Novel organic–inorganic pervaporation membrane with a superhydrophobic surface for the separation of ethanol from an aqueous solution

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In the pervaporation (PV) of organics from aqueous solutions, the adsorption step is usually the rate-limiting step, which affects membrane separation performance. To enhance the affinity of membrane surface to organics or to weaken the affinity to water in order to increase membrane separation performance, many methods have been developed to modify the characteristics of the membrane surface. In this work, a superhydrophobic surface was introduced to decrease the affinity of the membrane surface to water. A simple and facile casting method was used for the preparation of a pervaporation membrane with superhydrophobic surfaces using SiO2 and polydimethylsiloxane (PDMS) as membrane materials. The effect of pre-polymerization of PDMS at different temperatures was first investigated. Then, different membrane substrates were studied. The results indicated that a higher roughness of the membrane substrate surface leads to the easy formation of a superhydrophobic surface and that a pervaporation membrane with superhydrophobic surface was obtained, whose water static contact angle is 152 ± 0.6° and water sliding angle is 5°. Subsequently, the home-made pervaporation membrane was characterized for its ability to separate a 5 wt% ethanol aqueous solution under different conditions. The results indicated that the separation factor obtained using the membrane with a superhydrophobic surface was nearly five times higher than that obtained using a membrane without a superhydrophobic surface. Furthermore, when the separation was performed at different feed concentrations, the trade-off phenomenon in the PV process was observed to be overcome using the membrane with a superhydrophobic surface. Thus, the results of this work are helpful to gain insight into the control of surface wettability to enhance membrane separation performance in pervaporation process.

1. Introduction

Pervaporation (PV) has gained considerable attention as a very useful energy-saving and cost-effective liquid separation technique [1–2]. Based on the solution–diffusion model describing PV, the surface structure and properties of the membrane play an important role in the membrane separation because penetrants must first adsorb onto the surface of the membrane before separation can occur. Thus, modification of the surface of the membrane to enhance the wettability for the preferred penetrants is often desirable [1]. However, some surface modifications were complicated and time-consuming to implement [2] because additional processing steps are required after membrane fabrication, which increases the manufacturing costs and complicates the processing [1]. Furthermore, recent surface modification techniques often use the alteration of the chemical composition of the membrane surface to change their surface properties, which has already been criticized for its inability to retain the modified properties with time [3].

In the preparation of a superhydrophobic surface, in addition to the alteration of the chemical composition of the membrane surface to change the surface properties, the change of the membrane structure, especially the roughness of the membrane surface, also affects the wettability of the surface because the wettability of a surface depends on both the surface chemistry and on the surface roughness [4]. Zhang et al. [5] reported that the contact angle on smooth POTS modified silicon surface is only 110°, while the contact angle on the rough surface modified with POTS can be as high as 157.1°. Thus, some authors have already focused on the
alteration of the surface roughness to enhance surface hydrophilic/hydrophobic property to increase the membrane separation performance [6–7]. For example, Liao et al. [7] fabricated an integrally modified membrane (I-PVDF) with a superhydrophobic surface for direct contact membrane distillation; the results indicated that a high and stable water flux of 31.6 L/m² h can be obtained, which is superior to all other PVDF flat-sheet membranes tested under the same or similar conditions.

Superhydrophobic surfaces are forms of highly hydrophobic surfaces with hierarchical roughness, whose water static contact angle is greater than 150° and water sliding angle less than 10° [8–9]. Therefore, superhydrophobic surfaces will make water much harder to adsorb onto the membrane surface [8], thereby resulting in a higher separation factor when it is used in the PV process due to its separation mechanism. Many very clever methods to produce superhydrophobic surfaces have been reported [9]. Although these methods are good for the preparation of superhydrophobic surfaces, most of the reported methods utilize harsh physical treatments and costly materials and exhibit poor ability to scale-up in practice [10]. For example, Chen et al. [11] developed a simple spin-coating method to successfully fabricate SiO₂/PS and SiO₂/PVC superhydrophobic composite coatings without any special equipment or rigorous conditions. However, the spin-coating method is still very hard process to scale-up. Thus, simple, inexpensive, and feasible methods are required for industrial applications of these types of superhydrophobic surfaces. The casting method has been proven to be a simple, inexpensive, and feasible method. In addition, casting can also be readily scaled-up in practice. As Latthe et al. [12] described in their review, the casting method is simple and does not require special equipment or rigorous conditions when it is compared with other sophisticated methods. Therefore, the casting method is used here to fabricate a pervaporation membrane with a superhydrophobic surface.

According to previous research, superhydrophobic surfaces should have low surface energy and a hierarchical surface roughness. Therefore, to enhance the superhydrophobic properties of the surface of a PV membrane, inorganic fillers of nano-silica were used as the roughness-enhanced material because nano-silica are suitable to form hierarchical roughness [13]. PDMS (polydimethylsiloxane) was chosen as the low surface energy material to reduce the membrane surface energy. The pieces of materials used are eco-friendly and cheap and thus will be beneficial for the practical application of superhydrophobic surfaces in the PV membrane industry.

In previous research, membranes with superhydrophobic surfaces have been widely studied. However, to the best of our knowledge; although superhydrophobic surfaces have already been used in applications such as membrane distillation and microfiltration, there have been little articles about the fabrication of superhydrophobic PV membrane surfaces and the study of the effect of superhydrophobic surfaces on the PV separation performance. Because a superhydrophobic surface will reduce the chemical affinity of water to the surface [8], high selectivity is thus expected. As a result, in this work, a dense PV membrane with a superhydrophobic surface was fabricated and the effect of both the pre-polymerization of PDMS and the substrate characteristics on the membrane superhydrophobic surface was studied. After the fabrication of a membrane with a superhydrophobic surface, the nanocomposite membrane was characterized using SEM imaging and contact angle analysis. In the pervaporation study, the simultaneous enhancement of both the separation factor and the flux is a significant challenge due to the trade-off phenomenon in pervaporation. In addition, many efforts are ongoing to overcome the trade-off phenomenon by improving the membrane performance using different methods, such as elevating the hydrophilicity of the membrane [14]. In this work, the trade-off phenomenon was investigated in the separation of an ethanol aqueous solution at different feed concentrations and different feed flow rates. This work provides an insight into the control of the surface wettability to enhance the membrane separation performance in the PV process.

2. Experiment

2.1. Materials

Polydimethylsiloxane (PDMS) was purchased from GE Toshiba Silicones Co., Ltd., Japan. Fumed silica with a particle diameter of 10–20 nm was purchased from Haiyi Scientific & Trading Co., Ltd., China. Porous microfiltration (MF) substrates of cellulose acetate (CA, 0.22 μm), polyethersulfone (PES, 0.22 μm), and polyvinylidene fluoride (PVDF, 0.22 μm) were purchased from SePro Corporation, USA, and Solvay Corporation, USA. Heptane and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the chemical reagents were used as received without further purification.

2.2. Fabrication of PV membranes with a superhydrophobic surface

The composite membranes with superhydrophobic surfaces were prepared as follows: PDMS polymer (RTV-615, part-A:part-B = 10:1) was dissolved in a certain volume of heptane to yield a 20 wt% polymer solution. Certain amounts (10–20 wt%) of SiO₂ were added into the PDMS polymer solution to form the membrane solution. The solution was stirred for approximately 5–6 h until a homogeneous suspension was obtained at 50 °C before casting the solution onto a substrate using a casting machine. The as-cast membrane was left overnight at room temperature, and then transferred over to a vacuum oven at 80 °C for 5 h for complete curing, as shown in Fig. 1. A composite membrane with a certain hydrophobic surface was obtained.

2.3. Characterization

The water contact angle and the sliding angle were measured on a drop shape analysis system (KROSS DSA100, Germany) using a 5-μL water droplet at ambient conditions.

The surface morphology of the composite membranes were coated with a conductive layer of sputtered gold to make it conductive to enable the characterization using a field-emission scanning electron microscopy (FE-SEM, Hitachi-4800, Japan) operated at 5 kV and 10 μA.

The viscosities of the polymer coating solution were determined by using a Brookfield viscometer (DV-II+P ro, Brookfield Engineering Laboratories, USA). The determination of viscosity was performed at 25 °C.

![Fig. 1. Schematic representation of the preparation of a membrane with a superhydrophobic surface using the casting method.](image-url)
The topographies of the substrates were measured using AFM (Autoprobe CP-Research, Bruker, USA) under ambient conditions at room temperature. The scan speed was 1.00 Hz. The images underwent second-order flattening using ProScan (version 2.1) software.

2.4. The solubility and diffusivity of ethanol and water in membranes

The solubility and diffusivity of ethanol and water in the membranes were determined using gravimetric method described elsewhere [15]. A known weight membrane strip with known thickness (l) were immersed in a pure ethanol and water solution separately at 20 °C for a given time (t). The membrane was then blotted quickly with tissue paper to remove the membrane surface solution before it was weighted by a digital analytical balance. The equilibrium solvent uptake (M_{s,∞}, in g of solvent per g of dry membrane) was determined until no further weight increase was observed for the membrane. And the ideal sorption selectivity (\(\alpha_s\)) was calculated as:

\[
\alpha_s = \frac{M_{\text{ethanol,}}}{M_{\text{water,}}}
\]  

where \(M_{\text{ethanol,}}\) and \(M_{\text{water,}}\) are the equilibrium solvent uptakes for the pure ethanol and water, respectively.

In order to calculate the diffusion selectivity, the diffusion coefficient was first estimated by a half-time method as follows [16]:

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

where \(t_{0.5}\) is the time at which \(M/M_s = 0.5\). And the ideal diffusion selectivity (\(\alpha_d\)) was calculated as follows:

\[
\alpha_d = \frac{D_{\text{ethanol}}}{D_{\text{water}}}
\]  

where \(D_{\text{ethanol}}\) and \(D_{\text{water}}\) are the pure ethanol and water diffusion coefficients, respectively.

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

\[
\alpha_{\text{ideal}} = \alpha_d \times \alpha_s
\]  

2.5. Pervaporation experiment

The pervaporation experiments were performed using a homemade apparatus, which was described in our previous work [17]. A flat membrane with an effective area of 7.065 cm² was sealed in a circular plate and frame pervaporation cell. The feed solution was maintained at the desired temperature using a water bath and a peristaltic pump for recirculation of the liquid mixture. During the experiments, the upstream of the membrane was maintained at atmospheric pressure and the downstream pressure was kept at 280 Pa, which was monitored using a Reborn ZDZ-52 Manometer (Reborn Corporation, China).

The initial experiment was normally conducted for 1 h to achieve steady state. When operating conditions were changed, half an hour was required to again reach steady state. After achieving steady state, samples of both the retentate and the permeate were collected for analysis. The permeate flux (J) was obtained by weighing the permeate product collected in a cold trap (W) for a given time (t), with its compositions determined using a Gas Chromatography (GC–2014, Shimadzu, Japan). The PV performance of the membrane was evaluated in terms of the permeate flux and selectivity. The permeate flux is calculated as:

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

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

The selectivity in this work was calculated and expressed by the separation factor, \(\alpha\), which is defined as follows:

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

where Y and X are the weight fraction of solutes in the permeate and feed, respectively. The sub-index A refers to ethanol and B refers to water.

3. Results and discussion

3.1. Membrane preparation

3.1.1. Effect of pre-polymerization of PDMS

In the fabrication of the organic–inorganic composite membrane, precipitation of inorganic fillers may occur during the preparation if the viscosity of the membrane solution is relatively low because of the insolubility of the inorganic fillers in any organic solvent and their higher density than most polymers, which results in the formation of an inhomogeneous top layer, subsequently leading to a decrease in the selectivity [18]. To prevent the precipitation of silica particles in the coating suspension, pre-polymerization was utilized to assist the dispersion of the particles, which is a technique often used to enhance the pre-polymerization of PDMS polymer in membrane solution (suspension). Jia et al. [19] and Moermans et al. [20] used pre-polymerization of the PDMS polymer network with all components present at an elevated temperature (70 °C). During this process, a partial polymerization occurred, which led to an increased viscosity of the suspension and an improved stabilization of the suspension. Furthermore, by using an elevated temperature to pre-polymerize the PDMS polymer, the time to achieve a suitable viscosity of the membrane solution is reduced. As shown in Fig. 2, when the temperature is higher, the time required to obtain a suitable viscosity is reduced, thereby reducing the cost. However, to ensure that the fillers can uniformly disperse into the polymer, the fillers require a sufficient amount of time to achieve a uniform dispersion. To balance these two opposing factors, a trial and error method was used to select a suitable temperature and time. From the results, the temperature of 50 °C was found to be suitable because at this temperature, the time for the membrane solution to achieve a suitable viscosity (13.19 mPa s) is approximately 5 h, which is sufficient for the fillers to uniformly disperse into the polymer, and the membrane solution can stabilize for a relative longer time for casting. In contrast

![Fig. 2. The relationship between the temperature and the time required to achieve a suitable viscosity of the membrane solution.](image-url)
with the viscosity obtained at the temperature of 60 °C, the membrane solution can only stabilize for less than 30 s, which is too fast to permit the casting of the membrane solution to the substrate. In addition, it is also very easy for the membrane solution to become more viscous at this high temperature. As a result, a temperature of 50 °C was chosen in the following experiments.

### 3.1.2. Membrane substrate effects

To study the effect of substrates on the superhydrophobic surface and avoid the effect of the membrane solution, the substrates were coated using an identical membrane solution containing 20 wt% SiO\(_2\) in PDMS polymer. Fig. 3 shows the static contact angle on different composite membranes, which indicates that the static contact angle on the composite membrane using the PVDF substrate is highest, followed by that using the PES substrate, and finally the CA substrate has the lowest static contact angle. In the composite membrane, the selective layer coated on a substrate forms a composite membrane. The properties of the substrate that can affect the composite membrane separation performance have previously been reported [21]. In this work, the factor that most affects the hydrophobic properties of the composite membrane is the roughness parameter, with the root mean square (RMS) of PVDF being highest at approximately 370.2 nm (as obtained by AFM), followed by that of PES, with a value of 168.6 nm, and finally that of CA, with a value of 152.2 nm, which is shown in Fig. 4. It is proposed that the roughness of the substrate surface favors the formation of a selective layer with a desired roughness when the selective layer is cast onto the rough substrate because when the substrate surface is rough, the selective layer can use the roughness of the substrate to form a suitable roughness without primarily using the agglomeration of silica. In contrast, when the substrate surface is very smooth, such as for a glass surface, which has already been used for the formation of a superhydrophobic surface, the agglomeration of silica is the primary method to form the roughness because of the requirements of the micro/nano-hierarchical structure. The higher the concentration of the aggregates is, the more difficult it is for the polymer to fill all the spaces between the particles in the aggregate, which leads to more interstitial cavities in the membrane, thereby leading to low selectivity [22]. With the help of the roughness of the substrate, the concentration of agglomeration is low, thereby enabling the polymer to fill the spaces between the particles in the aggregate. Therefore, using the above-described approach, a dense pervaporation membrane with a superhydrophobic surface was obtained.

### 3.2. Membrane characterization

Fig. 5 shows images of a water droplet static contact angle (A), water sliding angles (B) and ethanol droplet static contact angle (C). As shown in Fig. 5(A), a water droplet could sit on the composite membrane surface with a water static contact angle of 152 ± 0.6 °. A 5-μL water droplet can easily roll off the surface when the surface was tilted by only 5° (Fig. 5(B)), indicating a Cassie-Baxter non-wetting state. In contrast with the water contact angle, ethanol easily spreads out on the surface, with its contact angle being less than 8° (Fig. 5(C)), exhibiting highly oleophilic properties. Scanning electron microscope (SEM) images of the composite
membrane reveal that hierarchical roughness surface was obtained, as shown in Fig. 6(A). The enhanced surface roughness could amplify the wettability of materials, making a hydrophobic surface more hydrophobic and an hydrophilic surface more hydrophilic [9]. Compared to Fig. 6(A), Fig. 6(B) shows that only nanoscale structure is present on the surface; such nanostructure cannot exhibit superhydrophobicity [23] Because a water droplet can penetrate into the nano-scale surface structure, leading to an opposite effect on the droplet adhesion, thereby making the surface less hydrophobic and resulting in a high contact angle hysteresis [23].

To further demonstrate the low adhesion of water on the surface, a series of snapshots, shown in Fig. 7, that exhibit the placement of a water droplet on a superhydrophobic surface were obtained using the contact angle instrument. It can be seen that when the water droplet moves from the air (Fig. 7(A)) to the surface (Fig. 7(B)), the water droplet does not spread out. In addition, with further downward movement of the needle, the exerted force on the water surface caused the shape of the water droplet to become deformed into an ellipse instead of spreading out onto the surface, due to its superhydrophobic characteristics, as shown in Fig. 7(C). When additional force is applied onto the water droplet, the water droplet readily slides to the side, as shown in Fig. 7(D), demonstrating the low contact angle hysteresis of the surface. When the needle is retracted slowly, the deformed and displaced water droplet can reform its water shape until finally the water droplet detaches completely from the surface without wetting the surface, as shown in Fig. 7(E) and (F). This phenomenon clearly illustrates the poor adsorption of water onto the superhydrophobic surface. For PV application, this is of utmost importance in improving the PV separation performance, considering the solution–diffusion mechanism.

Fig. 8 shows the effect of the water sliding angle on the separation factor. To study the effect of the water sliding angle on the membrane performance and to avoid the effect of the water static contact angle, the water static contact angle was controlled in the range of 145–152° and different water sliding angles were studied to investigate their effects on the separation performance. The water sliding angle is a criterion for evaluating the surface hysteresis, which usually arises from the contact line pinning due to the surface roughness and heterogeneity [24]. This approach enables the differentiation between strong adhesion and weak adhesion of a liquid at a solid surface [25]. Although the water static contact angle can exceed 142° due to the surface roughness, an insufficient roughness caused the system to be in the Wenzel state or in a mixed wetting situation and thus water can still penetrate into the cavities, resulting in an elongated (continuous) three-phase contact line. Thus, the adhesion of liquid at the solid surface is strong, which finally affects the membrane separation performance. As shown in Fig. 8, with a decrease in the water sliding angle, the separation factor increases. This behavior is the result, when the solution–diffusion model is considered, of the strong adhesion of water at membrane surface, which will favor the adsorption of water onto the membrane surface, resulting in a larger volume of water to transport through the membrane, leading to low selectivity. When water sliding angle is low, adhesion...
of water and its corresponding affinity with the membrane surface is low [8], resulting in less water adsorbed onto the membrane and thus transporting through it, resulting in enhanced selectivity. Thus, it is shown in Fig. 8 that the separation factor increased accordingly with the decrease in the water sliding angle.

Furthermore, Fig. 8 also shows that the separation factor is low when compared to the pure PDMS, which is usually from 4.4 to 10.8 at different concentrations and temperatures. This behavior is believed to be caused by the addition of silica into the PDMS, which induced non-selective defects (voids large enough to permit Knudsen flow) that are selective to smaller molecules [26]. As shown in Table 2, although the permeate solubility of ethanol and water in SiO2/PDMS membrane would increase with the increasing incorporated content of SiO2 and both diffusivity selectivities of ethanol and water increased with the SiO2 incorporation, the solubility selectivity decreased, leading to lower separation factor. This suggested that the solubility is the rate-limiting step in the separation. This phenomenon involving decreased selectivity of membrane over ethanol due to the addition of fumed silica was previously reported [27]. However, the separation factor obtained using a superhydrophobic surface (high static contact angle and low sliding angle) still increased nearly five times compared to the membrane with the high static contact angle and high sliding angle. This behavior is also illustrated in the observation that the water sliding angle is more important in the determination of the membrane separation performance. Furthermore, in future articles, porous particles, such as silicalite-1 or MOF fillers, which can enhance the adsorption of organics in the fillers, will be used to enhance the separation factor of the hybrid membrane.

3.3. Separation performance of a PV membrane with a superhydrophobic surface

The separation performance of a membrane is affected by operating parameters. To fully evaluate the separation performance of a PV membrane with a superhydrophobic surface at different operating parameters, the effects of operating parameters (e.g., feed concentration and temperature) on the separation performance were studied in the separation of an ethanol–water mixture.

### 3.3.1. Effect of temperature

Fig. 9(A) shows the effect of temperature on the fluxes and the separation factor in the separation of an ethanol–water solution. It can be seen that increasing the temperature leads to an increase of the ethanol and water fluxes through the membrane. This increase is because the driving force of the PV process is the difference of partial pressures between the two sides of the membrane; increasing the feed temperature enhances the difference of the partial pressures, thereby increasing the driving force for ethanol and water permeation. Furthermore, a higher temperature promotes the motion of polymer molecules and weakens the interaction between the permeate molecules and polymer molecules, thus reducing the transfer resistance of permeate molecules through the membrane and facilitating their diffusion through the membrane. Fig. 9(A) also shows that the separation factor increases with increasing temperature, which results from the higher apparent activation energy of ethanol than that of water. As shown in Fig. 9(B), the temperature dependence of the permeate flux follows an Arrhenius equation, where the apparent activation energy can be calculated from the slope of the linear fit of the experimental data. A higher value of the apparent activation energy of the permeate molecules implies an increased sensitivity to temperature. The apparent activation energy of ethanol is calculated to be 34.28 kJ/mol, which is higher than that of water at 23.13 kJ/mol. Thus, increasing the temperature leads to a higher separation factor.

As discussed above, temperature can affect the membrane permeability and the driving force in pervaporation. The effect of temperature on the membrane permeability can be best evaluated by the permeation activation energy ($E_p$), which is the energy required for a liquid species to transport across the membrane. The heat of evaporation ($\Delta H_v$) can be used to roughly measure the temperature dependence of the driving force. Therefore, the apparent activation energy ($E_a$) can be expressed as the permeation activation energy: 

$$E_a = \frac{\Delta H_v}{\gamma}$$

### Table 1
Solubility parameters (Mpa$^{1/2}$) of ethanol, water, and PDMS[29].

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\delta_3$</th>
<th>$\delta_2$</th>
<th>$\delta_1$</th>
<th>$\delta_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>15.8</td>
<td>8.8</td>
<td>19.4</td>
<td>24.1$^*$</td>
</tr>
<tr>
<td>Water</td>
<td>15.5</td>
<td>16</td>
<td>42.4</td>
<td>17.1$^b$</td>
</tr>
<tr>
<td>PDMS</td>
<td>15.9</td>
<td>0.1</td>
<td>4.7</td>
<td></td>
</tr>
</tbody>
</table>

$^*$ $\delta_0$, Difference of the solubility parameters of ethanol and water ($\delta^*$) and of ethanol and PDMS ($\delta^b$).

### Table 2
Effects of SiO2 content on saturation sorption uptake, sorption ideal selectivity and diffusion ideal selectivity, and ideal selectivity of the membrane for pure ethanol and water at 20°C.

<table>
<thead>
<tr>
<th>SiO2 content (wt%)</th>
<th>$\gamma_{\text{ethanol}}^{\text{sat}}$</th>
<th>$\gamma_{\text{water}}^{\text{sat}}$</th>
<th>$\gamma_{\text{ethanol}}^{\text{membrane}}$</th>
<th>$\gamma_{\text{water}}^{\text{membrane}}$</th>
<th>$\gamma_{\text{ethanol}}$</th>
<th>$\gamma_{\text{water}}$</th>
<th>$\gamma_{\text{ethanol}}^{\text{ideal}}$</th>
<th>$\gamma_{\text{water}}^{\text{ideal}}$</th>
<th>$\gamma_{\text{ethanol}}^{\text{ideal}}$</th>
<th>$\gamma_{\text{water}}^{\text{ideal}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.046</td>
<td>0.0015</td>
<td>30.7</td>
<td>0.41</td>
<td>12.6</td>
<td>4.7</td>
<td>30.7</td>
<td>0.41</td>
<td>12.6</td>
<td>4.7</td>
</tr>
<tr>
<td>10</td>
<td>0.063</td>
<td>0.0052</td>
<td>12.1</td>
<td>0.75</td>
<td>9.08</td>
<td>1.9</td>
<td>12.1</td>
<td>0.75</td>
<td>9.08</td>
<td>1.9</td>
</tr>
<tr>
<td>20</td>
<td>0.087</td>
<td>0.014</td>
<td>6.21</td>
<td>0.91</td>
<td>5.65</td>
<td>0.5</td>
<td>6.21</td>
<td>0.91</td>
<td>5.65</td>
<td>0.5</td>
</tr>
</tbody>
</table>
energy ($E_p$) plus the heat of evaporation ($\Delta H_e$), $E_p$ can thus be obtained by subtracting the heat of evaporation from the apparent activation energy.

The separation mechanism of pervaporation is described by a solution–diffusion model, which includes three consecutive steps: dissolution, diffusion and desorption. The permeation activation energy ($E_p$) can also be expressed as the sum of the energies of these three steps. The desorption step is generally regarded as a fast step, due to the very low pressure applied in the permeate side, and the membrane permeability is mainly determined by the solubility and diffusivity of the penetrants in the membrane. To determine which step is the rate-limiting step, the activation energies of these two steps were compared, where the activation energy of diffusion for the compounds diffusing through the membrane is represented by $E_d$ and the enthalpy of dissolution for the compounds to be dissolved into membrane is $\Delta H_d$. $E_d$ is generally positive, while $\Delta H_d$ is usually negative, due to the exothermic sorption process. Consequently, if the dissolution step is the rate-limiting step, then $|\Delta H_d| > |E_d|$, and $E_p$ will be negative; if the diffusion step is the rate-limiting step, then $|\Delta H_d| < |E_d|$, and $E_p$ will be positive. The heats of evaporation ($\Delta H_e$) of ethanol and water are 41.42 kJ/mol and 42.78 kJ/mol, respectively. Compared with the apparent activation energy, the value found for $E_p$ for ethanol and water in pervaporation was negative, which indicated that the dissolution step is the rate-limiting step. This dissolution limitation also explains why ethanol can permeate through the hydrophobic membrane preferentially over water and become enriched in the permeate, despite of the larger molecular size of ethanol compared to water.

### 3.3.2. Effect of feed concentration

Fig. 10 shows the effect of feed concentration on the flux and separation factor of the membrane at 40 °C. It is shown that as the feed ethanol concentration increases from approximately 1.1 wt% to 5.6 wt%, the ethanol flux increases and water flux remains constant, resulting in an increasing separation factor from 4.7 to 5.9 and a higher total flux, which is in contrast to the trade-off phenomenon frequently observed between the flux and the separation factor in pervaporation experiments [28]. This behavior is because in pervaporation experiments, many factors, such as the interaction between the penetrants and the membrane, contribute to the separation characteristics of a specific membrane [29]. With the increasing surface hydrophobicity of the membrane, the sorption of the membrane surface to ethanol will be enhanced and the sorption to water reduced. In addition, ethanol did not reach its saturated adsorption level at the superhydrophobic surface of the membrane, as usually occurs for a membrane without a superhydrophobic surface in this range of feed ethanol concentrations [29]. In hydrophobic pervaporation, sorption is both the first step and the rate-limiting step, which determines the separation performance of membrane, as discussed above. With the increase in the feed ethanol concentration, ethanol has a higher chance to interact with the membrane surface, thus enabling it to permeate through the membrane. Furthermore, an increase in the feed ethanol concentration normally results in an increasing activity and partial pressure, which will enhance the driving force for the permeation of ethanol and consequently lead to a higher flux. As for the permeation of water, its constant flux may result from the compromise between the diminished feed water concentration that leads to a lower water flux and the coupling phenomena between ethanol and water that leads to a higher water flux. Therefore, the ethanol flux increases and the water flux remains constant in the range of the experimental conditions, leading to a higher separation factor and thus a higher feed ethanol concentration. As a result, the membrane with a superhydrophobic surface can overcome the trade-off phenomenon in the PV process. This result is similar to the results obtained by Kariduraganavar et al. [14,30]. They reported that with the enhancement of the hydrophilicity in the separation of water–isopropanol mixtures, the trade-off phenomenon was overcome due to the increasing selective adsorption.

### 3.3.3. Effect of the feed flow rate

At a constant feed flow rate, the rate-limiting step occurs at the step of adsorption in the hydrophobic pervaporation, as discussed above. In this section, different feed flow rates were considered to investigate their roles in the hydrophobic pervaporation. Fig. 11 shows the effect of the feed flow rate on the flux and the separation factor of the membrane with a feed concentration of 4.8 wt% at 40 °C. It is shown that increasing the feed flow rate produces a higher flux and a higher separation factor. To understand what renders this separation performance, one may look into the solution–diffusion mechanism in pervaporation and the system differences in terms of the penetrant-penetrant and penetrants-membrane interactions. According to the solution–diffusion mechanism, ethanol must diffuse first from the bulk solution to the upstream side of the membrane before adsorption and diffusion through membrane can occur. Yang et al. [15] reported the diffusivity coefficient in PDMS to be approximately $0.88 \times 10^{-10}$–$4.5 \times 10^{-10}$ m$^2$/s and $1.3 \times 10^{-9}$–$2.0 \times 10^{-9}$ m$^2$/s for ethanol and water, respectively. The ethanol diffusivity in water is in the range of $0.84 \times 10^{-9}$–$1.3 \times 10^{-9}$ m$^2$/s. However, for
ethanol aqueous solution, the faster water molecules can force ethanol molecules to diffuse faster, even moving with the approximate diffusion rate of water in PDMS, which is higher than the diffusivity of ethanol in water. Ortiz et al. [31] also reported that the resistance of the membrane can be neglected when using a thin PDMS membrane to recover organic compounds from its aqueous solution. Furthermore, as shown in Table 1, the solubility parameter difference between ethanol and PDMS is less than that between ethanol and water, indicating that ethanol is apt to preferentially adsorb onto the membrane surface from its aqueous solution when the ethanol–water solution contacts the membrane surface. Once ethanol is dissolved onto the membrane surface, it readily diffuses and transports through membrane. This behavior indicates that the adsorption and diffusion of ethanol through the membrane are faster than its transport from the bulk solution to the upstream side of the membrane; as a result, the feed ethanol concentration gradient layer adjacent to the surface of membrane becomes established with the running of the experiments. When the feed flow rate increases, the ethanol concentration gradient layer becomes thinner and more ethanol can absorb onto the membrane, leading to a higher permeate flux. With more ethanol adsorbed onto the membrane surface, the hydrophobic characteristics of the membrane surface decreases, resulting in a higher water flux. However, the water flux enhancement depends on the amount of ethanol adsorbed due to the superhydrophilic surface, and the enhanced degree of water flux is less than that of ethanol, leading to a higher separation factor. This behavior indicates that the diffusion of ethanol from the bulk solution to the upstream side of the membrane has a notable effect on the separation characteristics in these experimental conditions, due to the superhydrophobic membrane surface.

4. Conclusions

In this study, a pervaporation membrane with a superhydrophobic surface has been prepared using a simple and facile casting method. The effects of pre-polymerization of PDMS at different temperatures and times were studied. The results indicated that 50 °C and 5–6 h was a good temperature and time, respectively, for the dispersion of SiO2 in the PDMS solution. The different substrates were then investigated to demonstrate that the relatively high surface roughness results in a pervaporation membrane with a superhydrophobic surface; when the water static contact angle was controlled to be in the range of 145–152°, the effect of the water sliding angle on the separation performance was investigated. The results indicated that a lower sliding angle leads to a higher separation factor. Investigations of the membrane separation performance under different operating conditions were conducted, and the results indicated that the trade-off phenomenon in the PV process was overcome in the separation of the ethanol–water solution using the pervaporation membrane with a superhydrophobic surface at different feed ethanol concentrations, and when the feed flow rate increased, the membrane separation performance also increased. The results demonstrated that a pervaporation membrane with a superhydrophobic surface is a promising approach to improve the pervaporation membrane performance. In addition, the proposed simple and facile casting method to fabricate the membrane is also a good method to scale up to industrially fabricate pervaporation membranes with a superhydrophobic surface.

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