Preparation and characterization of PVA thin-film composite membrane for pervaporation dehydration of ethanol solution

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Abstract: These days, ethanol fuel has been widely consumed worldwide to replace gasoline due to its possible environmental and long-term economic advantages. In detail, the ethanol fuel (purity ≥ 99.5 wt%) has been produced by traditional separation processes such as azeotropic distillation or molecular sieve adsorption, which excessively employs energy and capital cost. The pervaporation has already been considered as an effective alternative to conventional methods because of its high separation efficiency and low power consumption. Pervaporation separation of ethanol/water solution using hydrophilic membranes has been extensively studied owing to their superior perm-selectivity. In this present work, the polyvinyl alcohol thin-film composite membrane is prepared by casting a thin crosslinked polyvinyl alcohol (PVA) film on the polyacrylonitrile (PAN) porous substrate. The effect of PVA concentration on the pervaporation performance of the fabricated membrane is studied. The physicochemical properties of the prepared membrane are characterized using FTIR, SEM images, and contact angle measurements. The separation performance in terms of permeation flux and selectivity is simultaneously evaluated through a pervaporation dehydration of ethanol/water mixture of 80/20 wt.% at 60 °C. The results show that the increase in PVA concentration leads to the decline in the hydrophilicity and the growth of the thickness and swelling degree of the membrane. Therefore, the selectivity of the membrane is found to improve significantly, while the permeation flux decreased with the PVA concentration ranging from 2.5 to 15 wt.%. Based on the results, the PVA membrane prepared from the 10 wt.% concentration is likely to provide high separation performance.

1. Introduction
Ethanol considered as one of the important solvents, has been widely used in many industrial processes, such as production of chemicals, foods, pharmaceuticals as well as blending gasoline. Especially, the need of ethanol with a high purity (≥ 99.5 wt.%) for making ethanol fuel has been increasing in recent years due to its environmental advantage, economic benefit, and the depletion of fossil fuel [1]. The ethanol fuel is produced from renewable feedstocks, namely cassava, corn, grain sorghum and sugarcane, through a fermentation, distillation, and dehydration process. In this process, the dehydration is extremely essential for producing ethanol fuel. The separation of water from an ethanol/water mixture is a major challenge because it is an azeotrope at 95.6 wt.% ethanol [2]. Thereby, the conventional azeotropic distillation or molecular sieve adsorption, which employ excessive energy and capital cost is becoming unfeasible for purifying ethanol.

Pervaporation (PV) has emerged as an efficient membrane process to separate heat sensitive, closing boiling and azeotropic mixtures in recent years due to its low energy consumption, benign operation conditions, no emission to the environment, and no involvement of entrainers in the feed solutions [3]. Hydrophilic membranes are intensively applied to address the pervaporation dehydration of the ethanol solution. A variety of hydrophilic polymers have been studied as membrane materials such as polyacrylonitrile (PAN), chitosan, sodium alginate, polyamide, and polyvinyl alcohol (PVA). Among the polymers, the PVA has been attracting great interest from researchers because of its excellent film forming, high hydrophilicity, good physical, chemical stability, low cost, and commercial availability [1-3]. However, the PVA membrane exhibits poor stability in aqueous solutions because the high affinity for water of the PVA causes the swelling phenomenon of the relative membrane, which detrimentally affects their selectivity. For this reason, the PVA membranes should be modified for forming more durable membranes applied in pervaporation dehydration of ethanol [1-3]. There are several methods to crosslink the PVA such as heat treatment, irradiation, and reaction with multifunctional compounds. Among them, the crosslinking by chemical reagents is a preferential adoption since a capability to tailor the morphology and the physicochemical properties of the PVA matrix can impact the separation performance of the membrane. The mechanical, swelling properties, morphology, and pervaporation performance of the PVA membrane are dependent on types of crosslinkers, crosslinking degree, PVA concentration and crosslinked conditions [1-3].

The present work focuses on the preparation of PVA thin-film composite membrane for dehydration of ethanol solution. For this, a thin PVA film in-situ crosslinked by glutaraldehyde (GA) is cast on the surface of a PAN porous substrate. The GA is used as the crosslinker in this study because it can rapidly react with hydroxyl groups on PVA at the ambient or medium temperature to obtain a tightly crosslinked network in the PVA matrix. Furthermore, the PAN can contribute to a prevention of swelling phenomenon in the PVA selective layer at the interface so that a high permeation flux and good selectivity of the relative membrane could be achieved. In this study, the effect of PVA concentration on the physicochemical properties and separation performance of the membrane are investigated.

2. Materials and methods
2.1. Membrane preparation
A PVA (Mw 146-186 kDa, 99%, Sigma) solution with a fixed concentration is prepared by dissolving the PVA in deionized (DI) water at 90 °C under agitation for 6 h. Next, the PVA solutions are cooled to room temperature and glutaraldehyde (GA) (25% in water, Sigma, USA) with the concentration of 3 wt.% is added under continuous stirring for 24 h. A 2M HCl solution as a catalyst is subsequently added under vigorous stirring for 3h to produce the casting solution. The resulting solution is degassed before casting. The thin-film composite membranes are prepared by casting the PVA aqueous solution on the PAN support membranes (PAN200, Ultura, USA) by using a casting knife with a constant gap of 70 µm. The membrane is dried at ambient temperature for 24 h. After that, the prepared membrane is crosslinked at 60 °C in 2 h [4-6]. Finally, the derived membrane is immersed in the 80 wt.% ethanol solution for 3 h and dried at room temperature for 24 h before pervaporation tests.
2.2. Membrane characterization
The surface chemistry of the crosslinked PVA membranes is characterized using an FTIR spectrometer (IFS28, Bruker) with an attenuated total reflection (ATR) supplied by the PIKE MIRacle™ (USA). A total of 60 scans are made for each sample with an apparatus resolution of 10 cm\(^{-1}\). The top surface and cross-section morphology of the membrane are visualized using the field emission scanning electron microscope (S-4800 FESEM, Hitachi). Furthermore, the thickness of the selective PVA layers is the average value of four different locations measured on the top of the membranes. The water contact angle (CA) of the membrane surface is measured using a contact angle analyzer (OCA25, Dataphysics). Five measurements are made at different locations at room temperature for each membrane sample, and the average value is reported. The swelling degree of the membranes (SD) is determined by immersing the dry derived membranes \(M_o\) with an area of 1 cm \(\times\) 1 cm into the deionized water and 80 wt% ethanol solution for 24 h at a room temperature before taking out and wiping the solution on the surface the membrane. Then the saturated membranes are weighed again \(M_s\). The SD is expressed by the equation:

\[
SD \% = \frac{M_s - M_o}{M_o} \times 100\%
\]

(1)

2.3. Pervaporation performance
The separation performance of the membrane is investigated for 80/20 wt.% ethanol/water mixtures, using a lab-scale pervaporation unit. The schematic diagram of the pervaporation setup is illustrated in Figure 1. A module membrane is designed with a membrane area of 19 cm\(^2\) with a channel height of 2 mm. The feed solution is circulated from the feed tank through the membrane cell with a flow rate of 72 ± 2 L/h by a pump. The temperature of the feed solution is 60 ± 1°C by a laboratory recirculating heater. The pressure of the feed side is at the atmospheric pressure and the pressure on the permeate side is maintained at 3 mbar by using a vacuum pump (Robinair, USA). The separation process is conducted for 2 h, and the permeate vapor is condensed in a cold trap by a laboratory chiller and heat exchanger using pure ethanol liquid (~ -20 °C). The collected permeate is weighed using a mass balance (accuracy ± 0.0001 g) for determining the permeation flux. The permeation flux \(J\) is determined using the following equation:

\[
J = \frac{Q}{A} \text{g}\text{m}^2\text{h}^{-1}
\]

where, \(Q\) (g), \(A\) (m\(^2\)) and \(t\) (h) represent the weight of permeate, effective membrane area and the operation time, respectively.

![Figure 1. The schematic diagram of the lab scale pervaporation unit.](image)

The composition of permeated product is specified by measuring the refractive indices with a digital differential refractometer (Reichert, AMETEK GmbH, Germany) combined with the aid of a calibration curve for ethanol/water mixture prepared using known quantities of the two components. The refractometry measurements are carried out at 25 °C. The separation factor (\(\alpha\)) is defined as:

\[
\alpha = \frac{y_{\text{Eth}}} {x_{\text{Eth}}} \frac{x_{\text{H2O}}} {y_{\text{H2O}}}
\]

(3)
where, \( x_W, x_{EtOH}, y_W, y_{EtOH} \) are the weight fractions of water and ethanol in the feed and permeate side, respectively. The data of permeation flux and separation factor reported in this work are based on the average of four experimental runs.

The water and ethanol permeances are calculated from the permeation flux as follow:

\[
J_{EtOH} = Q_{H_2O}(P_{feed}^{H_2O} - P_{permeate}^{H_2O}) \\
J_{EtOH} = Q_{EtOH}(P_{feed}^{EtOH} - P_{permeate}^{EtOH})
\]

(4)  (5)

where, \( P \) is the partial vapor pressure of each component on the membrane feed side. The partial vapor pressure of either water or ethanol could be calculated from their thermodynamic properties

\[
P_{feed}^{H_2O} = x_{H_2O}Y_{H_2O}P_{sat}^{H_2O} \\
P_{feed}^{EtOH} = x_{EtOH}Y_{EtOH}P_{sat}^{EtOH}
\]

(6)  (7)

where, \( \gamma \) is the activity coefficient of a component in the feed liquid and it is calculated by Wilson’s equation [4], and \( P_{sat} \) is the saturation vapor pressure of pure component at the feed temperature which is determined from Antoine equation [4].

The pervaporation separation index (PSI) of the membranes is calculated by the following equation:

\[
PSI = J \times (\infty - 1)
\]

(8)

To investigate the effect of PVA concentration on the physicochemical properties and ethanol/water separation efficiency of the crosslinked PVA membrane, the membrane fabrication conditions are presented in detail according to Table 1.

**Table 1.** Membrane fabrication conditions to investigate the effect of PVA concentration.

| PVA concentration (wt.%) | Crosslinking Agent | Crosslinking Agent Concentration (wt.%) | Heat treatment temperature (°C) |
|--------------------------|--------------------|----------------------------------------|-------------------------------|
| 5-15                     | GA                 | 3                                      | 30                            |

Indeed, the GA is used as a crosslinking agent because it sensitively reacts with OH functional groups in the PVA membrane. Specifically, the lattice reaction between the GA and the OH functional groups in the PVA that creates acetal and ether bridges in the PVA membrane can take place at room temperature to medium temperature.

![Figure 2. Infrared spectrum of the membrane formed with different concentrations of PVA.](image)
Figure 3. SEM images of PAN substrate and PVA membranes prepared with different concentrations: PAN (a,f); PVA5% (b,g); PVA 7.5% (c,h); PVA10% (d,i); PVA15% (e,k).
3. Results and discussion

3.1 Effect of PVA concentration on the physicochemical properties of the membrane.

The infrared spectra of the PVA membranes fabricated with different PVA concentrations are presented in Figure 2. A large peak appears in the wave number of 3000 - 3600 cm\(^{-1}\), representing the characteristic vibration of the hydroxyl functional groups in the PVA selective layer. The increase in the peak intensity reveals that the number of OH groups increases as increasing the PVA concentration. Moreover, it is obvious that there are two additional peaks at 1050 cm\(^{-1}\) and 1140 cm\(^{-1}\), which is representative for the vibration of acetal groups (-\(\text{C-O-C-O}\)) and ether groups (-\(\text{C-O}\)), respectively. Indeed, by increasing the concentration of PVA, the peak intensity which characterizes acetal group's vibration is likely to become more obvious. This confirms the presence of the crosslinked PVA layer on the PAN porous substrate [7, 8]. Additionally, the number of OH groups in the membrane increases as increasing the PVA concentration.

The surface and cross-section morphology of the PAN porous substrate and cross-linked PVA membranes fabricated with different PVA concentrations are shown in Figure 3. The Figure 3a and the Figure 3f show that the PAN substrate consists of two parts: a polyester fiber layer with a thickness of ca. 100 µm and a PAN microporous layer with a thickness of ca. 55 µm. The PAN substrate has a very small pore structure (about 0.5 µm) on the surface and a larger porous structure on the bottom side in contact with the polyester fiber layer. For the crosslinked PVA membranes shown in Figure 3(g-k), the thickness of the membrane tends to increase when increasing the PVA concentration. The thickness of the PVA selective layers fabricated by the various PVA concentration of 5.0 wt.%, 7.5 wt.%, 10.0 wt.%, and 15.0 wt.% are 1.8 µm, 4.5 µm, 9.4 µm, and 15.9 µm, respectively. The membrane surface is observed to be smoother and less defective as increasing the PVA concentration. The SEM images show that the crosslinked PVA membrane prepared with a 10 wt.% PVA concentration exhibits a smooth surface with no visible pores.

![Figure 4](figure.png)

**Figure 4.** Contact angles and the swelling degrees in water and 80/20 %wt ethanol/water mixture of PVA membranes crosslinked at different concentrations of PVA.

The Figure 4 illustrates the contact angle of the PVA membranes formed by the different PVA concentrations with deionized water and the swelling degree of the membranes in the aqueous medium as well as the 80 wt.% ethanol solution. In fact, the contact angle represents the hydrophilicity of the membrane. The lower contact angle shows the higher hydrophilicity of the membrane. As shown in Figure 4, the hydrophilicity of the crosslinked PVA membranes is observed to decrease as increasing the PVA concentration. The studies of investigation on surface molecular conformations of Li et. al reported that the water evaporation is slow when the membrane is heat-treated at low temperature. Thereby, the OH groups in the PVA matrix tend to shrink, while the methyl groups are located on the membrane surface leading to a decrease in the hydrophilicity of the membrane [9, 10]. Furthermore, the increase in the PVA concentration leads to the enhancement of the swelling degree of the
membrane. This can be explained that the growth of membrane thickness with increasing PVA concentration leads to an increase in the adsorption capacity for the aqueous solution inside the membrane. However, the observation indicates that the swelling degree of the membrane in the 80 wt.% ethanol is lower than that in the deionized water because the PVA membrane shows a greater affinity for water molecules than that for the ethanol one. Therefore, the diffusion of ethanol molecules through the cross-linked PVA membrane is more difficult than water molecules.

3.2 Effect of PVA concentration on the performance separation of the membrane.

The pervaporation performance of the crosslinked PVA membranes prepared by the various PVA concentrations is evaluated by separating the 80 wt.% ethanol at 60 °C under a pressure at 3 mbar. The permeation fluxes through the membrane are shown in Figure 5. The results show that the PAN substrate membrane is not capable of separating the ethanol/water mixture and having a flux of 5445 g.m⁻².h⁻¹. The permeation flux is significantly lowered as increasing the PVA concentration. However, the decrease in the permeation flux for the ethanol components is more remarkable than that for the water components. This phenomenon is reported by previous studies [11, 12].

![Figure 5. Mixed flux, water flux and ethanol flux across the membrane prepared with different concentrations of PVA.](image)

![Figure 6. Water permeability and ethanol permeability of the membranes prepared with different concentrations of PVA.](image)
Figure 7. Selectivity and separation efficiency index (PSI) of the membranes formed at different concentrations of PVA.

The Figure 6 shows the water and ethanol permeabilities of the PVA membranes prepared by different PVA concentrations. Both water and ethanol permeabilities are observed to decrease with an increasing PVA concentration. This could be due to the increase in the thickness of the selective PVA layer with a dense structure preventing the diffusion of water and alcohol molecules within the membrane. Moreover, the difference in the molecular size between the ethanol molecules (0.52 nm) and the water molecules (0.26 nm) results in the faster diffusion of water species in the PVA membrane compared to that of ethanol species [12, 13, 14].

The Figure 7 shows the selectivity and pervaporation separation index (PSI) of the prepared membranes with the different PVA concentrations. The results reveal the improvement of the selectivity of the membrane with an increase in the PVA concentration. The increasing rate of the selectivity sharply grows when increasing PVA concentration from 5 wt.% to 10 wt.%, which is due to the reduction of defects in the denser membrane. Besides, the permeability of the components within the membrane decreases with the membrane thickness. However, the observation confirms that the membrane selectivity increases slowly as further PVA concentration of 10 wt.%. The results are consistent with the dissolution-diffusion theoretical model used to explain the transport in the pervaporation membrane [15]. The PSI of the membrane is found to increase with the PVA concentration ranging from 5 wt.% to 10 wt.%. However, this index decreases when increasing the PVA concentration from 10 wt.% to 15 wt.%, which is due to a significant decline in the water permeation flux of the membrane.

Based on the results, it could be indicated that the PVA membrane prepared from the 10 wt.% PVA concentration is suitable for the fabrication of crosslinked PVA thin-film composite membrane with high selectivity and good PSI for separating the ethanol/water mixture.

4. Conclusion
The PVA thin-film composite membrane in-situ crosslinked by glutaraldehyde has been successfully fabricated for pervaporation separation of the ethanol/water azeotropic mixture. The impact of PVA concentration on the physicochemical property and separation performance of the membrane has been investigated. Increasing the PVA concentration increases the thickness and hydrophobicity of the PVA layer, which contributes to the decline of permeation flux. Particularly, the reduction of the ethanol permeability is more significant than that of the water permeability. However, the denser surface and higher thickness of the PVA layer as increasing the PVA concentration is found to significantly improve the selectivity of the membrane. The results suggest that the PVA concentration of 10 wt.% is suitable for developing the PVA thin-film composite membrane with sufficient permeation flux and high selectivity for the separation of the ethanol/water azeotropic mixture. The obtained membrane
exhibited a permeation flux of ca. 1.4 kg.m\(^{-2}\)h\(^{-1}\) and the selectivity of ca. 68, for the separation of the 80 wt% ethanol/water mixture.

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