

Ethanol-Responsive Characteristics of Polyethersulfone Composite Membranes Blended with Poly(*N*-isopropylacrylamide) Nanogels

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ABSTRACT: Ethanol-responsive smart membranes with different microstructures are prepared from blends of polyethersulfone (PES) and poly(*N*-isopropylacrylamide) (PNIPAM) nanogels by immersion precipitation phase inversion method in a convenient and controllable manner. The introduction of PNIPAM nanogels forms the microporous structures on the surface of the top skin layer and on the pore walls of the finger-like porous sublayer of membranes. The ethanol-responsive characteristics of the proposed PES composite membranes are systematically investigated. With increasing ethanol concentration in the range from 0 to 15 wt %, the trans-membrane flux of ethanol solution increases. The microstructures and the resultant ethanol-responsive characteristics of the composite membranes can be regulated by the content of PNIPAM nanogels blended in the membranes. The more the content of PNIPAM nanogels blended in the membranes, the more the number of the submicron pores is, and thus the better the ethanol-responsive characteristics of the composite membranes. The proposed ethanol-responsive smart membranes are expected to be combined with the traditional pervaporation membranes as a smart valve to achieve continuous and highly efficient ethanol production during the biological fermentation. The preparation technique and results in this study provide valuable guidance for further design and the industrial-scale fabrication of novel composite membranes for application in ethanol separation systems. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41032.

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INTRODUCTION

Ethanol plays an important role in our daily life and in industrial, medical and food fields.¹ Ethanol is used to manufacture organic compounds, and is also the key component of liquor and renewable fuels. It is an important production technology to produce ethanol from the biomass resources. However, traditional biological fermentation technology has been limited by the tolerance capability of the yeast to the ethanol concentration.² The growing ethanol concentration in the fermentation tank results in the inactivity of the yeast and causes the low efficiency of the ethanol production. Therefore, a separation technology is required to effectively reduce the ethanol solution concentration to achieve the continuous and efficient ethanol production.

The pervaporation membranes have been widely reported to selectively separate ethanol from fermentation broth.^{3–10} However, the ethanol concentration in the fermentation tank is difficult to be maintained at a stable value, because the currently-

existed membranes cannot self-regulatively adjust the trans-membrane flux of ethanol in response to the change of the ethanol concentration during the biomass fermentation process. Meanwhile, the mass transfer performance of the pervaporation membranes is much sensitive to the environmental temperature.¹¹ The efficiency of ethanol fermentation will be lowered when the membranes are not operated at the optimal ethanol concentration and temperature. Fortunately, the developing smart membranes have the capability to autonomously adjust the permeation performance according to the external environmental stimuli, such as temperature,^{12–15} pH,^{16–18} and ion signal.^{19,20} Act as smart valves, the ethanol-responsive smart membranes are developed to self-regulatively adjust the trans-membrane permeability responding to the ethanol concentration. It is expectable to ensure the ethanol concentrations in the fermentation broths to be in a relatively stable level via combining the smart membranes with traditional pervaporation membranes. So far, there have been several reports on ethanol-

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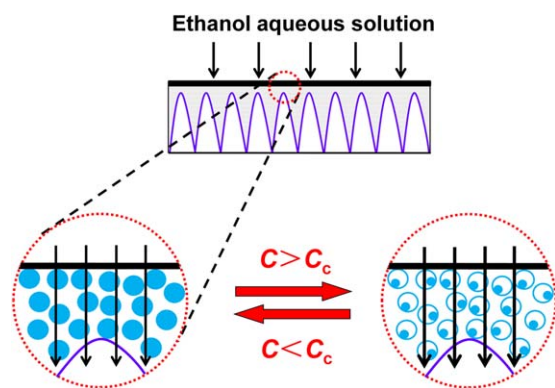


Figure 1. Schematic illustration of ethanol-responsive permeation across the PES composite membrane blended with PNIPAM nanogels. “ C ” and “ C_c ” stand for the ethanol concentration in the solution and the critical ethanol concentration, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

responsive membranes, which focus on the membranes prepared by grafting ethanol-responsive polymers into the porous membranes. Ito et al.² grafted poly(*N*-isopropylacrylamide) (PNIPAM) polymer chains onto the porous polyethylene (PE) substrates by using plasma grafting polymerization, and the resultant membranes achieved the ethanol-responsive gating function. Li et al.²¹ adjusted the ethanol-responsive critical concentration by grafting PNIPAM copolymers using atom transfer radical polymerization (ATRP). Although these smart membranes may be used to autonomously adjust the permeation performance of ethanol solution across the membranes, their preparation processes are somewhat complex and the grafting polymerization is still hard to achieve evenly in the deep membrane pores.²² In general, it is still difficult for the currently-existing grafting polymerization techniques to be applied in the large-scale industrial production of ethanol-responsive smart membranes.

Recently, the immersion precipitation phase inversion method has been used to prepare composite membranes from blends of membrane-forming materials and functional nanogels.^{23–25} Compared with the grafting polymerization techniques, this technique is more convenient and controllable; therefore, it is highly promising to be applied in the industrial-scale production of smart membranes.²³ Zhao et al.²⁶ prepared polyethersulfone (PES) composite membranes by blending PES/poly(*N*-vinyl pyrrolidone) (PVP) semi-interpenetrating network nanoparticles, and the hydrophilicity and the blood compatibility of the membranes were improved. The pH-sensitivity and the ion exchange capacity of the PES composite membranes are improved by blending poly(acrylic acid) (PAA) nanoparticles into PES membranes.²⁷ Moreover, Wang et al.²³ prepared the thermo-responsive composite PES membranes from blends of PES and PNIPAM nanogels. However, to the best of our knowledge, there has not been any report on ethanol-responsive composite membranes prepared by simply blending smart nanogels into membrane-forming materials using the immersion precipitation phase inversion method.

In this study, ethanol-responsive composite membranes are prepared by blending ethanol-responsive nanogels into membrane-

forming materials through the immersion precipitation phase inversion method. The permeation performances of ethanol solution across the composite membranes responding to the ethanol concentration are systematically investigated. The ethanol-responsive composite membranes can automatically regulate the trans-membrane flux responding to the environmental ethanol concentrations, as shown in Figure 1. In the ethanol solution with low concentration, the ethanol-responsive PNIPAM nanogels embedded in the composite membranes swell, which leads to the low permeability of ethanol solution across the composite membranes. However, when the ethanol concentration reaches to the critical ethanol response concentration (C_c), the ethanol-responsive PNIPAM nanogels shrink and the trans-membrane flux dramatically increases. Therefore, the ethanol-responsive composite membrane acts like a smart valve that self-regulatively adjusts the trans-membrane permeability responding to the ethanol concentration in the feed. The results in this study provide valuable guidance for further design and fabrication of novel ethanol-responsive composite membranes for application in ethanol separation systems.

EXPERIMENTAL

Materials

Polyethersulfone (PES) with molecular weight of 40 K is pre-dried at 120°C and used as the membrane-forming material. Monomer *N*-isopropylacrylamide (NIPAM; Sigma–Aldrich) is purified by recrystallization with a hexane-acetone mixture (50/50, v/v). *N,N*-dimethylacetamide (DMAc), *N,N*-methylenebisacrylamide (MBA) and ammonium persulfate (APS) are used as solvent, cross-linker and initiator, respectively. All the chemicals including ethanol (99.7%) are analytical grade. The water used in the experiments is well-deionized water from Millipore Milli-Q Plus water purification system.

Synthesis and Characterization of PNIPAM Nanogels

PNIPAM nanogels are synthesized by precipitation polymerization^{28,29} at 70°C. Monomer NIPAM (0.1 mol L⁻¹), cross-linker MBA (1, 5, and 10 mol %) and initiator APS (1 mol %) are dissolved in 200 mL of deionized water. The whole reaction is carried out in an anaerobic atmosphere for 6 h at a constant temperature of 70°C. Subsequently, the dispersion solution of PNIPAM nanogels is washed by centrifugation at the rotational speed of 8000 r min⁻¹ for six times. The resultant PNIPAM nanogels are dried by freeze-drying and reserved for further preparation of the composite membranes.

The morphology of the air-dried PNIPAM nanogels is observed by a Scanning Electron Microscope (SEM; JSM-7500F, JEOL). The size change of the PNIPAM nanogels in aqueous solution responding to ethanol concentration and temperature is determined by the Dynamic Light Scattering (DLS; Zetasizer Nano-ZS, Malvern). The dispersion solutions of PNIPAM nanogels are diluted to the concentration of 0.03 wt % for measurements.

Preparation and Characterization of Ethanol-Responsive PES Composite Membranes Blended with PNIPAM Nanogels

Ethanol-responsive PES composite membranes blended with PNIPAM nanogels are prepared by the immersion precipitation

phase inversion method. Because of its good mechanical, chemical, and thermal stability, PES is selected as the membrane-forming materials.^{30,31} About 17.5 wt % PES and a certain amount of freeze-dried PNIPAM nanogels are uniformly blended into DMAc solvent to form the casting solution. The casting solution is casted onto a glass plate and the wet membrane is formed by scraping at a constant speed of 1.725 m min⁻¹. The wet membrane is subsequently immersed in a water bath of 20°C for coagulating-forming. Later, the membranes are rinsed and soaked in the fresh deionized water for a week to get rid of the residual chemicals. The thickness of the composite membranes is measured by a digital thickness gauge and the average value is determined by measuring the different positions of the membranes for several times.

The SEM (G2 Pro, Phenom) is employed to observe the top and cross-sectional microstructures of the PES composite membranes. The membranes are mechanically fractured in liquid nitrogen to protect the integrity of the cross-sectional microstructures.

Ethanol-Responsive and Thermo-Responsive Permeability of Composite Membranes

A microfiltration apparatus with the controlled thermostatic unit is employed to investigate the dual ethanol-responsive and thermo-responsive permeability of the as-prepared membranes. The investigated membrane is preimmersed in the test solution to make the membranes fully soaked. Before the experiments, the membrane is placed in the microfiltration apparatus, and stabilized at a given temperature for 30 min. After bringing in a constant trans-membrane pressure of 0.2 MPa for a period of time, both the mass of test solution permeating across the investigated membrane and its corresponding time are recorded. The trans-membrane flux of the composite membrane is defined as the mass of test solution permeating through the membranes per unit membrane area and time, which is calculated by eq. (1):

$$J = \frac{m}{S \times t} \quad (1)$$

where J is the solution flux permeating through the membrane at a certain temperature [kg m⁻² h⁻¹], m is the mass of solution permeating through the membrane during the measured time [kg], S is the effective membrane area for the permeation [m²], and t is the measured time [h]. The trans-membrane fluxes of ethanol solutions with different concentrations (5–15 wt %) are measured. The investigated temperature range changes from 15 to 45°C.

To quantitatively study the thermo-responsive permeability of the composite membranes, an index that called as the thermo-responsive factor ($R_{T/15}$) is introduced. The thermo-responsive factor $R_{T/15}$ is defined as the ratio of the flux at a given temperature T to the flux at 15°C, which is calculated by eq. (2):

$$R_{T/15} = \frac{J_T}{J_{15}} \quad (2)$$

where J_T is the flux of water or ethanol solutions permeating through the composite membranes at a given temperature of T [kg m⁻² h⁻¹], and J_{15} is the flux across the membrane at 15°C

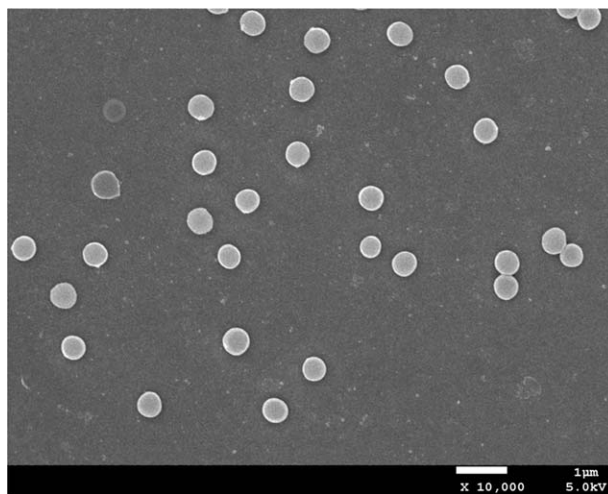


Figure 2. SEM image of the PNIPAM nanogels. The scale bar is 1 μm.

[kg m⁻² h⁻¹]. Similarly, a coefficient named the ethanol-responsive factor ($R_{CE/0}$) is defined as the ratio of the flux of ethanol solution to the water flux through the membrane at the same temperature in order to investigate the ethanol-responsive characteristics of composite membranes, as shown in eq. (3):

$$R_{CE/0} = \frac{J_{CE}}{J_0} \quad (3)$$

where J_{CE} is the flux of the ethanol solution permeating through the membrane at a certain temperature [kg m⁻² h⁻¹], and J_0 is the water flux permeating through the membrane at the same temperature [kg m⁻² h⁻¹].

RESULTS AND DISCUSSION

Morphology and Ethanol-Responsive Phase Transition Characteristics of PNIPAM Nanogels

The SEM image of PNIPAM nanogels prepared by precipitation polymerization exhibits good monodispersity and sphericity, as shown in Figure 2. The average diameter of the air-dried PNIPAM nanogels is about 600 nm.

The hydrodynamic size variation of the PNIPAM nanogels with the cross-linker concentration of 5 mol %, as functions of ethanol concentration and temperature, is shown in Figure 3. PNIPAM nanogels are initially in a swollen state in pure water and 20°C, and then shrink to the minimum as the ethanol concentration increasing. When the ethanol concentration increases further up to 45 wt %, the PNIPAM nanogels begin to reswell again. The swollen-to-shrunken-to-swollen behavior is due to both the rupture of hydrogen bonds between the amide groups on PNIPAM chains and water molecules, and the formation of the hydrogen bonds between the PNIPAM chains and ethanol molecules in ethanol/water mixtures.^{21,32–34} In pure water at 20°C, the water molecules form the hydrogen bonds with the amide groups of PNIPAM polymeric chains, which leads to the swelling of PNIPAM nanogels. With the increase of the ethanol concentration, the ethanol molecules are intended to concentrate around the PNIPAM chains to destroy the initial hydration effect. Finally, when enough ethanol molecules are introduced to exceed the critical response concentration C_c , the activation

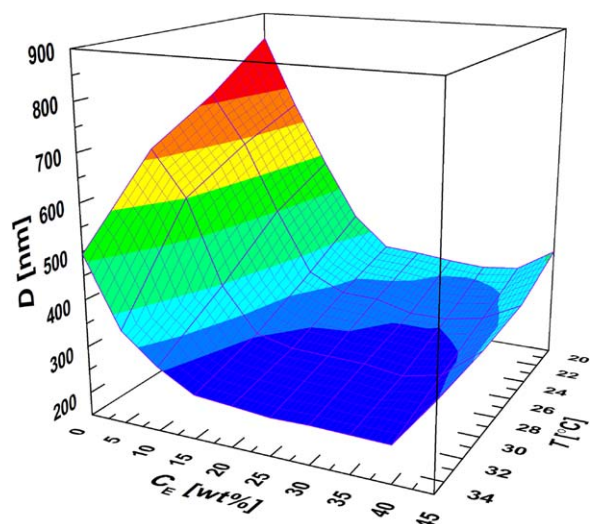


Figure 3. The hydrodynamic diameter change of the PNIPAM nanogels as functions of ethanol concentration and temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

energy of the ethanol solution is larger than the cohesive force of the PNIPAM chains. Therefore, the new hydrogen bonds between the ethanol molecules and PNIPAM chains are formed, resulting in the swelling of PNIPAM nanogels again. In addition, the environmental temperature also affects the volume change of the PNIPAM nanogels. With the increase of temperature, the PNIPAM nanogels show swollen-to-shrunken volume change due to the rupture of hydrogen bonds between the water molecules and PNIPAM polymeric chains. The result illustrates that the volume change behavior of PNIPAM nanogels is influenced by the change of both ethanol concentration and temperature.

The hydrodynamic diameter variation of PNIPAM nanogels with different cross-linker concentrations (1 and 10 mol %) responding to ethanol concentration and temperature are also investigated. The PNIPAM nanogels with crosslinker concentration of 5 mol % are chosen to fabricate PES composite membranes to further investigate the characterization of microstructure and the ethanol-responsive characteristics (please see Figure S1 and the discussion in Supporting Information).

Effect of Blended PNIPAM Nanogels on the Microstructure of Composite Membranes

The SEM images of the top surface and cross-sectional views of the blank and composite membranes are shown in Figures 4 and 5, respectively. The code M-0 represents the blank membrane without PNIPAM nanogels blended, while M-5, M-10, and M-15 represent the composite membranes blended with 5, 10, and 15% of mass fractions of PNIPAM nanogels, respectively. The typical structure of the dense skin layer and finger-like porous sub-layer prepared by the immersion precipitation phase transition method is observed in the SEM images of the blank membrane. However, the addition of PNIPAM nanogels results in a microporous structure of the composite membranes. There are many submicron pores appearing on the top surface and pore walls of the composite membranes. Moreover, the

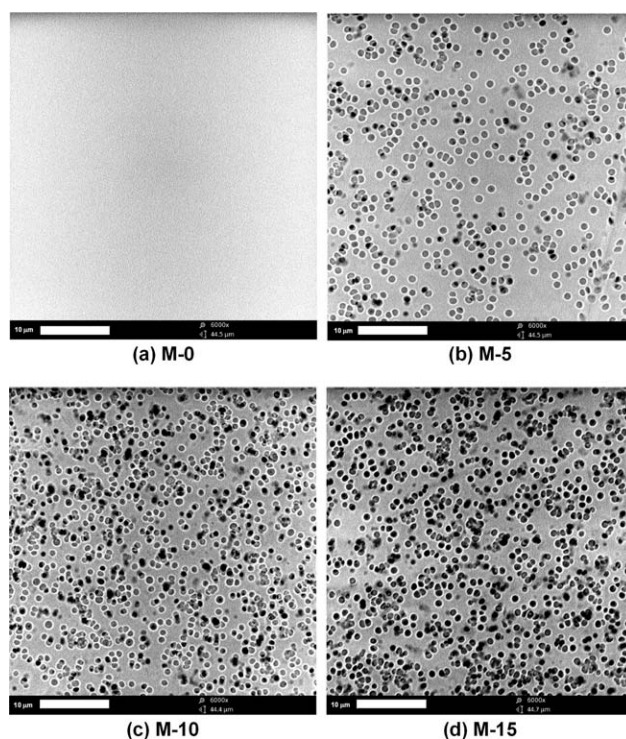


Figure 4. SEM images of top surface views of the membranes. (a) M-0, (b) M-5, (c) M-10, (d) M-15. The scale bars are 10 μm .

number of the submicron pores of composite membranes increases with increasing the mass fraction of PNIPAM nanogels, as shown in Figures 4(b–d) and 5(b–d). The formation of

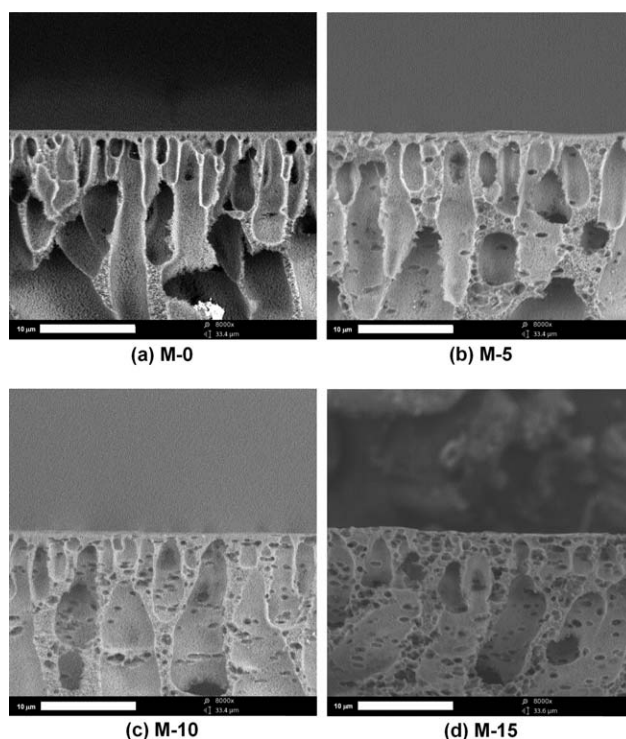


Figure 5. SEM images of cross-sectional views of the membranes. (a) M-0, (b) M-5, (c) M-10, (d) M-15. The scale bars are 10 μm .

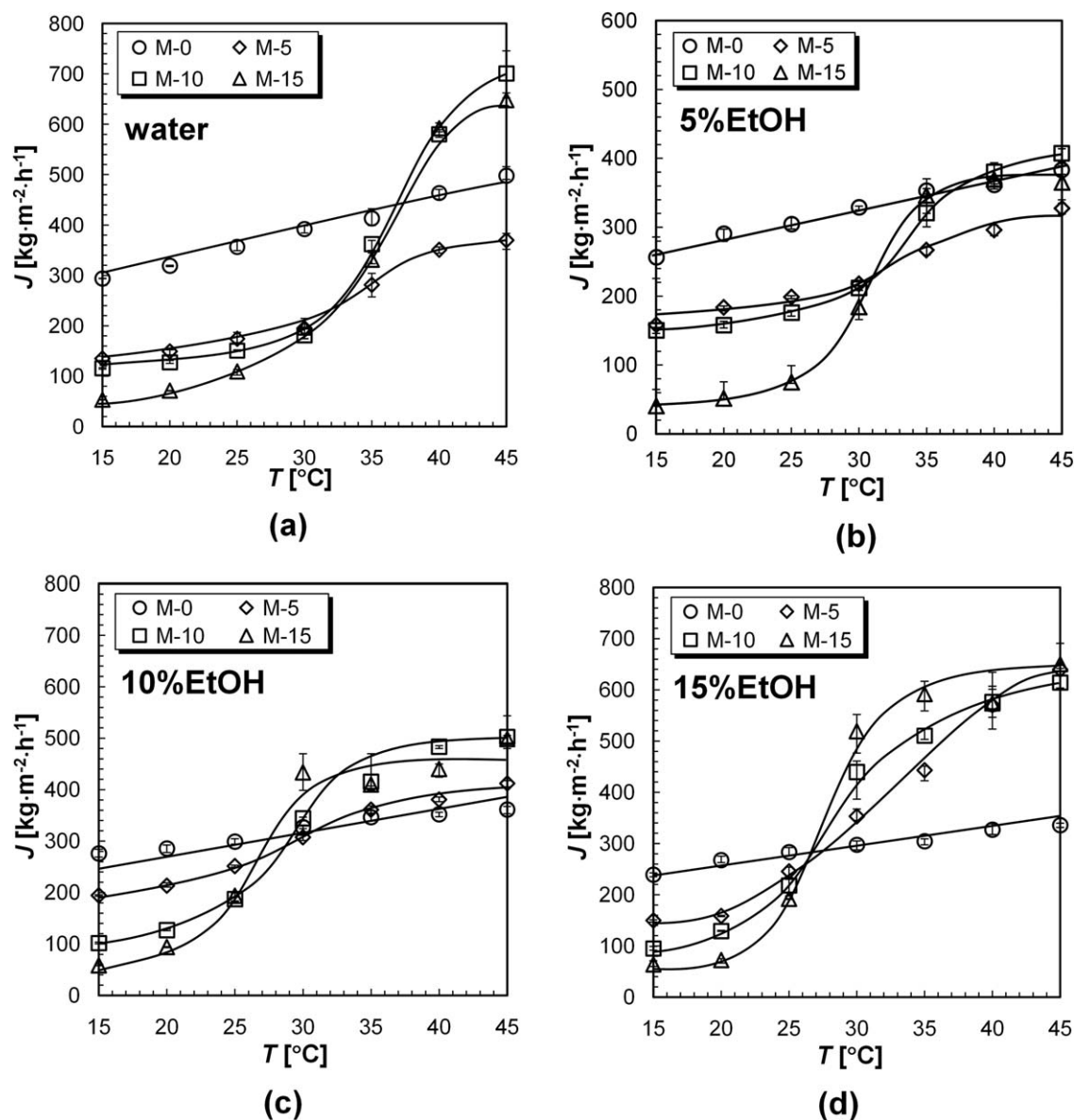


Figure 6. Temperature-dependent ethanol solution fluxes with different concentration across the composite membranes with different microstructures. Ethanol concentrations are (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, and (d) 15 wt %, respectively.

the submicron pores is attributable to the effects of both the hydrophilicity of PNIPAM nanogels and the viscosity of the casting solution on the thermodynamic instability and the kinetic rate during the phase separation process.^{35,36} When the PNIPAM nanogels are added, the casting solutions with higher viscosity affect the exchange rate between solvent and nonsolvent. The hydrophilicity of PNIPAM nanogels enhances the thermodynamic instability of the casting solution, disturbing the diffusion direction of the liquid–liquid phase separation. Subsequently, the driving force for precipitation is reduced and the microphase separation is occurred in partial area, and then the membranes with submicron pores on the surface and walls of the finger-like pores are formed. However, there is no trans-membrane micro-pores observed in cross-section of dense skin layer of composite membrane (please see Figure S2 in Supporting Information). Therefore, the ethanol-responsive permeability

and thermo-responsive permeability of PES composite membranes will be greatly influenced by the volume change of PNIPAM nanogels blended in the composite membranes as the functions of ethanol concentration and temperature.

Dual Ethanol-Responsive and Thermo-Responsive Characteristics of Composite Membranes with Different Microstructures

Considering that temperature is one of the most important variables in fermentation performance,^{37,38} it is important to investigate the effect of temperature change on the flux of ethanol solution during the permeation process. Effects of environmental temperature on the fluxes (J) of water and ethanol solutions through the composite membranes with different microstructures are shown in Figure 6. For the blank membrane (M-0), the fluxes of pure water or ethanol solutions simply increase

with increasing the environmental temperature. However, for the composite membranes (M-5, M-10, and M-15), both the fluxes of pure water and ethanol solutions significantly change at a certain temperature as the environmental temperature increases. The temperature at which the flux changes significantly is referenced as the response temperature of composite membranes. At temperatures below the response temperature of composite membranes, the fluxes of water and ethanol solutions through the membranes are low, because the swollen PNIPAM nanogels result in high resistance for the trans-membrane permeation. However, the fluxes become higher at the temperatures above the response temperature because the PNIPAM nanogels shrink and a lot of microchannels are formed around the nanogels, which facilitate the trans-membrane permeation. The more the PNIPAM nanogels embedded in the membranes, the lower the fluxes through the composite membranes at temperatures below the response temperature, and the higher the fluxes at temperatures above the response temperature. The response temperatures of the composite membranes with different microstructures in the same solution are almost the same, while shift to lower values in the ethanol solutions compared with that in water. Moreover, the higher the concentration of ethanol solution is, the lower the response temperature. The response temperatures of the three composite membranes in water and 5, 10, and 15 wt % of ethanol solution are 35, 32, 30, and 28°C, respectively. The increase of the ethanol concentration is helpful to destroy the hydrogen bonds between water molecules and PNIPAM polymeric chains; as a result, the response temperature of the composite membranes decreases as the ethanol concentration increases. There is no mass loss of the PNIPAM nanogels from the as-prepared composite membranes during the whole permeation process, and the responsive permeation characteristics show satisfactorily reversible and reproducible in the experiments.

The values of thermo-responsive factor $R_{T/15}$ in the water and ethanol solutions are shown in Figure 7. The $R_{T/15}$ values of the blank membrane slightly increase with increasing temperature no matter how the ethanol concentration varies, which results from the decrease of the solution viscosity with increasing temperature. For example, the maximum thermo-responsive factor $R_{45/15}$ of blank membrane in water is 1.7 calculated by the measured water flux. This value is quite close to 1.8 that obtained by substituting the solution viscosity values at different temperatures into the Hagen–Poiseuille's Equation.¹² The result shows that the blank membrane without blended PNIPAM nanogels has no thermo-responsive characteristics.

The $R_{T/15}$ values of the composite membranes show dramatically change at temperature across the response temperature of membranes no matter how the ethanol concentration varies. In the same solution, the $R_{T/15}$ values of the composite membranes with the different microstructures are significantly influenced by the content of the embedded PNIPAM nanogels. The more the PNIPAM nanogels blended in the membrane, the larger the $R_{T/15}$ value at the same temperature T . For example, the maximum thermo-responsive factor $R_{45/15}$ of M-5, M-10, and M-15 membranes in the 10 wt % of ethanol solution is 2.1, 5.0, and 8.5, respectively. The result shows that the composite membranes

blended with more PNIPAM nanogels are always more sensitive to the change of temperature.

The thermo-responsive characteristics of the composite membranes are enhanced with increasing ethanol concentration as shown in Figure 7. At the operation temperature of 45°C, for example, the maximum $R_{45/15}$ value of the M-10 membrane at the ethanol concentration of 5 wt % is 2.7, which increases to 6.5 at the ethanol concentration of 15 wt %. With the increase of the ethanol concentration, there are enough ethanol molecules so that it is easy to destroy the hydrogen bonds between PNIPAM chains and water molecules. As a result, the increasing ethanol concentration triggers the volume phase transition of the PNIPAM nanogels and enhances the flux of ethanol solution through the composite membrane. The results verify that the thermo-responsive characteristics are influenced by both ethanol concentration and the microstructures of the composite membranes.

Ethanol-Responsive Characteristics of Composite Membranes

Three-dimensional diagrams are plotted to illustrate the ethanol-responsive characteristics of the composite membranes with different microstructures at different ambient temperatures, as shown in Figure 8. Taking into account the possible application of composite membranes in ethanol fermentation, the ethanol-responsive characteristics of the composite membranes at both the general ambient temperature of 20 and 25°C, and the commonly used operation temperatures of 30 and 35°C during fermentation processes are focused in this part. Moreover, the ethanol-responsive characteristics of composite membranes in the concentration range of ethanol from 0 to 15 wt % are investigated, considering that the optimal tolerance concentration of yeast is ~8–10 wt %.²

The flux of ethanol solution across the blank membrane (M-0) decreases from 420 kg m⁻² h⁻¹ to 270 kg m⁻² h⁻¹ with increasing ethanol concentration from 0 to 15 wt % and decreasing temperature from 35 to 20°C. The viscosity of ethanol solution increases with increasing ethanol concentration at a constant temperature, while increases with decreasing temperature at a constant ethanol concentration.³⁹ According to the Hagen–Poiseuille's equation, the increase in the viscosity of ethanol solution leads to the decline of the trans-membrane flux of the blank membrane. Therefore, for the blank membrane, a lower ethanol concentration and a higher temperature result in a higher trans-membrane flux. However, the fluxes of ethanol solutions through the composite membranes blended with different contents of PNIPAM nanogels (M-5, M-10, and M-15) increase with increasing the ethanol concentration or the temperature. When the ethanol concentration increases from 0 to 15 wt % and the ambient temperature increases from 20 to 35°C, the trans-membrane fluxes of ethanol solutions across the M-5, M-10, and M-15 membranes dramatically increase from 150, 125, and 70 kg m⁻² h⁻¹ to 450, 500, and 580 kg m⁻² h⁻¹, respectively. Clearly, the more the PNIPAM nanogels blended in the composite membranes, the higher the fluxes through the composite membranes at higher ethanol concentration and higher temperature. The difference between the minimum and maximum fluxes through the composite membranes is gradually extended with increasing content of PNIPAM nanogels. For

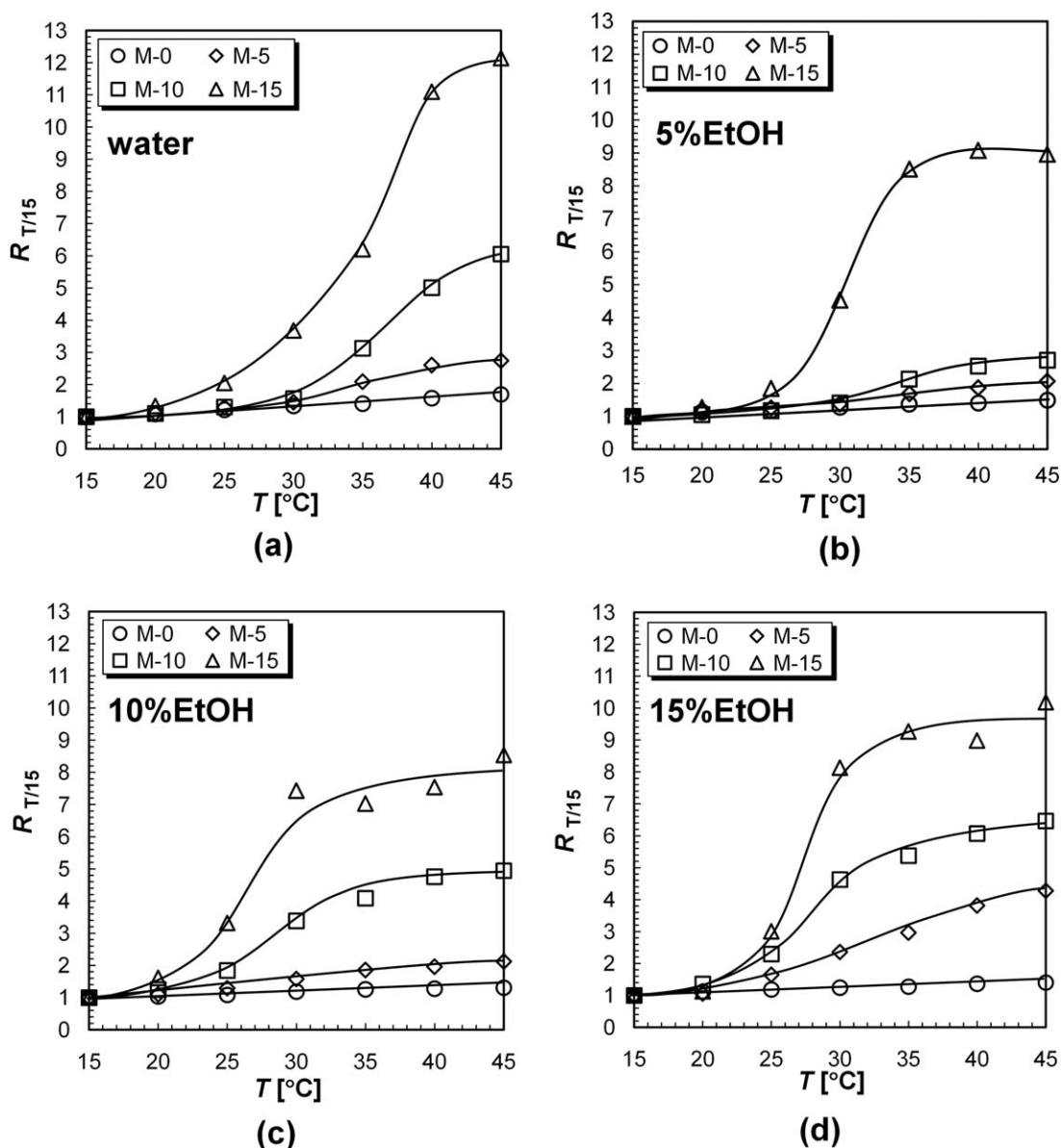


Figure 7. Thermo-responsive factors of the composite membranes with different microstructures in different ethanol solutions. Ethanol concentrations are (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, and (d) 15 wt %, respectively.

example, the maximum flux of M-5 membrane is approximately three times as the minimum value in the ranges of the investigated ethanol solutions and temperatures. However, the ratio of the maximum flux to minimum flux of M-15 membrane rises to 8.2 with increasing the content of PNIPAM nanogels to 15 wt %. At a lower ethanol concentration and a lower temperature, the PNIPAM nanogels are in a swollen state. The swollen PNIPAM nanogels inside the composite membranes tend to choke pores, resulting in a decrease in the trans-membrane flux. On the contrary, at a higher concentration and a higher temperature, the embedded PNIPAM nanogels are in a shrunken state. In this case, the shrunken PNIPAM nanogels blended inside the composite membranes tend to create channels around them, leading to an increase in the trans-membrane flux. With increasing the content of PNIPAM nanogels embedded in the

composite membrane, more pores are choked in the composite membrane and thus the trans-membrane flux decreases at a lower ethanol concentration and a lower temperature. At a higher ethanol concentration and a higher temperature, larger channels exist in the composite membrane and thus the trans-membrane flux increases. Therefore, the M-15 membrane, which is provided with the highest content of PNIPAM nanogels among the investigated membranes, exhibits the best thermo-responsive and ethanol-responsive characteristics in this study. Compared with the linear PNIPAM grafted membranes reported in the literatures,^{2,21} the PES composite membranes blended with PNIPAM nanogels show more superior performance of high trans-membrane flux and ethanol-responsive flux variation simultaneously (please see more detailed information in Supporting Information).

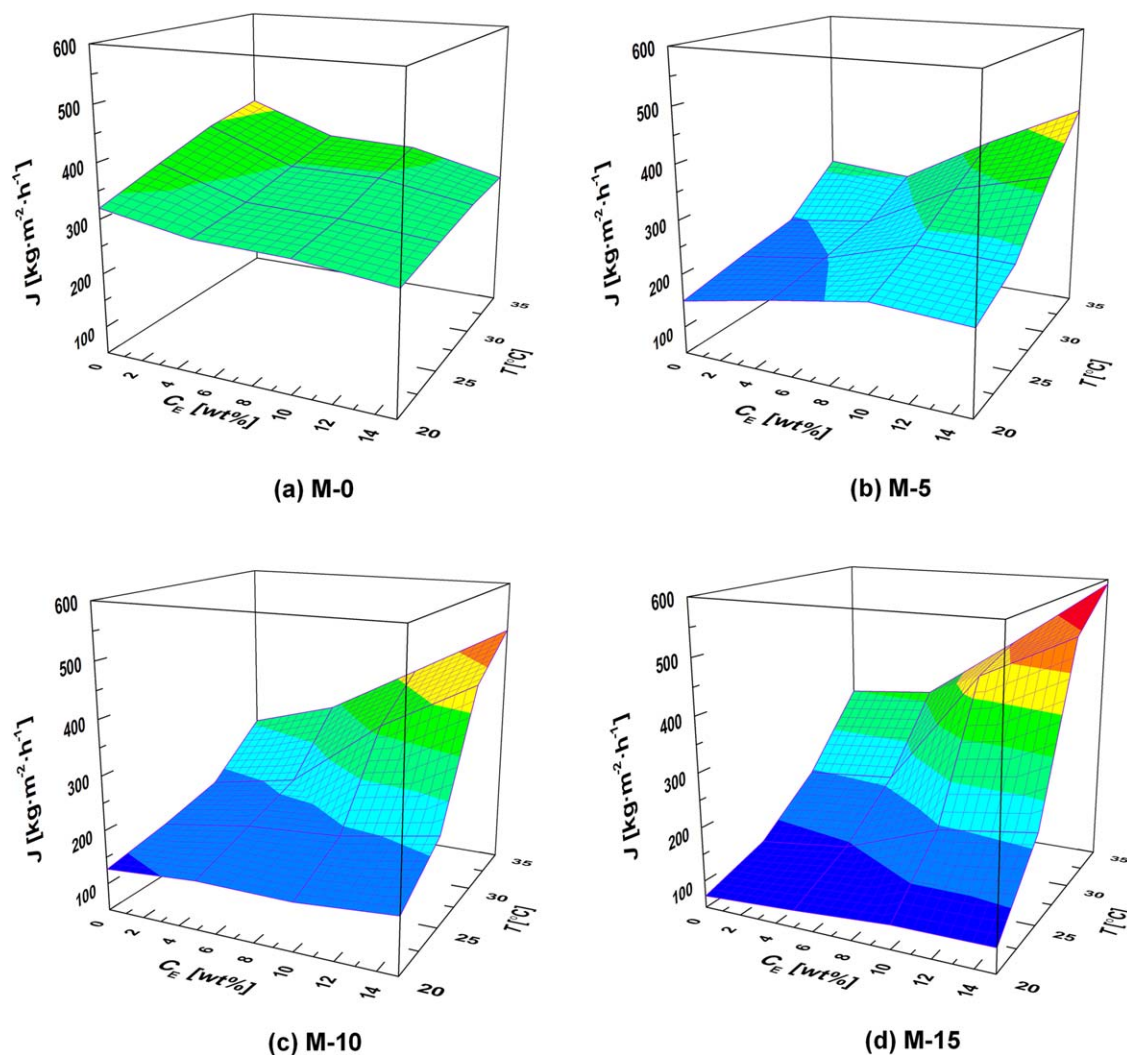


Figure 8. Fluxes of ethanol solutions across the composite membranes as functions of ethanol concentration and temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The effect of the operation temperature on the ethanol-responsive characteristics of the composite membranes is shown in Figure 9. For the blank membrane (M-0), the value of ethanol-responsive factor $R_{CE/0}$ slightly and simply decreases with increasing concentration of the ethanol solution within the investigated operation temperature range. It is attributable to that the viscosity of the ethanol solution slightly increases with increasing ethanol concentration from 0 to 15 wt %. The operation temperature has nearly no effect on the $R_{CE/0}$ value of the blank membrane. Taking M-10 membrane as an example of composite membrane, however, the $R_{CE/0}$ value increases with increasing ethanol concentration. The $R_{CE/0}$ value of M-10 at 30°C increases from 1.2 to 2.4 when the ethanol concentration goes up from 5 to 15 wt %. In addition, the operation temperature shows a heavy effect on the $R_{CE/0}$ value of the composite membrane. Specifically, the $R_{CE/0}$ value of the composite membrane increases first and then decreases with increasing operation temperature at a certain ethanol concentration. The maximum $R_{CE/0}$ value of M-10 membrane, which is the ratio of the flux of ethanol solution with concentration of 15 wt % to

water flux, is 1.2 at 20°C, 1.4 at 25°C, 2.4 at 30°C and 1.9 at 35°C, respectively. As mentioned above, with increasing the ethanol concentration from 0 to 15 wt %, the response temperature of composite membrane decreases from 35°C in water to 28°C in 15 wt % of ethanol solution. Moreover, the trans-membrane flux of the composite membrane at temperatures above the response temperature is larger than that below the response temperature. At operation temperatures of 20 and 25°C, which are below the lowest response temperature of 28°C in the ethanol solution, the trans-membrane flux of the composite membrane slightly increases with increasing ethanol concentration. Therefore, the maximum $R_{CE/0}$ value of M-10 membrane in the ethanol solution of 15 wt % slightly increases to 1.2 at 20°C and 1.4 at 25°C, respectively. At operation temperature of 35°C, which is above the response temperature of the composite membrane either in water and ethanol solution, the trans-membrane flux also slightly increases with increasing ethanol concentration. The maximum $R_{CE/0}$ value of M-10 membrane in the ethanol solution with the concentration of 15 wt % increases to 1.9 at 35°C. At 30°C, however, the trans-

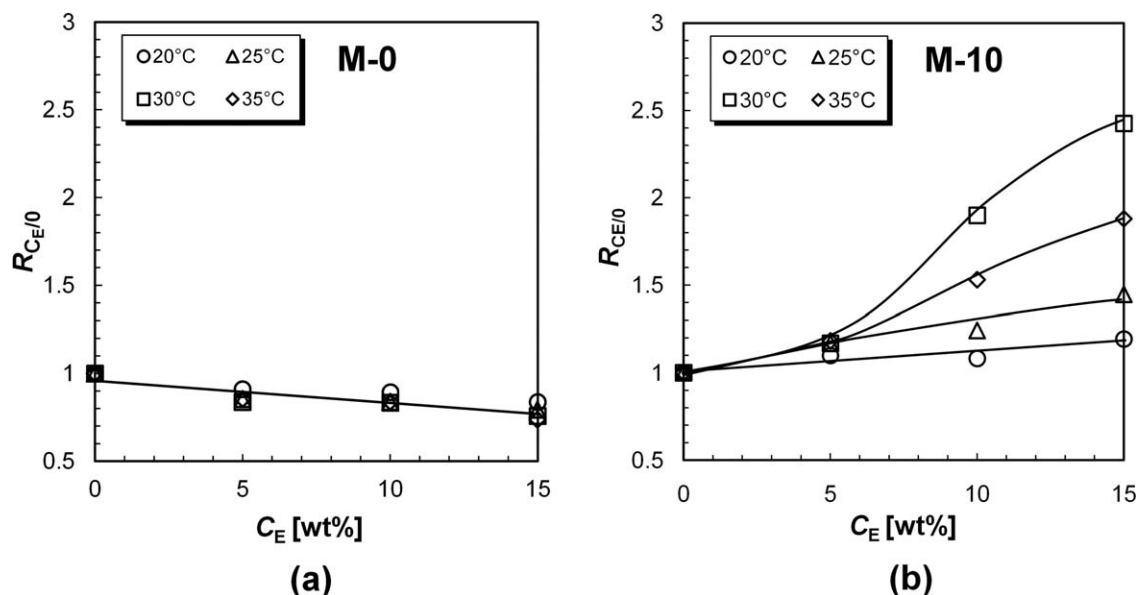


Figure 9. Effects of the operation temperature on the ethanol-responsive factor ($R_{CE/0}$) for the blank membrane M-0 (a) and the composite membrane M-10 (b).

membrane flux of ethanol solution with concentration of 15 wt % becomes much larger than that of water. It is attributable to that the operation temperature of 30°C is higher than the response temperature of 28°C in ethanol solution of 15 wt %, while lower than that of 35°C in water. As a result, the maximum $R_{CE/0}$ value of M-10 membrane at 30°C reaches to the maximum value of 2.4 in the investigated operation temperature range. The results show that the composite membrane blended with PNIPAM nanogels is provided with the best ethanol-responsive characteristics at the operation temperature of 30°C.

The effect of the content of PNIPAM nanogels embedded in the composite membranes on the ethanol-responsive characteristics is illustrated in Figure 10. The ethanol-responsive factor $R_{CE/0}$ at the same temperature and the same ethanol solution increases with increasing the content of the embedded PNIPAM nanogels. For example, at 30°C and ethanol concentration of 15 wt %, the $R_{CE/0}$ value of the M-15 membrane is 2.6, which is larger than 2.4 of M-10 membrane and 1.8 of M-5 membrane. Moreover, the effect of the content of PNIPAM nanogels on the $R_{CE/0}$ value becomes more significant as the concentration of ethanol solution increasing. The higher the content of PNIPAM

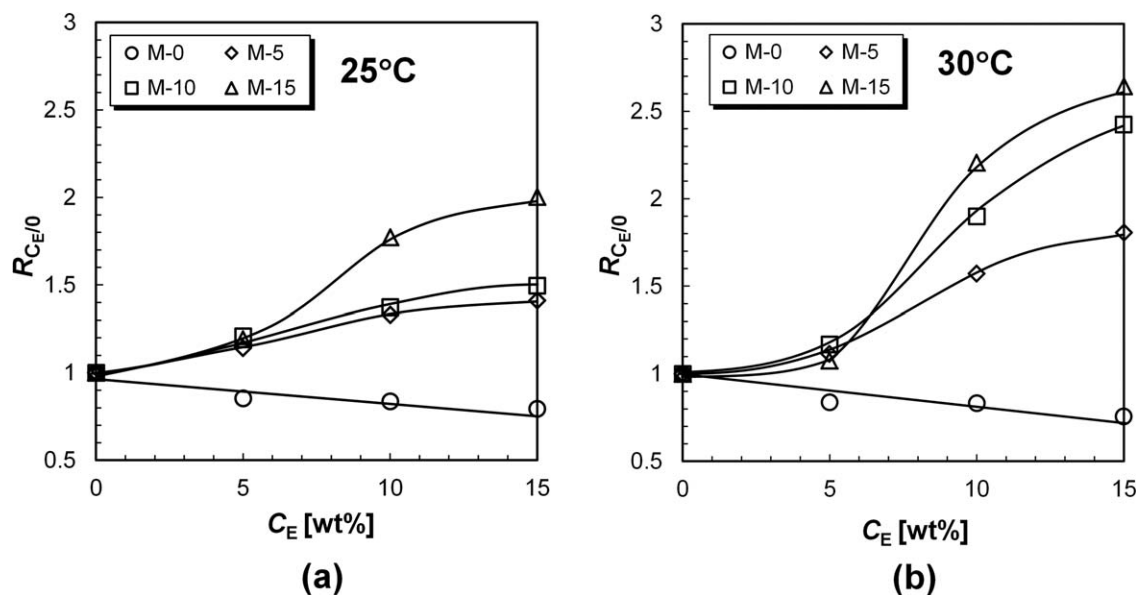


Figure 10. Effects of the mass fraction of PNIPAM nanogels on the ethanol-responsive factor ($R_{CE/0}$) at different operation temperatures. (a) 25°C, and (b) 30°C.

nanogels, the larger the difference between the trans-membrane fluxes of ethanol solution and that of water, especially when the ethanol solution is above the critical ethanol response concentration (C_c). In the ethanol solution at 25 and 30°C, especially when the concentration is higher than C_c , more microchannels form in the composite membrane with higher content of PNIPAM nanogels compared with that in water. The ethanol-responsive mechanism of PES composite membrane with PNIPAM nanogels is the same as that of PNIPAM nanogels as mentioned above. In addition, compared with that at 25°C, the maximum ethanol-responsive factor $R_{CE/0}$ of the same composite membranes at 30°C is higher. When the operation temperature increases from 25 to 30°C, the maximum $R_{CE/0}$ values of the M-5, M-10, and M-15 membranes respectively go up to 1.8, 2.4, and 2.6 from 1.4, 1.5, and 2.0. The results verify again that 30°C is the optimum operation temperature for the ethanol-responsive composite membranes.

CONCLUSIONS

In summary, ethanol-responsive PES composite membranes blended with PNIPAM nanogels are successfully developed by introducing the immersion precipitation phase inversion method. The blending of PNIPAM nanogels results in microporous structure in the PES composite membranes. The as-prepared composite membranes with different contents of PNIPAM nanogels exhibit satisfactory ethanol-responsive characteristics. The trans-membrane fluxes of ethanol solution across the composite membranes increase as both the concentration of ethanol solution and the operation temperature increasing. The optimum operation temperature for the ethanol-responsive composite membranes is 30°C, at which the membranes are provided with the best ethanol-responsive characteristics. At 30°C, the maximum ethanol-responsive factor $R_{CE/0}$ value of M-10 membrane reaches to a maximum value of 2.4. The ethanol-responsive characteristics of the composite membranes are heavily influenced by the content of PNIPAM nanogels blended in the membranes. The more the PNIPAM nanogels blended in the membranes, the larger the $R_{CE/0}$ values, the better the ethanol-responsive characteristics of the membranes. The preparation technique and results in this study provide a valuable guidance for further design and large-scale production and/or application of ethanol-responsive smart membranes.

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