PDMS/PVDF composite pervaporation membrane for the separation of dimethyl carbonate from a methanol solution

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1. Introduction

Dimethyl carbonate (DMC), which is a notably useful and “green” material, is widely used in chemical and petrochemical industries [1,2]. Many methods such as urea alcoholysis [1], transesterification [3], oxidative carbonylation of methanol [4], etc., are used to synthesize DMC. However, the obtained raw product using these methods is often an azeotropic mixture of DMC and methanol with a DMC-to-methanol weight ratio of 30:70 under normal pressure in the separation process [2,5,6]. Thus, the separation of the DMC–methanol azeotropic mixture is important and energy-intensive [7,8]. A large amount of energy is consumed at this step if conventional methods are used, such as pressure swing distillation, azeotropic distillation, extractive distillation and adsorption [9].

To reduce the energy consumption in the separation of the DMC–methanol azeotropic mixture, pervaporation (PV) has attracted increasing interest because this method has no vapor-liquid equilibrium limitation [8]. Therefore, the DMC–methanol azeotropic mixture can be economically and efficiently separated by pervaporation. Furthermore, pervaporation has other advantages such as high separation efficiency, less environmental pollution etc. [2,10]. Therefore, it is regarded as the most effective separation technology for azeotropic mixtures [2].

To pervaporate a DMC–methanol azeotropic mixture, two types of membranes were investigated: methanol-selective membrane materials such as polyamide-6 [7] and DMC-selective membrane materials such as PDMS [2]. Although the pervaporation performances using methanol-selective membrane may be acceptable, the major component in the DMC–methanol azeotropic mixture is methanol, which accounts for approximately 70 wt%. From an energy consumption view point, pervaporation is especially useful for removing minor components in the mixture because it does not require heating the entire feed stream as in distillation [11]. Therefore, more energy may be required to use methanol-selective membrane in the pervaporation of the DMC–methanol azeotropic mixture [2], which makes it less suitable to apply in the actual industry. Li’s group [2,6,12] developed two types of membranes to study their separation performance in the pervaporation of the DMC–methanol azeotropic mixture. They reported in their latest paper that the DMC-selective membrane is proven to be better in the pervaporation of DMC–methanol azeotropic mixture than the methanol-selective membrane does.

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There are few reports on the use of PDMS material to separate DMC from the methanol solution. Although Li’s group used the PVDF-supported silica/PDMS composite membrane to separate DMC from the methanol solution, membrane-swelling effects on the membrane performance have not been studied. Furthermore, although the addition of silica to the PDMS polymer suppresses the excessive membrane swelling to a certain extent and improves the plasticization resistance, the membrane performance improved only slightly, and because of the silica incorporation, the membrane they used is relatively thick (approximately 27 μm ± 3 μm), which decreased its economic efficiency in the industry. Because the energy consumption in the pervaporation is relatively small, the main capital cost of the pervaporation process is actually dominated by the membrane units and the membrane replacements [13]. It can be expected that membranes with higher flux and constant selectivity or higher selectivity will finally reduce the membrane cost. This is because that the increased flux of the membrane allows a smaller membrane area to be used to treat the same volume of solvents and furthermore smaller membrane area also can reduce the membrane skid cost [14]. However, Huang et al. [15] reported that when the membrane thickness is thinner than 19 μm, the selectivity would sharply decrease. Dong et al. [16] also reported that when the thickness is below 10 μm, its separation factor linearly decreased in the separation of butanol from the aqueous solution using PDMS.

In this paper, the DMC-selectivity membrane material PDMS was used to prepare the pervaporation membrane. PDMS is a type of rubber silicon that has been widely studied in pervaporation such as separating butanol from aqueous solutions [10,11,16] because of its strong hydrophobic property and excellent film-forming properties. Furthermore, according to the solution-diffusion model, a larger difference in affinity between DMC-PDMS and methanol-PDMS makes them easier to be efficiently separated [17]. The affinity between organics and PDMS polymer can be estimated using the difference in solubility parameters. The calculated difference in solubility parameter of DMC-PDMS is 6.3 MPa1/2, which is lower than that of methanol-PDMS (21.4 MPa1/2), and their difference is above 15, which is higher than that of DMC-PEBA (Polyether block amide), DMC-PTMSP (poly[(1-trimethylsilyl-1-propyne)], etc. PDMS is also a product that can easily be used industrially. Silica is generally used as filler in the fabrication of PV membranes and can suppress membrane swelling [2,18]. However, the incorporation of silica sometimes weakens the separation factor because of the incompatibility between the fillers and the polymers and the increasing free volume after the silica incorporation [19]. Therefore, in this work, the solubility and the diffusivity of pure DMC and methanol in homogeneous membranes without substrates were first investigated using pure PDMS and PDMS/silica membrane with different silica contents. Then, membranes with different thicknesses were fabricated using PDMS as the membrane material to obtain a thickness of less than 10 μm, and their separation performances were investigated. The effects of temperature and feed composition on separation performances were studied. Finally, the stability of the membrane was evaluated for 15 days under various conditions.

2. Experiments

2.1. Materials

Polydimethylsiloxane (PDMS) was purchased from GE Toshinba Silicones Co., Ltd., Japan. Fumed silica with a particle diameter of 10–20 nm was purchased from Haiyi Scientific & Trading Co., Ltd., China. Polyvinylidene fluoride (PVDF, 0.22 μm) was purchased from Solvay Corporation, USA. n-Heptane, methanol, and dimethyl carbonate were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All chemical reagents were used as received without further purification.

2.2. Membrane preparation

Although a thinner membrane leads to a higher flux, thin membranes often lack mechanical stability, particularly when vacuum is applied on the permeate side [20]. Therefore, a substrate was used to support the thin selective layer to form a composite membrane. The composite membrane was prepared as follows: membrane solutions with different PDMS concentrations were prepared by dissolving polydimethylsiloxane (PDMS) with a ratio of part A to part B of 10:1 in heptane under vigorous agitation at 50 °C for approximately 5 h until the viscosity reached approximately 13 mPas. Prior to coating, the substrate was immersed in distilled water at room temperature overnight. Residual water at the substrate surface was quickly wiped off with a filter paper when the substrate was removed from water. Then, the membrane solution was poured and spread over the substrate surface using a coating knife with different heights to give different PDMS selective layer thicknesses. The as-cast membrane was left overnight at room temperature and subsequently transferred to a vacuum oven at 80 °C for 5 h for complete curing.

2.3. Characterization

The fractured section of the composite membrane was fractured in liquid nitrogen. The fractured-section morphology of the composite membranes was coated with a conductive layer of sputtered gold to make it conductive so that it can be characterized using field-emission scanning electron microscopy (FE-SEM, Hitachi-4800, Japan), which was operated at 5 kV and 10 μA.

The viscosities of the polymer coating solution were determined using a Brookfield viscometer (DV-Ill pro, Brookfield Engineering Laboratories, USA). The viscosity was determined at 25 °C.

The pore volumes of the membranes were obtained using N2 as the analysis adsorptive at −196 °C with an Accelerated Surface Area and Porosimetry system (ASAP 2020, Micromeritics Corporation, USA). The samples were evacuated at 200 °C for 2 h prior to adsorption.

2.4. Pure-solvent solubility and diffusivity in the homogeneous PDMS membrane

The solubility and diffusivity of DMC and methanol in homogeneous membranes without the PVDF support with the thickness of 50–60 μm were determined using a gravimetric method, which is described elsewhere [21,22]. Furthermore, in order to make the comparison more precisely, the size and shape of membrane strips were same. Membrane strips with known weight (M0) and thickness (t) after drying to constant weight were separately immersed in a pure methanol and a pure DMC solution at 25 °C. After a given time (t), the membrane was quickly and carefully blotted with tissue paper to remove any surface solution. Then, the membrane was weighed using a digital analytical balance to obtain the mass (Mt) in g of solvent per g of dry membrane) of the solvent that was sorbed in the membrane. The equilibrium solvent uptake (M∞, measured in g of solvent per g of dry membrane) was measured until no further weight increase was observed for the membrane. And the solvent sorption history (Mt vs time) is plotted, which is shown in Fig. 1. The equilibrium solvent uptake (M∞) is also called the membrane swelling degree (SD), which denotes the swelling degree of the membrane.
Furthermore, according to the equilibrium solvent uptake, the ideal sorption selectivity \( \alpha_i \) is calculated using [21]:

\[
\alpha_i = \frac{M_{\text{DMC},\infty}}{M_{\text{MeOH},\infty}}
\]

where \( M_{\text{DMC},\infty} \) and \( M_{\text{MeOH},\infty} \) are the equilibrium solvent uptakes for the pure DMC and the pure methanol, respectively.

According to Balik et al. [23], different types of methods can be used to estimate the diffusion coefficient \( D \) of a solvent in polymers if the diffusion coefficient is in an order of magnitude for a particular system. Here, a half-time method was used to obtain the diffusion coefficient of DMC and methanol in the membrane because it does not require a complicated computer method and is as accurate as other methods for a particular system [23]. Furthermore, when membranes are increasingly swollen in the sorption process, the diffusion coefficient theoretically varies. However, in order to make the comparison of diffusivities among different membranes simple and legible, it is assumed that diffusion coefficient is constant in the sorption process, and thus the constant diffusion coefficient obtained from the half-time method is used in this work. The diffusion coefficient of the solvent in a membrane is described as follows according to the half-time method:

\[
D = \frac{0.04919^2}{t_{0.5}}
\]

where \( t_{0.5} \) is the time when \( M_1/M_\infty = 0.5 \). The diffusion coefficient ideal selectivity \( \alpha_D \) was calculated as follows:

\[
\alpha_D = \frac{D_{\text{DMC}}}{D_{\text{MeOH}}}
\]

where \( D_{\text{DMC}} \) and \( D_{\text{MeOH}} \) are the pure DMC and pure methanol diffusion coefficients, respectively.

2.5. Pervaporation experiment

The schematic diagram of the pervaporation process was described elsewhere [24]. All measurements were performed in duplicate; the average value of two data values was used in this work. The pervaporation experiments were performed with a flat thin-film composite membrane in a simple circular flat pervaporation cell, which was made of stainless steel with an effective membrane area of 7.065 cm\(^2\).

A Longer WT600-1F Peristaltic Pump (Longer Corporation, China) was used to recirculate the feed solution with a flow rate of 0.6 L/min unless otherwise specified. During the experiments, the upstream of the membrane was maintained at atmospheric pressure, and the downstream pressure was maintained at 210 Pa at all times unless otherwise specified. The temperature of the pervaporation setup and the feed solution were controlled within ±0.1 °C using a Scientz Water Bath (Ningbo Scientz Corporation, China).

The initial experiment was normally conducted for 1 h to attain a steady state. Then, samples of both retentate and permeate were collected for analysis. The permeate flux \( J \) was obtained by weighing the weights of the collection in a cold trap \( (W_i) \) for a given time \( t \), and the concentrations of DMC were measured using Gas Chromatography (GC-2014, Shimadzu, Japan). The PV performance of the membrane was evaluated in terms of the permeate flux, the normalized flux and the separation factor. The permeate flux and the normalized flux \( (J') \) (normalized to 100 \( \mu \)m) were calculated as follows:

\[
J = \frac{W_i}{At}
\]

\[
J' = \frac{W_i}{At} \times \frac{1}{100}
\]

where \( A \) is the effective membrane area.

The selectivity in this work was calculated and expressed by the separation factor \( \beta \) as follows:

\[
\beta = \frac{Y_A/X_A}{Y_B/X_B}
\]

where \( Y \) and \( X \) are the weight fractions of the solutes in the permeate and the feed, respectively. The sub-indices \( A \) and \( B \) refer to DMC and methanol, respectively.

The permeabilities of DMC and methanol in the membrane were calculated according to the following equation [25]:

\[
\Phi_i = \frac{J_i J}{M_i (\mu_i \rho_i p_{\text{atm}} - p_i^e)}
\]
where \( M_i \) is the molecular weight and \( p^i_{\text{sat}} \) is the vapor pressure of component \( i \), which is calculated using the Antoine equation. \( x_i \) and \( y_i \) are the mole fraction and the activity coefficient of component \( i \) in the feed, respectively. \( p_i^p \) is the partial pressure of component \( i \) in the permeate. And due to the low total pressure in the upstream side and the organic/organic mixture, the activity coefficient of component \( i \) can be assumed to be unity, which was also confirmed by the simulation of DMC–methanol mixture with aspen plus using the Wilson equation. Therefore, the permeance \( (\Phi_i/l) \) of component \( i \) can be calculated as follows [25,26]:

\[
\Phi_i = \frac{J_i}{M_i(x_i^{\text{sat}} p_i^{\text{sat}} - p_i^p)}
\]

(8)

The ideal selectivity of the membrane \( \alpha_{\text{ideal,c}} \) is defined as follows:

\[
\alpha_{\text{ideal,c}} = \alpha_s \times \alpha_D
\]

(9)

### 3. Results and discussion

#### 3.1. The solubility and the diffusivity of DMC and methanol in membranes

In pervaporation, the transport of liquids through the membrane can be described using the solution-diffusion model, which includes three consecutive steps: adsorption, diffusion, and desorption. The desorption step is often considered as a fast step because of the low vacuum pressure at the downstream, which was also experimentally verified by Crowder et al. [27]. Thus, the effects of sorption and diffusion on the membrane-separation performance were investigated.

#### 3.1.1. The solubility of DMC and methanol in homogeneous membranes

Fig. 1 shows the typical sorption history of pure methanol and DMC uptakes in PDMS, 10 wt% SiO\(_2\)/PDMS, and 20 wt% SiO\(_2\)/PDMS homogeneous membranes. The observed equilibrium methanol and DMC uptakes in membranes increased with the increasing SiO\(_2\) content in PDMS. The methanol and DMC uptakes increased from 0.0148 to 0.0551 \( \text{gmethanol/gmembrane} \) and 0.163 to 0.200 \( \text{gDMC/gmembrane} \), respectively, when the SiO\(_2\) content in PDMS increased from 0 wt% to 20 wt%. DMC is more preferentially sorbed into the membranes than methanol. As also reported by Nijhuis [28], in all cases, the preferentially permeating organic molecule is also sorbed preferentially, and the determining step in the selective transport is the preferential uptake of the organic molecule [9].

Furthermore, with increasing SiO\(_2\) content in PDMS, the equilibrium methanol uptake increased approximately 2.7-fold, whereas the DMC uptake increased by 23 %, which resulted in a decreased sorption selectivity with the increasing silica content in membrane as shown in Table 1. To illustrate the phenomenon, the equilibrium uptakes of methanol and DMC first divided the SiO\(_2\) content to eliminate the effect of SiO\(_2\) on the equilibrium uptakes, and it is found that the equilibrium uptake of methanol in the PDMS polymer continued to increase; however, the equilibrium uptake of DMC in the PDMS polymer remained constant. This result occurs because the surface of SiO\(_2\) is covered by various silanol groups and siloxane bridges, which make them more compatible with methanol; thus, more methanol was sorbed into the membranes with increasing SiO\(_2\) content. However, DMC itself has no silanol groups. Thus, the increase in the SiO\(_2\) content has a small effect on its sorption. This result was similar with Lue et al. [21], where a 3-fold increase in water uptake was observed when the zeolite addition increased from 0 to 30 wt%, and they ascribed this phenomenon to the capillary condensation mechanism. The different increasing degrees of the equilibrium uptakes for methanol and DMC with increasing SiO\(_2\) content decreased the sorption selectivity as shown in Table 1.

#### 3.1.2. The diffusivity of DMC and methanol in membranes

Fig. 1 shows that the required time for methanol and DMC to attain their equilibrium uptakes decreased with increasing SiO\(_2\) content, which indicates that the diffusion of methanol and DMC in membranes increased. To quantitatively illustrate the diffusion change with the increasing SiO\(_2\) content, a half-time method was used to estimate the diffusion coefficient of pure solvents in membranes. First, the equilibrium solvent uptake vs time \( (s) \) was plotted. A regression curve was obtained based on the experimental data with \( R^2 \geq 98 \% \). According to this method, the methanol and DMC diffusion coefficients in PDMS membranes were estimated to be \( 5.07 \times 10^{-11} \) and \( 2.85 \times 10^{-11} \text{m}^2/\text{s} \), respectively. With the incorporation of 20 wt% SiO\(_2\) into PDMS, the corresponding diffusivities increased to \( 6.08 \times 10^{-11} \) and \( 6.98 \times 10^{-11} \text{m}^2/\text{s} \), respectively. The diffusion coefficient increased approximately 1.20-fold for methanol and 2.45-fold for DMC, which increased the diffusion selectivity as shown in Table 1. This is because when SiO\(_2\) was incorporated into PDMS, the hydrophilic surface of SiO\(_2\) (because of the silanol groups on its surface) made them incompatible with hydrophobic PDMS polymer, and the void-defect channels appeared at the interface between SiO\(_2\) and PDMS. The instrumental analysis using Micromeritics ASAP 2020 showed that the maximum pore volume for 20 wt% silica content is 0.000231 cm\(^3\)/g, whereas that for 10 wt% silica content and the pure PDMS membrane is 0.000119 cm\(^3\)/g and null, respectively. Higher pore volume results from the high pore size distribution [29,30]. As we know, the PV membrane is dense. Theoretically, there is no pore volume in the perfect PV membrane. Therefore, the increase in pore volume with the increasing silica content in the PV membrane might result from the void-defects at the interface between the PDMS polymer and the inorganic silica because of its incompatibility. With the increasing void-defects, the diffusion resistance of methanol and DMC would both decrease, leading to an increasing diffusion coefficient. However, the diffusion resistance of methanol is lower than that of DMC due to its smaller kinetic diameter [9], therefore the change of diffusion coefficient of methanol is less sensitive to the increasing void-defects, which makes the enhanced degree of diffusion coefficient for the smaller methanol molecule less, resulting in higher diffusion selectivity with increasing SiO\(_2\) content as shown in Table 1.

Table 1 also shows that the sorption selectivity and the diffusion selectivity have opposite trends with the increasing SiO\(_2\) content in PDMS, and the calculated ideal selectivity follows the same trend with the sorption selectivity, which indicates that the sorption step is the rate-limiting step in the pervaporation of the DMC–methanol mixture. As observed in Table 1, increasing the SiO\(_2\) content in PDMS decreases the selectivity. The pure PDMS composite membrane was used in the following experiments to
study the effect of the operating parameters on the separation performance.

3.2. Membrane thickness effects

In pervaporation, the permeate flux is inversely proportional to the membrane thickness, and the selectivity should be independent of the membrane thickness, assuming that the membrane is homogeneous if the membrane is perfect [31]. Therefore, the membrane thickness can theoretically be extremely thin to increase the flux, so that the membrane cost decreases. To obtain the thinnest membrane using our fabricating method, membranes with different thicknesses were fabricated and used to separate the DMC–methanol mixture as shown in Fig. 2. It is observed that when the membrane thickness decreased, the flux increased exponentially from approximately 0.6 kg/m² h at 160 µm to above 15 kg/m² h at approximately 3 µm, which is consistent with the solution-diffusion mechanism. However, the selectivity does significantly vary when the thickness is below 6 µm, where the selectivity decreased linearly from approximately 3.8 to 2.6 at approximately 3 µm. This difference was assumed to originate from the change in the structural property of the membrane. As in Jadav et al. [32], PDMS membranes with different thicknesses from 0.2 to 150 µm were characterized using small-angle neutron scattering, ATR-IR, X-ray diffraction, scanning electron microscopy and differential scanning calorimetry. The results showed that thinner membranes had relatively more crystalline domains, were less hydrophobic and had higher amounts of chain aggregates, which were responsible for the low selectivity but the high flux. Furthermore, the membranes with a thickness above 6 µm (as shown in Fig. 3(A and B) and (D and E)) are notably smooth, whereas Fig. 3(C) and (F) shows that the membrane appeared uneven and less smooth because the 3 µm PDMS membrane is not continuous. In the composite-membrane preparation, when the selective layer of the composite membrane is notably thin, more chain aggregates form, which is consistent with the non-continuous nature and larger structural defects [32], which leads to higher flux and lower selectivity. Thus, the 6-µm-thick composite membrane was used in the following experiments. The membrane with a thickness of 6 µm that was obtained by our group can offer a normalized flux of 0.4872 kg/m² h, which is three times higher than the value obtained by Li’s group (0.162 kg/m² h) [2].

3.3. Pervaporation experiment

In the industrial pervaporation of DMC from a methanol solution, the operating parameters such as the feed concentration and the feed temperature are important factors that affect the economic efficiency of the separation because these operating parameters affect the separation performance. These factors are also notably important for the selection of suitable membrane materials to pervaporate the DMC–methanol azeotropic mixture. Furthermore, the membrane stability and the operation durability are notably important for its industrial application. Therefore, the effects of the operating parameters on the membrane performance and membrane stability were examined.

3.3.1. Effect of feed concentration

Fig. 4(A) and (B) shows the effects of the feed DMC concentration on the DMC and methanol fluxes at different temperatures. When the feed DMC concentration increased, the DMC flux increased accordingly; however, the changing trend of the methanol flux was complicated. When the feed temperature was below 30 °C, the methanol flux decreased with increasing feed DMC concentration; when it was 40 °C, the methanol flux was approximately constant at the feed DMC concentration between 20 wt% and 60 wt%; when it was above 40 °C, there was a maximum methanol flux. This trend occurred because when the DMC–methanol mixture is pervaporated using the PDMS membrane, DMC is the main factor that affects the membrane properties such as membrane swelling (because its solubility parameter is close to that of the PDMS polymer). The smaller difference in solubility parameter of the organic and PDMS membrane leads to higher affinity [33,34] and results in more membrane swelling, as shown in Fig. 1, which consequentially makes the permeances of DMC higher as shown in Fig. 5. Furthermore, the increasing feed DMC concentration also enhanced the partial pressure difference between the upstream side and the downstream side according to Henry’s law:

\[ p_i = h \times c_i \]

(10)

Where \( p_i \) is the equilibrium partial pressure of component \( i \), \( h \) is the Henry constant, and \( c_i \) is the mole fraction of component \( i \) in the solution. To further understand the relationship between the partial pressure and the flux, using modified Eq. (7) to express the flux as follows:

\[ J_i = \frac{\Phi_i}{M_i} \times \frac{c_i}{c_{i,tot}} \times (p_i - p_t) \]

(11)

This equation explicitly shows the positive influence of the vapor pressure on flux. Higher temperature also leads to higher vapor pressure and drives the DMC permeation, which results in higher flux. Therefore, higher feed DMC concentration and temperature led to higher flux.

However, for methanol, the observed membrane swellings in the methanol solution and DMC solution are approximately 1.48% and 16.3%, respectively, which indicates that unlike DMC, methanol did not significantly affect the swelling degree of the membrane. The existence of DMC in the membrane can promote the methanol permeation because the polymer swelling, which is induced by the more permeable molecule DMC, “opens the meshes of the network” to allow the less permeable molecule methanol to transport through the membrane more easily [17]. Thus, the methanol flux expressed a complex changing trend with increasing feed DMC concentration and increasing temperature because besides the effects of the feed methanol concentration and temperature on its flux, membrane swelling could also affect the methanol flux. On the one hand, the methanol flux would increase with enhanced membrane swelling and increasing temperature; on the other hand, the methanol flux would decrease with decreasing feed methanol concentration. These contradictory effects led to complicated methanol fluxes, which indicated that in pervaporation, when the membrane swelling is large, the flux trend of exclusive penetrants would be greatly affected by the membrane swelling.
In order to make comparison of pervaporation data more clearly under different operating conditions, the effects of the feed DMC concentration on the permeances of DMC and methanol at different temperatures were plotted as shown in Fig. 5. It is shown in Fig. 5(A) that when the driving force contribution is removed, the permeances of DMC are feed concentration dependent and its permeances decrease with their increasing feed concentration. Adsorption is the rate-limited step as discussed above, and with the linearly increasing feed concentration, the adsorption of DMC on membrane will gradually approach saturation and thus the increase in DMC concentration in membrane will gradually slow down, leading to lower permeance with increasing feed concentration. Baker et al. [25] reported this similar result to be a crowding (saturation) effect of ethanol diffusion through the zeolite pores in their separation of ethanol/water solution using mixed-matrix membrane. As the permeance curves in Fig. 5(A) show, the permeances decrease as temperature increases. Diffusivity almost always increases with the increase in temperature, while adsorption usually decreases due to its exothermic process. Thus, higher temperature leads to lower adsorption in membrane and the permeance of DMC is lower. For methanol, same results can be obtained.

Fig. 6 shows the effect of the feed DMC concentration on the separation factor and the DMC concentration in permeate at different temperatures. Increasing the feed DMC concentration decreases the separation factor and the DMC concentration in permeate, which is often observed in pervaporation when the membrane permselectivity mainly originates from the solubility selectivity [11]. As shown in Fig. 1, membranes are more easily swollen in the DMC solution than in the methanol solution, which resulted in enlarged free volumes in the membrane polymer and higher permeation flux [16]. Methanol has a smaller molecular size [9] and higher saturated vapor pressure than DMC. Therefore, methanol molecules transport more easily through the membrane with larger driving force [2], which decreases the separation factor. Furthermore, in the adsorption process of the membrane to the penetrants, the dissolution is not a fast transient process because of the membrane resistance, the interactions between the penetrants
and the membrane, etc., which implies that the adsorbed amount of penetrants into the membrane cannot maintain the pace with the increase of the feed DMC concentration. When the solvent adsorption approaches saturation in the membrane polymer, the increasing rate of the solvent concentration that is dissolved in the membrane would gradually decrease [11]. As a result, the separation factor decreased with increasing feed DMC concentration.

### 3.3.2. Effect of feed temperature

Fig. 7 shows that at a given feed concentration, increasing temperature would increase the DMC and methanol fluxes. This phenomenon might occur because the driving force and the free volumes increased, and the membrane resistance decreased at higher temperature. The driving force in the pervaporation is the difference in the partial pressures between the two sides of the membrane. The downstream side of the membrane is always maintained at the vacuum stability. With increasing temperature, the saturated partial pressure of the penetrants increased accordingly, which increased the flux when it is calculated using Eq. (11). Furthermore, higher temperature promotes the movement of the membrane polymer, which enlarges the free volume, weakens the interaction between the permeate molecules and the membrane polymer, reduces the transfer resistance and facilitates their diffusion through the membrane [16,33].

Fig. 8 shows the temperature dependency of the DMC and methanol fluxes at different feed DMC concentrations, which was found to follow an Arrhenius equation:

\[
J = J_0 \exp\left(-\frac{E_a}{RT}\right) \tag{12}
\]

where \(J\) is the permeate flux, \(J_0\) is the permeate rate constant, \(R\) and \(T\) are the universal gas constant and temperature in Kelvin, respectively, \(E_a\) is the apparent activation energy, calculated from the slope of \(\ln J\) versus \(1/RT\) plot. Using this equation, the apparent activation energies of DMC and methanol were obtained as shown in Fig. 9. Methanol has larger apparent activation energy than
DMC, which indicates a more sensitive behavior toward temperature alteration. Therefore, the methanol flux increases faster than the DMC flux with increasing temperature, which decreases the separation factor as shown in Fig. 6. Furthermore, the apparent activation energy of DMC decreased when the feed DMC concentration increased, which implies that less energy is required for DMC to permeate through the membrane at higher feed DMC concentrations. As discussed in Section 3.3.1, a higher feed DMC concentration led to higher membrane swelling and higher free volume, which decreased the membrane resistance to the DMC permeation. As a result, the apparent activation energy of DMC decreased at higher feed DMC concentrations. However, for methanol, the highest apparent activation energy was obtained at 60 wt% feed DMC concentration. This result might prove that in the pervaporation of the DMC–methanol mixture, DMC is more permeable, and its solubility parameter is closer to that of the membrane polymer, which increases its influence on the membrane performance. Thus, in addition to its own feed concentration and temperature, the methanol flux is affected by many other factors such as the feed DMC concentration, the membrane swelling, and the temperature, which makes it complicated. The reasons for the change in the apparent activation energy of methanol are currently under investigation by our group.

3.3.3. Membrane stability

To make the PDMS composite membrane made by our lab available for industrial applications, the membrane stability and the operation durability are notably important [2]. To evaluate the stability of the homemade PDMS composite membrane, one PDMS composite membrane has been studied to separate the DMC–methanol mixture at different operating conditions for more than 3 months, which implies its high operation durability. Then, this membrane was used to separate the 28 wt% ± 2 wt% DMC–methanol mixture at 40 °C for 15 days. As shown in Fig. 10, the membrane does not show any degradation of the flux and the DMC concentration in permeate during the experimental time, which implies that the membrane performance was stable for the separation of the DMC/methanol mixture. The future long-term stable investigation of homemade PDMS composite membranes is under construction to observe the longest stable time.

4. Conclusions

A defect-free PDMS/PVDF composite membrane with a thickness of 6 μm was successfully fabricated to separate DMC from a
methanol solution. The efficient cross-linked structure of the PDMS polymer is the main factor to form thin PDMS composite membranes. The sorption selectivity is considered a rate-limiting step in the separation of DMC from the methanol solution. Higher temperature and higher feed DMC concentration resulted in higher membrane swelling, which would greatly improve the flux of the less permeable molecule methanol and decrease the separation factor. The membrane exhibited a separation factor of 3.95 and a normalized total flux of 0.4872 kg/m²h in the pervaporation of 28 wt% DMC–methanol mixture at 40°C. Moreover, the membrane also showed a long stability during the testing period of 15 days. Therefore, the developed PDMS membrane is a promising candidate for practical applications in DMC production.

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