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PERVAPORATION OF ETHANOL/WATER MIXTURES WITH HIGH FLUX BY ZEOLITE-FILLED PDMS/PVDF COMPOSITE MEMBRANES[*]

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Abstract Thin-film zeolite-filled silicone/PVDF composite membranes were fabricated by incorporating zeolite particles into PDMS (poly(dimethylsiloxane)) membranes. The morphology of zeolite particles and zeolite filled silicone composite membranes were characterized by SEM. The zeolite-filled PDMS/PVDF composite membranes were applied for the pervaporation of ethanol/water mixtures and showed higher flux compared with that reported in literatures. The effect of zeolite loading and Si/Al ratio of zeolite particles on pervaporation performance of ethanol/water mixtures was investigated. With the increase of zeolite loading from 10% to 30%, the total flux increased significantly from 265.0 g/(m^{2}h) to 820.7 g/(m^{2}h) with 5 wt% ethanol feed concentration at 50°C, and the separation factor increased from 11.3 to 13.7. The effects of operation temperature and ethanol feed concentration on pervaporation performance were also studied. As the temperature increased from 40°C to 80°C, the separation factor varied from 12.1 to 13.7 which maintained the maximum value at 50°C, and the total flux increased exponentially from 435.5 g/(m^{2}h) to 2993.8 g/(m^{2}h) with 30% zeolite loading. Besides, the zeolite filled PDMS/PVDF composite membrane with 30% zeolite loading was ethanol perm-selective over a wide range of ethanol feed concentration (5 wt%–90 wt%), and especially showed excellent pervaporation performance in the low concentration range.

Keywords: Zeolite; PDMS; High flux; Pervaporation; Ethanol recovery.

INTRODUCTION

Fermentation ethanol has become one of the most important renewable energy resources due to its potential to reduce pollution and dependence on petroleum resources[1−3]. The ethanol recovery from aqueous solutions with low concentration has been received great attention recently. The current method used for ethanol recovery and purification in fermentation process is distillation followed by molecular sieve adsorption[4]. As a promising separation method, pervaporation has been considered to be an alternative to distillation due to its low energy consumption, optimized integration of pervaporation with fermentor and economical competition *etc*[5].

Many hydrophobic polymers were developed as ethanol perm-selective membrane materials, such as silicon-containing polymers, fluoro-containing polymers, and other modified polymers[6]. And mixed matrix membranes by incorporating highly selective zeolite molecular sieves into PDMS have showed much better selectivity for ethanol compared with common unfilled polymeric membranes. te Hennepe *et al.*[7, 8] developed silicalite-1 filled silicone rubber membranes, with separation factor for ethanol increasing from 7.6 to 16.5 and total flux increasing from 24.0 g/(m^{2}h) to 50.7 g/(m^{2}h) at 22.5°C. Jia *et al.*[9] prepared ultra-thin zeolite-PDMS composite

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membranes, with selective layer as thin as 3 μm, which showed a selectivity of 34 and total flux of 150 g/(m^{2}h) at 22°C, and the homogeneous membrane with a thickness of 125 μm showed a selectivity of 59, the highest value for ethanol/water separation factor so far, with total flux of only 71.0 g/(m^{2}h) at 22°C. Chen *et al.*[10] reported that the silicalite-1 filled PDMS membranes showed a selectivity of 29.3 and the total flux of almost 120.0 g/(m^{2}h) at 50°C. Although the selectivity of zeolite filled PDMS membranes was enhanced significantly, almost all of the total flux reported obtained no obvious improvement, which restricted its application for ethanol recovery seriously.

Efforts have been made in our work to improve the total flux of zeolite filled PDMS membranes significantly to meet the needs of practical application of PDMS. The whole preparation process of composite zeolite filled PDMS/PVDF membranes with high reproducibility and maneuverability was described in detail. The effect of various preparation and operation conditions on their pervaporation performance was also investigated.

EXPERIMENTAL

Materials

Pure α,ω-polydimethylsiloxanediol (PDMS) was purchased from Beijing Chemical Reagents Corporation, with kinetic viscosity of 5.0×10^4 Pa·s. ZSM-5 zeolite with Si/Al ratio of 38, 100 and 300 was purchased from Nankai University. *n*-Hexane and di-*n*-butyltin dilaurate (DBTOL) were obtained from Beijing Jingyi Chemical Reagents Corporation and were used as received. Phenyltrimethoxylsiane (PTMOS) was supplied by New Chemical Materials Corporation of Yingcheng Debang. Polyvinylidene fluoride (PVDF) 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 Zeolite-Filled Silicone/PVDF Composite Membranes

The PVDF porous substrate was prepared by dissolving PVDF in TEP to form a 15% dope solution, which was cast onto the surface of the non-woven fiber and immersed into water to induce polymer precipitation. The residual solvent was exchanged with ethanol for 5 min and dried at room temperature. The thickness of the single PVDF layer was controlled in the range of 30−33 μm determined by field emission scanning electron microscopy (FESEM).

The purchased zeolite powder was heat-treated at 600°C for 5 h and sieved on a 100 mesh sieve. A prescribed amount of PDMS and the sieved zeolite powder were added into *n*-hexane with vigorous magnetic stirring first, and then laid in water bath for ultrasonic vibration. The suspension was reset for magnetic stirring, and proper amount of PTMOS and DBTOL was added to induce the prepolymerization. As the suspension became highly viscous to form an almost homogeneous zeolite and PDMS phase, it was cast onto the PVDF porous substrate directly. And the composite membrane was dried at room temperature for 12 h and then placed in oven at 80°C for 5 h to remove the residual solvent. The weight ratio of zeolite to PDMS varied from 10% to 40%. The weight ratio of PDMS, *n*-hexane, PTMOS and DBTOL was 30:70:3:1.

For characterization purpose, zeolite-filled PDMS homogeneous membrane sample was also prepared. The homogeneous zeolite-filled PDMS suspension was coated onto a Teflon plate directly, and other post-treatments were all the same as mentioned above. The thickness of the homogeneous membrane was controlled to be about 100 μm.

Characterization

The zeolite particle size and the morphology of PDMS/PVDF composite membranes were obtained by using a field emission scanning electron microscope (FESEM, JEOL JSM-7401F) at 1.0 kV.

Zeolite filled PDMS homogeneous membrane samples with various zeolite loadings were immersed in 5 wt% and 100 wt% ethanol aqueous solutions at 25°C for 48 h. As the sorption equilibrium was obtained, the sample was taken out rapidly and wiped with tissue paper to remove the adherent solution and weighed immediately. The sorption capacity (SC) was defined as:

$$\mathrm{SC} = \frac{W_\mathrm{s} - W_\mathrm{d}}{W_\mathrm{d}} \tag{1}$$

Where W_d and W_s are the weight of the dry and swollen membrane samples, respectively.

The mechanical properties of zeolite-filled PDMS homogeneous membranes were measured at room temperature with 25% relative humidity using a GT-T5-2000 tensile testing machine with a crosshead speed of 50 mm/min. The sample width and length were 10 mm and 50 mm, respectively.

Pervaporation Process

The pervaporation experiments were conducted by using an apparatus developed by our laboratory[11] as shown in Fig. 1. The experiments were carried out with 5%–90% ethanol aqueous solutions. The operation temperature varied from 40°C to 80°C with permeate-side pressure of *ca.* 100 Pa. The effective area of the membrane was 0.0022 m^2.The permeation vapor was condensed and collected using a liquid nitrogen trap. The composition of permeate collected in the trap was analyzed by gas chromatography to determine the separation factor and total flux. The total flux J and separation factor α are defined as follows:

$$J = \frac{Q}{A \cdot T} \tag{2}$$

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

$$\alpha = \frac{Y_\mathrm{A} \cdot X_\mathrm{B}}{X_\mathrm{A} \cdot Y_\mathrm{B}} \tag{3}$$

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.

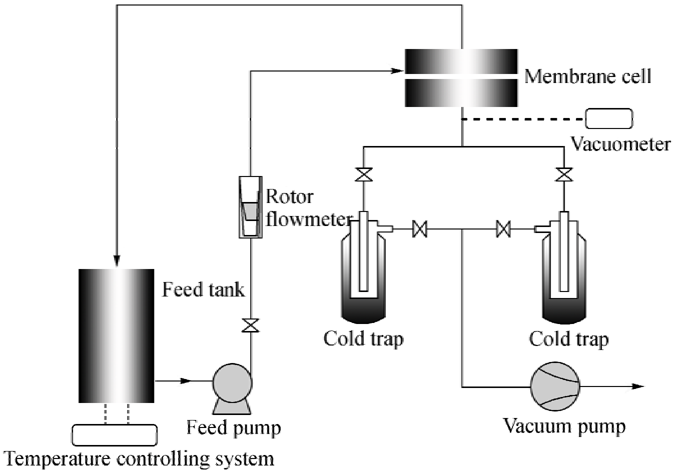

Fig. 1 Schematic diagram of the pervaporation apparatus

Sorption and Diffusion Selectivity

Dry zeolite-filled PDMS homogeneous membranes were laid in conical flasks filled with 5 wt% ethanol aqueous solution. The conical flasks were sealed and kept in water bath to maintain constant temperature. The membranes were kept in the ethanol aqueous solution for 48 h to maintain sorption balance. Then the membrane was taken out and wiped with tissue paper to remove the adhered liquid. The wet membrane was immediately put into sealed three-neck flask connected with the standard sorption measurement apparatus developed by our own laboratory as shown in Fig. 2. The sorption and diffusion selectivities are defined as follows:

$$\alpha_{\text{sorp}} = \frac{Y_A \cdot X_B}{Y_B \cdot X_A} \tag{4}$$

$$\alpha_{\text{diff}} = \alpha / \alpha_{\text{sorp}} \tag{5}$$

Where X_A and X_B represent the ethanol and water concentrations (wt%) of the initial ethanol solution in conical flask respectively, and Y_A and Y_B represent the ethanol and water concentrations (wt%) in the membranes maintained sorption balance which were determined by GC (gas chromatography).

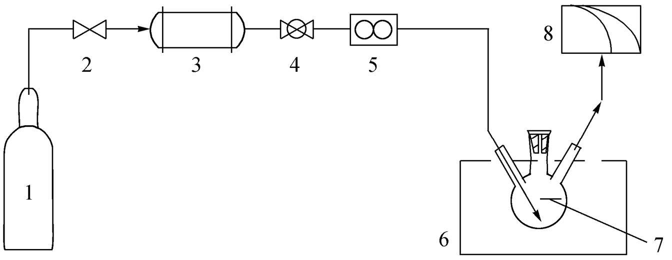

Fig. 2 Schematic diagram of the measurement of sorption selectivity
1) Hydrogen generator; 2) Valve; 3) Desiccating tube; 4) Steady flow valve; 5) Flowmeter; 6) Oil bath with thermocontrol; 7) Membrane; 8) Gas chromatography

RESULTS AND DISCUSSION

Characterization

The morphology of zeolite particles and the zeolite filled PDMS/PVDF composite membrane with 30% zeolite loading is presented in Fig. 3. The zeolite particle size ranged from 0.5 μm to 1.5 μm, and the top PDMS layer of the composite membranes was about 10 μm. It can be found that the zeolite particles distributed uniformly in the PDMS membrane, and the top layer was cast onto the PVDF porous substrate tightly and properly.

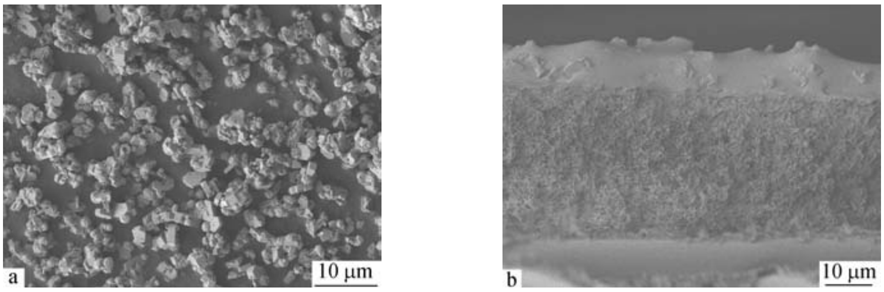

Fig. 3 SEM images of zeolite particles (a) and zeolite filled PDMS/PVDF composite membranes (b)

The sorption capacity of zeolite filled PDMS membranes with various zeolite loading is listed in Table 1. As the zeolite loading increased from 10% to 40%, it was found that the sorption capacity of zeolite filled PDMS membranes increased in both of pure ethanol and 5 wt% aqueous ethanol solutions. It was indicated that the adsorption of zeolite pores to ethanol and water molecules was enhanced as zeolite loading of PDMS membranes increased in both of the pure ethanol and aqueous ethanol solutions.

Table 1. Relationship between the swelling degree and the zeolite content

Ethanol concentration (wt%)	Sorption capacity (%)			
	10 wt%[a]	20 wt%	30 wt%	40 wt%
5	0.30	0.63	1.00	1.23
100	2.11	3.71	4.92	6.43

[a] The ratio of zeolite/PDMS

In order to investigate the effect of zeolite loading on the mechanical properties of zeolite filled PDMS membranes, the tensile strength, Young's modulus and extension ratio with different zeolite loadings were tested, and the results are given in Fig. 4. As shown in Fig. 4, both of the tensile strength and Young's Modulus of zeolite filled PDMS membranes increased as the zeolite loading increased from 10% to 40%, which may result from the increased rigidity of PDMS chains by incorporation of zeolite particles. The extension ratio maintained the maximum value of 220% with the zeolite loading of 20% and then decreased as the zeolite loading increased. It was considered that the excess incorporation of zeolite decreased the mobility of the PDMS chain and consequently depressed the extension ratio of PDMS membranes.

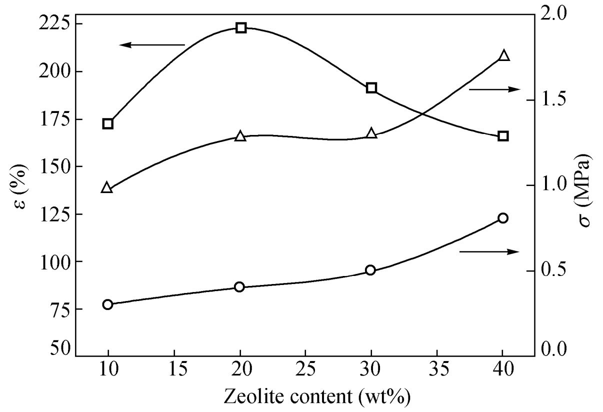

Fig. 4 Mechanical properties of zeolite filled PDMS/PVDF composite membranes with various zeolite content
○ Young's modulus (MPa); □ Extension ratio (%); △ Tensile strength (MPa)

Preparation of Zeolite-Filled PDMS/PVDF Composite Membrane

Since the zeolite particles and PDMS were obviously different in physicochemical properties[10, 12–14], both the precipitation and aggregation of zeolite crystallites would lead to the inhomogeneity of the zeolite filled PDMS suspension, which were the main challenging problems for contribution of zeolite to the enhancement of pervaporation performance. Therefore, it was essential to disperse zeolite particles homogeneously and keep the suspension stably. There were mainly two routes to solve the problems[9]: application of ultra-fine zeolite particles and prepolymerization of PDMS polymers.

In our work, PTMOS was chosen as the crosslinker to initiate the prepolymerization of PDMS, which made the viscosity of the suspension increasing very quickly due to the high reactivity of PTMOS and prevented the homogeneous suspension from precipitation very effectively. Moreover, PTMOS as a tri-functional crosslinker showed better pervaporation performance than others, especially in favor of improvement of total flux of PDMS membranes, which was investigated in our previous work[11]. The zeolite particles used in this paper was 0.5–1.5 μm, and the zeolite-filled PDMS layer was 10 μm, almost ten times of the zeolite particles, which ensured that the mixed matrix membrane was free from cracks and pinholes.

Pervaporation Performance

Effect of zeolite loading on pervaporation performance

According to the solution-diffusion model[15, 16], pervaporation performance mainly depends on two factors: the selective sorption or selective diffusion or both of them. The incorporation of molecular selective zeolite uniformly into PDMS matrix would improve both of the selectivity and total flux of the membranes[17–20]. This was almost consistent with the experimental results shown in Fig. 5. Zeolite with Si/Al ratio of 300 was incorporated in PDMS membranes. In the range of operation temperature tested from 40°C to 80°C, the total flux of the composite membrane increased all along as the zeolite loading increased from 10% to 40%. This result was obviously different with the zeolite filled PDMS membranes reported in literatures. Chen *et al.*[10]

found that as the silicalite-1 content increased from 10% to 50%, the total flux declined from 120 g/(m^{2}h) to 75 g/(m^{2}h). It was considered that the totally different effect of zeolite loading on total flux was attributed to the hydrophobicity difference of zeolite. ZSM-5 zeolite with Si/Al ratio 300 used in our work was not so hydrophobic and highly selective to ethanol as silicalite-1, and the zeolite pores may act as channels for both of ethanol and water molecules, which lead to the remarkable enhancement of the total flux as the zeolite loading increased. But hydrophobic silicalite-1 maintained much better selectivity for ethanol molecules, which led to the sharp decrease of water flux of silicalite-1 filled PDMS composite membranes as the zeolite loading increased. It was also found that the separation factor increased as zeolite loading increased from 10% to 30%, and dropped sharply as the zeolite loading reached 40%. It was thought to be caused by the defects and pinholes due to the aggregation of zeolite particles in the ultra-thin PDMS membranes. Although the selectivity of ZSM-5 filled PDMS/PVDF composite membranes was a little lower than that of silicalite-1 filled PDMS membranes reported, their total flux was almost one magnitude higher than that of the common silicalite-1 filled PDMS membranes, which was of great importance for the practical application of PDMS membranes for ethanol recovery from aqueous solutions.

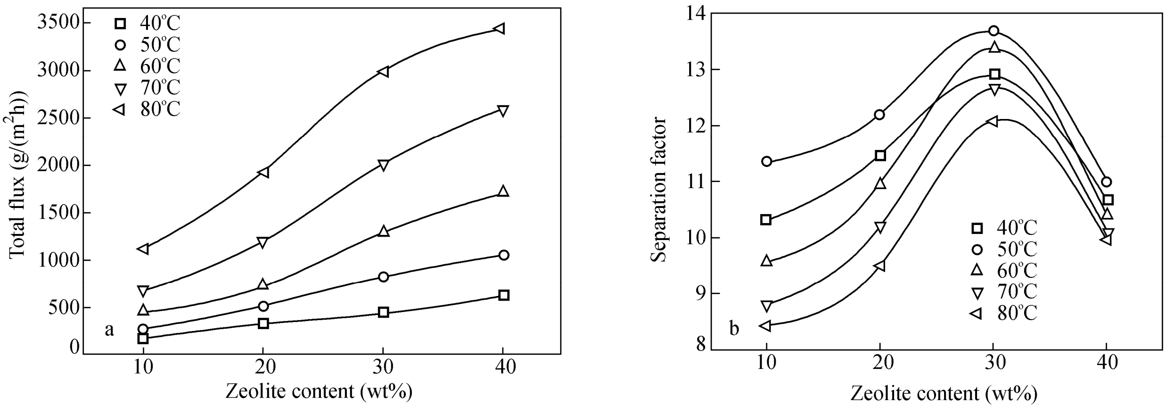

Fig. 5 Effect of zeolite content on the pervaporation performance of PDMS/PVDF composite membranes
a) Total flux versus zeolite content; b) Separation factor versus zeolite content

Effect of Si/Al ratio on pervaporation performance

For comparison purpose, the effect of zeolite with various Si/Al ratios on pervaporation performance was also investigated as shown in Fig. 6. An increase of Si/Al ratio from 38 to 300 with 40% zeolite loading resulted in an increase of both the total flux and separation factor. As the hydrophobicity of zeolite increased with the

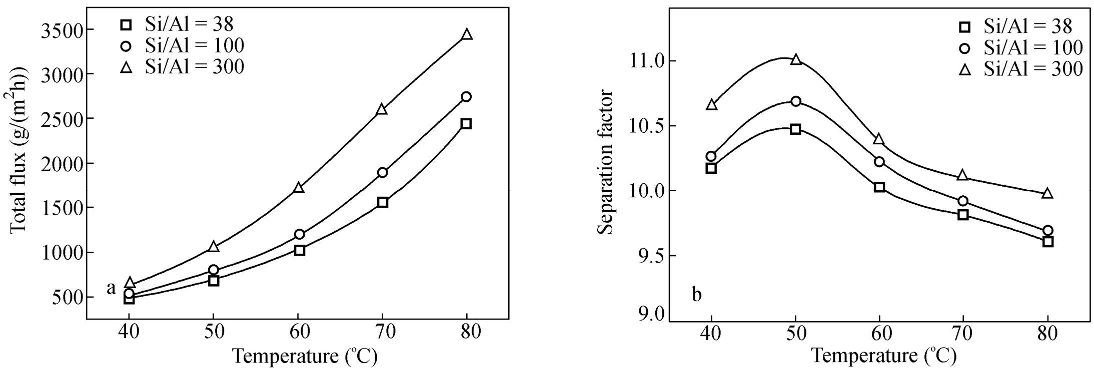

Fig. 6 Effect of Si/Al ratio on the pervaporation performance of PDMS/PVDF composite membranes
a) Total flux versus temperature; b) Separation factor versus temperature

increase of Si/Al ratio in the low range from 38 to 300, the zeolite pores became more selective to ethanol molecules, which led to the increase of separation factor. From the analysis of variation of ethanol flux and water flux, it was deduced that both of them increased as Si/Al ratio increased and the increasing extent of ethanol flux was higher than that of water flux, which resulted in the improvement of both total flux and separation factor. As the Si/Al ratio reached a certain value, such as full-silicon, the zeolite filled PDMS composite membrane may not follow the disciplines mentioned above, and further studies are needed.

Effect of ethanol feed concentration on membrane performance

The effect of ethanol feed concentration on membrane performance is shown in Fig. 7. In the whole range of 5%–90% ethanol feed concentration, the filled PDMS/PVDF membrane with 30% zeolite loading at 50°C showed ethanol perm-selective properties. As presented in Fig. 7, the separation factor decreased sharply as the ethanol concentration increased, the total flux increased from 820.7 g/(m^{2}h) at 5 wt% to 4831.2 g/(m^{2}h) at 90 wt% at 50°C, whose trend appeared to follow an exponential increase with ethanol feed concentration.

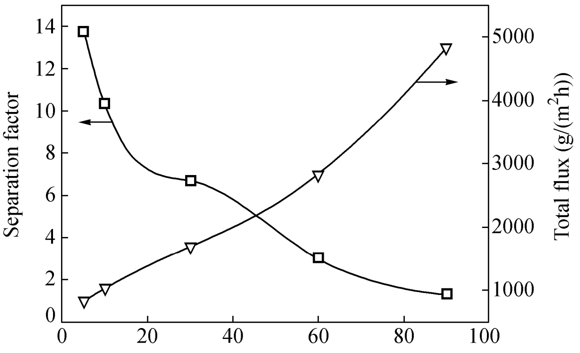

Fig. 7 Effect of ethanol feed concentration on the pervaporation performance of PDMS/PVDF composite membrane

Time-dependence of the pervaporation performance

Since the enhancement in pervaporation performance of zeolite filled PDMS membranes was usually attributed to the molecular selective properties, it was doubt that whether the pervaporation process could go along at steady-state for ages due to the complex structure of matrix membranes. To testify the improvement in pervaporation performance obtained in our work to be intrinsic and persistent, a long time pervaporation experiment was conducted as shown in Fig. 8. First, the experiment was carried out for 240 min with every interval of 40 min, then interrupted for a weekend, and followed by the continuous testing for another 240 min.

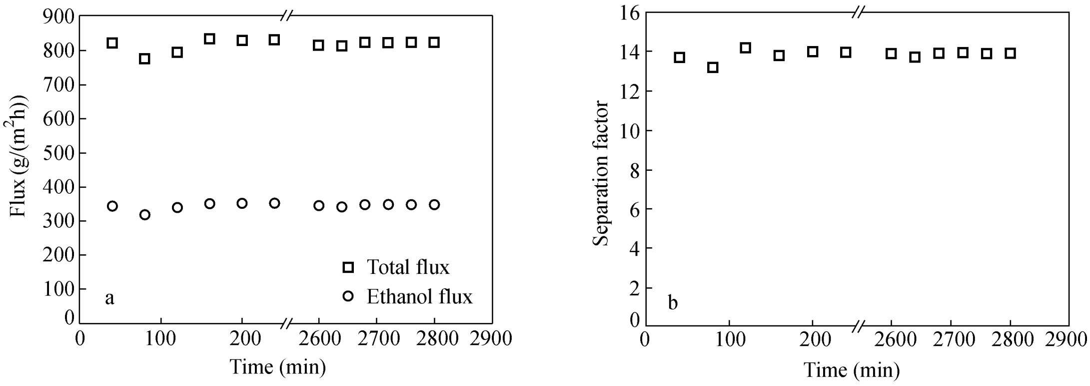

Fig. 8 Time dependence of the pervaporation performance of zeolite filled PDMS/PVDF composite membrane
a) Flux versus time; b) Separation factor versus time

As shown in the figure, the separation factor and total flux as well as ethanol flux declined slightly at the initial of each test, which may be resulted from the swelling of PDMS membranes. And the decline in the second test showed much more slightly than that in the first one. By restarting the test, the pervaporation performance was almost constant which proved that the zeolite filled PDMS composite membrane would keep the good performance in a long term.

Comparison of pervaporation performance

For comparison purpose, the pervaporation performance of different zeolite-filled PDMS membranes with separation priority reported by other groups is listed in Table 2. It was found that the total flux of the zeolite-filled PDMS/PVDF membranes developed in our work was remarkably higher than that reported in literatures, which also maintained acceptable selectivity for ethanol. Besides, the high stability of pervaporation performance was testified in long run. Moreover, the preparation process of ZSM-5 filled PDMS/PVDF membranes with low zeolite loading of 30% was of high reproducibility and maneuverability.

Table 2. Pervaporation performance of different zeolite-filled PDMS membranes

Membrane	Membrane thickness (μm)	Zeolite loading (wt%)	Ethanol feed concentration (wt%)	Temperature (°C)	Total flux (g/(m^{2}h))	α	Ref.
Silicalite-1 filled PDMS membrane	150 (casting thickness)	40^a	5–5.5	22	362	14.9	[7]
Silicalite-1 filled PDMS membrane	150 (casting thickness)	60^a	5–5.5	22	507	16.5	[7]
Silicalite-1 filled PDMS membrane	125	77^a	7.0	22	89	59	[9]
Silicalite-1 filled PDMS/PEI composite membrane	20	77^a	5.1	22	150	34	[9]
Silicalite-1 filled PDMS/PEI composite membrane	12	62^a	6.5	22	150	16	[9]
Silicalite-1 filled PDMS/PEI composite membrane	4	62^a	7.0	22	560	14	[9]
USY filled PDMS membrane	100	50^a	5.0	30	61	16.1	[19]
ZSM-5 filled PDMS membrane	100	50^a	5.0	30	46	14	[19]
Silicalite-1 filled PDMS membrane	100	10^a	4.4	50	120	29.6	[10]
Silicalite-1 filled PDMS membrane	100	30^a	4.4	50	130	18.2	[10]
Silicalite-1 filled PDMS membrane	100	50^a	4.4	50	92	17.3	[10]
ZSM-5 filled PDMS/PVDF composite membrane	10	30^b	5.0	50	821	13.7	This work
ZSM-5 filled PDMS/PVDF composite membrane	10	30^b	5.0	60	1290	13.4	This work
ZSM-5 filled PDMS/PVDF composite membrane	10	30^b	5.0	70	2011	12.6	This work

^{a}The ratio of zeolite/(zeolite + silicone rubber); ^{b}The ratio of zeolite/silicone rubber

Based on the comparison, it was concluded that the excellent pervaporation performance of the ZSM-5 filled PDMS/PVDF membranes was attributed to the thin PDMS film layer, cross-linking reagent PTMOS, less hydrophobicity of ZSM-5, as well as the preparation process. PTMOS as a tri-functional crosslinker, was in favor of enhancement of total flux due to the low crosslinking density, and contributed to the highly viscous and stable suspension of zeolite filled PDMS due to its high reactivity. The zeolite used in our work was not as hydrophobic as silicalite-1, which may be another important factor contributing to the high total flux and acceptable selectivity of the composite membranes. As the Si/Al ratio increased, the hydrophobicity of zeolite increased and silicalite-1 showed the highest hydrophobicity. As reported by Chen *et al.*[10], the water flux decreased sharply with increasing the silicalite-1 content in PDMS membranes because high hydrophobicity of silicalite-1 particles showed strong repellency to water molecules. The Si/Al ratio of zeolite in our work was equal to or below 300, which was not so hydrophobic as silicalite-1 and showed much less repellency to water molecules. And the zeolite also maintained certain hydrophobicity and ethanol selectivity. This may contribute to the high total flux and acceptable selectivity of the zeolite filled PDMS composite membranes.

Sorption and Diffusion Selectivity

The sorption and diffusion selectivities were measured to investigate the pervaporation mechanism of zeolite-filled PDMS homogeneous membranes. The result was shown in Fig. 9. It was found that the sorption selectivity increased as increasing zeolite loading, and the diffusion selectivity followed the reversed order. The sorption and diffusion selectivities also followed the opposite tendency with increasing temperature. Both of the solution and diffusion contributed to the separation factor of zeolite-filled PDMS membranes. With high zeolite loading at low temperature, sorption selectivity of membranes contributed more than the diffusion selectivity, while diffusion selectivity of membranes was dominated with low zeolite loading at high temperature.

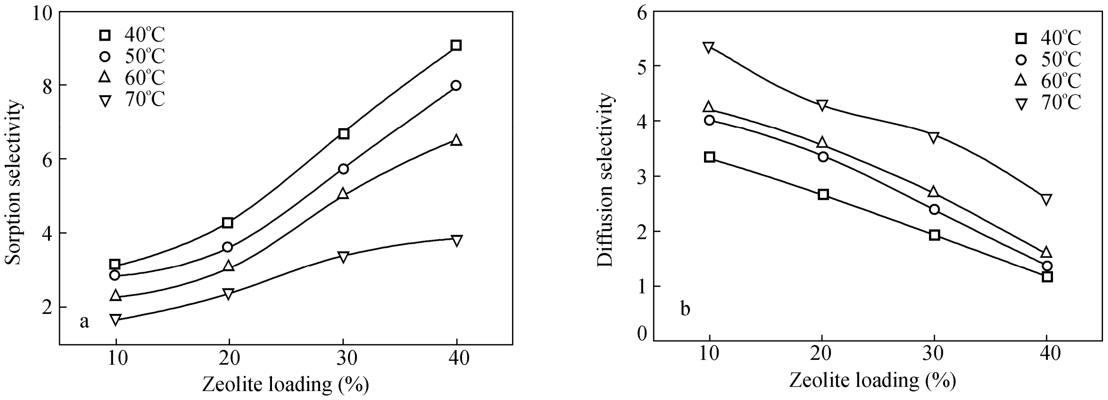

Fig. 9 Sorption and diffusion selectivity of zeolite-filled PDMS membranes

CONCLUSIONS

Zeolite filled PDMS/PVDF composite membranes with thin-film top layer of 10 μm were fabricated by incorporation of zeolite particles into PDMS solutions. It was found that the total flux of the composite membrane was remarkably higher than that of filled PDMS membranes reported in literatures with acceptable selectivity. Increase of zeolite loading (10%–30%) and Si/Al ratio (from 38 to 300) improved both the total flux and separation factor. The zeolite filled PDMS membrane with zeolite loading of 30% gave a total flux of 821.0 g/(m^{2}h) and a separation factor of 13.7 with 5 wt% ethanol concentration at 50°C. As the temperature increased from 40°C to 80°C, the separation factor varied from 12.1 to 13.7 which maintained the maximum value at 50°C, and the total flux increased exponentially from 435.5 g/(m^{2}h) to 2993.8 g/(m^{2}h) with 30% zeolite loading. Besides, the zeolite filled PDMS/PVDF composite membrane with 30% zeolite loading was ethanol perm-selective in a wide range of ethanol feed concentration (5 wt%–90 wt%), and especially showed excellent pervaporation performance in the low concentration range. The excellent pervaporation performance obtained was proved to be quite stable and persistent.

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