. Surface modification by grafting hydrophilic polymers such as poly (ethylene glycol) was also developed to improve membrane antifouling performance [32]. However, neither of the above methods can obtain antifouling performance without causing a significant decrease in flux due to resistance of the additional layer. Therefore, our objective is to improve membrane antifouling performance without sacrificing membrane flux and investigate the relationship between membrane surface morphology and its antifouling performance.

In this study, HMPA was used as an additive in the aqueous solution to prepare polyamide TFC membranes with enhanced flux and good salt rejection, which has not been reported. The addition of HMPA influenced the forming rate of polyamide layer and its chemical composition. Membrane surface morphology and hydrophilicity also changed. It was found that different HMPA concentrations led to membrane morphology with different peak-valley distance and peak spacing width which might affect their antifouling performance. As a result, colloidal silica fouling experiments in laboratory scale were conducted to investigate the relationship between surface morphology and its antifouling performance.

2. Experimental

2.1. Materials and chemicals

The microporous polysulfone membrane was obtained from Vontron Membrane Technology Co., Ltd., China. The key monomers m-phenylenediamine (MPD) and trimethyl chloride (TMC) were purchased from Aladdin Reagent Co., Ltd., China (purity >99%) and Qingdao Benzo Chemical Co., Ltd., China (purity >99%), respectively. Hexamethyl phosphoramide (HMPA) was of analytical grade and purchased from Aladdin Reagent Co., Ltd., China. Other reagents were of analytical grade unless otherwise specified, and used without further purification.

Commercial colloidal silica (M-5, Cabot Chemical Co., Ltd.) was used as a model colloidal foulant. The colloidal silica was supplied in a powder form and was used as obtained. Colloidal silica suspension was prepared by dispersing silica powder in deionized water (conductivity <3μS/cm) through intense stirring for 1 h and then ultrasonication for 6 h. The mean hydrodynamic diameter of the colloidal silica was approximately 250 nm determined by dynamic light scattering (BI200SM, Brookhaven, US).

2.2. Membrane preparation

Aromatic polyamide TFC membranes were prepared through interfacial polymerization between MPD in the aqueous solution and TMC in the organic solution (n-hexane). Triethylenamine (TEA) and camphor sulfonic acid (CSA) were added into the aqueous solution to adjust the pH value of the solution. Sodium dodecyl sulfate (SDS) was used to improve the wettability of the top surface of the polysulfone support by the aqueous MPD solution. HMPA was added in the aqueous solution, with four different concentrations of 1.0, 2.0, 3.0 and 4.0 wt%, respectively (refer to Table 1).

First, the MPD aqueous solution was contacted with the top surface of the polysulfone support for 1 min, followed by removing the excess solution and blowing the coated surface with an airknife until no residual liquid. Afterwards, TMC solution was coated thereon and reacted for 1 min. Finally, the excess organic solution was removed and the resulting membrane was heated in an air-circulated dryer at 80 °C for 5 min. Any significant defects on the membrane surface were made visible by spraying the membrane with a dye solution containing rhodamine B (500 mg/L), which preferentially stained polysulfone red in any regions where the polyamide layer incompletely covered the polysulfone support [33]. The dyed membrane was washed thoroughly with tap water until no color was visible. Those almost defect-free samples were selected and washed completely with deionized water and stored in NaHSO3 solution (0.5 wt%) until their RO performance evaluation and fouling experiments were conducted. The membrane samples for other characterization were stored in deionized water. The MPD–TMC TFC membrane without HMPA addition was also prepared for a comparison purpose. All above operations were performed in laboratory scale to investigate the antifouling performance.

In Table 1, Compositions of aqueous and organic solutions for the TFC membranes, the aqueous solution consists of MPD, HMPA, TEA, and CSA at different concentrations, while the organic solution contains TMC and SDS at different concentrations. The membrane samples were characterized by measuring the performance at the initial stage of RO operation. The results of these experiments are presented in Table 2, which shows the changes in flux, salt rejection, and antifouling performance before and after the addition of HMPA.

Table 1: Compositions of aqueous and organic solutions for the TFC membranes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aqueous solution (wt%)</th>
<th>Organic solution TMC (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPD</td>
<td>HMPA</td>
</tr>
<tr>
<td>MH-0</td>
<td>2.0</td>
<td>0</td>
</tr>
<tr>
<td>MH-1</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>MH-2</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>MH-3</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>MH-4</td>
<td>2.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

In the first set of experiments, the aqueous solution contained MPD and HMPA at different concentrations, while the organic solution contained TMC and SDS at different concentrations. The table shows the water permeability and salt rejection of the membrane samples at different conditions. The results indicate that the addition of HMPA significantly improved the flux and reduced the salt rejection, which suggests that HMPA has a positive effect on antifouling performance. The results also show that the addition of HMPA at higher concentrations resulted in better performance, indicating that the optimal concentration of HMPA is between 2.0 and 4.0 wt%.
conducted in a clean room and the temperature was maintained at 20 ± 1 °C with a relative humidity of 50–60%. The HMPA additive membranes are referred to as MH-1, MH-2, MH-3, MH-4 and the non-additive membrane is referred to as MH-0.

2.3. Diffusion kinetics

Ultraviolet–visible (UV–vis) spectroscopy (DH-2000, Ocean Optics) was used to characterize the diffusion rate of MPD without and with different HMPA concentrations from the aqueous phase to the organic phase. First, a total volume of 0.5 ml aqueous solution (MPD: 0.2 wt%, HMPA: 0, 1.0, 2.0, 3.0 and 4.0 wt%, respectively) was added into the bottom of a cuvette with a microsyringe carefully and the liquid–air interface was below the light source. Then 1.0 ml hexane was injected immediately into the cuvette to overlay the aqueous layer and Spectra Suite Spectrometer Operating Software was started simultaneously to record UV absorption spectra. Each diffusion process was conducted for 10 min. MPD has two characteristic absorption bands, K band (240 nm) and B band (288 nm) in the ultraviolet region, whereas HMPA has only K band (234 nm). When MPD and HMPA coexist in hexane, their K bands overlap to yield one K band. Thus, the B band of MPD was chosen to characterize the MPD concentration variation in hexane. The average value of absorbance was obtained from three diffusion processes for each HMPA concentration. The relative error was smaller than 3%.

2.4. Chemical characterization

Chemical composition of the TFC membrane surface was characterized by X-ray photoelectron spectroscopy (XPS) (PHI-1600, USA) using Mg Kα X-ray source. The electron emission angle was set at 45° to give a sampling depth of <100 Å. XPS spectra were analyzed through PHI-MATLAB software package. Chemical structure of the skin layer was characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy using an FTS-6000 system with a germanium crystal at a 45° angle of incidence, providing a penetration depth of approximate 600 nm. The membrane samples were removed from storage in deionized water and completely dried under vacuum before XPS and ATR-FTIR characterization.

2.5. SEM and AFM

Scanning electron microscopy (SEM) images of the surface and the cross-section for the TFC membranes were obtained on Nova NanoSEM 430 (FEI, USA). For the cross-section observation, the membrane samples were frozen in liquid nitrogen and fractured. All membrane samples were coated with gold by a sputter-coating machine.

Surface morphology of the TFC membranes was performed by atomic force microscopy (AFM) (Aí-IIIa, China) using tapping mode in air. Scanning area was 10 μm × 10 μm and scanning rate was set to 1 Hz. The surface roughness is reported in terms of the average roughness ($R_a$), root mean square roughness ($R_{rms}$) and relative surface area ($\Delta$) (actual surface area divided by the projection area [34]). All the surface roughness values presented were an average data obtained from five membrane samples for MH-0, MH-1, MH-2, MH-3 and MH-4 membrane, respectively. The membrane samples were removed from storage in deionized water and completely dried under vacuum before SEM and AFM characterization.

![Fig. 1. Effect of HMPA concentration on the absorbance variation of MPD in hexane.](image)

![Fig. 2. Chemical structure of the skin layer of aromatic polyamide TFC membrane.](image)

![Fig. 3. ATR-FTIR spectra of the aromatic polyamide TFC membranes.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>O (%)</th>
<th>N (%)</th>
<th>N/O</th>
</tr>
</thead>
<tbody>
<tr>
<td>MH-0</td>
<td>74.0</td>
<td>15.6</td>
<td>10.4</td>
<td>0.667</td>
</tr>
<tr>
<td>MH-1</td>
<td>72.9</td>
<td>15.5</td>
<td>11.6</td>
<td>0.748</td>
</tr>
<tr>
<td>MH-2</td>
<td>73.1</td>
<td>15.2</td>
<td>11.7</td>
<td>0.770</td>
</tr>
<tr>
<td>MH-3</td>
<td>73.2</td>
<td>15.0</td>
<td>11.8</td>
<td>0.787</td>
</tr>
<tr>
<td>MH-4</td>
<td>73.4</td>
<td>14.8</td>
<td>11.8</td>
<td>0.797</td>
</tr>
</tbody>
</table>

Theoretical values:
- Fully cross-linked: 75.0, 12.5, 12.5, 1.0
- Fully linear: 71.4, 19.1, 9.5, 0.5
2.6. Static contact angle measurement

The hydrophilicity of membrane surface was characterized based on water contact angle measurement with sessile drop method. Contact angles were measured at room temperature by a contact angle goniometer (OCA15EC, Dataphysics, Germany) equipped with a video camera. A total of 2 µL deionized water droplet was placed on a dry membrane surface using a motor-driven microsyringe. SCA 202 software was used to calculate the static contact angle. The sample preparation for contact angle measurement was as follows. Firstly, the membrane samples were soaked in 15 vol.% ethanol for 10 min at 50 °C and then washed completely with deionized water. Next, the membrane samples were soaked in deionized water for 24 h and changed water three times to remove the residual chemicals as much as possible. The contact angles of all the membrane samples were measured immediately after they were completely dried under vacuum and cooled to room temperature. In order to minimize the inaccuracy of measurement, at least eight contact angles on different locations of the membrane samples were averaged to get a reliable result.

Fig. 4. SEM images of the TFC membranes: MH-0 (a, b), MH-1 (c, d), MH-2 (e, f), MH-3 (g, h), and MH-4 (i, j).
2.7. RO performance evaluation

The RO performance for all the TFC membranes was conducted with 2000 mg/L NaCl solution at a pressure of 225 psi (1.55 MPa) in a cross-flow membrane filtration unit. The system has been depicted in our previous paper [35]. A high-pressure pump delivered the feed solution from a 10 L vessel into the membrane cell. The pressure and cross-flow rate were controlled by a bypass valve and a back-pressure valve at the inlet and outlet of the membrane cell, respectively. The feed solution temperature was controlled at 25 ± 0.1 °C by a circulating chiller. The membrane samples (effective area: 17.34 cm²) were soaked in deionized water for at least 2 h and changed water every 30 min before tested. The steady flux was obtained after running for at least 1 h. The flux was determined by directly measuring the permeate weight and recorded in real time on a laboratory computer. The salt concentrations of the feed and the permeate were measured using a conductivity meter (DDSJ-308A, Cany Precision Instrument Co., Ltd., China). The salt rejection was calculated using the following equation:

\[ R(\%) = \left(1 - \frac{c_p}{c_f}\right) \times 100 \]

in which \(c_p\) is the permeate conductivity and \(c_f\) is the feed conductivity. All the results presented were an average data obtained from four membrane samples for MH-0, MH-1, MH-2, MH-3 and MH-4 membranes, respectively.

2.8. Fouling experiments

Membrane samples were soaked in deionized water for at least 2 h and changed water every 30 min prior to loading onto the filtration unit. The fouling experiments were conducted in a cross-flow filtration unit (see Section 2.7). The protocol for all colloidal fouling experiments was as follows. Firstly, a membrane sample was pre-pressured with deionized water at a pressure of 225 psi (1.55 MPa) for at least 1 h until a steady flux was achieved. Next, 4 L electrolyte solution (10 mM NaCl) was used as the feed solution and circulated until a steady flux was obtained. The operating pressure was adjusted to obtain the predetermined initial flux. After the initial flux stabilized, 2 L colloidal silica suspension (600 mg/L) and 1.17 g sodium chloride were added to the feed tank to provide 6 L suspension containing 200 mg/L colloidal silica and 10 mM NaCl. The pH value of the feed was 6.8 ± 0.2. The temperature in all experiments was fixed at 25 ± 0.1 °C and the cross-flow rate was kept at 1.0 L/min. The flux was monitored continuously during the fouling experiment and recorded in real time on a laboratory computer. The retentate was circulated to the feed tank.

3. Results and discussion

3.1. Diffusion kinetics

The absorbance of MPD at B band with time is shown in Fig. 1. It can be seen that the absorbance of MPD becomes stronger which
means higher concentration of MPD in hexane when more HMPA is added in the aqueous solution. This suggests that HMPA can accelerate significantly the diffusion rate of MPD from the aqueous phase to the organic phase. And the higher the HMPA concentration in the aqueous solution is, the faster the diffusion rate of MPD from the aqueous phase to the organic phase. The addition of HMPA induces more MPD molecules to transfer into the organic phase resulting in a thicker reaction zone. The role of HMPA in facilitating diffusion of MPD is attributed to the ion pairs formed between HMPA and MPD molecules in the aqueous phase. These ion pairs can cross the liquid–organic interface easily due to their lipophilic nature. Besides, HMPA can increase the reaction rate between MPD and TMC. In the organic phase the MPD-HMPA ion pairs undergo a nucleophilic displacement reaction with TMC to form polyamide. The resulting chloride ions form new ion pairs with HMPA and return to the aqueous phase and the cycle continues [36,37]. As a result, the cross-linking extent and thickness of the polyamide skin layer increase due to the addition of HMPA in the aqueous solution during the interfacial polymerization, which can be demonstrated by XPS, ATR-FTIR and SEM results (see Sections 3.2 and 3.3).

3.2. Chemical structure of TFC membranes

The chemical structure of the skin layer of the TFC membrane is presented in Fig. 2, which consists of the fully cross-linked portion and the fully linear portion containing pendant carboxylic acid.

Table 3
Analysis of peak areas for the TFC membranes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A1 (1663 cm⁻¹)</th>
<th>A2 (1609 cm⁻¹)</th>
<th>A3 (1541 cm⁻¹)</th>
<th>A4 (1587 cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MH-0</td>
<td>0.764</td>
<td>0.141</td>
<td>0.431</td>
<td>0.642</td>
</tr>
<tr>
<td>MH-1</td>
<td>1.033</td>
<td>0.218</td>
<td>0.640</td>
<td>0.477</td>
</tr>
<tr>
<td>MH-2</td>
<td>1.106</td>
<td>0.234</td>
<td>0.776</td>
<td>0.459</td>
</tr>
<tr>
<td>MH-3</td>
<td>1.350</td>
<td>0.306</td>
<td>0.993</td>
<td>0.415</td>
</tr>
<tr>
<td>MH-4</td>
<td>1.466</td>
<td>0.352</td>
<td>1.186</td>
<td>0.359</td>
</tr>
</tbody>
</table>

Table 4
Surface roughness analysis and contact angles of the TFC membranes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rₜ (nm)</th>
<th>Rₚₑₘ (nm)</th>
<th>Δ</th>
<th>Contact angle, θ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MH-0</td>
<td>46.9 ± 2.4</td>
<td>58.5 ± 2.0</td>
<td>1.29 ± 0.01</td>
<td>62.1 ± 2.5</td>
</tr>
<tr>
<td>MH-1</td>
<td>56.9 ± 1.2</td>
<td>71.8 ± 1.4</td>
<td>1.35 ± 0.02</td>
<td>45.9 ± 3.4</td>
</tr>
<tr>
<td>MH-2</td>
<td>58.3 ± 1.8</td>
<td>73.6 ± 1.6</td>
<td>1.36 ± 0.02</td>
<td>45.4 ± 3.1</td>
</tr>
<tr>
<td>MH-3</td>
<td>58.4 ± 1.7</td>
<td>75.9 ± 1.6</td>
<td>1.28 ± 0.01</td>
<td>42.8 ± 4.1</td>
</tr>
<tr>
<td>MH-4</td>
<td>60.1 ± 1.6</td>
<td>76.1 ± 1.7</td>
<td>1.36 ± 0.01</td>
<td>40.3 ± 4.2</td>
</tr>
</tbody>
</table>

a Average value ± standard deviation.

Fig. 5. Skin layer thicknesses of the TFC membranes.

Fig. 6. Typical vertical height profiles of the TFC membranes by AFM: MH-0 (a), MH-1 (b), MH-2 (c), MH-3 (d), and MH-4 (e).
to both the N–H in-plane bending and the C–N stretching vibration. The band at 1609 cm\(^{-1}\) is ascribed to polyamide aromatic ring breathing. The band at 1587 cm\(^{-1}\) is one of characteristic bands for polysulfone. The areas of the four peaks (A1, A2, and A3 for polyamide, A4 for polysulfone) of all the TFC membranes were calculated and listed in Table 3. The areas of three peaks (1663, 1609, and 1541 cm\(^{-1}\)) for polyamide increase with increasing HMPA concentration. This indicates that more polyamide deposits over the polysulfone support with increasing HMPA concentration. The peak area of 1587 cm\(^{-1}\) for polysulfone decreases with increasing HMPA concentration. This also suggests that a thicker polyamide skin layer is formed over the polysulfone support, and thus shortens the penetration depth of radiation into the polysulfone support and results in a smaller peak area for the polysulfone support. Combined with the XPS results, it can be inferred that the addition of HMPA leads to an increase in both the thickness and the cross-linking extent of the polyamide skin layer. The increase in the thickness of the polyamide skin layer can be demonstrated by SEM results (see Section 3.3).

3.3. Morphology of TFC membranes

Representative surface morphology and cross-section structures of the TFC membranes formed with different HMPA concentrations in the aqueous solution are shown in Fig. 4. It can be seen that MH-0 membrane surface exhibits ring-like ridges. However, with the increase of HMPA concentration, the membrane surface morphology develops from leaf-like structure to rough irregular clusters. In the representative cross-section images, the interface between the polyamide skin layer and the polysulfone support has been marked using a black bar. The skin layer thickness of each membrane (MH-0, MH-1, MH-2, MH-3, and MH-4) was measured from five membrane samples, and for each sample, ten positions were measured. Fig. 5 shows the average values of skin thickness distri...
layer thickness and their standard deviations (50 positions for each membrane). It can be seen that the average skin layer thickness gradually increases from 180 nm (MH-0) to 290 nm (MH-4).

Membrane surface roughness in terms of the average roughness ($R_a$), root mean square roughness ($R_{ms}$) and relative surface area ($\Delta$) by AFM is reported in Table 4. The results suggest that $R_a$ and $R_{ms}$ values of the additive membranes are at least 10 and 13 nm higher than those of the non-additive membrane. As for additive membranes, higher HMPA concentration just causes a small increase in $R_a$ and $R_{ms}$ values. The relative surface areas of additive membranes are nearly identical with the exception of MH-3 membrane, whose lower relative surface area may be due to its wider peak spacing.

Fig. 6 shows the typical vertical height profiles along the horizontal line of the scanning area ($10\mu m \times 10\mu m$) for all the membranes. The definitions of peak-valley distance and peak spacing width are also presented in Fig. 6(a). The peak-valley distance and peak spacing width were measured from ten different vertical height profiles of five samples for each membrane (MH-0, MH-1, MH-2, MH-3, and MH-4). The distributions of peak-valley distance and peak spacing width for each membrane are shown in Figs. 7 and 8, respectively. The average values of peak-valley distance and peak spacing width for each membrane are also presented in these figures. It can be seen that the average peak-valley distance increases in order of MH-0 < MH-1 < MH-2 < MH-3 < MH-4. The average peak spacing width increases according to MH-0 < MH-1 < MH-2 < MH-4 < MH-3.

3.4. Hydrophilicity of TFC membranes

The lower contact angle means the greater tendency for water to wet the membrane surface and the better hydrophilicity. The contact angles of the TFC membranes are presented in Table 4. It can be seen that the contact angle decreases drastically from 62.1° to 45.9° when 1 wt% HMPA is added in the aqueous solution. The additive membranes have similar contact angles. The
wettability of a solid surface is governed by both the chemical composition and the surface geometrical structure [38]. According to the XPS results, the membranes with more HMPA addition should exhibit worse hydrophilic surfaces due to their higher cross-linking extent and less pendant carboxylic acid. Therefore, the increased hydrophilicity of the additive membranes might be caused by the increased roughness. However, according to Wenzel equation [39], the increase in relative surface area (Δ) (or roughness factor) shown in Table 4 can only cause a slight decrease in contact angle (less than 2°). This might be because the area of membrane surface obtained from AFM images is not the true area of the surface [34,40]. Moreover, we think that some residual chemicals in the membranes might also contribute to the decrease in contact angle. To find the exact reason for the decrease in contact angle needs further study.

3.5. RO performance of TFC membranes

The RO performance for all the TFC membranes is presented in Fig. 9. It can be seen that the addition of HMPA contributes much to flux enhancement. The optimum concentration of HMPA is 3 wt% which can provide membrane (MH-3) with the flux of 51.67 L/m² h while maintaining good salt rejection of 98.27%. The flux of MH-3 membrane increases by 73% and the salt rejection loss is less than 0.21% compared with the non-additive membrane (MH-0). In a previous study, it was reported that the membrane using NMP (2.0 wt%) as an additive showed 38% increase in flux and 0.1% loss in salt rejection [24]. It was also reported that using DMSO (2.0 wt%) as an additive led to more than threefold increase in flux and 3.42% loss in salt rejection [25]. By comparison, HMPA is a better choice to improve membrane flux while maintaining high salt rejection.

Kwak and his colleagues [25] found that the cross-linked polyamide layer was composed of two types of pores having radii of about 2.1–2.4 Å (network pore) and 3.5–4.5 Å (aggregate pore). The increase in size and number of network pores in the polyamide skin layer by adding DMSO during interfacial polymerization enhanced the permeability of water molecules across the membrane. They also inferred that the increase in size of aggregate pores led to larger defect pores that allow salt ions across the membrane, and as a result, the salt rejection decreased. Because HMPA and DMSO are both polar aprotic solvents, the addition of HMPA has the same effect as DMSO on increasing membrane flux and decreasing salt rejection. However, HMPA leads to less increase in flux and less decrease in salt rejection than DMSO. This might be because the size and number of network pores and the size of aggregate pores of TFC membranes with HMPA addition are smaller than those of TFC membranes with DMSO addition.

3.6. Fouling experiments

Because the membranes (MH-0, MH-1, MH-2, MH-3 and MH-4) had different membrane resistances, different operating pressures were applied to obtain the same initial flux (j0 = 35.0 L/m² h). The operating pressures for MH-0, MH-1, MH-2, MH-3 and MH-4 membranes were 227 psi (1.56 MPa), 180 psi (1.24 MPa), 163 psi (1.12 MPa), 160 psi (1.10 MPa) and 158 psi (1.09 MPa), respectively. The evolution of relative flux as a function of filtration time with different membranes is shown in Fig. 10. A short-term increase in flux is observed upon introduction of colloidal silica into the feed, which was attributed to the depolarization of the salt boundary layer due to the local mixing by the flowing layer of colloidal particles [41]. The flux decline percentage for a given filtration time (10 h) is in the following order: MH-1 (12.8%) < MH-2 (13.6%) < MH-0 (14.5%) < MH-3 (15.8%) < MH-4 (16.6%).

The results suggest that hydrophilicity of membrane surface is not the leading factor for colloidal fouling because MH-3 and MH-4 membranes have better hydrophilic surfaces than MH-0 membrane but their fouling is more severe. Moreover, conventional roughness parameters such as Rq, Rms and Δ are insufficient to explain the fouling behavior because the lower values of Rq, Rms and Δ for MH-0 membrane have not brought it better antifouling performance. According to the discussion in Section 3.3, the average peak-valley distance is from 161 to 242 nm and average peak spacing width is from 386 to 949 nm, which are of the same order of magnitude as the mean hydrodynamic diameter of the model colloidal silica (M-5, 250 nm). We think that the average peak-valley distance and average peak spacing width on the membrane surface are related to the membrane fouling behavior. On one hand, the wider peak spacing reduces the chance of colloidal silica depositing into the valley; on the other hand, the larger peak-valley distance makes the deposited colloidal silica difficult to be flushed out by the shear flow. From Figs. 7 and 8, it can be seen that the average peak-valley distance increases in order of MH-0 < MH-1 < MH-2 < MH-3 < MH-4 and the average peak spacing width increases in order of MH-0 < MH-1 < MH-2 < MH-4 < MH-3. Therefore, MH-1 and MH-2 membranes with smaller peak-valley
distance and wider peak spacing possess better antifouling performance. However, the results may be different when the size of colloidal silica is much bigger or smaller compared with the peak-valley distance or peak spacing width on the membrane surface. Therefore, further study needs to be conducted to investigate the fouling behavior of colloidal particles of different sizes.

4. Conclusions

Polyamide TFC RO membranes with improved performance were prepared by adding HMPA in the aqueous solution during the interfacial polymerization. The addition of HMPA facilitated the diffusion rate of MPD from the aqueous phase to the organic phase resulting in a thicker reaction zone. HMPA could also increase the reaction rate between MPD and TMC. As a result, the addition of HMPA led to an increase in both the thickness and the cross-linking extent of the polyamide skin layer, which could be seen from both the chemical analysis and membrane cross-section morphology. The membrane surface morphology developed from leaf-like structure to rough irregular clusters with increasing HMPA concentration. The peak-valley distance and peak spacing width on the membrane surface also changed. The membrane surface became more hydrophilic due to the addition of HMPA. The membranes with the addition of HMPA showed a large increase in flux and the optimum concentration is 3 wt% which can provide membranes with smaller average peak-valley distance and average peak spacing width on the membrane surface also related to the membrane fouling behavior. The wider peak spacing reduced the chance of colloidal silica depositing into the valley, and the larger peak-valley distance made the deposited colloidal silica difficult to be flushed out by the shear flow. It was found that MH-1 and MH-2 membranes with smaller average peak-valley distance and wider average peak spacing showed better antifouling performance.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20676095), the Program for New Century Excellent Talents in University, the Cheung Kong Scholar Program of China (No. 20676095), the Program for New Century Excellent Talents in University, and the Program of Introducing Talents of Discipline to Universities (No. B06006).

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