



## Study on a novel polyester composite nanofiltration membrane by interfacial polymerization. II. The role of lithium bromide in the performance and formation of composite membrane

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### ABSTRACT

Composite membranes were prepared by interfacial polymerization of trimesoyl chloride (TMC) with (i) triethanolamine (TEOA), and (ii) *N*-methyl-diethanolamine (MDEOA) on addition of various contents of LiBr in aqueous phase. The influence of LiBr in aqueous phase on the composite membrane performance and surface morphologies was investigated. For monomer TEOA, the pure water flux of composite membrane enhanced as the LiBr content increased and it reached a maximum at 3% of LiBr, then decreased. However, the extreme value of the salt rejection functioned with the content of LiBr changed to 1% (a turning point), at which the membrane displayed a lowest salt rejection. The change in performance of the composite membrane with the content of LiBr was due to the competition of two factors. One was the interaction of Li<sup>+</sup> ion with the hydroxyl oxygen atom of alcohol amine, which could induce an increase in the density and reactivity of OH groups in the aqueous phase, forming a dense skin layer of the composite membrane as a result. The other factor was the complexation of Li<sup>+</sup> ion with the carbonyl in TMC, causing the acid chloride group of TMC preferring to hydrolyze which could induce to construct a hydrophilic and loose surface layer. The role of LiBr in the formation of the composite membrane was further testified by investigating another monomer MDEOA. The analysis of the composite membrane formation in the presence of LiBr was validated by reaction coefficient, contact angle, streaming potential, SEM, and AFM.

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### 1. Introduction

Nanofiltration (NF) is a novel membrane separation technique developed in the 1980s based on reverse osmosis (RO) [1]. It is a pressure driven membrane process and is applicable for separating dissolved components having a molecular weight cutoff (MWCO) of about 200–1000 Da and molecular size of about 1 nm [2]. It can also be used to separate inorganic salts with much smaller size than pore size according to electrostatic repulsion [3]. Thus, NF technique is suitable for water purification, the separation of amino acids, peptides and antibiotics, the treatment of industrial effluents and organic solutions [4–6].

Most of NF membranes are thin-film composites by interfacial polymerization where a dense, ultra-thin selective layer is produced separately onto a porous support having good mechanical properties. As a result, the functions of the selective layer and the support are independently optimized [7]. The performance of

the composite membrane is determined by the chemistry and the preparation conditions of the ultra-thin selective layer [8]. Most of studies have focused on improving membrane performance by optimizing preparation parameters. These include parameters such as monomer concentration, partition coefficients of the monomers, reaction time and post-treatment [8–13]. Furthermore, additives in aqueous phase which can influence monomer solubility, diffusivity, hydrolysis, or protonation or to scavenge inhibitory reaction byproducts also play an important role in determining the structure of the interfacially polymerized film and subsequently the membrane performance [9,14]. For example, addition of small amounts of hydrophilic water-soluble polymer or a polyhydric alcohol to the amine solution can produce high-flux reverse osmosis membranes with good rejection [6,15,16]. Sodium hydroxide, dimethyl piperazine, triethylamine (TEA), and other acylation catalysts accelerate the *m*-phenylenediamine (MPD)–trimesoyl chloride (TMC) reaction by removing hydrogen halide formed during amide bond formation [9,17]. Among the additives, alcohols, ethers and sulfur-containing compounds are commonly used [18]. However, few studies have been performed using an inorganic salt as an additive in aqueous phase during the interfacial polymerization. In

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fact, addition of inorganic salt to the casting solution may be very effective in preparing membranes with high performance by casting method because they are considered to be able to change the solvent properties and/or the interaction between the molecule chains [19,20]. Kraus et al. found that salts contained in aromatic polyamide solutions had a considerable effect on the performance and structure of reverse osmosis membranes cast from these solutions [21]. Kim et al. studied the effect of  $ZnCl_2$  on the formation of polysulfone membrane and found the addition of  $ZnCl_2$  induced the intermolecular association of PSf chains, and consequently produced the ultrafiltration membrane having small pores without any significant change in porosity [19]. Recently, Idris et al. revealed that the presence of lithium halide as additives exhibited significant influence on the performance of membrane [22,23]. Among the three lithium halide additives investigated, LiBr seemed to improve the performance of the PES membranes tremendously. From this point of view, how will TFC membrane performance and morphologies be in the presence of the inorganic salt as an additive by the interfacial polymerization?

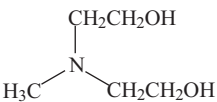
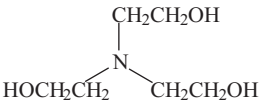
In our previous work, triethanolamine (TEOA), which is environmental-friendly, economical and easy to be obtained, was utilized as an active monomer of aqueous phase in preparation of thin-film composite (TFC) membrane [24]. A novel TFC membrane for nanofiltration was also developed by interfacial polymerization of TEOA and trimesoyl chloride (TMC) on the polysulfone supporting membrane. As a continuation, the influence of inorganic salt in aqueous phase on the composite membrane performance and surface morphologies was studied. In the present study, we firstly investigated the role of lithium bromine in the membrane formation during interfacial polymerization because the lithium halide additives were commonly used in the membrane preparation.

## 2. Experimental

### 2.1. Materials

The microporous polysulfone supporting membrane was supplied by the Development Center of Water Treatment Technology, Hangzhou (China). Triethanolamine (TEOA) and *N*-methyl-diethanolamine (MDEOA) (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were respectively used as an active monomer of aqueous phase. Table 1 shows the molecular structures of the alcohol amines used in the study. Trimesoyl chloride (TMC) (Qindao Sanli Chemical Engineering Technology Co., Ltd.) was used as an active monomer in the organic phase whereas *n*-hexane (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was utilized as an organic phase solvent. Lithium bromide monohydrate (LiBr·H<sub>2</sub>O) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Analytical grades of sodium dodecyl sulphate (SDS) (Wenmin Biochemistry Science and Technology Co., Ltd.), glycerol, Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, NaOH, and Na<sub>2</sub>CO<sub>3</sub> were used.

**Table 1**  
The molecular structure and abbreviation of the alcohol amine.

Abbreviation	Chemical name	Molecular structure
MDEOA	<i>N</i> -Methyl-diethanolamine	
TEOA	Triethanolamine	

### 2.2. Membrane preparation

The composite membranes were prepared by conventional interfacial polymerization technology. The fabrication process involved initial preparation of an aqueous phase solution: the alcohol amine (6% w/v), SDS (0.3% w/v) and LiBr (ranged from 0% to 7% w/v) were placed in deionized water with the pH adjusted to approximately 12 by a mixture of NaOH and Na<sub>2</sub>CO<sub>3</sub>, blended in 1:2 proportion; whereas the organic phase solution was composed of TMC (0.2% w/v) in *n*-hexane. Therefore, the microporous PSf supporting membrane was immersed into the aqueous phase for about 30 min at 35 °C. After removing excess liquids on the membrane surface, the membrane was further soaked in the organic phase for 35 min. Finally, the membrane was post-treated in an oven at 60 °C for about 30 min for further polymerization, leading to the formation of a skin layer. The resulting membranes were thoroughly washed with deionized water before carrying out evaluation studies.

### 2.3. Monomer characterization

#### 2.3.1. Preparation of TMC–LiBr complex

LiBr was ground into powder and dried in a vacuum oven at 100 °C for about 24 h to remove the water. And then, TMC and LiBr were mixed in molar proportion of 4:1 and warmed slowly at 40 °C to achieve a clear solution. After cooling to room temperature, complex of TMC–LiBr was obtained.

#### 2.3.2. Transmission FT-IR

The FT-IR spectra were recorded with a 4 cm<sup>-1</sup> spectra resolution on a Nicolet Nexus 470 spectrometer equipped with a DTGS detector by signal-averaging 64 scans. Two pieces of microscope CaF<sub>2</sub> windows, which have no absorption bands in the MIR region, were used to prepare a transmission cell. Before the measurements of transmission FT-IR, the TEOA, glycerol, and MEDOA aqueous solution containing various contents of LiBr was dropped onto the CaF<sub>2</sub> salt plate, respectively. TMC and the complex of TMC–LiBr were respectively blended with KBr powder, pressed into a tablet. The baseline correct processing was performed by the software of OMNIC 6.1.

#### 2.3.3. Viscosity and reaction coefficient

Viscosity of the TEOA and MDEOA aqueous solution with various contents of LiBr was determined using a viscosity meter (Cannon–Fenske Routine Viscometer) in a 35 °C water bath.

The reaction coefficient (*R*) is defined as the ratio of alcohol amine in organic phase to its concentration in water of a two-phase water/*n*-hexane after 35 min—the time over which interfacial polymerization reaction is evaluated. To obtain the reaction coefficient, a solution of 6% (w/v) alcohol amine (TEOA or MDEOA) and amount of LiBr in water was added to 20 mL of organic phase containing TMC in a separating funnel. After 35 min, the aqueous solution of alcohol amine was removed. The concentrations of alcohol amine in the aqueous solution before and after contact with the organic phase were determined by using ultraviolet-visible spectrophotometer (Lambda 35, PerkinElmer, USA).

### 2.4. Membrane characterization

#### 2.4.1. Pure water flux and rejection

The measurements of pure water flux and salt rejection were performed using a cross-flow membrane module as shown in our recent article [24], and it had a membrane effective area of 60 cm<sup>2</sup>. Before measurement, all the membranes were pretreated at a high pressure drop of 0.7 MPa for approximately 20 min. Then, the pure

water flux and rejection tests were conducted at an operation pressure of 0.6 MPa. The water flux was calculated in Eq. (1):

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

where  $V$  is the total volume of permeated pure water,  $A$  is the membrane area, and  $t$  is the operation time. Deionized water was used for this measurement. The rejections were measured using a 5 mmol/L  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  solution, respectively. The operation pressure was 0.6 MPa. The concentrations of the permeation and feed solutions were determined by electrical conductivity using an auto temperature compensation conductivity meter (HANA Model EC215, Italy). The rejection,  $R$ , was calculated in Eq. (2):

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

where  $C_p$  and  $C_f$  are the concentrations of the permeation and feed solutions, respectively.

#### 2.4.2. Streaming potential

The setup to determine streaming potential was almost similar to that described by our previous paper [24]. Reversible  $\text{Ag}/\text{AgCl}$  electrodes, placed on both sides of the membrane, were used to measure the resulting electrical potential difference ( $\Delta E$ ) as the pressure difference across the membrane ( $\Delta P$ ) changed through a digital electrometer (VC 890D, Shenzhen Victor Hi-tech Co. Ltd.). Then the streaming potential was calculated in Eq. (3):

$$\text{SP} = \frac{\Delta E}{\Delta P} \quad (3)$$

The pressure difference ranged from 0 to  $4 \times 10^5$  Pa. The 5 mol/m<sup>3</sup> KCl solution was put in the unit by  $\text{N}_2$  pressure controlled by a gauge.

#### 2.4.3. Contact angle measurement

Water was used as the probe liquid for determination of the hydrophilicity at the membrane surface. The static contact angle of water on the surface of a polymer membrane was measured by using OCA15 (Dataphysics Co., Germany) and following the sessile drop method at 25 °C and a relative humidity of 65%. Drops were formed using a 10- $\mu\text{l}$  Hamilton positive displacement syringe. The average value of contact angles on each polymer membrane was calculated using at least five different locations on each membrane.

#### 2.4.4. Membrane morphology

The surfaces of composite membranes were observed using a scanning electron microscope (TESCAN 5136MM). Air-dried membrane samples were prepared for SEM imaging by coating the surfaces with a conductive layer of sputtered gold. The surface roughness of the composite membrane was measured by AFM analysis (Nanoscope IV). Membrane samples were fixed on a specimen holder and  $1.5 \mu\text{m} \times 1.5 \mu\text{m}$  areas were scanned in the tapping mode in air. The surface roughness was reflected in terms of the average plane roughness ( $R_a$ ) and root mean square roughness (rms).

### 3. Results and discussion

#### 3.1. Effect of LiBr content on the composite membrane performance and morphologies

Fig. 1 (a) shows the pure water permeation rates for the membranes prepared by the interfacial polymerization of TEOA and TMC on addition of various contents of LiBr in aqueous phase. The pure water flux of composite membrane enhances as the LiBr content increases and it reaches a maximum at 3% (w/v) of LiBr. The order

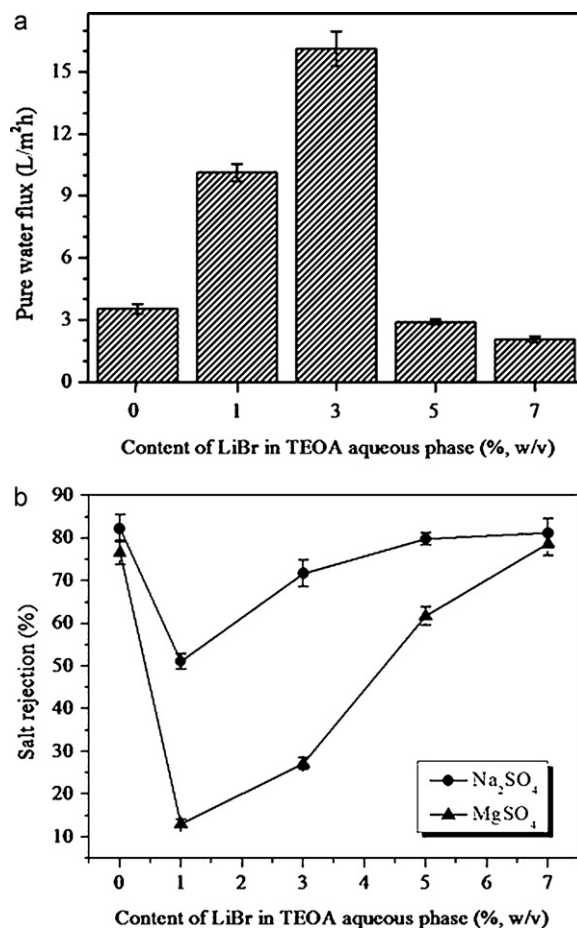
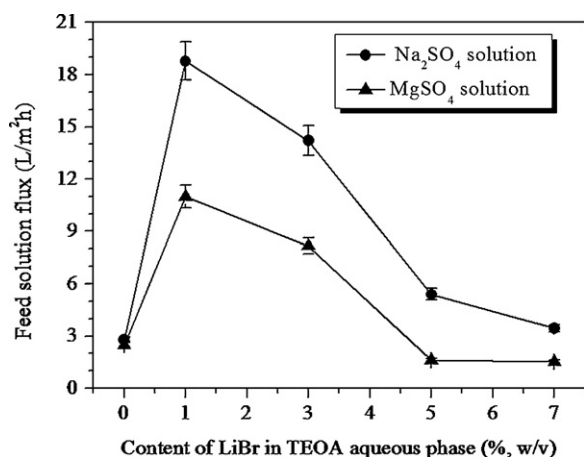


Fig. 1. Pure water permeation rates (a) and salts rejections (●- represents  $\text{Na}_2\text{SO}_4$  and ▲- represents  $\text{MgSO}_4$ ) for the membranes prepared by the interfacial polymerization of TEOA and TMC on addition of various contents of LiBr.

of the flux according to the content of LiBr is: 3% > 1% > 0% > 5% > 7%. However, the extreme value of the salts rejection functioned with the content of LiBr changes to 1% (w/v) (as shown in Fig. 1 (b)) (a turning point) at which the membrane displays a lowest salts rejection, not only to  $\text{Na}_2\text{SO}_4$  but also to  $\text{MgSO}_4$ . Generally, the pure water flux is related with the membrane structure, whereas, the rejection is concerned not only with the membrane structure but also with affinity and adsorption effects of membrane surface. Therefore,  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  salt solution flux of the membranes was examined and the result demonstrated in Fig. 2. Clearly, the contents of LiBr corresponding to the maximum flux of  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  solution are both at 1% (w/v). Thus, the asynchronous change of pure water flux and salts rejection with increasing of LiBr content is mainly attributed to the adsorption effect of membrane surface. Furthermore, from Fig. 1 (b), it could also be seen that the rejection of membrane to  $\text{Na}_2\text{SO}_4$  is always higher than that to  $\text{MgSO}_4$ . We speculate that the electrical character of the membrane surface skin layer promotes the difference in rejection to the electrolyte solution with different valence cation as described in Ref. [24]. We then determined the surface charge characteristics of the composite membranes by measuring the streaming potential of the membranes and found the composite membrane surfaces were negatively charged in the neutral experiment solution. According to the electrostatic effect [25,26], the rejection of the membranes to  $\text{Na}_2\text{SO}_4$  should therefore be higher than that to  $\text{MgSO}_4$ .

Fig. 3 presents the SEM images of the surfaces of the TEOA/TMC composite membranes prepared with various contents of LiBr. The surface morphology of composite membrane is distinctly depen-



**Fig. 2.** Flux of the salt solution (● represents Na<sub>2</sub>SO<sub>4</sub> and ▲ represents MgSO<sub>4</sub>) versus the content of LiBr for composite membranes prepared by the interfacial polymerization of TEOA and TMC.

dent on the content of the LiBr used. The comparison of Fig. 3 (a)–(e) and (f) shows that the convex area on the surface increases after the interfacial polymerization. The variation of the surface morphologies confirms that the dense layer is formed after interfacial polymerization. Moreover, as the content of LiBr increases, the surface of composite membrane becomes smoother and the surface coverage becomes lower. The composite membrane with 3% LiBr seems to have the lowest surface coverage. However, the surface becomes rougher at greater amounts of LiBr. The roughness of membrane surface can be quantified from the AFM results as presented in Fig. 4 and Table 2. According to Table 2, the order of increasing roughness using rms (root mean square height) is: 3 wt% < 1 wt% ≈ 0 wt% < 5 wt% < 7 wt%. The results from AFM analysis are consistent with the morphologies observed by SEM images. The formation of this dense active layer is the key factor for the

**Table 2**

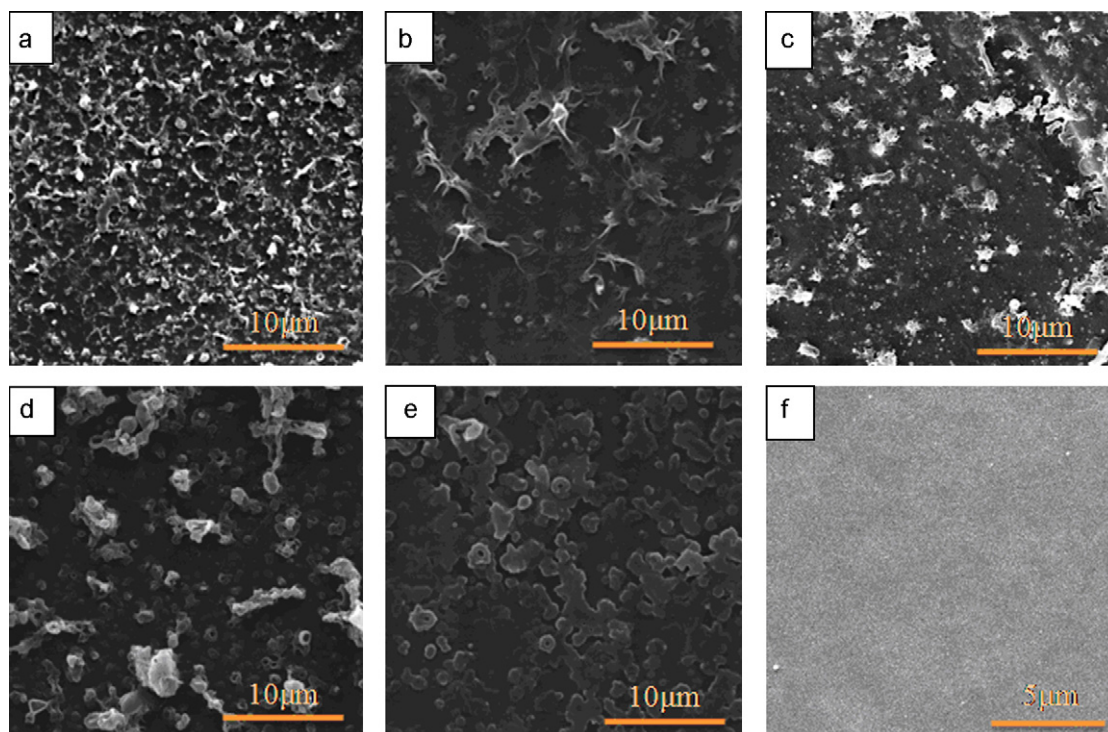
Surface roughness values of the TEOA/TMC composite membranes with different contents of LiBr by AFM.

The content of LiBr (w/v)	Rms (nm)	Ra (nm)
0%	22.670	16.584
1%	20.341	16.591
3%	18.927	14.978
5%	26.289	21.018
7%	36.111	27.059

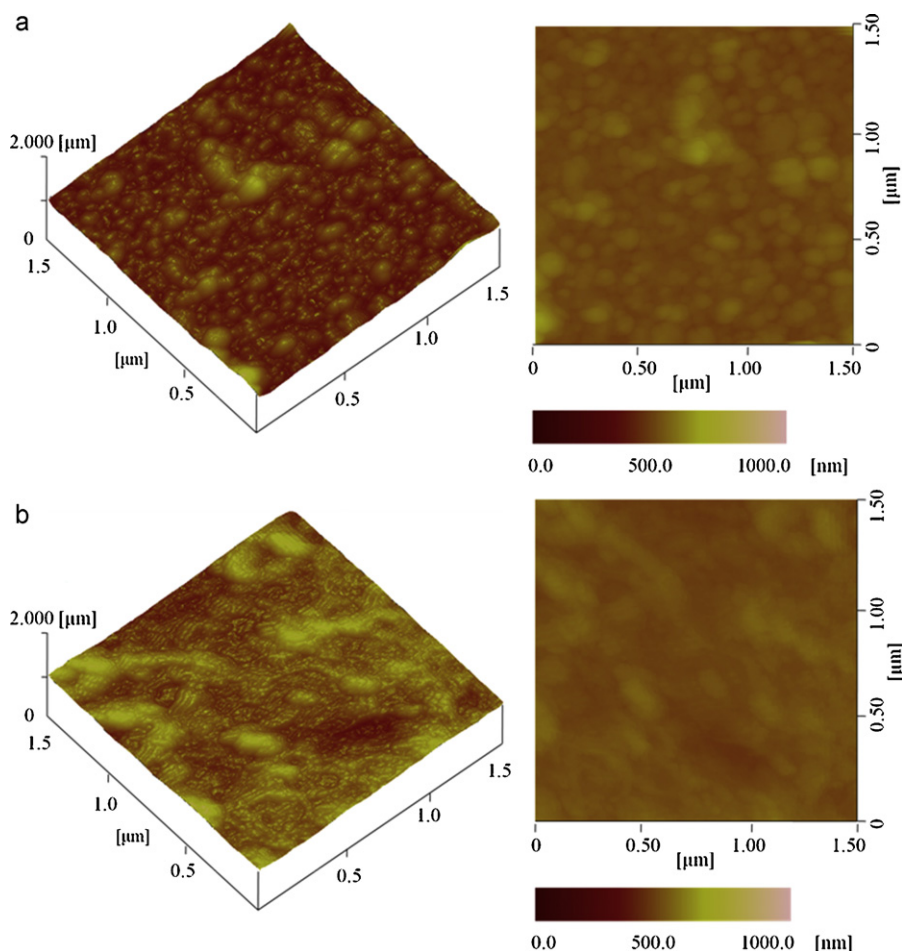
separation properties of the composite membrane, which could be testified by the results of pure water flux and salts rejection. The role of LiBr in the membrane performance and morphologies during interfacial polymerization is assumed that LiBr might govern the properties of alcohol amine solution as well as the hydrolyzation of organic phase monomer in the reaction zone. Membrane formation process is analyzed in detail in Section 3.2.

### 3.2. The role of LiBr in the composite membrane formation

To investigate the role of LiBr in the composite membrane formation, the property of the TEOA aqueous phase in the presence of LiBr was primarily studied by examining the FT-IR spectra for the TEOA solutions with various contents of LiBr and the result demonstrated in Fig. 5 (a). The obvious absorptions within 3700–3000 cm<sup>-1</sup> region and that around 1640 cm<sup>-1</sup> are the stretching vibration and the in-plane bending of OH group in TEOA (or water) molecule respectively. It is interestingly found from Fig. 5 (a) that the addition of LiBr to TEOA solution affects the peak position of OH band, in which the stretching vibration shifts to a higher wavenumber. The peak position of ν(OH) functioned with the ratio of LiBr to TEOA is presented in Fig. 5 (b). As is well known, the OH stretching vibrations are predicted to exhibit sequential red shift with the increasing strength of the hydrogen bond [27]. Thus, the sequential positive shift of TEOA–TEOA (or H<sub>2</sub>O) hydrogen bonded OH stretching band indicates that the hydrogen bonds of OH are



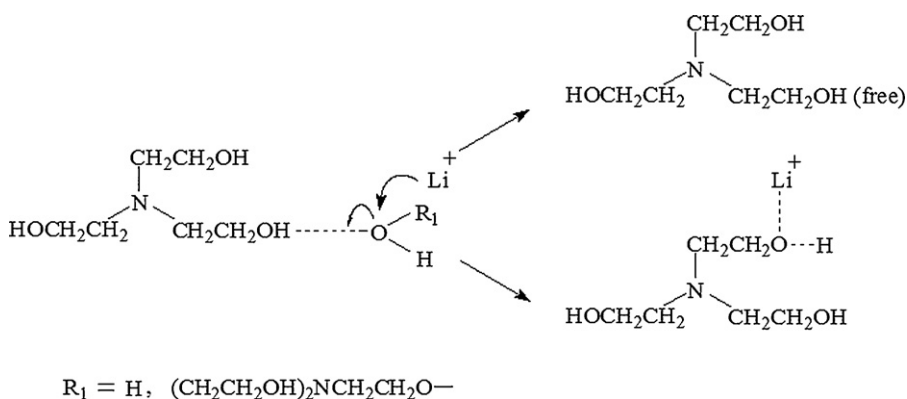
**Fig. 3.** SEM images of the membrane surface morphologies prepared by the interfacial polymerization of TEOA and TMC on addition of various contents of LiBr (a) 0%, (b) 1%, (c) 3%, (d) 5%, (e) 7%, and (f) PSF supporting membrane.



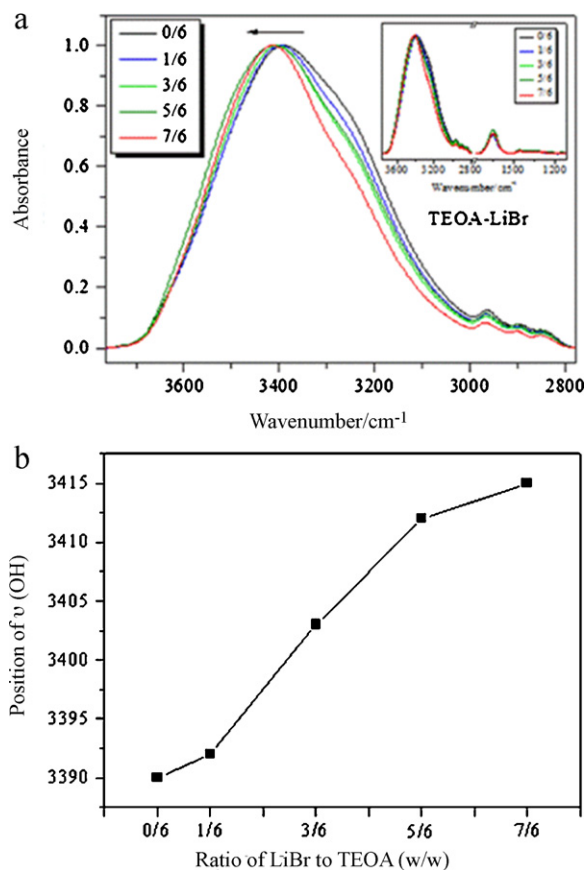
**Fig. 4.** AFM images of the surfaces of composite membranes prepared by the interfacial polymerization of TEOA and TMC on addition of various contents of LiBr: (a) 0%, and (b) 3%.

broken up in the existence of LiBr. Therefore, it could be clearly deduced that LiBr could interact with TEOA. It had been reported that lithium salts could interact strongly with amide group [28,29]. The interaction of lithium ions with amide group occurs through the oxygen, since resonance in the molecule causes the oxygen to be the site of negative charge [30,31]. Therefore, it is speculated that the LiBr–TEOA interaction takes place mainly through the hydroxyl oxygen atom due to the oxophilic nature of lithium ion and much less steric interaction. Interaction with nitrogen, on the other hand, would cause a decrease in the C–N frequency [31], which is contrary to experimental evidence (the peak shift of C–N absorption is not

observed in Fig. 5 (a)). To further testify the interaction of lithium ion with hydroxyl oxygen atom, the FT-IR spectra for aqueous solutions of glycerol (its structure is presented in Fig. 6 (a)) containing various contents of LiBr were investigated and the result is shown in Fig. 6 (b). There is a blue shift as well when LiBr is added to the glycerol aqueous solution. The peak position of  $\nu$  (OH) functioned with the ratio of LiBr to glycerol is presented in Fig. 6 (c). The blue shift of  $\nu$  (OH) indicates the hydrogen bonds of OH are weakened due to the interaction of  $\text{Li}^+$  ion and the hydroxyl oxygen atom of glycerol or water. Spectroscopic investigation further confirms that lithium ion interacts with TEOA mainly through the hydroxyl oxy-



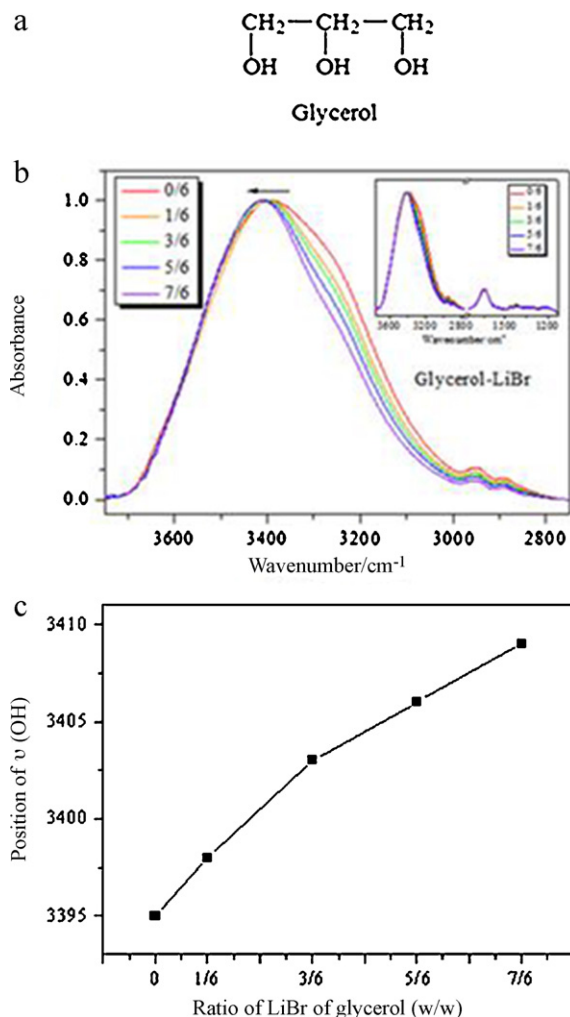
**Scheme 1.** Interaction between  $\text{Li}^+$  ion and the hydroxyl oxygen atom of TEOA.



**Fig. 5.** FT-IR spectra of the TEOA aqueous solutions containing various ratios of LiBr to TEOA (a), and the peak position of  $\nu$  (OH) versus the ratio of LiBr to TEOA (b).

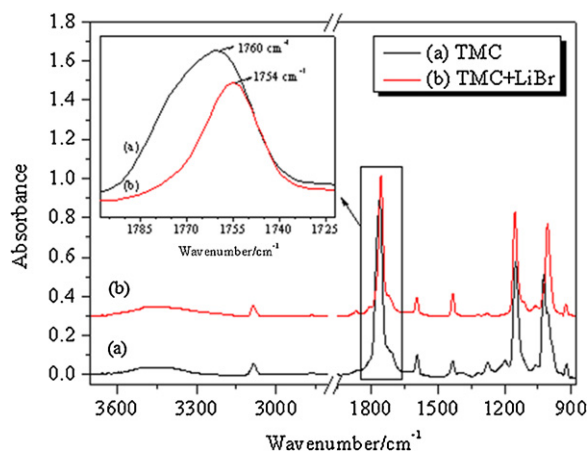
gen atom, which would induce two effects as shown in Scheme 1. One is the increase of the number of free TEOA, which could result in an increase in the density of reactable OH groups. The other effect is the enhancement of the reactivity of OH groups of TEOA due to the interaction of  $\text{Li}^+$  ion with hydroxyl oxygen atom that weakens the strength of the OH bond.

Besides, when aqueous phase solution containing LiBr contacts with organic phase, the interfacial polymerization of TEOA and TMC would occur and simultaneously LiBr diffuses from aqueous phase into organic phase. Pertinent studies of amide salt solutions reported that inorganic salts formed complexes with the carbonyl groups in polar, aprotic solvents, such as dimethylformamide (DMF), dimethylacetamide (DMAC) and *N*-methyl-2-pyrrolidone (NMP), via an ion-dipole interaction [28–33]. Thus, in the case of the system of LiBr and TMC,  $\text{Li}^+$  ion would complex with the carbonyl ( $\text{C}=\text{O}$ ) in the TMC molecule. This complex formation behavior can be confirmed by infrared spectroscopy. Fig. 7 presents the spectra of TMC and its complex with LiBr. The absorption of carbonyl group in the complex of TMC–LiBr is located at  $1754\text{ cm}^{-1}$ , which is lower than that in TMC around  $1760\text{ cm}^{-1}$ . The red shift of the carbonyl could be explained in terms of the reduction of the electron density in double bond of carbonyl, through the donation of electron to LiBr for interaction. Spectroscopic examination suggests that  $\text{Li}^+$  ion complexes with the carbonyl group, thus activating the carbonyl of TMC. As a consequence, the hydrolysis rate of acyl chloride of TMC is increased. Although the esterification rate of TMC with TEOA is also probably enhanced as a result of the activation of carbonyl of TMC, its role in membrane formation is minor compared with that of the hydrolyzation of acyl chloride that could be concluded from the result of the membrane streaming potential as described in detail in Fig. 11 of Section 3.3.

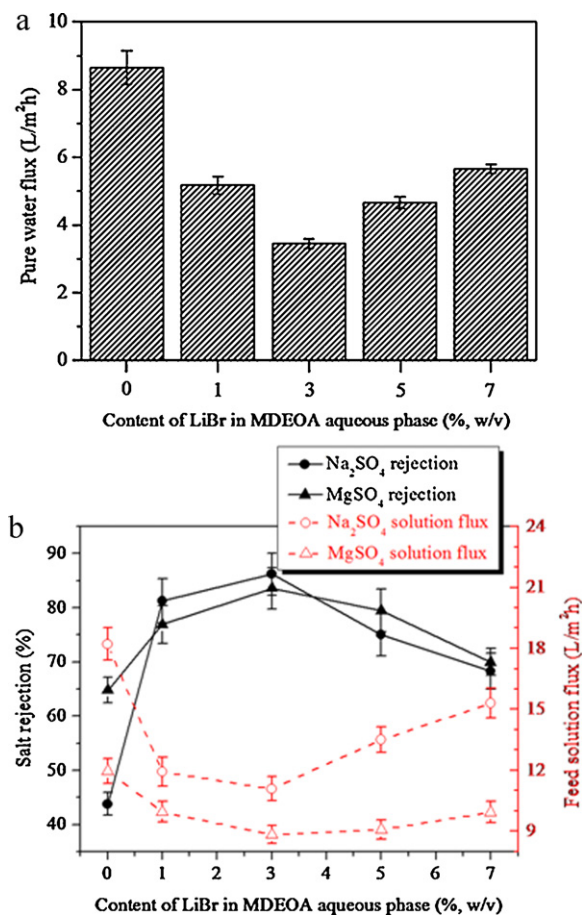


**Fig. 6.** The molecular structure of glycerol (a), FT-IR spectra of the glycerol aqueous solutions containing various ratios of LiBr to glycerol (b), and the peak position of  $\nu$  (OH) versus the ratio of LiBr to glycerol (c).

To sum up, the addition of LiBr in aqueous phase during the interfacial polymerization of TEOA and TMC would result in two functions on the membrane formation. One is the interaction of  $\text{Li}^+$  ion with the hydroxyl oxygen atom of TEOA, which could induce to an increase in the density and the reactivity of OH groups in the aqueous phase, forming a dense skin layer of the composite mem-



**Fig. 7.** FT-IR spectra of TMC and complex of TMC–LiBr.

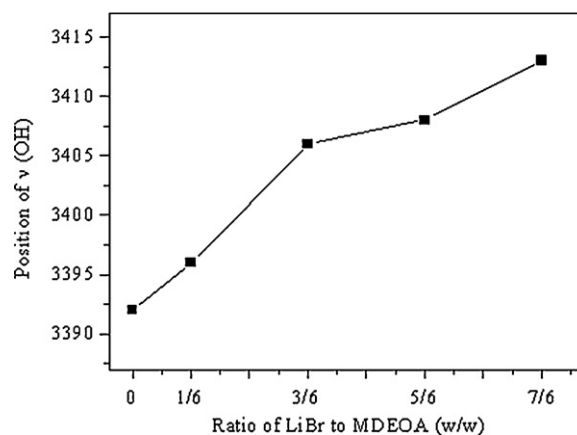


**Fig. 8.** Pure water permeation rates (a), and salts rejections (●— represents Na<sub>2</sub>SO<sub>4</sub> and ▲— represents MgSO<sub>4</sub>) and flux of salts solution (○— represents Na<sub>2</sub>SO<sub>4</sub> and □— represents MgSO<sub>4</sub>) for the membranes prepared by the interfacial polymerization of MDEOA and TMC on addition of various contents of LiBr.

brane as a result. The other factor is the complexation of Li<sup>+</sup> ion with the carbonyl in TMC, causing the acid chloride group of TMC preferring to hydrolyze which could induce to construct a hydrophilic and loose surface layer. The change in performance of the composite membrane with the content of LiBr (as shown in Fig. 1) is mainly due to the competition of two factors. For lower content of LiBr, the complexation of Li<sup>+</sup> ion with the carbonyl of TMC might play a more important role in membrane formation, which leads to the formation of a more hydrophilic and permeable surface layer. Thus, the flux of the composite membrane increases when the content of LiBr increases from 0 to 3%. However, when the content of LiBr increases further, especially past 3%, the interaction of Li<sup>+</sup> ion with the hydroxyl oxygen atom of TEOA is likely to have a great impact on the membrane formation, which results in formation of a dense skin layer. So, the flux of the composite membrane decreases.

### 3.3. Influence of LiBr on the performance of the composite membrane prepared from different aqueous phase monomers

Another monomer in aqueous phase—N-methyl-diethanolamine (MDEOA) was also studied in the presence of LiBr as additive in aqueous phase to testify the role of LiBr in the formation of the composite membrane. The performance of the composite membrane by the interfacial polymerization of MDEOA and TMC in the presence of various contents of LiBr is illustrated in Fig. 8. Interestingly, different from the influence of LiBr on the performance of the TEOA/TMC composite membrane, the flux of the MDEOA/TMC composite membrane firstly decreases with LiBr



**Fig. 9.** The peak position of ν(OH) in FT-IR spectra versus the ratio of LiBr to MDEOA.

content until it reaches 3% and then increases. The order of the salts rejection (Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>) changed with the LiBr content is completely contrary compared with that of the flux. The property of the aqueous phase promotes the difference in the performance of the composite membrane prepared by two monomers of TEOA and MDEOA.

To clarify the influence of LiBr on the property of MDEOA aqueous phase, the FT-IR for MDEOA aqueous solutions with various contents of LiBr were also examined. Similarly, addition of LiBr to MDEOA solution also affects the peak position of OH band, in which the stretching vibration shifts to a higher wavenumber (Fig. 9). This means Li<sup>+</sup> ion also interacts with the hydroxyl oxygen atom in MDEOA, which leads to an increase in the density and the reactivity of OH groups in the MDEOA aqueous phase. Then, why the addition of LiBr to the MDEOA aqueous phase has a different effect on the performance of the composite membrane compared with monomer TEOA?

Because the performance transition points of the membranes are situated at 3% LiBr content for two monomers of aqueous phase, the following investigation about the content of LiBr is focused on 0% and 3%. The membrane interfacially polymerized by MDEOA (or TEOA) and TMC on addition of LiBr is designated as LMDEOA/TMC (or LTEOA/TMC) composite membrane in the following discussion.

As mentioned above, the addition of LiBr in aqueous phase during interfacial polymerization would result in two functions on the membrane formation. One is the interaction of Li<sup>+</sup> ion with hydroxyl oxygen atom in alcohol amine, and the other factor is the complexation of Li<sup>+</sup> ion with the carbonyl in TMC. If LiBr interacts with TMC, it must diffuse from aqueous phase into organic phase. Thus, the viscosity of the aqueous phase plays an important role in the diffusion of LiBr, finally influencing the complexation of Li<sup>+</sup> ion with the carbonyl in TMC. Table 3 shows the viscosities of the TEOA and MDEOA aqueous solutions and of them on addition of 3% LiBr. The addition of LiBr works to increase the viscosity of alcohol amine solution. The increase in viscosity arises from strong interaction between LiBr and alcohol amine (TEOA or MDEOA). Furthermore, the viscosity of the MDEOA aqueous solution is always higher than that of TEOA solution no matter whether containing LiBr. Therefore, the diffusion rate of LiBr from MDEOA aqueous phase to organic phase must be lower. As a result, the effect of complexation of Li<sup>+</sup> ion with the carbonyl of TMC is minor for monomer MDEOA. Correspondingly, the role of interaction of Li<sup>+</sup> ion with the hydroxyl oxygen atom of MDEOA is predominant during the formation of composite membrane, which leads to form a dense skin layer. So, the flux of the MDEOA composite membrane with 3% LiBr is lower than that without LiBr. The result above could be validated by the reaction coefficient (R) of two phases as shown in Table 3.

**Table 3**

The viscosity and reaction coefficient of the aqueous phase for MDEOA and TEOA monomer with various contents of LiBr.

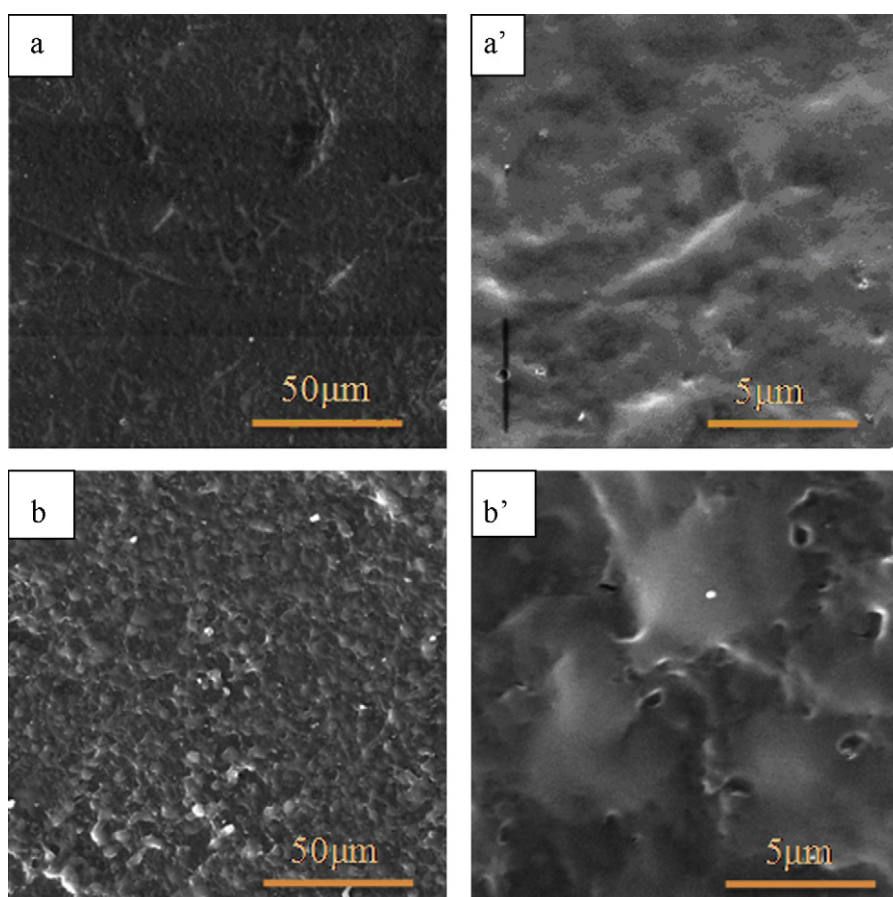
Aqueous phase	TEOA	TEOA + 3%LiBr	MDEOA	MDEOA + 3%LiBr
Viscosity (cP)	0.7980 ± 0.0012	0.8887 ± 0.0010	1.0091 ± 0.0016	1.0329 ± 0.0007
Reaction coefficient	4.31 ± 0.07%	7.79 ± 0.14%	1.09 ± 0.04%	7.73 ± 0.12%

The addition of LiBr makes an increase in the reaction coefficient for two monomers (MDEOA and TEOA) of aqueous phase, in which the *R* value for TEOA increases from 4.31% to 7.79% and increases from 1.09% to 7.73% for MDEOA. This implies that the existence of LiBr in alcohol amine aqueous phase indeed increase the reaction degree of interfacial polymerization due to the fact that the interaction of Li<sup>+</sup> ion with the hydroxyl oxygen atom of alcohol amine increases the density and the reactivity of OH groups in aqueous phase. Furthermore, this effect of LiBr on MDEOA aqueous phase is more predominant (the *R* value increases from 1.09% to 7.73%), which induces to form a denser skin layer.

SEM images are obtained for MDEOA/TMC and LMDEOA/TMC membranes (Fig. 10). Fig. 10 (a) and (b) are images of them at ×500 magnification respectively. Fig. 10 (a') and (b') are images at ×5000 magnification respectively. From Fig. 10 (a) the morphology of the MDEOA/TMC membrane is entirely different from the TEOA/TMC membrane (as shown in Fig. 3 (a)). The TEOA/TMC membrane surface contains many tightly packed and small nodular structures, whereas, the MDEOA/TMC membrane surface is relatively flat with some protuberances (Fig. 10 (a) and (a')). This is due to the formation of polymer with a lower molecular weight during the interfacial polymerization of MDEOA and TMC because the number of functional groups in the MDEOA molecule is relatively

fewer than that in the TEOA. Moreover, the surface of LMDEOA/TMC membrane is relatively rougher and more pronounced edges than that of the MDEOA/TMC membrane. The result proves that the addition of LiBr promotes the reaction between MDEOA and TMC.

Fig. 11 shows the streaming potentials of the composite membranes respectively prepared by the aqueous phase monomers of MDEOA and TEOA with and without LiBr. The addition of LiBr causes the surfaces of the composite membranes to possess higher negative charges no matter the type of monomer. The result reveals that the activation of carbonyl due to the complexation of Li<sup>+</sup> ion with it mainly causes an increase in the hydrolysis rate of acyl chloride, forming a hydrophilic surface layer with carboxylic acid (–COOH) groups. Moreover, the increment of negative charges resulted from the addition of LiBr for TEOA membrane is markedly larger than that for MDEOA membrane. The result reinforces the analyses that the complexation of Li<sup>+</sup> ion with the carbonyl of TMC plays a more important role in membrane formation of monomer TEOA, leading to the formation of a more hydrophilic structure, whereas for monomer MDEOA, interaction of Li<sup>+</sup> ion with the hydroxyl oxygen atom of aqueous phase has a greater impact on the membrane formation, which results in an increase in the density of the surface layer. Furthermore, it is noted that the density of negative charge is relatively low for MEDOEA membrane. Therefore, both size exclu-



**Fig. 10.** SEM images of the membrane surface morphologies of MDEOA with (a) 500× magnification and (a') 5000× magnification, and LMDEOA with (b) 500× magnification and (b') 5000× magnification.



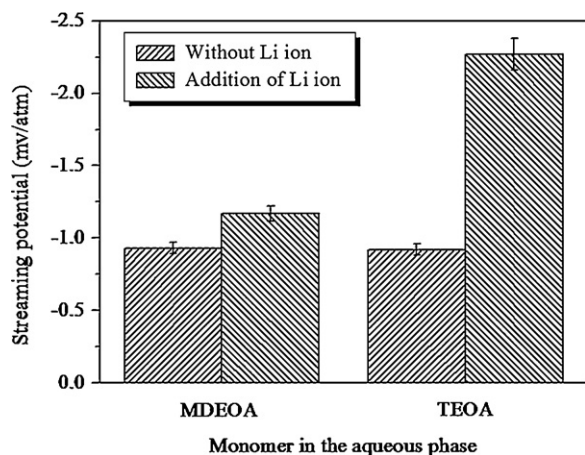


Fig. 11. Streaming potential of the composite membranes interfacially polymerized by two aqueous phase monomers (MDEOA and TEOA) with TMC on addition of Li ion or not.

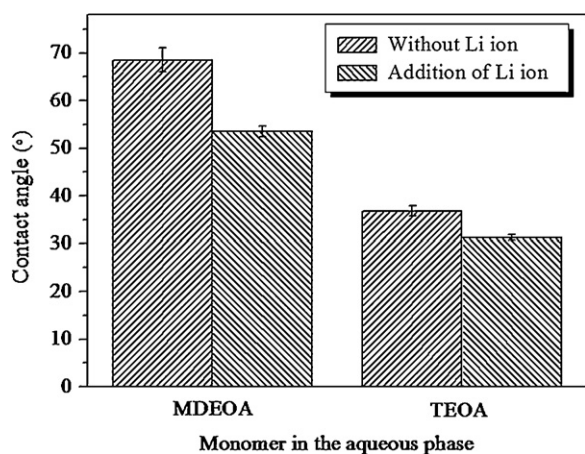


Fig. 12. Contact angle of the composite membranes interfacially polymerized by two aqueous phase monomers (MDEOA and TEOA) with TMC on addition of Li ion or not.

sion and charge exclusion contribute together to the separation result, which exhibits the alternation rejection levels of  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  with the LiBr content as shown in Fig. 8 (b).

The surface hydrophilicity of membranes is evaluated from the average equilibrium sessile drop contact angles of the de-ionized water on dried membrane surfaces (Fig. 12). Seen from Fig. 12, the contact angles of membranes on addition of LiBr are all smaller than that of membranes without LiBr. This implies that the addition of LiBr in the aqueous phase may have increased the membrane hydrophilicity during interfacial polymerization due to the effect of complexation of  $\text{Li}^+$  with TMC.

#### 4. Conclusions

The present paper investigated the role of LiBr in the performance and formation of the composite membrane by interfacial polymerization. For monomer TEOA, the pure water flux of composite membrane enhanced as the LiBr content increased and it reached a maximum at 3% (w/v) of LiBr. However, the extreme value of the salts rejection functioned with the content of LiBr changed to 1% (a turning point), at which the membrane displayed a lowest salts rejection, not only to  $\text{Na}_2\text{SO}_4$  but also to  $\text{MgSO}_4$ . The asynchronous change of pure water flux and salts rejection with increasing of LiBr content was mainly attributed to the adsorption effect of membrane surface. The change in performance of the

composite membrane with the content of LiBr was due to the competition of two factors. One was the interaction of  $\text{Li}^+$  ion with the hydroxyl oxygen atom of alcohol amine, which could induce to an increase in the density and the reactivity of OH groups in the aqueous phase, forming a dense skin layer of the composite membrane as a result. The other factor was the complexation of  $\text{Li}^+$  ion with the carbonyl of TMC, causing the acid chloride group of TMC preferring to hydrolyze which induced to construct a hydrophilic and loose surface layer. The interactions of  $\text{Li}^+$  ion with monomers were confirmed by the FT-IR spectroscopy. The role of LiBr in the formation of the composite membrane was further testified by investigating the MDEOA monomer. The addition of LiBr to the MDEOA aqueous phase had a different effect on the performance of the composite membrane compared with monomer TEOA. The flux of the MDEOA/TMC composite membrane firstly decreased with LiBr content until it reached 3% and then increased. The order of the salt rejection changed with the LiBr content was completely contrary compared with that of the flux. The different result of membrane performance influenced by LiBr for two monomers was due to the alteration of the predominant effect functioned. The analysis of the membrane formation on addition of LiBr was validated by reaction coefficient, contact angle measurement, streaming potential, SEM, and AFM.

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