Preparation of Asymmetric Chitosan Hollow Fiber Membrane and Its Pervaporation Performance for Dimethyl Carbonate/Methanol Mixtures

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ABSTRACT: Chitosan hollow fiber membranes (CHFMs) were successfully fabricated by a phase inversion method. The CHFMs obtained by ethanol–hexane exchange drying displayed integrally skinned asymmetric morphologies by field-emission scanning electron microscope observation. The CHFMs could be used for the pervaporation separation of dimethyl carbonate (DMC)/methanol mixtures. Swelling properties of the polymer material were investigated, and the effects of feed composition and operating temperature on the pervaporation separation performance of the CHFMs were evaluated. The relationship of permeation flux and temperature was in agreement with the Arrhenius equation. It was demonstrated that the integrally skinned asymmetric CHFMs exhibited an effective method for the separation of DMC/methanol azeotropic mixtures. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2875–2882, 2010

Key words: chitosan; hollow fiber membranes; asymmetric morphology; pervaporation; dimethyl carbonate

INTRODUCTION

Dimethyl carbonate (DMC) is considered to be an important and environmentally benign chemical that has wide applications in the past few years.[1] It can be used as an agent to replace some virulent carcinogens, such as phosgene and dimethyl sulfate, because of two methyl groups and one carbonyl group in its molecule.[2] It is also used as a component of electrolyte solvent mixtures in Li-ion battery because of its acceptable anodic stability for the 4 V cathodes used in Li-ion batteries, as well as lithiated graphite. What is more, DMC shows other properties such as high polarity, sufficiently low toxicity, and acceptable safety features.[3] DMC has also been proposed as an alternative fuel additive for its high oxygen content (53 wt %), good blending properties, favorable distribution in gasoline/water, low haze point, low toxicity, and fast biodegradation.[4]

Five methods have been mainly used to synthesis DMC: (a) phosgenation of methanol (MeOH); (b) MeOH oxy-carbonylation; (c) carbonylation of methylnitrite; (d) ethylene carbonate or urea transesterification; (e) direct synthesis of DMC starting from carbon dioxide.[1] Usually, DMC is obtained as a mixture with MeOH. Separation is a critical aspect of producing DMC. In the major commercial process for DMC production, various separation processes (e.g., extractive distillation, liquid–liquid extraction, and pressure swing distillation) have been proposed to separate and purify DMC from DMC/MeOH azeotropic mixtures (comprising of approximately 30/70 DMC/MeOH by weight under normal pressure).[4] Generally, separation of the azeotropic mixtures is a high-energy consumption and complicated operation process by these conventional separation technologies.

In recent years, pervaporation is widely considered as an attractive alternative to other conventional separation methods for a variety of processes, especially exhibits advantages for the separation of azeotropic and close-boiling mixtures.[5,6] Compared with these conventional separation technologies, it has higher separation efficiency and lower energy costs. In addition, it has other advantages of simplifying process plants and avoiding possible

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pollutants used in conventional separation process to break up azeotropic composition.

Membrane materials will directly determine the properties of membranes prepared. Selection of the polymer materials for the pervaporation separation is mainly based on three important features: high chemical resistance, sorption capacity, and good mechanical strength of the polymer membrane in the solution.[6] It should have good interaction preferably with one of the components of the mixture for separation. As for DMC/MeOH mixtures, MeOH is more hydrophilic and polar than DMC due to dipole moment of hydroxyl group. As a result, the interaction between the polar material and MeOH should be stronger than DMC, which results in large affinity of MeOH for hydrophilic or polar polymer materials. Therefore, it should be possible to improve MeOH/DMC selectivity by using a polar or hydrophilic membrane.[7] Currently, some polymer materials used to prepare pervaporation membranes for separating DMC/MeOH mixtures have been researched: chitosan,[8,9] poly(vinyl alcohol) (PVA),[10,11] poly(acrylic acid) (PAA)/PVA,[12] ion exchange materials,[13] and so on. Among these polymer materials, chitosan is a derivative of chitin that is one of the most abundant natural polymers. Figure 1 shows the structure of chitosan.[14] It was used as a membrane material for separating DMC/MeOH mixtures because of its high hydrophilicity, more affinity to MeOH than DMC, good film forming property, and chemical stability. Furthermore, chitosan offers a possibility to obtain a high separation property due to its reactive amino groups and hydroxyl groups can be used for chemical modifications.[8,9,15]

Homogeneous dense flat membranes have been mostly prepared to study the characteristics of membranes for DMC/MeOH separation in these previous works.[8–13] These membranes are easy to be prepared and can directly show the intrinsic separation properties of those polymer materials. Compared with flat membranes, hollow fiber membranes have the following advantages: (a) higher membrane packing density (i.e., membrane area per unit module volume); (b) self-supporting ability; and (c) the hollow fibers themselves form the vacuum vessel if the shell fed mode of operation is used.[15] Furthermore, asymmetric hollow fiber membrane morphology offers a possibility of making a barrier with a thin effective separation layer, which enables higher flux while maintaining desirable separation ability.

Asymmetric hollow fiber membranes are typically prepared from a single polymer solution via the phase inversion process first developed in 1960 by Loeb and Sourirajan. Phase separation processes in polymer solutions in relation to membrane formation have been reviewed by van de Witte et al.[16] It is generally considered that the top skin layer primarily determines the separation properties of an asymmetric membrane. Through proper control and adjustment of the membrane preparation conditions, integrally skinned asymmetric hollow fiber membranes with high flux and satisfactory selectivity for pervaporation separation can be produced. Some polymer materials have been used in the preparation of integrally skinned asymmetric hollow fiber membranes for pervaporation, such as polysulfone, poly (vinylidene fluoride), polyimide, and so on.[17–20] Different from these materials, chitosan is a highly crystalline and strongly hydrophilic material. Both phase inversion process and drying process are important to obtain integrally skinned asymmetric chitosan hollow fiber membranes (CHFMs). To our best knowledge, it has not been reported on preparation of integrally skinned asymmetric CHFMs and their use for pervaporation of DMC/MeOH mixtures.

In this study, we developed integrally skinned asymmetric CHFMs to separate DMC from DMC/MeOH mixtures. The CHFMs were prepared through a dry/wet phase inversion process and dried by ethanol–hexane exchange drying. Swelling properties of the polymer material and pervaporation separation performances of the CHFMs were investigated.

EXPERIMENTAL

Materials

Chitosan (degree of deacetylation 94%, M_n 875 kDa) was purchased from Zhejiang Yuhuan Ocean Biochemistry, China. Acetic acid solution was used as solvent for chitosan. DMC was purchased from Alfa Aesar Company. Other chemical reagents and solvents were analytical purity from commercial sources and used without further purification. The feed mixtures used for the pervaporation experiments were prepared by blending MeOH and DMC with predetermined compositions.

Preparation of membranes

Preparation of chitosan homogeneous dense membranes

Chitosan homogeneous dense membranes were prepared by solution casting method. Chitosan was dissolved in dilute acetic acid solution. The polymer solution, comprising of 1.5 wt % of chitosan, 2.5 wt % of acetic acid, and 96.0 wt % of de-ionized water, was filtered to remove any nondissolved residue before being cast onto a clean glass plate at ambient conditions. The polymer solution was dried naturally in the air for 48 h to form a homogeneous dense membrane. The dried chitosan membranes were treated in an alkali solution containing 0.6*M* of sodium hydroxide. After alkaline treatment, chitosan

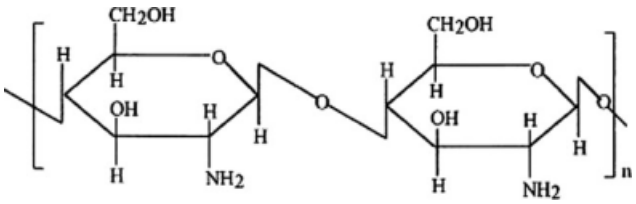

Figure 1 Structure of chitosan.

membranes were rinsed thoroughly in deionized water to wash out any residual sodium hydroxide. The membrane was then dried in the air. The thickness of dried membrane was determined to be about 11 μm using a digital micrometer.

Fabrication of CHFMs

Chitosan was dissolved in acetic acid solution. CHFMs were fabricated by a dry/wet spinning process. Details of spinning parameters are listed in Table I. The degassed homogenous polymer solution and bore liquid were extruded through the spinneret die to form a nascent hollow fiber membrane and then passed through an air gap before entering the coagulation bath of alkaline solution. Spinning rate was controlled by N_2 pressure and flow rate of bore fluid was controlled with a syringe pump. The as-spun CHFMs were washed thoroughly with deionized water and stored for further drying process.

Drying of membranes

Removing water directly from a wet membrane in the air may cause changes of the membrane morphology. Solvent exchange drying was used widely as an effective method to minimize changes of membrane morphology, especially for a hydrophilic membrane, such as cellulose hollow fiber membrane.[21–24] Chitosan is a strongly hydrophilic linear polymer material, and its chemical structure unit is similar to that of cellulose, only the group of 2-OH is replaced by $-NH_2$. Therefore, solvent exchange drying was also used in this study.

The wet CHFMs were immersed in ethanol followed by hexane, and then dried naturally in ambient air at room temperature. In each solvent exchange step, a solvent was refreshed for twice and the retention period in each fresh solvent was more than 8 h with stirring. Every time, the volume of solvent was more than 300 times to that of the former solvent stayed in the CHFMs.

Morphological study of CHFMs

For morphology, the CHFMs samples were immersed in liquid nitrogen and fractured to obtain tidy fiber cross-sections, followed by coating with platinum in a sputtering device. The surface and cross-section morphologies of CHFMs were observed under a field-emission scanning electron microscope (FESEM) (model: S-4700, Hitachi Company, Japan).

Degree of swelling and solubility selectivity

Before each experiment, the predried chitosan membranes were weighed and then immersed quickly in different known concentrations of DMC/MeOH mixtures at 50°C for 48 h to reach an equilibrium swelling. These membranes were taken out from the solutions and weighed after the surface liquid was removed quickly. All experiments were repeated at least for three times, and the results were averaged. The degree of swelling (DS) of the membrane was calculated by Eq. (1):

$$\mathrm{DS} = \frac{W_s - W_d}{W_d} \times 100\% \tag{1}$$

where W_s and W_d are the weights of the swollen membrane and the dried membrane, respectively.

The swollen membranes were placed in a vacuum system, and the solution sorbed into the membranes was completely trapped with liquid nitrogen. The composition was analyzed by a gas chromatography (model: 7890II Tianmei, China). The solution composition in the membrane and in the feed yielded the solubility selectivity, as expressed in Eq. (2):

$$\alpha_s = \frac{y^{\mathrm{m}}_{\mathrm{MeOH}}/y^{\mathrm{m}}_{\mathrm{DMC}}}{x^{\mathrm{F}}_{\mathrm{MeoH}}/x^{\mathrm{F}}_{\mathrm{DMC}}} \tag{2}$$

where $x^{\mathrm{F}}_{\mathrm{MeOH}}$ and $x^{\mathrm{F}}_{\mathrm{DMC}}$ are the weight fractions of MeOH and DMC in the feed, $y^{\mathrm{m}}_{\mathrm{MeOH}}$ and $y^{\mathrm{m}}_{\mathrm{DMC}}$ are those in the membrane, respectively.

TABLE I
Experimental Parameters for the Spinning of CHFMs

Parameter	Value
Dope solution composition (wt %)	(Chitosan/acetic acid/water) 8.5/5.7/85.8
Spinneret temperature (°C)	25
Room temperature (°C)	25
Room relative humidity (%)	50–60
Air gap distance (cm)	5
External/internal coagulant temperature (°C)	25
External coagulant bath composition (wt %)	(NaOH/water) 10/90
Bore fluid composition (wt %)	(NaOH/water) 25/75
Bore fluid flow rate (cm^3/min)	0.95
Spinneret (inner diameter/outer diameter) (mm)	1.1/2.2

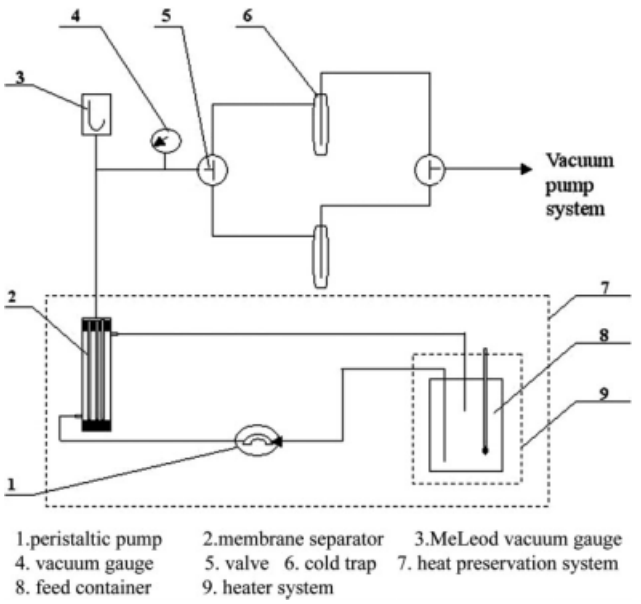

Figure 2 The apparatus used for pervaporation experiments.

Module fabrication and pervaporation tests

CHFMs module was made by putting 15 fibers in a stainless steel tube (tube length: 22 cm). The effective membrane area per module is about 120 cm^2. The test system used for pervaporation experiments is shown schematically in Figure 2. Pervaporation experiments were carried out at 20 to 50°C. The feed solution was pumped into the shell side of the module and the permeate came out from the lumen of CHFMs. The permeation flux was determined by:

$$J = \frac{W}{A \cdot t} \tag{3}$$

where J, W, A, and t represent the permeation flux ($g/(m^2\ h)$), weight of the permeate (g), the effective membrane area (m^2), and operation time (h), respectively. A vacuum pump was used to maintain the downstream pressure at 150–300 Pa. The permeation flux was determined by measuring the weight of permeate. The compositions of the feed solutions and permeates were also measured by gas chromatography. The separation factor (α) for MeOH was defined as:

$$\alpha = \frac{y_{\mathrm{MeOH}}/y_{\mathrm{DMC}}}{x_{\mathrm{MeOH}}/x_{\mathrm{DMC}}} \tag{4}$$

where x_{MeOH} and x_{DMC} are the weight fractions of MeOH and DMC in the feed, y_{MeOH} and y_{DMC} are those in the permeate, respectively.

The permeance of the membrane for component i (P_i) equaled the permeation flux divided by driving force[12]:

$$P_i = \frac{J_i}{x_i \gamma_i p_i^{\mathrm{sat}} - y_i p^{\mathrm{P}}} \tag{5}$$

where P_i (mol/(cm^2 s cmHg)), J_i the permeate flux of component i (mol/(cm^2 s)), x_i the mole fraction of component i in the feed side, γ_i the activity coefficient of component i, p_i^{sat} the saturated vapor pressure of component i (cmHg), y_i the mole fraction of component i in the permeate, and p^{P} is the permeate pressure (cmHg). The permeance selectivity (β) was defined as the ratio of the permeances:

$$\beta = \frac{P_a}{P_b} \tag{6}$$

where indices a and b refer to the fast permeable component and the slow permeable component, respectively.

RESULTS AND DISCUSSION

Morphology of the CHFMs

The CHFMs were prepared by dry/wet phase inverse process, which was commonly used to fabricate polymeric membrane. But the CHFM forming process was more complex because its process involved a neutralization reaction between acidified polymer solution and sodium hydroxide in the coagulation bath. Delayed phase separation processes have been observed during the phase inversion process.

Figure 3 shows FESEM images of outer surface and cross-section of the CHFM after solvent exchange drying. Photo (a) shows the integral cross-section morphology. No finger-like macrovoid can be found. Photo (b) shows the morphology of outer surface. A dense morphology can be seen from it. Photos (c) and (d) show the morphologies of cross-section near the outer surface at magnification of 10,000 and 50,000, respectively. A thin dense skin layer can be found near the outer surface. Photo (e) and (f) show the morphologies of cross-section in the middle part and near the inner surface, respectively. Sponge-like porous substrate can be seen due to the delayed phase separation process. In a word, an integrally skinned asymmetric structure has been formed after solvent exchange drying. This could possibly be explained as follows.

When the nascent chitosan hollow fibers encountered the alkaline solution of sodium hydroxide in the coagulation bath, cationic amine groups ($-NH_3^+$) were converted into free amine groups ($-NH_2$).[25] The homogeneous polymer solution was transformed into a two-phase system in which the polymer-rich solid phase formed the rigid membrane structure, while the polymer poor liquid phase

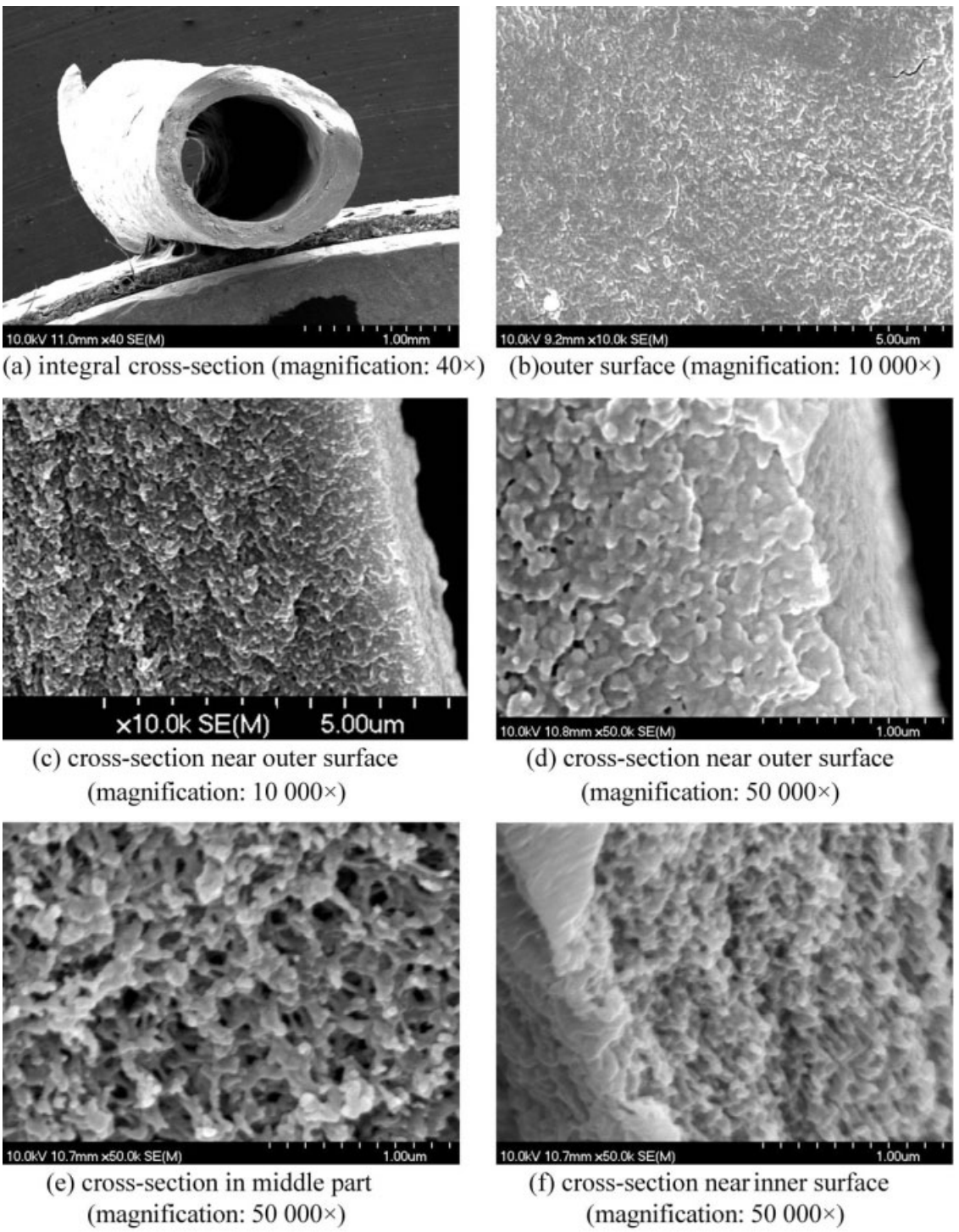

Figure 3 FESEM images of outer surface and cross-section of the CHFMs.

formed the voids. Then gelation and crystallization of chitosan might start from the surface. A skin layer was formed on the surface of the membrane due to rapid polymer precipitation. Simultaneously, the skin layer slowed down the entry of sodium hydroxide into the underlying polymer solution to react with acetic acid. Consequently, the polymer precipitated much more slowly, forming a porous substrate. Consequently, a sponge-like porous asymmetric structure was formed due to delayed phase separation.

The sorption properties of chitosan homogeneous dense membranes

A change in the feed composition would directly affect the sorption phenomena (DS) at the liquid

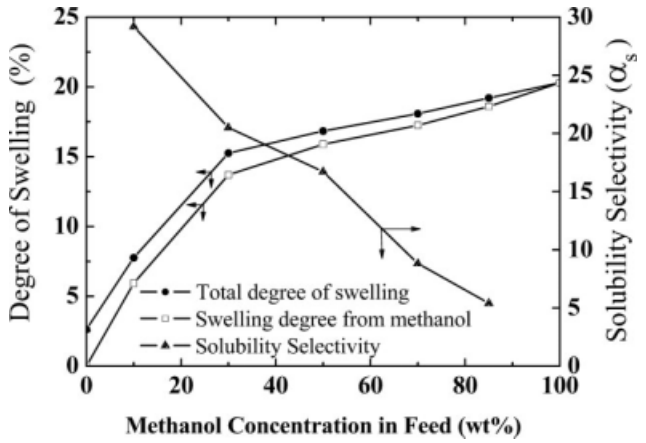

Figure 4 Effect of MeOH concentration on swelling degree and solubility selectivity of chitosan homogeneous dense membrane in the DMC/MeOH mixtures at 50°C.

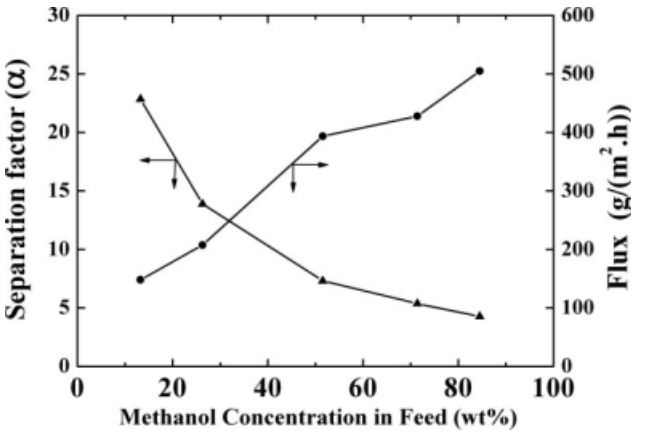

Figure 5 Effect of MeOH concentration in feed on separation factor and permeation flux of CHFMs for separating DMC/MeOH at 50°C.

membrane interface, as proved by the solution-diffusion principle. Figure 4 shows the effect of MeOH concentration on the DS and solubility selectivity of chitosan homogeneous dense membrane in the DMC/MeOH mixtures at 50°C. The membrane was only slightly swollen by pure DMC. With the increase of MeOH concentration, the total swelling degree of membrane increased but the solubility selectivity decreased. It can be considered that the membrane is preferentially solvated by MeOH as MeOH share strong interactions with chitosan through hydrogen bonds, whereas interactions between DMC and chitosan are weak. Generally, the chemical structures of polymer and the solvent would control the swelling of the membrane: swelling will be enhanced when the solubility parameter (δ) of polymer and solvent are close.[26] Solubility parameter of chitosan, MeOH, and DMC are listed in Table II. Solubility parameter of chitosan is closer with that of MeOH than DMC, so the DS should be enhanced gradually with increasing MeOH concentration. The decrease in solubility selectivity with increasing methanol concentration was due to an increased affinity of DMC for chitosan-methanol mixtures.

TABLE II
Solubility Parameters (δ) of Chitosan and Four Liquids[24,27]

Species	δ $(cal/mL)^{0.5}$
Chitosan	21.1
Methanol	14.5
DMC	10.1
Water	23.4
Ethanol	12.7
Hexane	7.3

Pervaporation properties of the CHFMs

Effect of MeOH concentration in feed on pervaporation performances

Feed concentration is one of the important factors during pervaporation processes. Figure 5 shows the permeation flux (J) and separation factor (α) of CHFMs under different MeOH concentration in the feed at 50°C. An increase in feed MeOH concentration tended to increase the permeation flux and decrease the separation factor. Usually, the increase in the permeation flux could be explained in terms of the increased DS in the pervaporation literature. In this case, as MeOH concentration in the feed mixture increased, because of a strong interaction between membrane and MeOH the membrane became more swollen. As a result, polymer chains became more flexible and both MeOH and DMC could easily permeate the membrane, which resulted in the decrease of separation factor.

In practice, permeance (P) is one of the intrinsic membrane properties used for asymmetric membrane for permeation. The permeance and permeance selectivity (β) are also used to describe the pervaporation performance.[28] Figure 6 shows the partial permeances under different MeOH concentration in the feed at 50°C. The saturated vapor pressure and activity coefficient of component data required to determine the permeances were calculated from the process simulation software (Aspen Plus 11.1). It can be seen from Figure 6 that DMC permeance increases continuously with decreasing DMC feed concentration. This increase in permeance correlates with the increase in MeOH content of the highly MeOH-hydrophilic chitosan membrane material. The membrane permeance selectivity (β) data show the chitosan membrane material to have high selectivity for MeOH over DMC for the entire concentration range. With the increase of MeOH concentration in feed, permeance selectivity of MeOH/

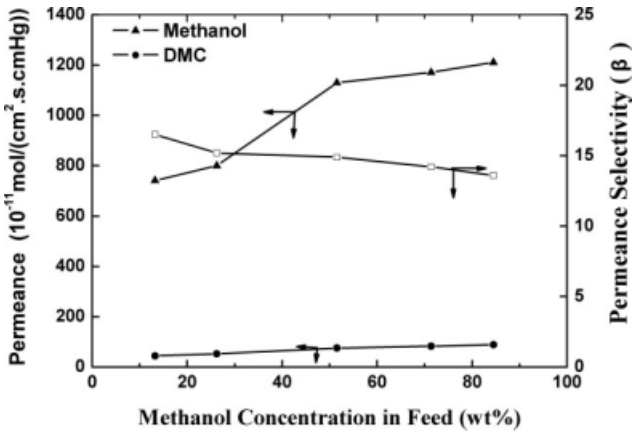

Figure 6 Effect of MeOH concentration in feed on partial permeance for separating DMC/MeOH at 50°C.

DMC decreased, which is similar to the conclusion of the hydrophilic PVA membrane for water/ethanol pervaporation system summarized by Wijmans.[28]

Effect of operation temperature on pervaporation performances

The effect of operation temperature on pervaporation performances of a 70 wt % MeOH feed had been investigated. Figure 7 shows the effect of temperature on the permeation flux and separation factor of the CHFMs. Permeation flux increased and separation factor decreased with temperature. Temperature affected the transport of components both in the liquid feed and in the membrane. Both diffusion of components in the liquid and sorption of components into membrane increased with feed temperature. In addition, at higher temperature the mobility of the chitosan chains led to an increase of the permeate molecules diffusion in free volume of the membrane. All these led to higher flux, whereas

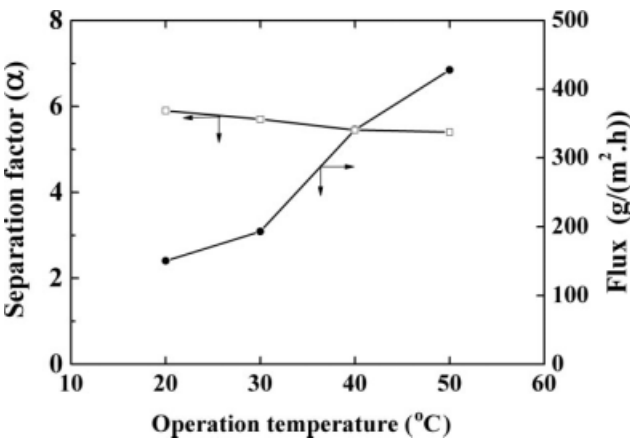

Figure 7 Effect of operation temperature on separation factor and pervaporation flux of CHFMs for the feed containing 70 wt % MeOH.

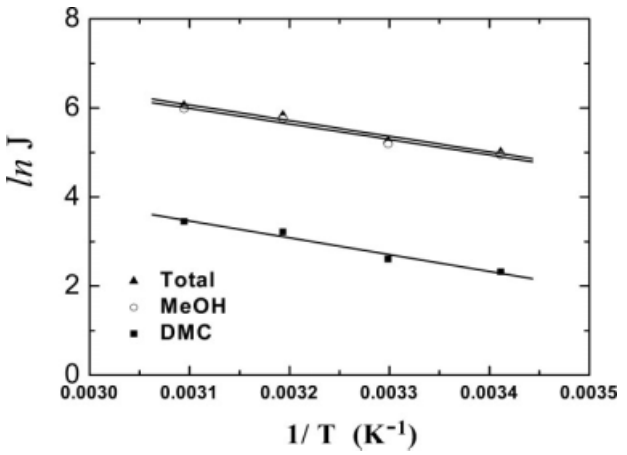

Figure 8 Arrhenius plot of ln J versus $1/T$ for 70 wt % of methanol in feed.

the separation factor was suppressed. Similar results were obtained for DMC/MeOH separation reported by Won et al.[9] On the other hand, with the operating temperature increasing, the vapor pressure of both MeOH and DMC in the feed compartment also increased, but the vapor pressure at the permeate side was not affected. All this resulted in an increase in the driving force with increasing temperature.

The temperature dependence of permeation flux could be expressed by an Arrhenius-type relationship[29]:

$$J = J_0 \exp\left(-\frac{E_p}{RT}\right) \tag{7}$$

where J represents permeation flux (g/(m^2 h)), J_0 is a constant representing pre-exponential factor, E_p represents activation energy for permeation, and RT is the usual energy term. From the Arrhenius relationship, the pervaporation activation energy (i.e., the energy barrier for the species to transport through the membrane) can be evaluated from Eq. (7). On the basis of the respective methanol and DMC fluxes obtained at pervaporation temperature of 20, 30, 40, and 50°C for 70 wt % of methanol in feed, Arrhenius plots are shown in Figure 8 for the temperature dependence of permeation flux. From a least square fit of these linear plots, the activation energies for total permeation, permeation of methanol and DMC were estimated, and the results were 29.2, 28.9, and 31.6 kJ/mol, respectively. This suggests that the permeating molecules of DMC require more energy to transport through the membrane, whereas methanol molecules take less energy.

Comparison between pervaporation and distillation

Figure 9 illustrates the permeation selectivity of the CHFMs compared with distillation separation based

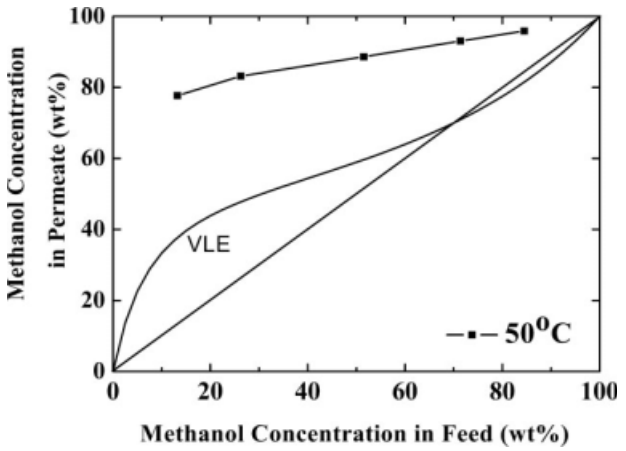

Figure 9 Permeate concentration versus feed concentration for pervaporation of DMC/MeOH, as compared with the VLE data.

on vapor–liquid equilibrium (VLE) at 50°C. Clearly, MeOH concentration in the permeate by pervaporation was much higher than that in the saturated vapor. MeOH concentration in the permeate exceeded that in the azeotrope even when the feed concentration of MeOH was only 10 wt % MeOH/DMC selectivity of the pervaporation was much higher than that of the distillation. These results indicated that pervaporation was more efficient for DMC/MeOH separation than distillation. What is more, the azeotrope, which was difficult to be separated by distillation, could be broken by pervaporation. The integrally skinned asymmetric CHFMs obtained in this work provide an effective method for separation of DMC/MeOH azeotropic mixtures.

CONCLUSIONS

Integrally skinned asymmetric CHFMs have been prepared by a dry/wet phase inversion process followed by ethanol–hexane exchange drying. It has been found that the total permeation flux of CHFMs increases but separation factor decreases with the increase of MeOH concentration and operation temperature for the pervaporation of DMC/MeOH mixtures. The relationship of permeation flux and temperature is in agreement with the Arrhenius equation. Integrally skinned asymmetric CHFMs provide an effective method for the separation of DMC/MeOH azeotropic mixtures.

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