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Effect of Isomeric Propanols on the Performances of Polyethersulfone Nanofiltration Membranes

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Abstract: In this work, polyethersulfone (PES) asymmetric nanofiltration (NF) membranes were prepared by immersion precipitation phase inversion process. The casting solution contained *N*-methyl-2-pyrrolidone (NMP) as solvent, 1-propanol and 2-propanol as nonsolvent additives, and polyvinylpyrrolidone (PVP) as pore former additive. Water was used as a coagulant. The effects of the PVP content in the casting solution and the exposed time on the performances of the NF membranes were investigated. It was found that with the increase of PVP content, the pure water flux (PWF) increased to the largest value and then decreased. The rejection to PEG 1000 always decreased. The largest value ($1281.40\,kg \cdot m^{-2} \cdot h^{-1} \cdot MPa^{-1}$) of PWF appeared when the content of 1-propanol was 9 wt.%. However, when 2-propanol was added in the casting solution, the largest value of PWF was only $678.37\,kg \cdot m^{-2} \cdot h^{-1} \cdot MPa^{-1}$ (the content of 2-propanol was 7 wt.% and other preparing conditions were unchanged). The results meant that both PWF and rejection of the membranes with 1-propanol as additive were higher than that of 2-propanol as additive. The possible reason was discussed from the viewpoint of the difference of solubility of propanols to PES and PVP.

Keywords: Nanofiltration, phase inversion, polyethersulfone, propanol

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INTRODUCTION

Nanofiltration (NF) membranes have a low molecular weight cut-off (MWCO, 200~1000 Da) and unique selectivity for monovalent and divalent ions. They have been applied in many industry fields such as food, pharmaceuticals, biotechnology, dye, petrochemicals, and waste water treatment (1). In recent years, researching the manufacture of NF membranes has become the focus in the separation membrane field, following the reverse osmosis (RO) and ultrafiltration (UF) membrane techniques (2).

Immersion precipitation phase inversion is a famous technique for the preparation of polymeric asymmetric separation membrane (3). For this process, a homogeneous casting solution consisting of polymer and solvent is immersed into a nonsolvent coagulation bath. The exchange between the solvent and the nonsolvent due to liquid-liquid demixing causes the polymer casting solution to precipitate, by which various membranes are formed. In order to enhance the performances of the membrane, some additives are often added to the casting solution (4–6). For example, several authors reported that adding PVP in the casting solution produced high porous and well-interconnected membranes (7). Other studies reported that adding alcohols could significantly change the formation of membranes. Chen et al. studied the effect of the polarity of alcohols on membrane formation (8). They found that the thickness of the top skin layer decreased with the increase of the polarity of alcohols in casting solution. Xu et al. also observed the influence of different aliphatic alcohols on the structures of membranes (9). We found, however, that there were no reports on the effect of isomeric alcohols (such as 1-propanol and 2-propanol) on the formation or performances of NF membranes.

Polyethersulfone (PES) is a kind of high performances polymer material, which is widely used to prepare microfiltration, ultrafiltration, and gas separation membranes, because it possesses many of the favorable characteristics (10). In this work, PES NF membranes were prepared by immersion precipitation phase inversion technique using PVP and propanols as additives. The isomeric effect of 1-propanol and 2-propanol on the performances of PES NF membranes was investigated.

EXPERIMENTAL

Materials

PES (Ultrason E6020P) was purchased from BASF Co., Germany. PVP (K30) was purchased from Fluka Chemika, Switzerland. 1-propanol, 2-propanol, *N*-methyl-2-pyrrolidone (NMP), PEG 1000 were purchased from Tianjin Kermel Chemical Reagents Development Centre, China. Distilled water was used throughout this study.

Preparation of NF Membranes

The procedure of preparing PES NF membranes was as follows. First, PES and PVP were dissolved in a mixture of NMP and nonsolvent additives (1-propanol and 2-propanol) to form homogeneous casting solutions containing 24 wt.% of PES. After degassing, the casting solutions were cast on non-woven fabric support with a casting knife. The notch of the knife was 360 μm. After exposing in air for a period of time, the membranes were immersed into a water bath (10°C). During the preparation of the membranes, the room temperature was maintained at 20°C, and the relative humidity was about 60%. After three times of solvent exchange process with water in 24 h, the membranes were used for nanofiltration tests.

Nanofiltration Experiments

Nanofiltration experiments were carried out by using self-made equipment at room temperature. The effective area of the membrane was 7 cm^2. The pressure in the cell was maintained at 0.5 MPa with nitrogen gas. Pure water flux (PWF) of membranes was calculated by the following equation:

$$PWF = \frac{m_{\text{water}}}{A \times t \times \Delta P}$$

Where m_{water} was the weight of permeated water, A was the area of membranes, t was the permeation time, and ΔP was the transmembrane pressure.

An aqueous solution containing 0.5 g/L of PEG 1000 was used as the feed solution for the rejection test. After running for 15 minutes, the concentration of permeation was measured and the rejection (R) was calculated by the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

Where C_p and C_f were the concentration of PEG 1000 in the permeation and feed side, respectively.

RESULTS AND DISCUSSION

Effect of Isomeric Propanols Content on the Performances of NF Membranes

The content effect of 1-propanol and 2-propanol on the performances of NF membranes was studied by varying the content of propanol in the casting solutions from 7 to 18 wt.%, when the content of PVP was fixed for 7 wt.%. Figures 1 and 2 show the performances of NF membranes prepared by adding 1-propanol and 2-propanol, respectively.

From Figs. 1 and 2, a similar trend can be found, which is with the increase of content of propanols from 7 to 12 wt.%, the PWF of the membranes increases but the rejection to PEG 1000 decreases. In general, nonsolvents incline to reduce the solvent power of the solvent to the polymer, which will make the interaction between polymer-solvent to become weak. And this will induce the occurrence of intermolecular interaction between polymer-polymer (11). In other words, adding nonsolvent additives can make the polymer solution to become unstable and induce the process of phase separation to be easy, which is inclined to form a porous skin layer at the surface of the membrane. This is the reason for increasing the content of propanols which can increase the PWF of the membranes.

However, when the content of propanols is over 12 wt.%, there are different trends for PWF: the PWF of the membrane with 1-propanol

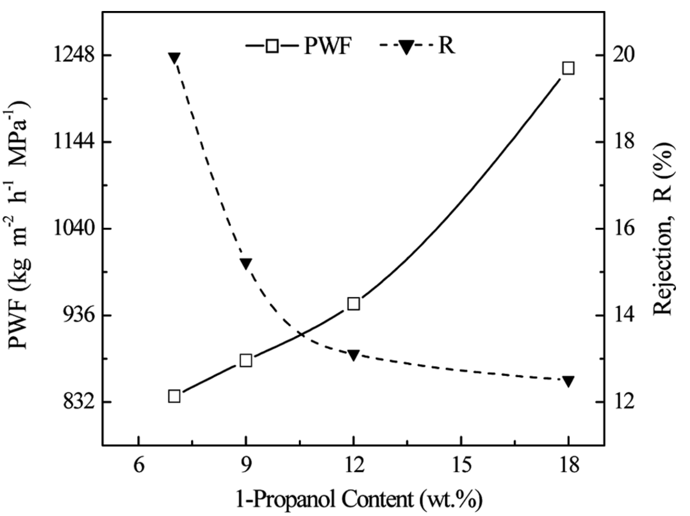

Figure 1. PWF and rejection at different 1-propanol content.

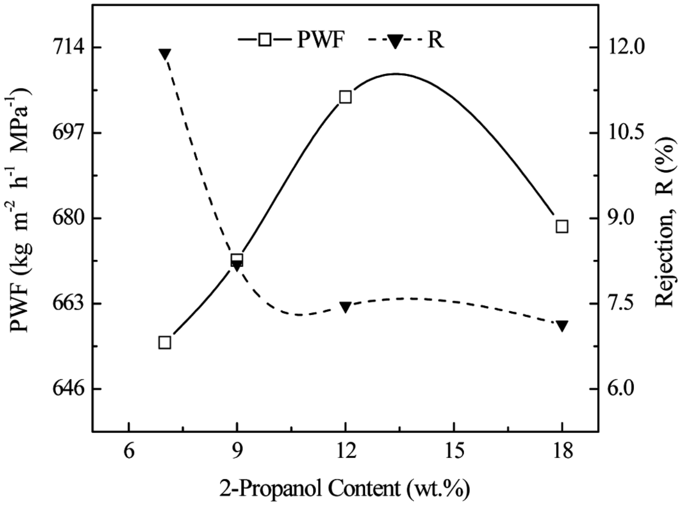

Figure 2. PWF and rejection at different 2-propanol content.

keeps increasing but the PWF of the membrane with 2-propanol decreases. Moreover, it is found that both the PWF and the rejection of the membrane with 1-propanol as additive are higher than that of with 2-propanol as additive. Figures 3 and 4 show the difference of PWF and rejection of the two kinds of membranes, respectively.

The reason for these phenomenon may be attributed to the different solubility of the propanols to PES and PVP. It has been known that the smaller difference of solubility parameters between a solvent and a polymer, the stronger solubility of the solvent is to the polymer (12, 13). The difference of the solubility parameters between two components ($\Delta\delta_{i-j}$) can be calculated by the following equation:

$$\Delta\delta_{i-j} = \sqrt{[(\delta_{d,i} - \delta_{d,j})^2 + (\delta_{p,i} - \delta_{p,j})^2 + (\delta_{h,i} - \delta_{h,j})^2]}$$

Where subscripts *d, p, h* stand for the dispersion interaction, the polar bonding and the hydrogen bonding, respectively. The subscripts *i* and *j* represent two components, respectively. The difference of solubility parameters between the two components of the casting solution is listed in Table 1. The data of solubility parameters were obtained from Reference (14).

It can be found that the solubility to PES decreases with NMP, 2-propanol and 1-propanol, while the order to PVP is increasing. As a polymeric additive, the addition of PVP reduced the solvent power for

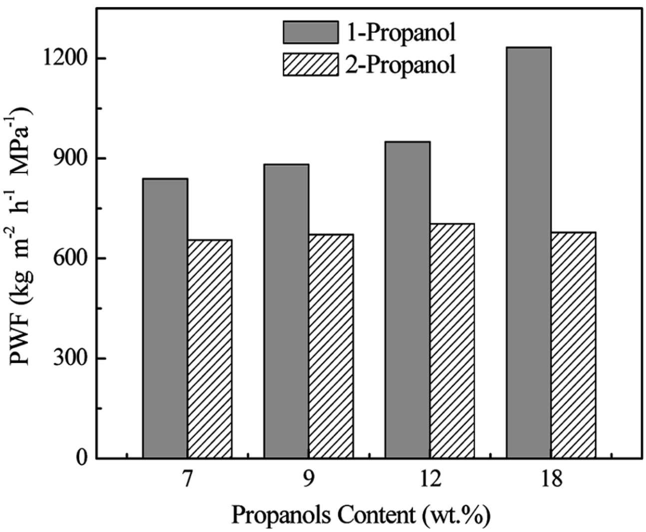

Figure 3. Influences of propanols content on PWF of membrane.

PES and made the viscosity of the casting solution to increase. This induced the solution to be unstable, and restricted the movement of the polymer chains. When adding 1-propanol in the casting solution, the

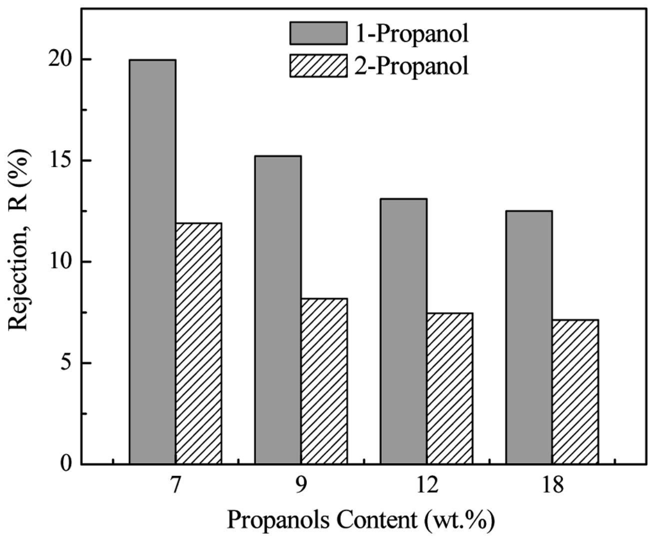

Figure 4. Influences of propanols content on rejection to PEG 1000.

Table 1. Difference of solubility-parameters between two components ($\Delta\delta_{i-j}$)

$\Delta\delta_{i-j}$ $(J \cdot cm^{-3})^{0.5}$	NMP	2-propanol	1-propanol	PVP
NMP	0	11.31	11.76	14.81
PES	2.03	9.78	10.38	14.36
PVP	14.81	9.42	8.36	0
Water	35.38	27.73	26.55	21.97

interaction between NMP/PVP was weakened since 1-propanol has stronger solubility to PVP than NMP. In other words, there was relatively more solvent (NMP) to dissolve PES. Consequently, the mobility of PES molecules increased when 1-propanol was added in the casting solution. Compared with 1-propanol, 2-propanol has stronger miscibility with NMP but weaker solubility to PVP. The better miscibility between the solvent and nonsolvent can make the phase separation of the casting solution to take more easily place because the nonsolvent competes with the polymer for the solvent (15). Due to both worse solubility of 2-propanol to PVP and the competition for NMP between 2-propanol and PES, the casting solution was less stable and its viscosity was higher than the casting solution adding 1-propanol.

According to the polarity concept, some researchers found that the interaction between water/2-propanol was stronger than the interaction between water/1-propanol (8). However, a contrary result is reached from the solubility parameters theory. As listed in Table 1, the difference of the solubility-parameters between water/2-propanol is larger than the value between water/1-propanol. It means that the interaction between water/2-propanol is weaker than the interaction between water/1-propanol. But the interaction between water/propanol is weaker than the interaction between water/PVP. Moreover, the interaction between PVP/propanol is quite stronger than the interaction between water/propanol. Consequently, direct liquid-liquid exchange between water and propanol seems to be impossible. Due to a stronger interaction existing between PVP/1-propanol than PVP/2-propanol, a rapid exchanging rate will happen between water and the casting solution containing 2-propanol, instead of 1-propanol, because the "activity" of PVP for exchanging with water in the casting solution containing 1-propanol will be more confined than in the casting solution containing 2-propanol. This will induce a rapid liquid–liquid demixing at the initial precipitation process and form a membrane structure with a porous skin layer. However, the high viscosity hampered the diffusion rate of molecules in the casting solution, which suppressed macrovoids formation in the sublayer during the precipitation progress (16). This influence on the structure of the membrane leads to the decrease of PWF. Therefore, the PWF of the membrane with 2-propanol as additive first increases and then decreases with the increase of the PVP content, and both PWF and the rejection of the membrane with 2-propanol as additive are lower than that of 1-propanol as additive, because the membrane adding 1-propanol will have more dense skin layer and porous support sublayer structure.

Effect of PVP Content on the Performances of NF Membranes

The effects of PVP content on the performances of PES NF membranes were researched by changing the content of PVP from 3 to 11 wt.% when the content of propanols was fixed at 7 wt.%. Figures 5 and 6 show PWF and rejection of the membranes when 1-propanol and 2-propanol were added in the casting solutions.

From Figs. 5 and 6, it can be found that with the increase of the PVP content, the PWF increases to a largest value and then decreases, but the rejection decreases. When adding PVP in the casting solution, there were two effects on the membrane formation process. First, the casting solution became unstable, and the phase separation process occurred easily. Second, the exchange rate between the solvent and the water became faster because PVP was a hydrophilic polymer. Therefore, the

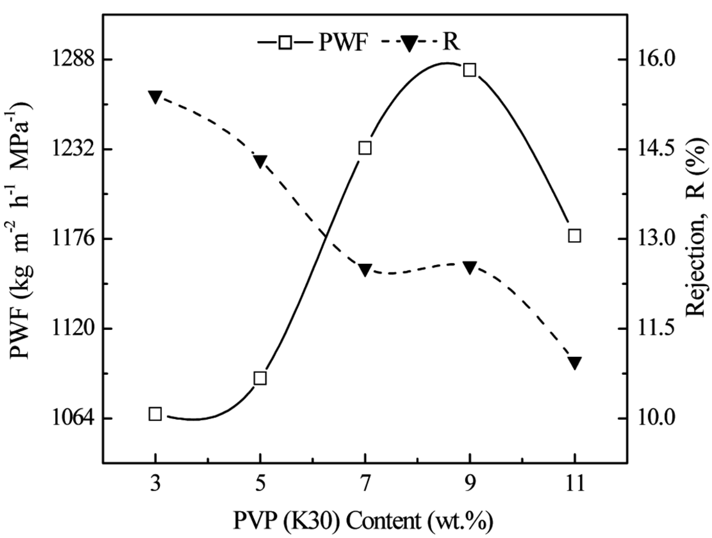

Figure 5. PWF and rejection at different PVP K30 content (nonsolvent additive was 1-propanol).

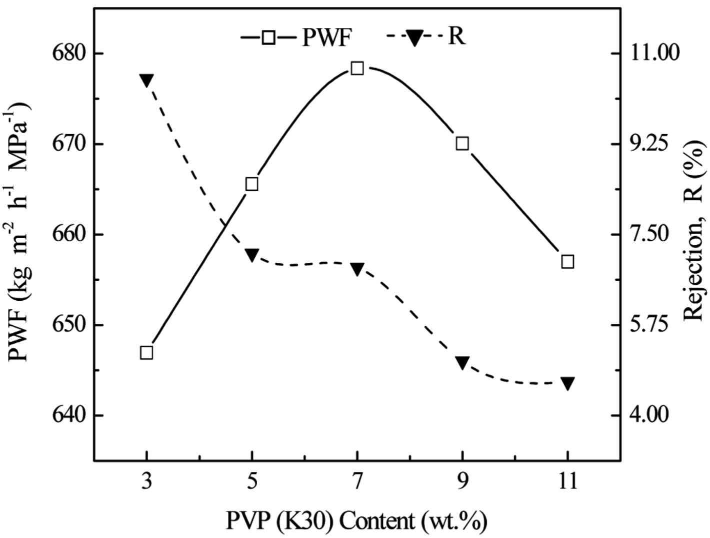

Figure 6. PWF and rejection at different PVP K30 content (nonsolvent additive was 2-propanol).

process of instantaneous liquid–liquid demixing took place in the initial precipitation process. This would lead to a porous skin layer in the membrane and the increase of PWF.

On the other hand, when adding PVP in the casting solution, the viscosity of the solution increased. The increase in viscosity suppressed the formation of macrovoids in the sublayer during the precipitation process, leading to the decrease of PWF. Consequently, the competition between these two mechanisms resulted in the trend shown in Figs. 5 and 6, which is that the PWF first increases and then decreases with the increase of PVP content but the rejection decreases. Due to the addition of 1-propanol enhances the mobility of polyethersulfone molecules, the largest value of PWF of the membrane appears at the content of 9 wt.% for 1-propanol, while it appears at 7 wt.% for 2-propanol.

Effect of Exposed Time on the Performances of the NF Membranes

The exposed time plays an important role in the process of preparing NF membrane by the immersion precipitation phase inversion technique. Figures 7 and 8 show the effect of the exposed time on the performance of the membranes when the content of PVP and propanols were 7 wt.% and 18 wt.%, respectively.

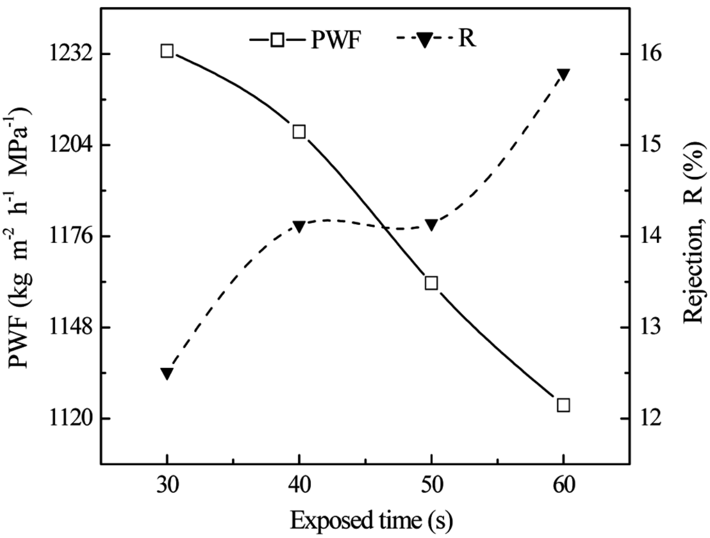

Figure 7. PWF and rejection at different exposed time (nonsolvent additive was 1-propanol).

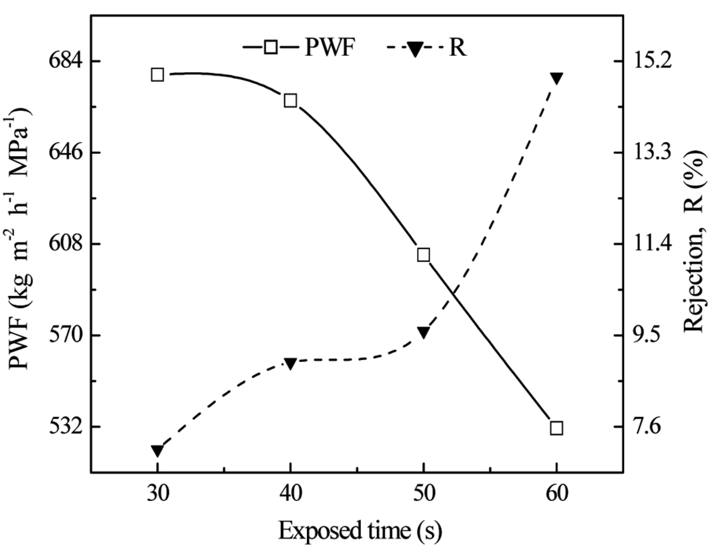

Figure 8. PWF and rejection at different exposed time (nonsolvent additive was 2-propanol).

From Figs. 7 and 8, it is found that with the increase of exposed time in air, the PWF of the membranes decreases but the rejection increases. Because propanols are volatile solvents at room temperature, the polymer content became higher at the interface between the polymer casting solution and air when the exposed time increased. Consequently, a thicker dense top layer formed which induced the decrease of PWF and the increase of the rejection. When adding the nonsolvent with lower boiling point in the casting solution, the influence of exposed time on the performance of the membrane will be more obvious. The boiling point of 1-propanol is 97.19°C, and b.p. of 2-propanol is 82.5°C. Consequently, the influence of exposed time on the performances of the membranes was significant when 2-propanol was added.

CONCLUSION

In this paper, polyethersulfone nanofiltration (NF) membranes were prepared by immersion precipitation phase inversion process with PVP and isomeric propanols as additives. It was found that 1-propanol and 2-propanol had different effects on the performances of the membranes. The possible reason was that their difference in solubility to PES and PVP induced the different influences. With the increase of PVP content from 3 to 11 wt.%, the PWF increased to the largest value and then decreased but the rejection decreased. The largest value of PWF appeared when the content of 1-propanol was 9 wt.%, and it appeared when the content of 2-propanol was 7 wt.%. This is a competition result between two different effects in the membrane formation process when adding PVP in the casting solution. We also found that the exposed time played an important role in the process of preparing NF membrane by immersion precipitation phase inversion technique. With the increase of the exposed time in air, the PWF of the membranes decreased but the rejection increased. Compared with adding 2-propanol, both PWF and the rejection of the membranes were higher when 1-propanol was added.

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