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Poly (dimethylsiloxane)-poly (tetrafluoroethylene)/poly (vinylidenefluoride) (PDMS-PTFE/PVDF) hollow fiber composite membrane for pervaporation of chloroform from aqueous solution

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Abstract−A novel PDMS-PTFE/PVDF hollow fiber composite membrane using PTFE-PDMS as the top active layer and PVDF hollow fiber as the support layer was prepared for the pervaporation of chloroform from water. Sorption and diffusion behaviors of chloroform and water in PDMS-PTFE membranes, which had different PTFE content, were investigated. The results showed that with increasing PTFE content from 0 wt% to 40 wt%, chloroform/water ideal separation factor first increased and then decreased, and permeabilities of both chloroform and water increased. For the 30% PTFE-PDMS membrane, when feed temperature ranged from 40 °C to 60 °C, permeabilities of both chloroform and water increased, but ideal separation factor for chloroform/water first increased and then decreased. Effects of operating conditions, such as feed flow rate, active layer thickness, feed concentration and feed temperature, on PV performances of the 30% PDMS-PTFE/PVDF hollow fiber membrane for the pervaporation of chloroform-water mixtures were studied. Examination showed that concentration polarization on the membrane surface occurred when feed flow rate was less than 3,000 mL/min. With the increase in active layer thickness from 13.8 to 78.0 μm, chloroform flux and water flux dropped from 21 to 13 $g\cdot h^{-1}\cdot m^{-2}$ and from 93 to 22 $g\cdot h^{-1}\cdot m^{-2}$, respectively, but the separation factor increased from 1494 to 3949. With an increase of feed concentration from 55 to 850 ppm, chloroform flux increased linearly but water flux remained constant, and separation factor decreased. With an increase of the feed temperature from 40 to 60 °C, both flux and separation factor increased, the variation of permeation flux followed the Arrhenius relationship, and the activation energy values were 21.65 and 9.6 KJ/mol for water and chloroform, respectively.

Keywords: Poly (dimethylsiloxane), Polytetrafluoroethylene, Hollow Fiber Membranes, Pervaporation

INTRODUCTION

Membrane pervaporation (PV) is a potentially attractive process for removing low concentration organic solvents from contaminated water [1-4]. Compared with traditional separation processes, the advantages of PV process are low operating temperature, minimal energy expenditure, no emission to environment, no requirement of additional components in the feed and no second environment pollution [3-5]. According to solution-diffusion theory, the transport of permeating molecules through a dense polymer membrane consists of three consecutive steps: sorption on the upstream surface of the membrane, diffusion through the membrane matrix and desorption from membrane downstream surface. Therefore, solubility and diffusivity are the two key factors which determine membrane separation efficiency. To understand the transport behavior of permeating molecules, numerous sorption and diffusion experiments have been carried out [6-8].

PDMS membrane is commonly used as a kind of organics-permselective membrane; it has perfect comprehensive properties of flux, selectivity and stability. To make the PV process more economically attractive, many studies have been done for the modifications of PDMS membranes so as to improve their organophilic properties [9-19]. We recently reported on the successful fabrication of a novel composite membrane of Poly (tetrafluoroethylene) (PTFE) filled PDMS membrane which has excellent hydrophobic properties [3]. Compared with unfilled PDMS membranes, this composite membrane exhibits striking advantages in total flux and separation factor when used for the removal of chloroform from aqueous solution. When the content of the PTFE additive in PTFE-PDMS membrane was 30 wt%, feed temperature was 50 °C and permeate-side vacuum was 0.101 MPa, the membrane had the best PV performance with the total flux of 31.8 $g\cdot h^{-1}\cdot m^{-2}$ and separation factor of 3215.

Hollow fiber composite membrane has higher packing density and larger membrane area for a fixed module volume than flat-sheet membrane does [20-22], so hollow fiber membrane seems to be the best alternative from an application point of view. In this study, PDMS-PTFE/PVDF hollow fiber composite membrane has been made with microporous PVDF hollow fiber membrane as the support layer. The sorption and diffusion properties of chloroform and water in homogeneous PTFE-PDMS flat sheet membranes were measured at 40 °C, 50 °C and 60 °C. For the PTFE filled composite membrane, the effects of operating conditions, such as feed flow rate, active layer thickness, feed concentration and feed temperature, on separation performances were examined.

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EXPERIMENTAL

1. Materials

PVDF hollow fibers, which were used as membrane support layers, were obtained from Shanghai Mega Vision Membrane Engineering & Technology Co. Ltd. (PR China). Their void fraction was 72.5%, pore diameter was 0.15 μm and inside diameter was 1.00± 0.03 mm. PDMS (Silicone Rubber 107, M_w5000); cross linking agent ethyl silicate and curing agent dibutyltin dilaurate were purchased from Shanghai resin Company (PR China). PTFE ultrafine particles (Dyneon TF-9207) were used as the additive, their primary and secondary particle sizes were 100 nm and 1.4 μm, respectively, according to Minnesota Mining and Manufacturing Company (America). PTFE roller sheets in 0.3 mm thickness were used in sorption experiments and were purchased from DuPont Company (America). Reagent grade *n*-heptane and chloroform were obtained from Shanghai Run Jie Chemical Reagent Company (PR China).

2. Membrane Preparation

Preparation methods of unfilled and PTFE filled PDMS homogeneous flat sheet membranes used for the sorption experiments in this study are described in the literature [3]. The membranes were designated as 0% PTFE-PDMS, 10% PTFE-PDMS, 20% PTFE-PDMS, 30% PTFE-PDMS and 40% PTFE-PDMS according to PTFE content in membranes. PTFE-PDMS/PVDF hollow fiber composite membranes used in our pervaporation experiments were fabricated by dip-coating method: wiped with tissue paper, PVDF hollow fibers were dipped into the 30% PTFE-PDMS casting solution for 10 seconds, dried in a sterile room at room temperature for 24 hours, and the coated membranes were ready for use. The fabricated hollow fiber membranes were designated as 30% PTFE-PDMS/PVDF. Different thickness PTFE-PDMS/PVDF hollow fiber membranes could be obtained by repeating above dip-coating process different times, the thickness of the active layer was measured by SEM experiment.

3. SEM Characterization

Hollow fiber membrane samples were fractured in liquid nitrogen, coated with gold, the membranes were characterized by a scanning electron microscope (SEM, JEOL Model JSM-5600 LV, Japan) to observe the structures of the cross-section of the membranes.

4. Sorption Experiments

PTFE-PDMS membranes (with different PTFE content and no support layer) were dried at 60 °C under vacuum for 8 h, weighed with a highly sensitive electronic balance (ALC-1100.2, Sartorius, German, sensitivity: 0.1 mg), the dried membranes then were immersed in pure chloroform (or pure water) at different temperatures. After a certain time, the swollen membranes were taken out. Wiped with filter papers to get off surface liquid, the membranes were weighed immediately. The membranes were then put back into the previous soaking solution of chloroform (or pure water) for the next weight measurement. This process was repeated until sorption equilibrium was obtained (when there was no significant weight increase for the swollen membrane) to get the dependence of sorption behavior and soaking time. The data in this paper were the average values of four to five measurements. S_i was sorption coefficient of pure solvent in the membrane and was determined by

$$S_i=(M_{i,\infty}-M_{i,0})/M_{i,0} \tag{1}$$

where i represents the solvents chloroform or water, $M_{i,\infty}$ is the mass of the fully swollen membrane and $M_{i,0}$ is the mass of the dried membrane.

The ideal sorption selectivity [23] α_s was calculated by

$$\alpha_s=S_C/S_W \tag{2}$$

where S_C and S_W are the swelling degrees of the membranes which were soaked in pure chloroform and pure water, respectively.

Diffusion coefficient (D) of water and chloroform in the membranes was measured from the initial linear sorption curves [23], and calculated from the slopes of M_t/M_∞ versus $t^{1/2}$.

$$M_t/M_\infty=4[Dt/(\pi L^2)]^{0.5} \tag{3}$$

where M_t refers to the mass of the absorbed solvent in swollen membrane at time t. L is the thickness of dry membrane.

Diffusion selectivity (α_D) was calculated by

$$\alpha_D=D_C/D_W \tag{4}$$

where D_C and D_W are the diffusion coefficients of pure chloroform and pure water, respectively.

The ideal separation factor α_p and the ideal permeability P_i [23] were calculated by

$$\alpha_p=\alpha_s\times\alpha_D \tag{5}$$

$$P_i=S_i\times D_i \tag{6}$$

5. PV Performance

The characteristics of the hollow fiber membrane module used in our pervaporation experiments are given in Table 1. Fig. 1 is the schematic diagram of homemade PV apparatus used in this case. Dilute chloroform/water solution used as the feed was circulated by a pump outside the hollow fiber membranes in the 40 L feed tank. The temperature of the tank was kept constant with a built-in booster heater controlled by a temperature controller. Permeate-side pressure was obtained by a vacuum pump. After the operation reached steady state, permeate vapor sample was collected in a liquid nitrogen trap which had been weighed previously. The cold trap with frozen sample was weighed, and then 100 mL pure water was poured into the cold trap. Then this mixture of pure water and sample was poured into a 3,000 mL beaker which with 2,400 mL pure water in it. Thereafter, the sample was dissolved in the beaker for 15 minutes under ultrasonic condition. The diluted sample was then analyzed by gas chromatography (Shimadzu, GC2014C), which had an electron capture detector (ECD) and a headspace sampling (HS-16A, Shanghai Kemeiao Scientific Instrument Co. Ltd., China). The concentration of the permeate vapor sample was calculated through

Table 1. Properties of hollow fiber membrane module

Housing material	PVC
Sealant	Epoxy resin
Inside diameter of the shell (mm)	63
Inside diameter of hollow fibers (mm)	1.00±0.03
Thickness of membrane wall (mm)	0.70
Number of hollow fibers	100
Effective length of hollow fibers (mm)	250
Total membrane effective area (mm^2)	125600

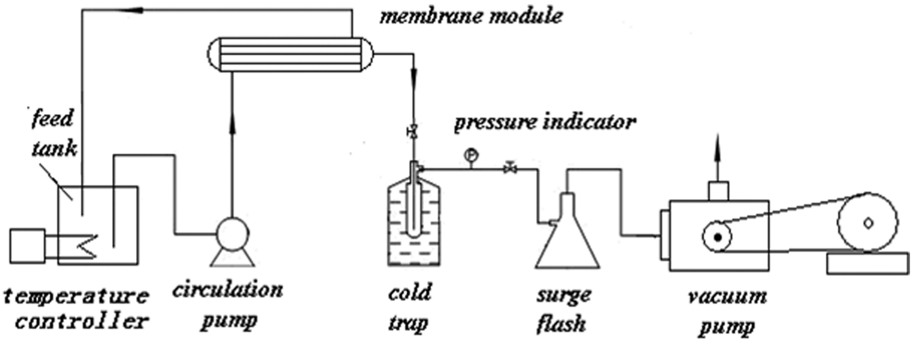

Fig. 1. Schematic diagram of pervaporation apparatus.

back-calculating method. Permeation flux J ($g\cdot m^{-2}\cdot h^{-1}$) and separation factor α are defined as

$$J_i=m_i/(\Delta t\times A) \qquad (7)$$

$$\alpha=(y_{chloroform}/y_{water})/(x_{chloroform}/x_{water}) \qquad (8)$$

where m_i is the total mass of permeate collected during the time interval Δt of about 30 minutes, A is the effective membrane area, x and y are the mole fraction of chloroform in permeate and in feed, respectively.

RESULTS AND DISCUSSION

1. Sorption Analysis

Fig. 2 and Fig. 3 illustrate the sorption history of chloroform and water in PTFE-PDMS membranes which had different PTFE content at different temperatures, respectively. From these figures we can see that for both PDMS and PTFE-PDMS membranes, chloroform uptake values were much bigger than those of water, which means that both PDMS and PTFE-PDMS membranes had a better solubility for chloroform than for water. From the pictures, also, the sorption coefficients of both chloroform and water decreased with the incorporation of PTFE and also decreased with the increase of PTFE content in membranes. According to the data of water contact angles we published before (Table 2, literature [3]), generally, with the increase of PTFE content in PTFE-PDMS membranes, water sorption coefficient decreases and chloroform sorption coefficient increases. But in this study, the chloroform sorption coefficient showed an opposite tendency. The reason could be that chloroform sorption coefficient in pure PTFE membrane was far less than that in pure PDMS membrane from the curves 1 and 6 in Fig. 2(a), so for PTFE-PDMS membranes, the chloroform sorption coefficient de-

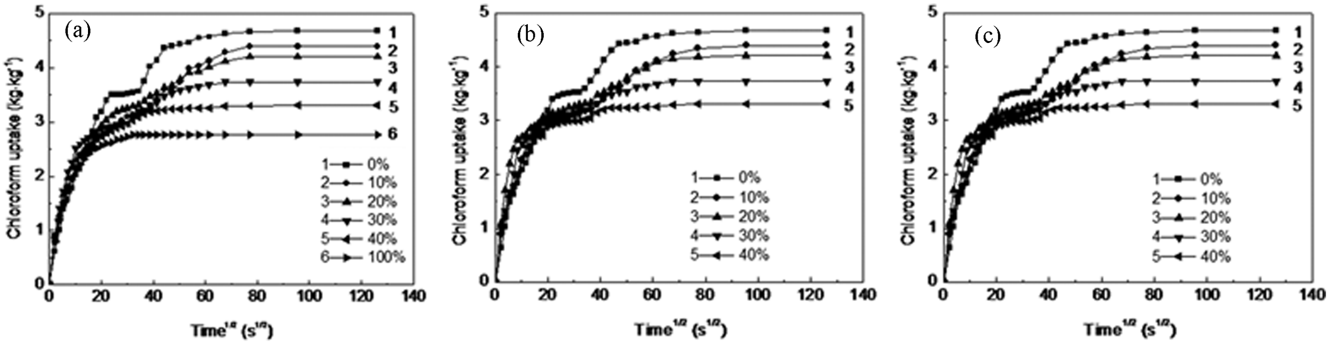

Fig. 2. Sorption curves for the uptake of chloroform in PTFE-PDMS membranes at different temperatures. (a) 40 °C, (b) 50 °C and (c) 60 °C.

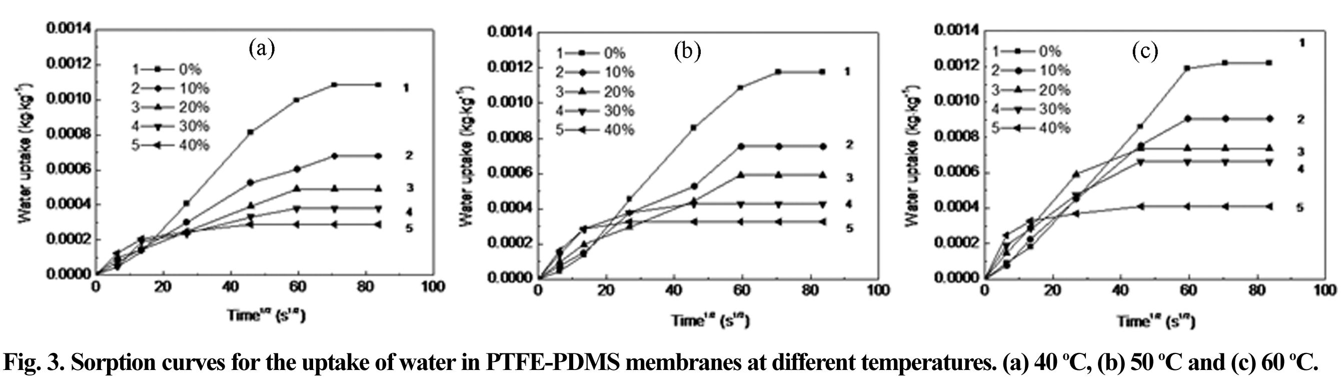

Fig. 3. Sorption curves for the uptake of water in PTFE-PDMS membranes at different temperatures. (a) 40 °C, (b) 50 °C and (c) 60 °C.

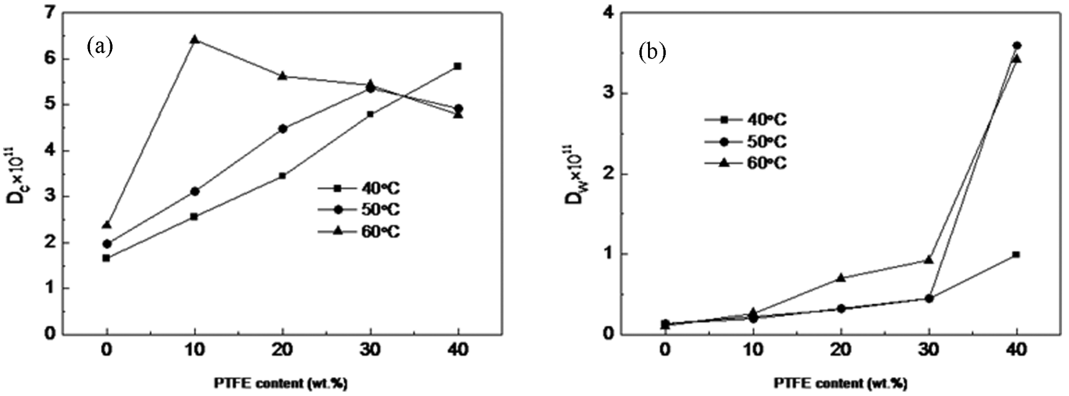

Fig. 4. Effects of PTFE content on diffusion coefficients at different temperatures. (a) Chloroform, DC; (b) Water, DW.

pends on PDMS content and increases with the increase of PDMS content in membranes. With an increase of operating temperature from 40 °C to 60 °C, sorption coefficients of both chloroform and water were basically invariant, which was not in accordance with Nguyen's study which used a deposited tetramethyl disiloxane membrane to study the sorption behavior of chloroform at different temperatures [24]. According to Nguyen, chloroform sorption coefficients decreased with increasing temperature from 30 °C to 50 °C, which means it is not favorable to chloroform sorption when feed temperature is high. The variations of water sorption coefficients in PTFE-PDMS membranes can be explained from the aspect of water condensation enthalpy according to the literature [25].

Diffusion coefficients of chloroform and water in different PTFE-PDMS membranes, which had different PTFE content at different temperatures, are presented in Fig. 4(a) and Fig. 4(b), respectively. We can see that the diffusion coefficients of both chloroform and water were increased by incorporating PTFE into PDMS membranes. With the increase of PTFE content from 0% to 40%, when feed temperature was 40 °C, chloroform diffusion coefficient increased, and when feed temperatures were 50 °C and 60 °C, chloroform diffusion coefficients first increased and then decreased. As for water diffusion coefficients under different temperatures, when PTFE content increased from 0% to 30%, they slowly increased; and when PTFE content further increased from 30% to 40%, they rapidly increased to the maximum. The reason for this is that the initial introducing of PTFE to the PDMS membranes caused the loose packing of PDMS chains, which was the main factor that controlled the diffusions of both chloroform and water [26]. But with the further increase of PTFE in PDMS membrane, the main control factor for the diffusion of chloroform might become the long and tortuous diffusion path caused by the interspaces among primary PTFE particles [23], and for the reason that the kinetic diameter of water molecule (0.37 nm) was smaller than that of chloroform molecule's (0.65 nm), the changing of the polymer chains caused by the incorporation of PTFE had little effect on the diffusion of water [27,28]. With an increase of operating temperature from 40 to 60 °C, the diffusion coefficients of both chloroform and water increased. It can be interpreted by the increase of the mobility of polymer chains and the increase of free volumes of the PTFE filled matrix [23,26].

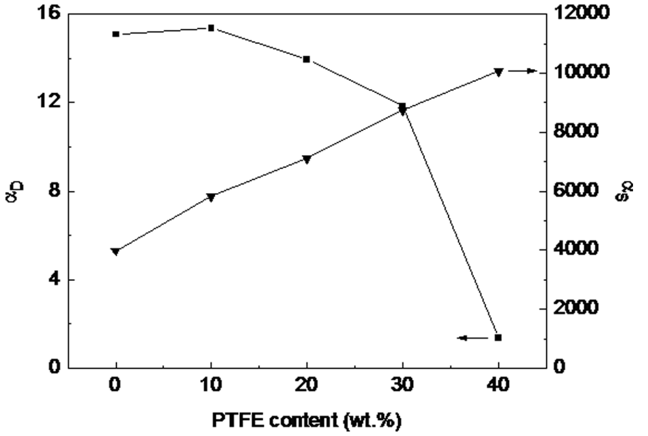

Fig. 5. Effects of PTFE content on chloroform/water sorption selectivity and diffusion selectivity.

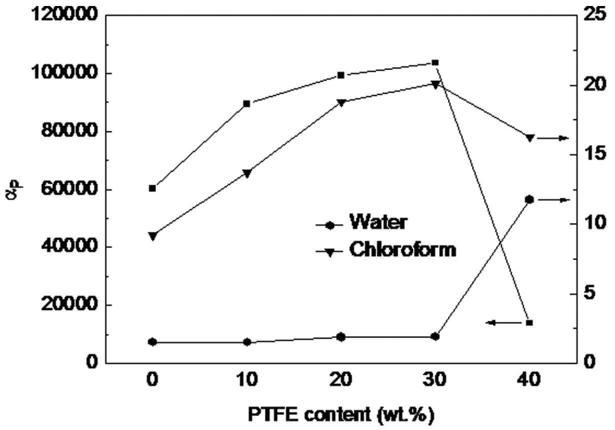

Fig. 6. Effects of PTFE content on ideal separation factor of chloroform/water and permeabilities of chloroform and water.

Fig. 5 shows the effects of PTFE content on chloroform/water solubility selectivity and diffusion selectivity at 50 °C. With an increase of PTFE from 0 wt% to 40 wt%, solubility selectivity increased and diffusion selectivity decreased. Possible explanations could be that with the increase of PTFE in membranes, membrane hydrophobicity increased (see Table 2 in literature [3]) which caused the increase of chloroform/water solubility selectivity. But because a water molecule is smaller than a chloroform molecule, the diffusion selectivity decreased. Effects of PTFE content on the ideal separation factor of chloroform/water and the permeabilities of chloroform and water

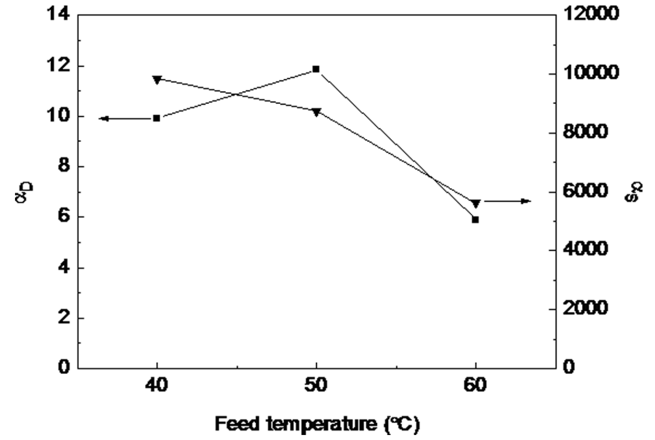

Fig. 7. Effects of feed temperature on chloroform/water sorption selectivity and diffusion selectivity.

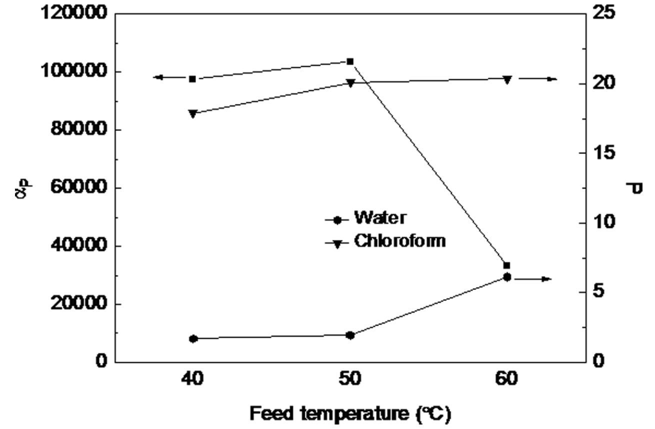

Fig. 8. Effects of feed temperature on the ideal separation factor of chloroform/water and the permeabilities of chloroform and water.

at 50 °C are presented in Fig. 6. With the adding of PTFE from 0 wt% to 30 wt%, both ideal separation factor and chloroform permeability first increased with the best ideal separation factor of 103640 and then decreased. Water permeability increased slightly when PTFE increased from 0 wt% to 30 wt%, then increased sharply. The changing trends in Fig. 6 are in accordance with our previous study results as shown in Fig. 8 of [3], but that chloroform permeability was significantly bigger than that of water's was not in agreement with our previous pervaporation results for the reason of the extremely low chloroform concentration in [3]. The effects of feed temperature on chloroform/water solubility selectivity and diffusion selectivity were studied using the 30% PTFE-PDMS membranes (Fig. 7). With an increase of feed temperature from 40 to 60 °C, solubility selectivity increased, but diffusion selectivity first increased and then decreased. The effects of feed temperature on chloroform/water ideal separation factor and the permeabilities of chloroform and water were also carried out using the 30% PTFE-PDMS membranes (Fig. 8). With an increase of operating temperature from 40 to 60 °C, both chloroform permeability and water permeability increased, but the ideal separation factor first increased a little and then decreased considerably. The data in Fig. 7 and Fig. 8 are important to define feed

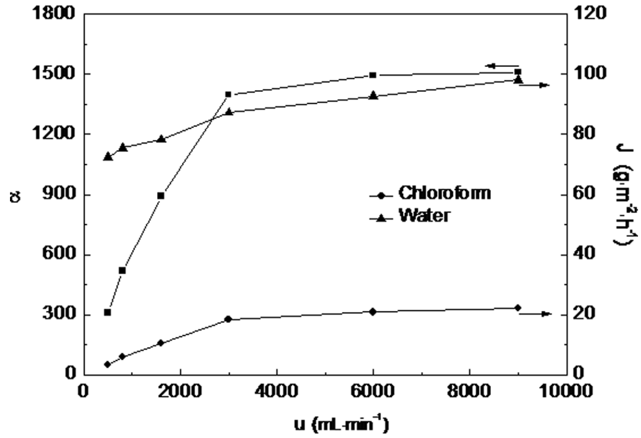

Fig. 9. Effects of feed flow rate on pervaporation performances.

temperature for the pervaporation process of chloroform/water mixtures.

2. PV Performance

2-1. Effect of Feed Flow Rate

Effects of feed flow rate on PV performances including chloroform flux, water flux and separation factor have been investigated through PV experiments using the 30% PTFE-PDMS/PVDF hollow fiber membrane; the results are in Fig. 9. Our experimental conditions were as follows: chloroform concentration 150 ppm, feed temperature 50 °C, permeate-side pressure 2.2 mmHg, and active layer thickness 13.8 μm. As Fig. 9 shows, with the increase of feed flow rate, all of the chloroform flux, water flux and separation factor increased rapidly at first and then leveled off at feed flow rate 3,000 mL/min. These results are in accordance with the findings reported in the literature [29] which used PDMS composite membranes to remove chloroform from aqueous solution. According to the study of [29], when membranes with high selectivity and high permeability were used for the pervaporation of low concentration aqueous, concentration polarization may have occurred in the boundary layer adjacent to the membrane surface. From Fig. 5 to Fig. 8, the PTFE-PDMS membranes had much higher permeability and selectivity for chloroform than for water, so we believe concentration polarization occurred in this study and it was confirmed by Fig. 9. As shown in Fig. 9, when feed flow rate increased from 500 to 3,000 mL/min, all of the chloroform flux, water flux and separation factor increased linearly. It means concentration polarization was the control step of mass transfer when flow rate was less than 3,000 mL/min. When feed flow rate was higher than 3,000 mL/min, with the increase of flow rate, there was not an obvious increase for chloroform flux, water flux and separation factor. So in this situation, membrane resistance became the control step of mass transfer. Consequently, to study membrane permeation properties for dilute solutions, feed flow rate must be big enough to eliminate the influence of concentration polarization. For this study, flow rate should be bigger than 3,000 mL/min.

2-2. Effect of Active Layer Thickness

Fig. 10 demonstrates the effects of active layer thickness of the 30% PTFE-PDMS/PVDF hollow fiber membranes on flux and separation factor for the 150 ppm chloroform solutions with a feed flow rate of 6,000 mL/min at 50 °C and 2.2 mmHg. The cross-sectional

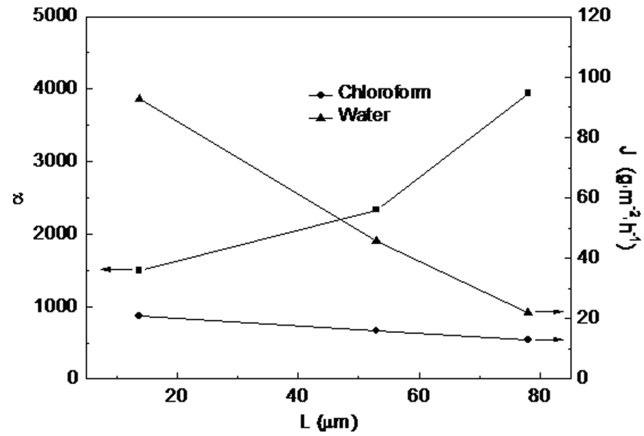

Fig. 10. Effects of active layer thickness on pervaporation performances.

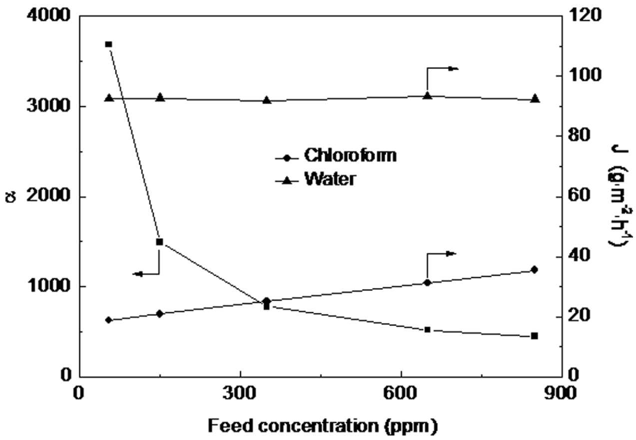

Fig. 12. Effects of feed concentration on pervaporation performances.

views of the 30% PTFE-PDMS/PVDF hollow fiber membranes with different thicknesses of active layer (13.8, 53.0 and 78.0 μm) are shown in Fig. 11.

From Fig.10, with the increase of the active layer thickness, chloroform flux and water flux dropped from 21 to 13 and from 93 to 22 g·h^{-1}·m^{-2}, respectively, whereas separation factor increased from 1494 to 3949. There usually is a trade-off between flux and separation factor depending on the membrane thickness; the results agreed well with the literature [30,31]. Through studying the impacts of film thickness on the structures and properties of PDMS membranes [31], Jadav thought, in thin films, there exists cluster and crystallization of polymer chains, which accordingly cause a loose structure of the thin polymer membranes, and this consequently results low selectivity and high permeability of the thin membranes. On the contrary, thick films had high selectivity and low permeability, which is also because thick films had extended diffusion range.

2-3. Effect of Feed Concentration

Fig. 12 shows the effects of feed concentration on flux and separation factor of the 30% PTFE-PDMS/PVDF hollow fiber membrane with 13.8 μm active layer under the experiment condition of feed flow rate of 6,000 mL/min, feed temperature of 50 °C and permeate-side pressure of 2.2 mmHg. From the figure, with the increasing of chloroform concentration from 55 to 850 ppm, chloroform flux increased linearly from 18.75 to 35.48 g·h^{-1}·m^{-2}, and water flux remained constant at around 92.30±1.00 g·h^{-1}·m^{-2}. According to solution-diffusion theory, when chloroform concentration increased, chloroform vapor pressure difference as the driving force across the membrane increased and caused the increase of chloroform flux.

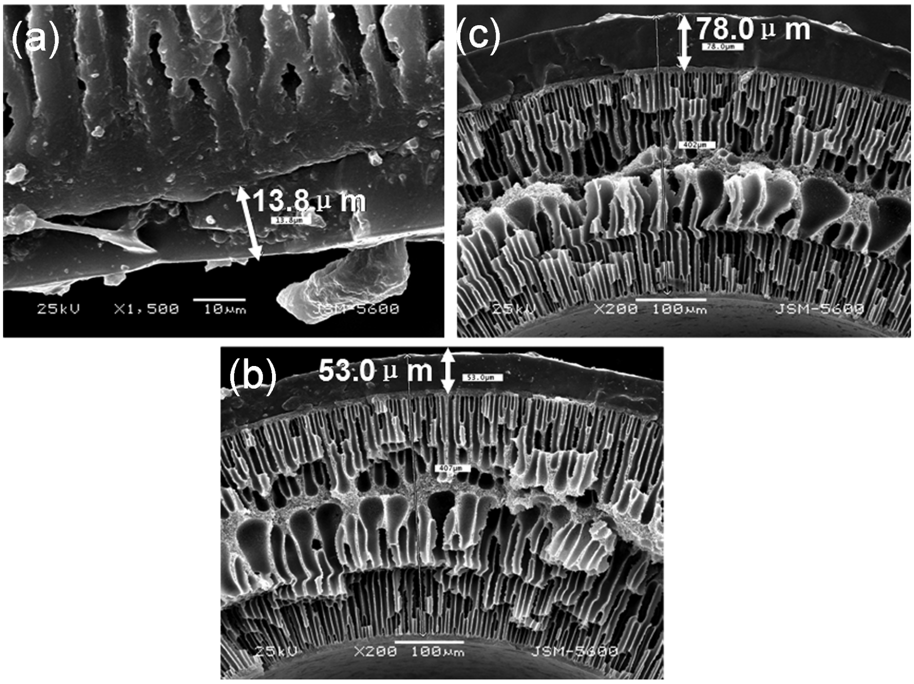

Fig. 11. SEM photographs of the 30%PTFE-PDMS/PVDF membranes with different thickness active layer.

Whereas with the increase of chloroform concentration from 55 to 850 ppm, there was no significant change in water concentration (only dropped from 99.945 to 99.915 wt%), so the pressure-difference driving force of water across the membrane was kept almost the same; therefore, we see an unchanged water flux. In addition, because the concentration of water was much higher than that of chloroform, we can see that water flux was significantly higher than that of chloroform. The same dependence of water flux on chloroform concentration was also observed by other authors' pervaporation experiments [32]. Separation factor decreased with the increase of chloroform concentration, and it could be explained by the definition Eq. (8) of separation factor.

2-4. Effect of Feed Temperature

Fig. 13 illustrates the effects of feed temperature on PV performances of the 30% PTFE-PDMS hollow fiber membrane with active layer thickness of 13.8 μm at chloroform concentration of 150 ppm, feed flow rate of 6,000 mL/min and permeate-side vacuum of 2.2 mmHg. As feed temperature increased, water flux, chloroform flux and separation factor increased nearly linearly, same as for the 30% PTFE-PDMS flat sheet membrane (Fig. 9 in literature [3]). Compared with flat sheet membrane, hollow fiber membrane showed higher flux but lower separation factor. Fig. 13 is also in accordance with the changing trends of chloroform permeability and water permeability in Fig. 8. The effects of temperature on fluxes followed the Arrhenius type function: J_i=J_0 exp (−E_a/RT). Plots of permeation fluxes (ln (J_i)) of chloroform and water versus reciprocal temperature (1/T) are shown in Fig. 14. Activation energy values calculated from slopes were 21.65 and 9.6 KJ/mol for water and chloroform, respectively, which indicated that water permeation was more sensitive to operation temperature than that of chloroform for the 30% PTFE-PDMS hollow fiber membrane.

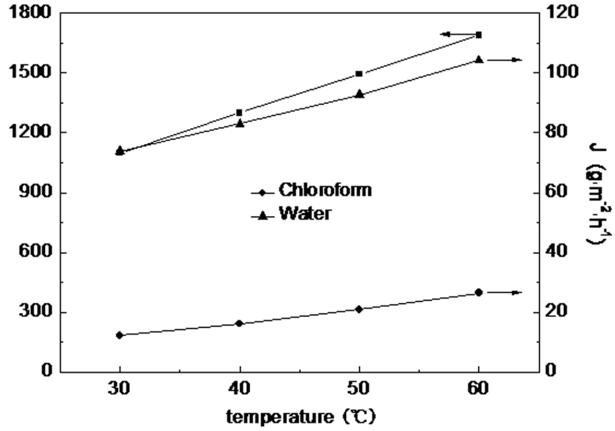

Fig. 13. Effects of feed temperature on pervaporation performances.

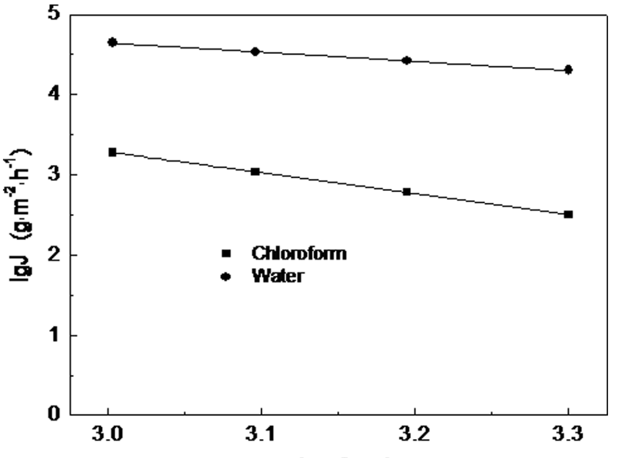

Fig. 14. Arrhenius plots of lnJ versus 1/T for the 30% PTFE-PDMS hollow fiber membrane.

CONCLUSIONS

A novel hollow fiber pervaporation membrane with PTFE-PDMS as the top active layer and PVDF hollow fiber as the support layer was developed for the PV of chloroform from water. Sorption experiments of PTFE-PDMS membranes with different PTFE content indicated that PTFE-PDMS membranes had better solubility and diffusivity for chloroform than for water. With the increase of PTFE content from 0 wt% to 40 wt%, sorption coefficients of both chloroform and water decreased; for the diffusion coefficient of chloroform, when experiment temperature was 40 °C, it increased, when experiment temperature was 50 °C or 60 °C, it first increased and then decreased; the diffusion coefficient of water first increased slowly when PTFE content was less than 30 wt%, and then it increased sharply; chloroform/water solubility selectivity increased but diffusion selectivity decreased at 50 °C. Consequently, chloroform/water ideal separation factor and chloroform permeability first increased and then decreased, whereas water permeability first increased steadily and then increased steeply. With an increase of operating temperature from 40 to 60 °C, for the 30% PTFE-PDMS membrane, sorption coefficients of both chloroform and water were basically invariant but their diffusion coefficients increased; solubility selectivity increased and diffusion selectivity first increased and then decreased. Consequently, permeabilities of both chloroform and water increased, and chloroform/water ideal separation factor first increased and then decreased.

PV performance was studied at different feed flow rates, active layer thicknesses, feed concentrations and feed temperatures using 30% PTFE-PDMS/PVDF hollow fiber membrane. When feed flow rate increased from 500 to 9,000 mL/min, chloroform flux, water flux and separation factor all first increased linearly and then leveled off. So when feed flow rate was less than 3,000 mL/min, the mass transfer control step was concentration polarization on the membrane surface, but when feed flow rate was higher than 3,000 mL/min, the mass transfer control step was membrane resistance. With the increase in active layer thickness from 13.8 to 78.0 μm, chloroform flux and water flux dropped from 21 to 13 $g\cdot h^{-1}\cdot m^{-2}$ and from 93 to 22 $g\cdot h^{-1}\cdot m^{-2}$, respectively but the separation factor increased from 1494 to 3949. When chloroform concentration increased from 55 to 850 ppm, the chloroform flux increased linearly, but water flux remained constant and separation factors decreased. As operating temperature increased from 40 to 60 °C, both the flux and separation factor increased; the variation of permeation flux followed the Arrhenius relationship, and the activation energy values from the slopes were 21.65 and 9.6 KJ/mol for water and chloroform, respectively.

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