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Enhanced Pervaporation Performance of Multi-layer PDMS/PVDF Composite Membrane for Ethanol Recovery from Aqueous Solution

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Abstract Multi-layer PDMS/PVDF composite membrane with an alternative PDMS/PVDF/non-woven-fiber/PVDF/PDMS configuration was prepared in this paper. The porous PVDF substrate was obtained by casting PVDF solution on both sides of non-woven fiber with immersion precipitation phase inversion method. Polydimethylsiloxane (PDMS) was then cured by phenyltrimethoxylsilane (PTMOS) and coated onto the surface of porous PVDF substrate one layer by the other to obtain multi-layer PDMS/PVDF composite membrane. The multi-layer composite membrane was used for ethanol recovery from aqueous solution by pervaporation, and exhibited enhanced separation performance compared with one side PDMS/PVDF composite membranes, especially in the low ethanol concentration range. The maximum separation factor of multi-layer PDMS/PVDF composite membrane was obtained at 60 °C, and the total flux increased exponentially along with the increase of temperature. The composite membrane gave the best pervaporation performance with a separation factor of 15, permeation rate of 450 g/m^2h with a 5 wt.% ethanol concentration at 60 °C.

Keywords Multi-layer · PDMS/PVDF · Composite membrane · Pervaporation

Introduction

The production of ethanol biofuels from biomass resources has caught increasing attention for the purpose of developing an alternative fuel to fossil ones [1–4]. Since microorganisms usually experienced strong ethanol inhibition as ethanol concentration exceeded 5~8 wt.%, ethanol recovery from the fermentation broth was needed [5]. Pervaporation has been considered as an efficient, cost-effective manner for ethanol recovery from fermentation broth due to its low energy consumption, optimized integration of pervaporation with fermentor, synergy of performing both ethanol concentration, and solvent dehydration, etc. [6–7].

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The properties of the membrane material and feed species are the main factors determining the separation performance achieved in the pervaporation process. There are several kinds of ethanol perm-selective membrane materials, such as silicone-containing polymers (PDMS, PTMSP, etc.) [8–10], fluorine-containing polymers [11–12], and other hydrophobic polymers [13]. As the current benchmark of hydrophobic membrane material, PDMS is often used for concentration of dilute ethanol aqueous solutions. However, the selectivity of pure PDMS reported is very low, with the separation factor for ethanol concentration from water ranging from 4.4 to 10.8 [14]. Much effort has been expended to improve the overall pervaporation performance of PDMS membranes due to its low-cost and easiness to handle, but there was no breakthrough in selectivity or permeation flux of pure PDMS membranes.

In the present paper, a multi-layer PDMS/PVDF composite membrane with an alternative PDMS/PVDF/non-woven-fiber /PVDF/PDMS configuration was prepared to surpass the limit of pure PDMS' selectivity for ethanol recovery from aqueous solutions. The multi-layer composite membrane showed enhanced separation performance of ethanol/water solutions compared with one side PDMS/PVDF composite membrane.

Experimental

Materials

Pure α,ω-polydimethylsiloxanediol (PDMS) was purchased from Beijing Chemical Reagents Corporation, with an average molecular weight of 50,000 determined by GPC. *n*-hexane and di-*n*-butyltin dilaurate (DBTOL) were obtained from Beijing Jingyi Chemical Reagents Corporation, and was used as received. Phenyltrimethoxylsiane (PTMOS) was supplied by New Chemical Materials Corporation of Yingcheng Debang. Polyvinylidene fluoride (PVDF, 1015) was used for the preparation of porous membrane support. Triethyl phosphate (TEP, reagent grade, Beijing Chemical Corporation) was used as the solvent for PVDF membrane formation. All reagents were used as received unless otherwise mentioned.

Preparation of Bi-layer PVDF Membrane

The bi-layer PVDF membrane was prepared by dissolving PVDF in TEP to form a 15 wt.% dope solution, which was cast on both sides of the non-woven fiber and immersed into water to induce polymer precipitation. The residual solvent was exchanged with alcohol for 5 min and dried at room temperature. The thickness of the single PVDF layer was controlled in the range of 45 μm~50 μm determined by a micro screw gauge.

Preparation of PDMS/PVDF Composite Membrane

Multi-layer PDMS/PVDF Composite Membrane

Pure PDMS and cross-linking reagent PTMOS were dissolved in *n*-hexane with vigorous stirring and then organometallic tin catalyst was added into the solution. The resulted homogeneous PDMS solution was coated onto the both sides of the porous PVDF substrate one side by the other and dried at room temperature for 48 h. The configuration schematic diagram of multi-layer PDMS/PVDF composite membrane was shown in Fig. 1. The

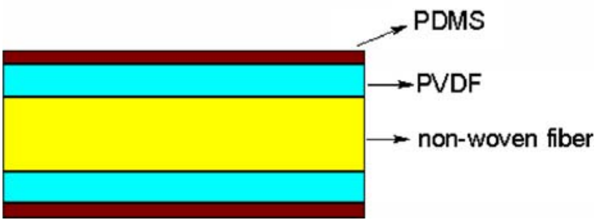


Fig. 1 Schematic diagram of multi-layer PDMS/PVDF composite membrane

thickness of the PDMS layer ranged from 5 to15 μm which was determined by field emission scanning electron microscope (FESEM, Quanta200 FEG). Simultaneously, the relative element composition in the cross-section of PDMS/PVDF composite membrane was recorded by EDX line scan.

Single-layer PDMS/PVDF Composite Membrane

The PVDF dope solution containing 15 wt.% PVDF obtained in 2.2 was cast onto only one side of the non-woven fiber and other post treatment was all the same as 2.2. The casting solution of PDMS was just coated onto the PVDF surface obtained above.

Pervaporation Separation Process

Pervaporation experiments were conducted by using an apparatus developed by our laboratory as shown in Fig. 2. The experiments were carried out with low ethanol feed concentration ranging from 5 to 30 wt%. And the operation temperature varied from 40 to 80 °C with the permeate side pressure of ca. 200 Pa. The permeation vapor was condensed and collected using a liquid nitrogen trap. The composition of permeate collected in the trap

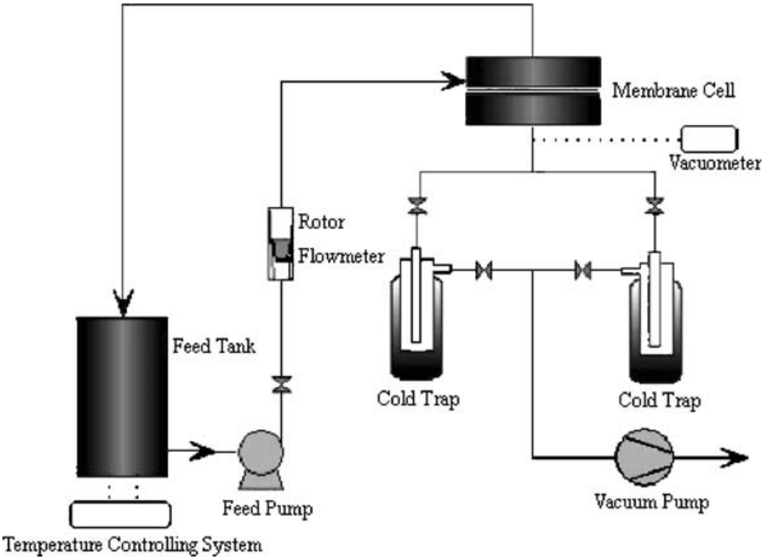


Fig. 2 Schematic diagram of the pervaporation apparatus

was analyzed by gas chromatography to determine the separation factor. The total flux and separation factor are defined as follows:

$$J = \frac{Q}{AT} \tag{1}$$

Where Q (g) is the total mass of permeate collected in T hours, and A (m^2) denotes the effective area of the membrane.

$$\alpha = \frac{Y_A \cdot X_B}{X_A \cdot Y_B} \tag{2}$$

Where X_A and X_B represent the ethanol and water concentrations (wt.%) in the feed solution respectively, and Y_A and Y_B represent the ethanol and water concentrations (wt.%) in the permeate.

Results and Discussions

Preparation of the Multi-layer PDMS/PVDF Composite Membrane

Since PVDF was a porous membrane, dilute PDMS homogeneous solution was liable to plugging in the pores of PVDF membrane surface and may lead to the notable increase in permeation resistance across the interface of PVDF and PDMS for small molecules. In our work, PTMOS was chosen as the cross-linking reagent to initiate the pre-polymerization of PDMS, which made the viscosity of the PDMS solution increasing very quickly due to the high reactivity of PTMOS. The reaction scheme was shown in Fig. 3. Moreover, PTMOS, as a tri-functional cross-linking, showed better pervaporation performance than others, especially in favor of improvement of total flux of PDMS membranes, which was investigated in our previous work [15]. Besides, the dependence of viscosity of PDMS solution on pre-polymerization time was monitored with a rotating cylinder viscometer (Brookfield, DV-II+Pro). As shown in Fig. 4, the PDMS solution was cast on the PVDF membrane as the viscosity reached above 1,000 mPa·s and the viscous PDMS solution can be effectively prevented from plugging in the pores of PVDF membrane. Figure 5 showed the morphology of one side of multi-layer PDMS/PVDF composite membrane and the relative element composition in the cross-section of PDMS/PVDF composite membrane recorded by EDX line scan. From

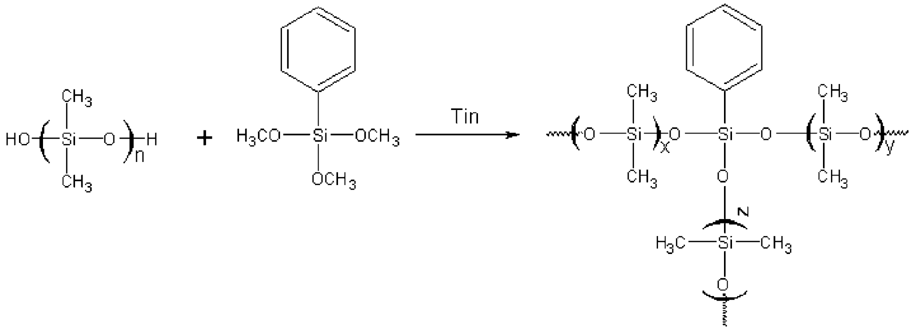


Fig. 3 Curing scheme of PDMS and PTMOS

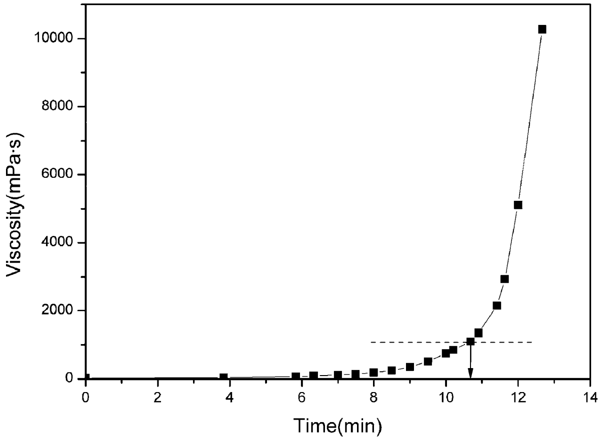


Fig. 4 Dependence of viscosity of PDMS solution on pre-polymerization time

the absence of major Si signals in the EDX line scan across the PVDF substrate, it also can be concluded that the PDMS existed mainly as a thin layer on the top and the surface of the support and only in small content as deposited inside the support, not plugging in the pores.

Pervaporation Performance

Effect of Ethanol Feed Concentration on Pervaporation Performance

The effect of ethanol feed concentration on the total flux and selectivity for ethanol aqueous solution were represented in Fig. 6. The thickness of PDMS layer was 10 μm. As the feed concentration increased from 5 to 30 wt%, the separation factor decreased from 15.0 to 4.1, and the total flux increased from 452.2 to 818.6 g/m^{2}h with the operation temperature of 60 °C. The effect of ethanol feed concentration on pervaporation performance of multi-layer PDMS/PVDF composite membrane was similar to that of PDMS composite membrane reported in literatures [16–18]. As the feed concentration increased, the free volume in PDMS membrane also increased due to the increase of swelling degree of PDMS membranes. Therefore, the chain mobility was enhanced, and the diffusivity of ethanol and water molecules became much easier which led to the increase of the total flux. The increase in the diffusivity of water resulted from the increase of free volume in PDMS which was much larger than the increase in the diffusivity of ethanol, since the molecular size of water was smaller than that of ethanol. Therefore, the separation factor decreased as the feed concentration increased.

The high permeation flux of multi-layer PDMS/PVDF composite membrane was attributed to the low transport resistance of small molecules across the interface of PDMS and PVDF. As confirmed in the EDX line scan, the PDMS pre-polymer did not plug-in the pores of PVDF, which led to the low transport resistance of small molecules across the interface of PDMS and PVDF. It was considered that there were two hybrid steps in the whole separation process: pervaporation across the first PDMS layer and evapomeation [19] across the second PDMS layer. The high selectivity was supposed to be attributed to both steps of the separation process. The improved selectivity of multi-layer PDMS/PVDF composite membrane may be explained with a hybrid of solution-diffusion and pore-flow model [20]. Further study is being carried on.

Fig. 5 Cross-section of one side of multi-layer PDMS/PVDF composite membrane together with the intensities of the Si Kα of the EDX line scan

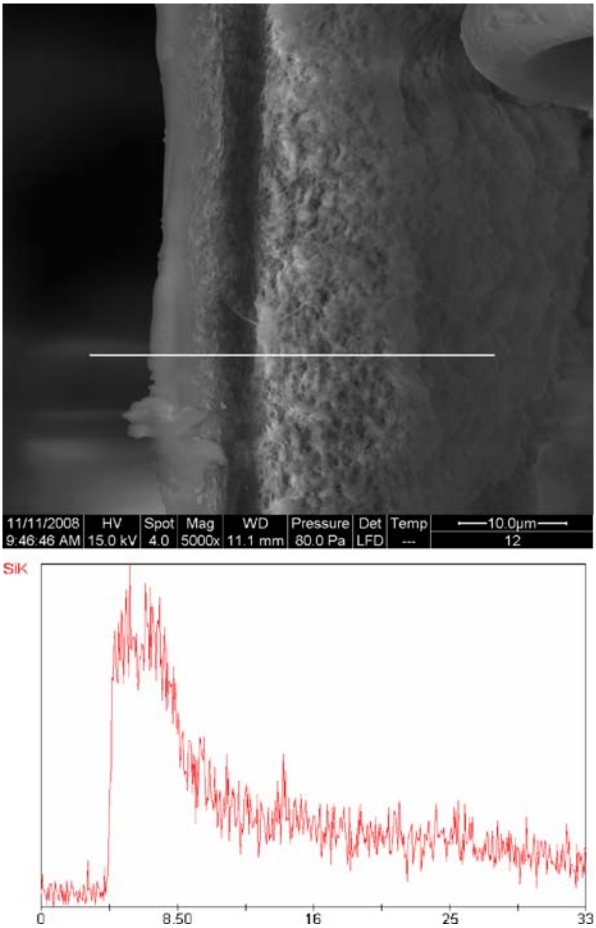
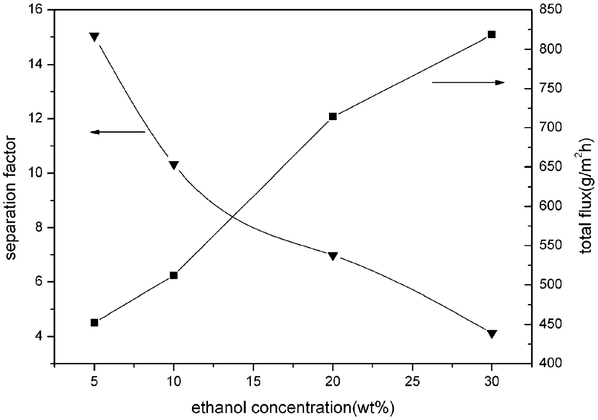


Fig. 6 Effect of ethanol feed concentration on the pervaporation performance of multi-layer PDMS/PVDF composite membrane



Effect of Operation Temperature on Pervaporation Performance

The effect of operation temperature on the pervaporation performance was represented in Fig. 7. The thickness of PDMS layer was 10 μm. The separation of ethanol aqueous solutions with four kinds of concentration was measured through varying the operation temperature. As the operation temperature increased, a novel phenomenon appeared that the separation factor showed a maximum value at 60 °C with the total flux increasing all along. Our results are, quite evidently, different from those reported in the literature. Li et al. [21] and Molina et al. [22] found that the selectivity of ethanol to water increased with increasing temperature. Vankelecom et al. [23] proposed that the separation factor of ethanol aqueous solution tended to decrease with increasing temperature using PDMS membranes. Many rational explanations of the experimental results are advanced, and most of them are based on the significant changes of solubility and diffusion of penetrating components with varying temperature. The novel phenomenon discovered in our experiment was also thought to be related with changes of permeation characteristics

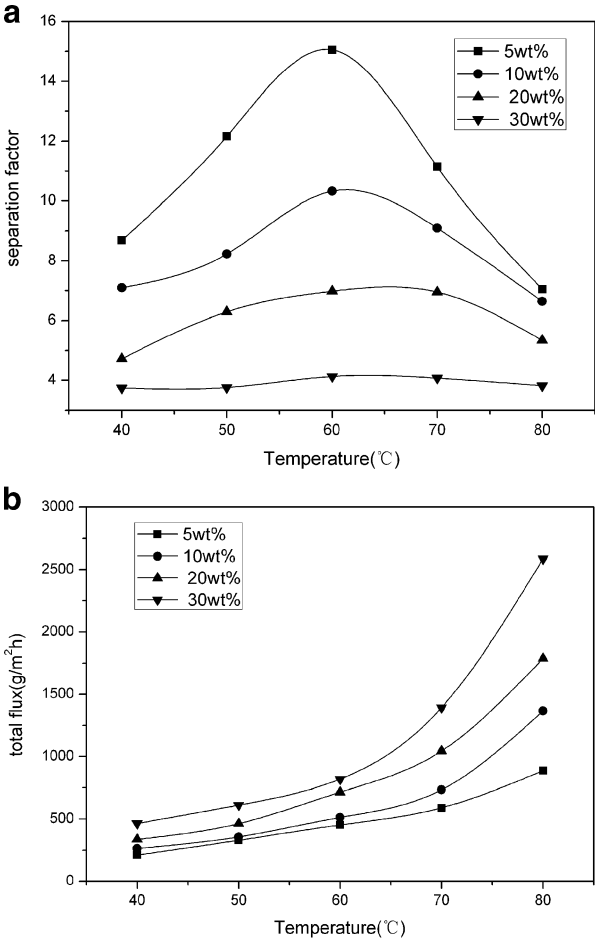


Fig. 7 Dependence of pervaporation performance of multi-layer PDMS/PVDF composite membrane on operation temperature **a** separation factor versus temperature; **b** total flux versus temperature)

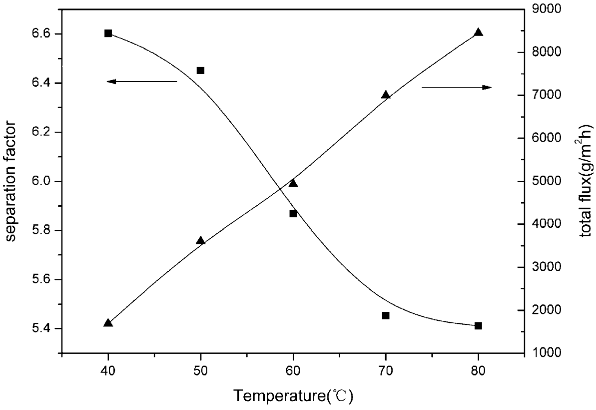


Fig. 8 Dependence of pervaporation performance of bi-layer PVDF porous membrane on operation temperature

caused by varying temperature, and especially associated with the much different permeation process of the multi-layer PDMS composite membrane.

For further study, the pervaporation performance of bi-layer porous PVDF membrane was also studied as shown in Fig. 8. As the operation temperature increased from 40 to 80 °C, the total flux increased almost linearly and the separation factor decreased all along. Moreover, the separation factor of bi-layer porous PVDF membrane maintained a maximum value of 6.6 at 40 °C. Although the variation tendency of pervaporation performance of PVDF membrane with temperature changes was not the same as that of multi-layer PDMS/PVDF membranes, it was considered that the PVDF porous substrate may play an important role in the higher selectivity of PDMS composite membranes for ethanol, since the PVDF showed a considerable selectivity for ethanol.

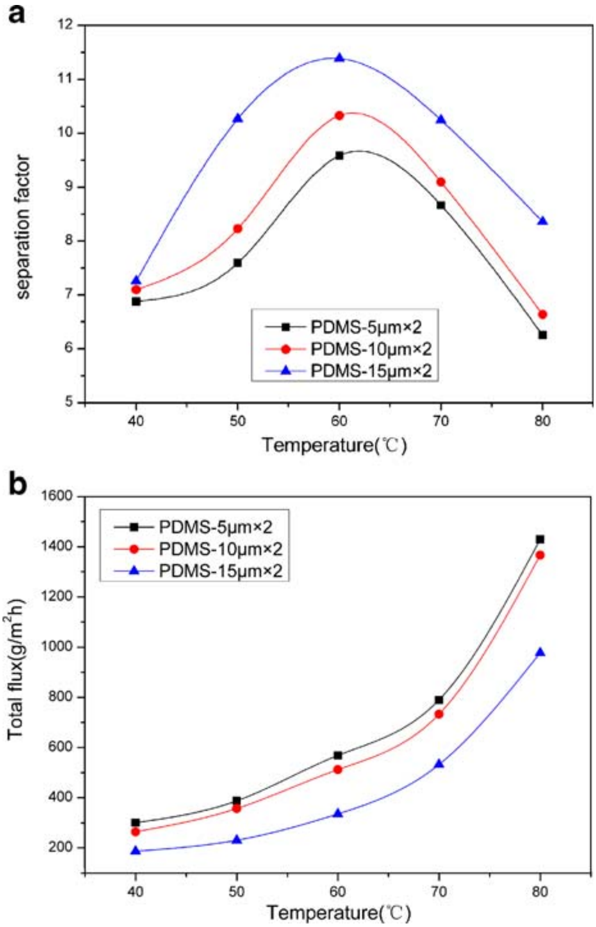
Effect of Thickness of PDMS Layer on Pervaporation Performance

The effect of thickness of PDMS layer on pervaporation performance of multi-layer was shown in Fig. 9. The ethanol feed concentration was 10 wt.%. As the PDMS layer increased from 5 to 15 μm, the separation factor increased and the total flux followed the reversed order. It was found that both of the separation factor and permeation flux can be maintained at a high level as the PDMS layer was 10 μm. The pervaporation performance of multi-layer PDMS/PVDF composite membranes can be adjusted by changing the thickness of selective PDMS layer.

Comparison of Pervaporation Performance with Single-layer PDMS/PVDF Composite Membrane

For comparison purposes, the pervaporation performance of single-layer PDMS/PVDF composite membrane developed with the similar method and materials was also investigated. The thickness of the PDMS layer is 10 μm, determined by micro screw gauge. The comparison was conducted with the same operation conditions as with 10 wt.% ethanol feed concentration. The comparison of pervaporation performance was represented in Fig. 10 The separation factor of the multi-layer composite membrane was much higher than that of single-layer PDMS/PVDF membrane in almost the whole range of operation temperature except at 40 °C. And the total flux followed the reversed order. It was clear that the total flux was depressed as the mass transport resistance of the multi-layer membrane

Fig. 9 Effect of thickness of PDMS layer on the pervaporation performance of multi-layer PDMS/PVDF composite membranes **a** separation factor versus temperature; **b** total flux versus temperature)

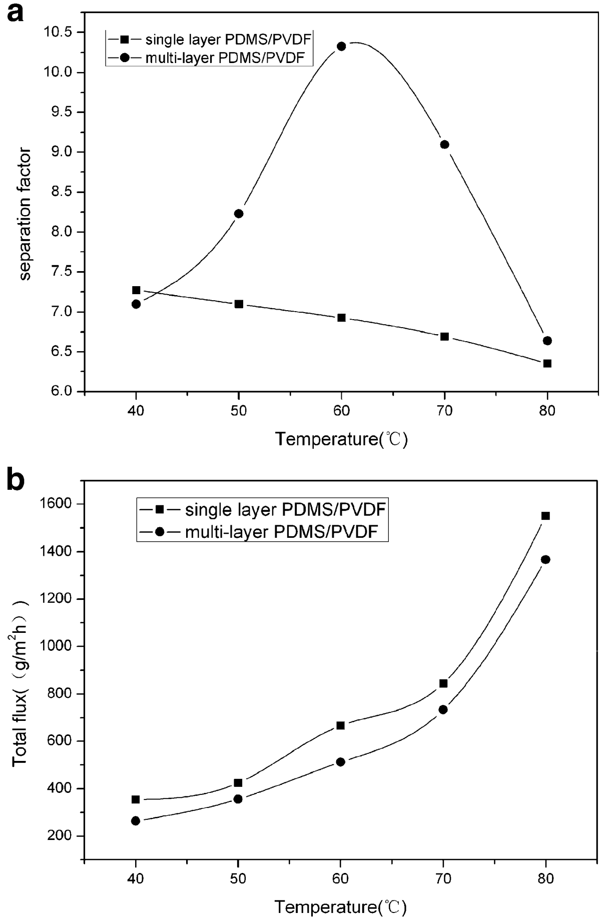


increased. However, the decrease of total flux of multi-layer composite membrane was much less than half of the total flux of the single-layer membrane, which indicated that the total mass transport resistance was not simply adding resistance of each layer.

Compared with the pervaporation performance of single-layer PDMS membranes for separation of ethanol/water mixtures reported in literatures [24–26], both the selectivity and total flux of multi-layer PDMS membranes maintained a high level. The highest selectivity of pure PDMS composite membrane reported in literatures was 14.0 (PDMS/PTEF) [26], while the best selectivity of multi-layer PDMS/PVDF composite membrane was 15.0, which indicated that the multi-layer configuration was very effective for the improvement of PDMS' pervaporation performance.

The low selectivity of pure PDMS was always considered to be the bottleneck of its industrial application for ethanol recovery. The multi-layer PDMS/PVDF composite membrane developed in our study surpassed the utmost of the selectivity of pure PDMS. The separation factor of the multi-layer composite membrane reached as high as 15 with the total flux of 452.2 g/m^{2}h with the feed concentration of 5 wt.% at 60 °C. The PDMS membrane with multi-layer configuration may open a door for its application in ethanol recovery in the future.

Fig. 10 Dependence of pervaporation performance of single-layer PDMS/PVDF composite membrane on operation temperature **a** separation factor versus temperature; **b** total flux versus temperature)



Conclusion

Multi-layer PDMS/PVDF composite membrane with an alternative PDMS/PVDF/non-woven-fiber/PVDF/PDMS configuration was prepared in this paper. As the operation temperature increased, the separation factor maintained a maximum value of 15.0 at 60 °C and the total flux increased all along. The composite membrane surpassed the limit of pure PDMS' selectivity for ethanol remarkably with the total flux decreasing a little compared with the single-layer PDMS/PVDF membrane. A hybrid solution-diffusion and pore-flow model was expected to be established in the future for the explanation of the excellent pervaporation performance of multi-layer PDMS/PVDF composite membrane and membrane configuration design. The PDMS with multi-layer configuration may also be expected to be the ethanol perm-selective materials for industrial application.

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