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The effect of polymer concentration and additives of cast solution on performance of polyethersulfone/sulfonated polysulfone blend nanofiltration membranes

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ABSTRACT

The effect of polymer concentration of polyethersulfone (PES) plus sulfonated polysulfone (SPSF) and additives of cast solution on performance of PES/SPSF blend nanofiltration (NF) membranes was investigated. The field emission scanning electron microscopy and X-ray photoelectron spectroscopy were used to analyze characteristic of PES/SPSF blend NF membranes. The water flux of PES/SPSF blend membranes decreased dramatically with an increase in polymer concentration of PES plus SPSF. The rejection of polyethylene glycol (PEG) and salts increased with increasing polymer concentration of PES plus SPSF. When acetone was used as an additive, the water flux declined with increasing mass concentration of acetone, but the rejection of PEGs and salts increased. The PES/SPSF blend NF membranes with mimimum rejection of sodium chloride indicated that it could separate monovalent salts from multivalent salts effectively, which would be potential application in softening water for drinking water resource.

Keywords: Poly(ether sulfone); Sulfonated polysulfone; Nanofiltration membrane

1. Introduction

Nowadays, nanofiltration (NF) is a relative new membrane process, and becoming more and more important in industries and environment. Its application is rapidly growing in water treatment for removal of natural organic substance, salts, and dyes due to its capabilities of removing all pathogens, multivalent ions, and small organic molecules in the molecular weight range of 200–1,000 g/mol [1–5]. NF membrane can be made by interfacial polymerization (IP) technique which is one of the most well-known processes for the formation of film of composite NF membranes,

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and by phase inversion method which can obtain asymmetric membrane. Many researchers use the IP technique which is a cross-linking on a microporous membrane surface. IP would give the composite membrane more chemical-resistant, greater water flux, and better separation [6–8]. However, preparation of composite NF membrane by IP technique is more sophisticated and laborious than fabrication of asymmetric NF membrane since the process of IP is carried out in two steps by the reaction of aqueous and organic solution. The process of fabrication of asymmetric NF only needs one step by the method of phase inversion. There is ongoing interesting in the development of NF membranes in a relatively simple way. Over the past few years, there are a number of studies that reported the preparation of charged asymmetric NF membranes only through the single-step process using charged polymeric material [9–13].

Polyethersulfone (PES) is widely used due to its thermal stability, mechanical strength, and chemical durability. However, the hydrophobic nature of PES is disadvantageous for preparation of NF membranes. Sulfonated polysulfone (SPSF) has adequate hydrophilic and can improve performances of membranes because of its much of sulfonic acid group on PSF chain. Besides, many of the researchers used this material to make ion exchange membranes. Thus, this material is hopefully to be developed to be a good NF membrane material [14]. But this material possesses weak strength, which would cause less stability under high pressure [15]. The blend PES/SPSF NF membrane is a combination of good hydrophilic of SPSF and mechanical strength of PES, which can improve the water flux and stability of blend membrane under high pressure and long operation time. Besides, the previous work showed that the combination of PES and SPSF could form asymmetric structure, which contained thin compact layer and thick substrate layer because of difference of PES and SPSF phase transfer rate [16]. But the membranes made of single PES or single SPSF had no apparent thin compact layer.

Generally, the water flux and separation performances of PES/SPSF NF membranes were strongly affected by the sulfonation degree of SPSF, ratio of PES/SPSF, and mass concentration of polymer and additives. The previous work about effect of sulfonation degree of SPSF and mass ratio of PES/SPSF on NF performance was reported [16]. It was noted that the PES/SPSF membrane with the PES and 10% sulfonation degree SPSF ratio of 6/4 (wt.%) showed a better NF performance. In this work, the effect of mass concentration of polymer and additives on NF performances of PES/SPSF membrane was studied.

2. Experimental

2.1. Materials

Ultrason® E3010 PES supplied by BASF Chemical Company and SPSF (10% of sulfonation degree) supplied by Tianjin Normal University were dried for 6 h on 105˚C in vacuum before use. *N,N*-dimethyl acetamide (DMAc) was used as solvent. Acetone, tetrahydrofuran (THF), and ether were used as additives. Polyethylene glycol (PEG) included PEG600 with Mw 600 g/mol, PEG800 with Mw 800 g/mol, and PEG1000 with Mw 1,000 g/mol; sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) were used to characterize membrane selectivity. All the chemicals purchased from Tianjin Chemical Company were analytical grade and used as received without further purification. All the solutions used in the experiments were prepared using deionized water.

2.2. Preparation of PES/SPSF blend NF membranes

The casting solutions which contained PES, SPSF, and additive with different mass concentration were prepared in DMAc. The DMAc and additive were added slowly into a 250 ml three-neck flask, respectively, and stirred to additive dissolved. Then, the dried SPSF were added into a mixture of DMAc and additive, and mixed thoroughly under constant mechanical stirring at room temperature. After SPES was dissolved completely, the dried PES was added into flask. And then this mixture was stirred for not less than 6 h to form homogenous solution. The casting solution was filtered by stainless steel mesh and degassed to remove microbubbles in casting solutions.

Asymmetric PES/SPSF NF membranes were prepared via phase inversion by immersion precipitation using casting solutions containing PES, SPSF, DMAc, and additive. The solution was sprinkled to clean and smooth glass plate, and cast by self-made casting knife with 0.25 mm thickness on the glass plate. The glass plate with casted solution was immersed in the ice-water bath after exposure in air 180 s on room temperature of 25˚C with 30% humidity. After primary phase separation and membrane formation, the membranes were stored in water for 24 h to guarantee the complete phase separation.

According to the previous work results [16], the optimized mass ratio was 6/4 (wt.%) for PES and 10% sulfonation degree SPSF, in which the NF membrane had the best water flux and relatively better rejection to PEGs and salts comparing to the membranes made by using others ratios. So in this work, the mass ratio

of PES and 10% sulfonation degree SPSF with 6/4 (wt.%) was used for NF membrane preparation.

2.3. Characterization of NF membranes

2.3.1. X-ray photoelectron spectroscopy (XPS)

The sulfur (S) element molar content on the surface of SPSF/PES blend membrane would be measured by XPS (XPS PHI-1600).

2.3.2. Field emission scanning electron microscopy (FESEM)

The outer surface and cross-section morphologies of the flat NF membrane were observed with field emission microscope (FESEM, HItachi-s-4800). The membrane samples were cryogenically fractured under liquid nitrogen for few minutes to reduce damage on cross-section morphology. As the membranes were nonconductive, the prepared samples were sputter coated with gold using auto fine coater.

2.3.3. Membrane performance characterization

The experiments were carried out in batch mode (both retentate and permeate were returned to feed tank) by using laboratory-scale, cross-flow membrane filtration equipment as shown in Fig. 1. The effective filtration area of the membrane was 22.06 cm^2. The feed reservoir temperature was maintained approximately at 25℃.

Asymmetric flat NF membranes were characterized by measuring the pure water flux, rejection of small organic molecules, and salt. A salt solution containing NaCl or Na_2SO_4 with 1,000 mg/L was used as feed solution. Organic substance solution containing PEG with 200 mg/L was used to be characterization of organic rejection.

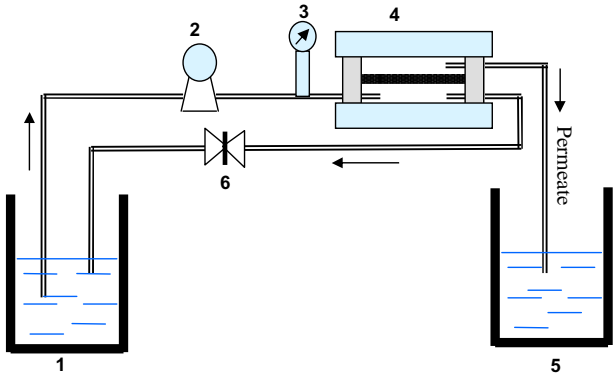

Fig. 1. Experimental drawing: (1) feed tank; (2) feed pump; (3) pressure sensor; (4) membrane cell; (5) permeate tank; (6) bypass control valve.

At first, the membranes were pre-compressed with deionized water at 0.6 MPa for 30 min. Then, the pure water flux was measured at transmembrane pressure 0.5 MPa. The temperature of feed was 25℃. The concentrations of NaCl and Na_2SO_4 in permeate were analyzed by conductivity measurement, and the concentration of PEG was analyzed by ultraviolet absorption (UV SHIMADZU UV-2450).

The water flux was calculated by the Eq. (1):

$$F\ (\text{Water flux}) = \frac{V}{A\Delta t} \tag{1}$$

where F (L m^{-2} h^{-1}) was water flux, V (L) is the volume of permeate pure water, A (m^2) is effective filtration area of membrane, and Δt (h) is filtration time.

The rejection was calculated using the following Eq. (2).

$$R\ (\%) = \left(1 - \frac{c_P}{c_f}\right) \times 100\% \tag{2}$$

where R (%) was rejection of solute. c_p (g/L) and c_f (g/L) represent the mass concentration of permeate and feed solution, respectively.

3. Results and discussion

3.1. Analysis of element on the surface of PES/SPSF blend membranes

As shown in Fig. 2, the molar contents of C, O, and S on the surface of PES/SPSF blend membrane with PES/SPSF ratio of 6/4 (wt.%) and 25 wt.% polymer concentration of PES plus SPSF were 85.78, 12.14, and 1.01%, respectively. There was a characteristic peak of S when the binding energy was 168.02 EV in Fig. 3 and intensity of S element peak increased with an increase in SPSF content in casting solution, which indicated that S content on the surface of PES/SPSF

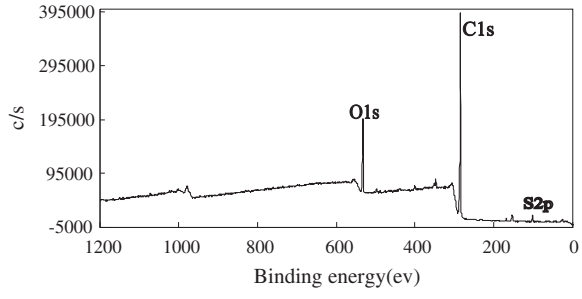

Fig. 2. XPS spectra of blending membrane: the ratio of PES/SPSF was 6/4 (wt.%), polymer concentration of PES plus SPSF was 25 wt.%; acetone mass concentration was 15 wt.%.

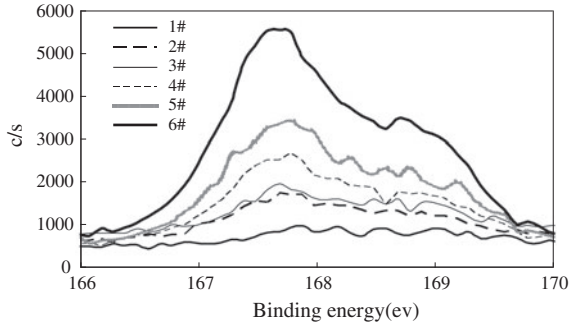

Fig. 3. XPS narrow scan for S element of membrane: 1# (PES membrane), 2#–6# (PES/SPSF blend membrane): ratios of PES/SPSF were 8/2 (wt.%), 6/4 (wt.%), 5/5 (wt.%), 4/6 (wt.%), and 2/8 (wt.%). Polymer concentration of PES plus SPSF was 25 wt.%; acetone mass concentration was 15 wt.%.

blend membrane increased with an increase in SPSF content in casting solution. This means that the content of sulfonic group on the surface of PES/SPSF blend membranes increased with an increase in SPSF content in casting solution. It seemed that the sulfonic group had a preferential orientation towards water during the membrane formation process, which caused sulfonic group of enrichment towards the surface of PES/SPSF blend membranes.

3.2. The effect of polymer concentration of PES plus SPSF on performance of PES/SPSF blend NF membranes

3.2.1. Morphology of cross-section structure of PES/SPSF blend NF membranes

Polymer concentration of PES plus SPSF presented total mass concentration of PES and SPSF. Fig. 4(B1)–(B6) shows the cross-section structures of PES/SPSF membranes at different polymer concentrations of PES plus SPSF. As shown from Fig. 4, there were skin layer and support layer with finger-like macropores in cross-section of PES/SPSF blend membranes. The scale of sponge-like structure increased with an increasing polymer concentration of PES plus SPSF while scale of finger-like pore declined. Besides, thickness of skin layer increased along with an increase in polymer concentration of PES plus SPSF.

3.2.2. Performances of PES/SPSF NF membranes

The results in Fig. 5 show that water flux decreased dramatically with increasing polymer concentration of PES plus SPSF. Increasing the polymer concentration of PES plus SPSF of casting solution could increase solution viscosity. Thus, the coagulation value reduced due to much interaction of solvent and polymer, and more interaction of nonsolvent and polymer that decreased dissolving power of solvent for polymer. Then this would further promote aggregation of polymer molecules through chain entanglement and the pore size, and porosity would decrease [17], which would decrease the water flux of PES/SPSF NF membranes.

From Fig. 5, rejection of PEGs increased with increasing mass concentration of the polymer PES and SPSF. However, rejection of PEG1000 reached about 99.9% with the polymer concentration of PES plus SPSF exceeding 28 wt.%. Rejection of PEG800 was more than about 98% when the polymer concentration of PES plus SPSF exceeded 32 wt.% and rejection of

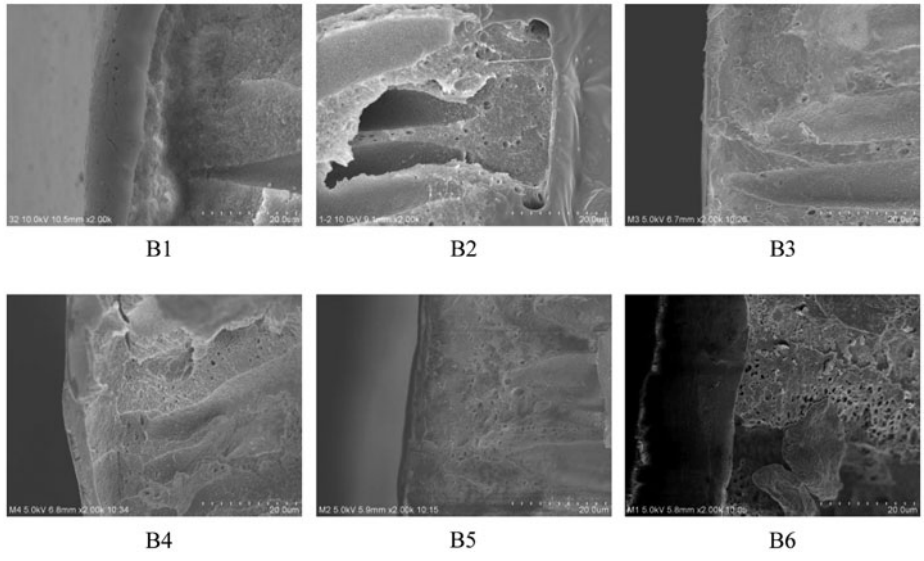

Fig. 4. The FESEM images of the cross-section of asymmetric NF membranes with different polymer concentration of PES plus SPSF: B1 (23 wt.%), B2 (25 wt.%), B3 (28 wt.%), B4 (30 wt.%), B5 (32 wt.%), and B6 (35 wt.%).

PEG600 was more than about 90% when the polymer concentration of PES plus SPSF exceeded 32 wt.%. It seemed that when the polymer concentration of PES plus SPSF increased, the aggregation of polymer molecules through chain entanglement would be promoted. Besides, when the polymer concentration of PES plus SPSF increased, the SPSF content in casting solution increased, which caused the solution hydrophilic would be stronger and phase transfer of membrane surface would be more intensified. These caused the pore size to decrease and membrane skin layer more compact [17,18], which resulted in an increasing rejection.

The results about rejection of salts in Fig. 6 shows that rejections of Na_2SO_4 and NaCl increased with increasing mass concentration of the polymer PES and SPSF. However, Na_2SO_4 rejection increased slightly when the mass concentration of the polymer PES and SPSF exceeded 28 wt.%. But NaCl rejection increased slightly with increasing polymer concentration of PES plus SPSF in range from 23 to 35 wt.%. Separation of ionic species by NF membranes was governed by both size exclusion and electrostatic interaction [19–22]. It seemed that the charge density of skin layer became higher as a result of increase of compactness of the skin layer with increasing polymer concentration.

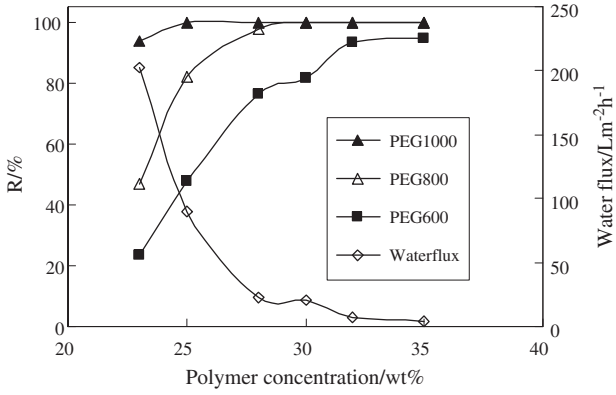

Fig. 5. Rejection of PEGs and water flux at different mass concentration of polymer: acetone mass concentration 15 wt.%.

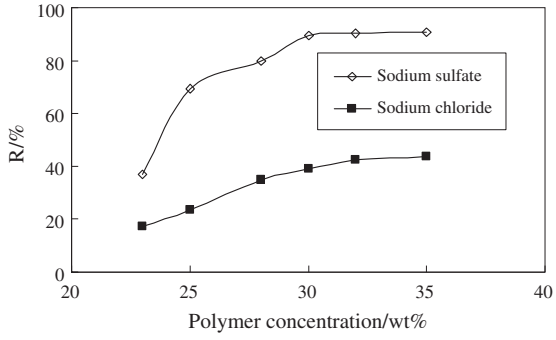

Fig. 6. Rejection of NaCl and Na_2SO_4 with different mass concentration of polymer: acetone mass concentration 15 wt.%.

3.3. The effect of additives on performance of PES/SPSF blend NF membranes

3.3.1. The effect of additive types

3.3.1.1. Morphology of PES/SPSF blend NF membrane cross-section structures. Fig. 7(C1)–(C3) presents the cross-section structures of PES/SPSF blend membranes prepared with casting solution containing different additives. There were finger-like macropores and asymmetric structures in three membranes from Fig. 7. Besides, porosities of all membranes were very good. However, the skin layer of membrane prepared with casting solution containing acetone was more compact apparently than others in cross-section structure of membranes.

3.3.1.2. Performances of PES/SPSF blend NF membranes. The results in Table 1 shows performances of PES/SPSF blend NF membranes prepared with casting solution containing different additives. The water flux of PES/SPSF blend membrane prepared by casting solution with THF was the highest in three membranes. However, its rejections of PEG and salts were the lowest. The PEG rejections and salts rejections of PES/SPSF blend membrane prepared by casting solution with acetone was the best, but its water flux was lower. A few results from the additives in casting solution had great effect on PES/SPSF blend performance due to difference of membranes structures which were prepared by casting solution with different additives. Obviously, the porosity of membrane prepared by casting solution with THF was higher than others membranes. The skin layer compactness of membrane prepared by casting solution with acetone was higher than others membranes. It might be the reason that the much higher concentration of polymer on the membrane surface layer was formed because the acetone would be evaporated during cast solution staying in the air, which would result in the more intact skin layer on the surface of air side.

3.3.2. The effect of additives mass concentrations

3.3.2.1. Morphology of PES/SPSF blend membrane cross-section structures. Fig. 8(D1)–(D5) shows the cross-section structures of PES/SPSF blend membranes

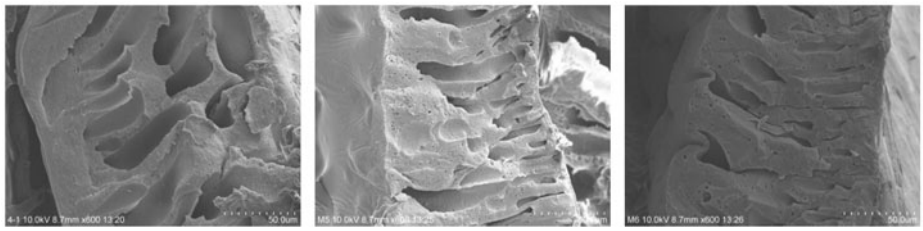

Fig. 7. SEM images of the cross-section of asymmetric NF membranes with different kinds of additives: additive in casting solution: C1 (acetone), C2 (ether), and C3 (THF). Polymer concentration of PES plus SPSF 25 wt.% and additive mass concentration 15 wt.%.

Table 1
Performances of PES/SPSF blend membranes prepared with casting solution containing different additives (polymer concentration of PES plus SPSF was 25 wt.% and additive mass concentration was 15 wt.%)

Membrane	Additive	Water flux ($L\,m^{-2}\,h^{-1}$)	Rejection of PEG1000	Rejection of PEG800	Rejection of PEG600	Rejection of Na_2SO_4	Rejection of NaCl
C1	Acetone	90.3	99.8	81.9	47.8	69.2	25.5
C2	Ether	143.5	96.7	79.1	45.7	55.5	25
C3	THF	304.6	74.2	57.5	20.5	33.3	20.8

prepared by casting solution with different additive mass concentrations. There were amazingly asymmetric structure with skin layer and support layer macropores. However, the columnar macropore can be seen in Fig. 8(D1), which is cross-section structure of the membrane prepared by casting solution with 8% additive mass concentration. With the increase of additive mass concentration, the macropore shape became cone shape from columnar shape. That is to say, the asymmetrical cross-structure was more apparently with an increase in additive mass concentration. What is more, the scale sponge-like structure increased while scale of finger-like pore declining along with increasing of additive mass concentration.

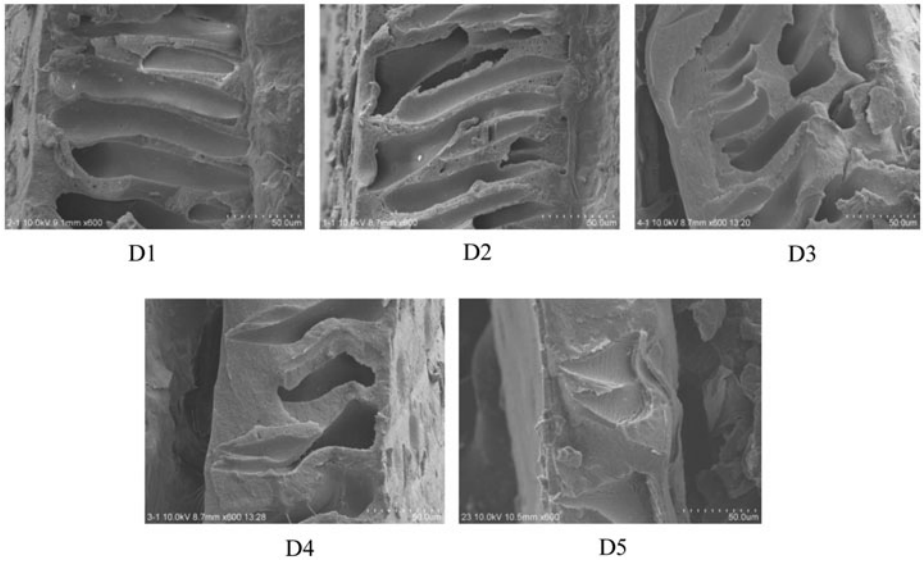

Fig. 8. SEM images of the cross-section of asymmetric PES/SPSF blend NF membranes with different mass concentrations of acetone: additive mass concentration: D1 (8 wt.%), D2 (11 wt.%), D3 (15 wt.%), D4 (18 wt.%), and D5 (20 wt.%).

3.3.2.2. Performances of PES/SPSF blend NF membranes. Fig. 9 shows that water flux declined with increasing acetone mass concentration. It seems that porosity declined and skin layer became more compact along with increasing of acetone mass concentration. As shown in Fig. 9, rejection of PEG increased with increasing acetone mass concentration. However, when the acetone mass concentration exceeded 15 wt.%, rejections of PEG1000 and PEG800 reached about 99.9 and 81%, respectively, and then increased very slowly. Increasing the acetone mass concentration of casting solution could cause more interaction of non-solvent and polymer that decreased dissolving power of solvent for polymer. Then this would further promote aggregation of polymer molecules through chain entanglement [17]. In addition, the higher concentration of acetone resulted in the evaporation of acetone on the membrane surface during exposure to the air, which would result in more dense skin on the surface of air side.

The results about rejection of salts in Fig. 10 indicate that rejections of Na_2SO_4 and NaCl increased with increasing acetone mass concentration. Rejection of Na_2SO_4 increased from 38.9 to 69.2% along with rejection of acetone mass concentration increasing from 11 to 15 wt.% and when acetone mass concentration exceeded 15 wt.%. However, when the mass concentration of the acetone increased in range from 5 to 20 wt.%, NaCl rejection increased slightly. The rejection of Na_2SO_4 for PES/SPSF blend NF membrane was much more than the rejection of NaCl, which indicated that it could separate monovalent salts from multivalent salts effectively.

As the previous discussion in section 3.2.2 indicated, it might be the reason for both size exclusion and electrostatic interaction to determine the rejection of Na_2SO_4 and NaCl. Increasing of the acetone mass concentration caused the skin denser on the membrane surface, which could make higher charge density on skin of the membrane. As the result, rejections of Na_2SO_4 and NaCl increased with increasing acetone mass concentration.

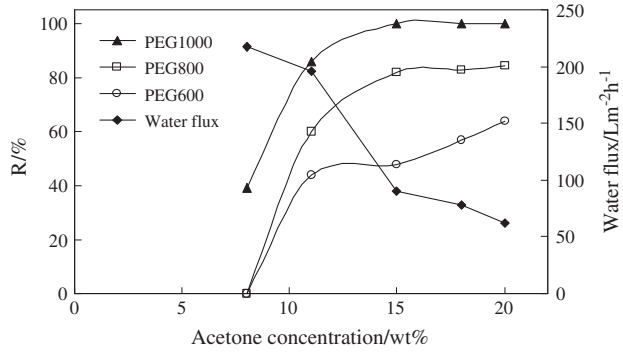

Fig. 9. Rejection of PEGs and water flux at different acetone mass concentrations: polymer concentration of PES plus SPSF was 25 wt.%.

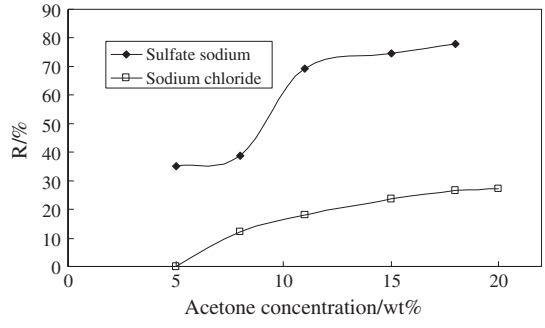

Fig. 10. Rejection of NaCl and Na_2SO_4 with different acetone mass concentration: polymer concentration of PES plus SPSF was 25 wt.%.

4. Conclusions

The novel PES/SPSF blend NF membranes with good performances had been prepared through blending SPSF with PES by phase inversion method. Results indicate that enrichment of sulfonic group occurred on the surface of PES/SPSF blend membranes. The water flux of PES/SPSF blend membranes decreased dramatically with increasing polymer concentration of PES plus SPSF. The rejection of PEG and salts increased with increasing mass concentration of the polymer PES and SPSF. The PES/SPSF blend membranes prepared by casting solution with acetone as additive had high PEG rejections and salts rejections with better compactness of membrane skin layer. The PES/SPSF blend NF membrane with less rejection of NaCl indicated that it could separate monovalent salts from multivalent salts effectively, which would be potential application in softening water for drinking water resource.

Acknowledgments

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