Investigation of Solute Diffusion through Polyvinyl Alcohol/ Polyallylamine Ultrafiltration Membrane

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Ultrafiltration membrane has been widely used for several applications due to their high separation capacity, high selectivity, and low operating pressure. In this work, solutes diffusion through polyvinyl alcohol/polyallylamine ultrafiltration membrane was investigated. The membrane was prepared by phase inversion method with glutaraldehyde as crosslinking agent. Meanwhile, NaCl and CaCl₂ were used as solutes, either as a single or double solute. The results showed that the increase of polyallylamine concentration led to the increase of membrane swelling degree. For both single and double solutes, diffusion of Na⁺ and Ca²⁺ were slightly decreased with the increase of swelling degree. However in double solute diffusion, there was interaction between Na⁺, Ca²⁺, and membrane that made Na⁺ ions moved faster and Ca²⁺ ions moved slower compared to single solute diffusion. In addition, the increase of solute concentration led to the increase of Na⁺ diffusion coefficient and the decrease of Ca²⁺ diffusion coefficient.

Keywords: polyallylamine, polyvinyl alcohol, swelling degree, solute diffusion, ultrafiltration membrane

INTRODUCTION

Ultrafiltration (UF) membrane has been widely used in water and wastewater treatment, chemical purification, gas separation, etc. UF offers some advantages, such as energy efficiency, high separation capacity, high selectivity, and relatively low cost (Khoiruddin, Widiasa et al. 2014, Aryanti, Yustiana et al. 2015, Himma, Anisah et al. 2016, Ariono, Aryanti et al. 2017, Wardani, Hakim et al. 2017). Several polymers have been used to prepare ultrafiltration membrane, such as polysulfone (Hamid, Ismail et al. 2011, Aryanti, Khoiruddin et al. 2013, Wardani, Hakim et al. 2017), polyvinyl alcohol (Vauclair, Tarjus et al. 1997, Wu, Lin et al. 2006, Josh, Haik et al. 2013, Jose, Shehzad et al. 2014), polyethersulfone (Rahimpour and Madaeni 2007, Razmjou, Mansouri et al. 2011, Moghimifar, Raisi et al. 2014),
polyvinyl chloride (Aryanti, Yustiana et al. 2015), polyvinyl fluoride (Du, Peldszus et al. 2009), polyacrylonitrile (Asatekin, Kang et al. 2007), etc. Among them, polyvinyl alcohol (PVA) is one of the promising material due to its excellent properties such as film formability, barrier to gases and liquids, hydrophilicity, good adhesion to various surfaces, chemical resistance and biodegradability (Wu, Gu et al. 2012, Josh, Haik et al. 2013, Jose, Shehzad et al. 2014). Besides, PVA is a polyelectrolyte material that contains of ionic groups, thus it can be used to produce charge UF membrane.

In several cases, the existence of charge on the membrane surface is required to improve its conductivity and permselectivity as well as its stabilities, including mechanical, chemical, and thermal stabilities (Khoiruddin, Ariono et al. 2017). Their separation ability depends not only by sieving mechanism, but also the electrolyte diffusion due to the exertion of electrostatic repulsive force against the electrolyte solute (Tsuru, Nakao et al. 1991). One of the most importance properties of charged membranes is their swelling behavior. Swelling is a dissolution process of a polymer in a defined solvent. It is greatly affected by the ionization of functional groups along the the polymer chain as well as the ionization of crosslinking agent molecules (Pieróg, Gierszewska-Drużyńska et al. 2009). In swelling membrane, the swollen polymer networks with pore/mesh of molecular size, usually between 20 and 100 Å (Peppas 1988). The mass transport of solutes in charged swelling membrane is based on the diffusivity of the penetrants into the mesh of the membrane.

In polyelectrolyte membrane, like PVA membrane, permeability mainly depends on the ions' mobility and their affinity with the membrane (Sun, Wu et al. 2014). Hydrophilic modification by blending PVA with other suitable hydrophilic polymers is one of alternative methods to improve the membrane affinity with the ions. Several modifications of PVA based ultrafiltration membrane have been studied (Yeom and Lee 1996, Mühlebach, Müller et al. 1997, Vauclair, Tarjus et al. 1997, Kim, Park et al. 2005, Wu, Lin et al. 2006, Wu, Gu et al. 2012, Josh, Haik et al. 2013, Jose, Shehzad et al. 2014). However, most of those studies used polyacrylonitrile (PAA) as additive. The use of polyallylamine (PAAm) as additive in PVA membrane preparation has not been found elsewhere. In this work, PVA/PAAm membrane was prepared by phase inversion method with glutaraldehyde as crosslinking agent. The addition of crosslinking agent is important to control the swelling behavior on the membrane. Meanwhile, NaCl and CaCl$_2$ were chosen as solutes, either as a single or double solute. This work then focused on the investigation of solute diffusion through PVA/PAAm membrane. The effect of PAAm addition and crosslinking ratio to membrane swelling degree was studied. In addition, the effect of membrane swelling to membrane performance, such as flux, rejection, and solute diffusion was also discussed.

**EXPERIMENTAL**

**Membrane Preparation**

Membrane was prepared from a mixture of PVA and PAAm with glutaraldehyde as
crosslinking agent. First, 10%-w PVA solution was heated until 90°C for two hours before cooled to 40°C. The PVA solution was mixed with PAAm, sulfate acid as catalyst, acetic acid as buffer, glutaraldehyde as crosslinking agent, and methanol as quencher. The composition of glutaraldehyde should be controlled to produce membrane with crosslinking ratio from 0.006 to 0.012 mol glutaraldehyde per mol PVA, as shown in Table 1. The mixed solution was casted on the Plexiglas and then dried in room temperature for about 6 days. After being dried, membrane was soaked in water for 24 hours to remove acid and methanol residual.

Table 1. Variation of membrane concentration and crosslinking ratio

<table>
<thead>
<tr>
<th>PAAm/PVA (w/w)</th>
<th>Crosslinking ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.006 0.008 0.010 0.012</td>
</tr>
<tr>
<td>0.08</td>
<td>0.006 0.008 0.010 0.012</td>
</tr>
<tr>
<td>0.12</td>
<td>0.006 0.008 0.010 0.012</td>
</tr>
</tbody>
</table>

Membrane Characterization

Membrane characterization was conducted to calculate the swelling degree of membrane by measuring membrane weight in the air and in n-hexane solution. Measurements were carried out at 25°C. The degree of swelling was calculated using following equation (Geens, Van der Bruggen et al. 2004).

\[
Q = \frac{\omega_a - \omega_h}{\rho_p} \rho_h
\]

where \(Q\) is membrane swelling degree, \(\omega_p\) is mass of dried membrane sample (g), \(\omega_a\) is mass of membrane sample in the air (g), \(\omega_h\) is mass of membrane sample in n-hexane (g), \(\rho_p\) is PVA density (g/cm\(^3\)), and \(\rho_h\) is n-hexane density (g/cm\(^3\)).

Diffusion Experiment

Diffusion experiment was conducted to determine diffusion performance through PVA/PAAm membrane. There are two types of solution were used in the diffusion experiment: (a) single solute solution of sodium chloride (NaCl) and calcium chloride (CaCl\(_2\)), (b) double solute solution (mixture of NaCl and CaCl\(_2\)). Variation of solute concentration on the diffusion experiment can be seen in Table 2.

Table 2. Variation of diffusion experiment

<table>
<thead>
<tr>
<th>Solute</th>
<th>Membrane thickness (cm)</th>
<th>Solute concentration (mmol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.03-0.07</td>
<td>52</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>0.03-0.07</td>
<td>-</td>
</tr>
<tr>
<td>Mixed solution A</td>
<td>0.03-0.07</td>
<td>26 26</td>
</tr>
<tr>
<td>Mixed solution B</td>
<td>0.03-0.07</td>
<td>52 52</td>
</tr>
</tbody>
</table>
Fig. 1 shows the experimental set-up of this work. First, feed tank D was filled with 6 L of electrolyte solution (NaCl, CaCl₂, or the mixture of NaCl and CaCl₂) while tank B was filled with aqua dm and cooler C was filled with cooling water. G2 valve was opened with flow rate about 0.3 mL/s until bottom part of module A was filled with water. Then, G1 valve was opened and pump was turned on until feed solution filled the top of module A. A 100 mL of permeate was taken to analyze the solute concentration. For single solute solution, permeate concentration was measured by argentometric method, while permeate from double solute solution was analyzed using atomic absorption spectroscopy (AAS).

The diffusion coefficient of Na⁺ and Ca²⁺ solutes was calculated by following equation:

$$D_i = \left( \frac{RT}{F} \right) u_i$$  \hspace{1cm} (2)

Here, $R$ is universal gas constant, $T$ is absolute temperature, $F$ is Faraday number, and $u_i$ is ion mobility of $i$.

RESULTS AND DISCUSSION

Membrane Characterization

In this work, PAAm was chosen as additive due to its hydrophilicity at normal and acid condition. Besides, the addition of PAAm is able to improve membrane affinity and selectivity (Harsch, Calderon et al. 2000, Hamerli, Weigel et al. 2003, Dejeu, Lakard et al. 2009). Meanwhile glutaraldehyde was used as crosslinking agent with crosslinking ratio of 0.006-0.012 mol glutaraldehyde per mol PVA. The crosslinking agent was added to control the swelling formation in PVA membrane. The PVA/PAAm membrane was characterized to study the relation of crosslinking ratio and PAAm addition to membrane swelling degree.

Fig. 2: Membrane swelling degree as the function of crosslinking ratio and membrane concentration

Fig. 2 shows that crosslinking ratio gave no significant effect to membrane swelling degree. The swelling degree was only...
slightly changed with the increase of crosslinking ratio. Meanwhile, the increase of PAAm concentration led to the increase of membrane swelling degree. The improvement could be due to additional sites like carboxylic acid groups from PAAm which strongly associated with membrane hydrophilicity (Jose, Shehzad et al. 2014, Khoiruddin, Ariono et al. 2017). The increase of hydrophilicity of membrane then led to the increase of water molecules that penetrate thorough membrane.

Diffusion of Single Solute

Membrane thickness can be used to indicate membrane swelling degree, where the increase of membrane thickness represents higher swelling degree. In homogeneous membrane, the permeability is greatly affected by membrane diffusivity and solubility, while independent to the membrane thickness. The diffusivity is uniform throughout the entire membrane. Meanwhile, for membrane with two or more different structure layers with different permeabilities, the overall permeability is affected by membrane thickness. It is due to the presence of boundary resistance between the structure layers (Hwang and Kammermeyer 1974).

Fig. 3 and Fig. 4 show the effect of PVA/PAAm membrane thickness on the membrane flux and rejection for single solute diffusion. It can be seen that flux for both Na$^+$ and Ca$^{2+}$ were decreased with the increase of membrane thickness. The flux obtained when using the thinnest membrane (0.03 cm) was approximately three times that of the thickest membrane (0.07 cm). Meanwhile, the Na$^+$ and Ca$^{2+}$ rejection were increased 0.5-0.8%. These results were in agreement with previous studies (Aptel, Cuny et al. 1974, Qunhui, Ohya et al. 1995, Sridhar, Srinivasan et al. 2003, Kanti, Srigowri et al. 2004, Villaluenga, Khayet et al. 2005) where the increase of membrane thickness led to the increase of solute rejection.
Corresponds to the flux and rejection data in Fig.3 and Fig.4, the diffusion coefficients for both Na\(^+\) and Ca\(^{2+}\) were decreased with the increase of swelling degree, as shown in Fig.5. Higher swelling degree was obtained by the increase of PAAm composition. As mentioned above, the addition of PAAm increase membrane hydrophilicity, thus higher amount of water penetrated to the membrane pores. The existence of the water molecules in the membrane pores made solutes difficult to penetrate through the membrane. Therefore, solute rejection was increased at higher swelling degree.

Furthermore, Fig.5 shows that diffusion coefficient for Na\(^+\) and Ca\(^{2+}\) between 4.2564 \(\times\) 10\(^{-6}\) to 6.8748 \(\times\) 10\(^{-6}\) cm\(^2\)/s. These results were compatible with diffusion coefficient that proposed by Schogl (Schlogl 1953), where diffusion coefficient of solute in membrane with water volume fraction more than 50% is about 10\(^{-6}\) cm\(^2\)/s. From Fig.5, it can be seen that the diffusion coefficients of Na\(^+\) were higher than Ca\(^{2+}\). It means that Na\(^+\) ions have higher mobility than Ca\(^{2+}\) ions since small molecules diffuse faster in solids than large molecules.

**Diffusion of Double Solute**

Fig.6 and Fig.7 show the effect of membrane thickness on the membrane flux and rejection for double solute diffusion. Mixed solution A consisted of 26 mmol/L Na\(^+\) and 26 mmol/L Ca\(^{2+}\), while mixed solution B consisted of 52 mmol/L Na\(^+\) and 52 mmol/L Ca\(^{2+}\). Same as single solute diffusion, flux was decreased and rejection...
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The diffusion coefficients for double solute diffusion were calculated by same method as single solute diffusion. The diffusion coefficients of double solute diffusion are presented in Table 3.

Table 3. Diffusion coefficient for double solute

<table>
<thead>
<tr>
<th>Solute concentration in feed (mmol/L)</th>
<th>Q</th>
<th>D x 10^6 (cm^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaCl</td>
<td>CaCl(_2)</td>
</tr>
<tr>
<td>26</td>
<td>4.577</td>
<td>7.783</td>
</tr>
<tr>
<td></td>
<td>5.337</td>
<td>7.774</td>
</tr>
<tr>
<td></td>
<td>6.614</td>
<td>6.775</td>
</tr>
<tr>
<td>52</td>
<td>4.577</td>
<td>7.820</td>
</tr>
<tr>
<td></td>
<td>5.337</td>
<td>8.026</td>
</tr>
<tr>
<td></td>
<td>6.614</td>
<td>7.182</td>
</tr>
</tbody>
</table>

was increased with the increase of membrane thickness.

In two solute diffusion, there is a positive or a negative influence on each other solute transport rate. The interaction of the solutes also has a significant effect on the sorption and penetration of the solute to the membrane (Izák, Hovorka et al. 2007). Compared to single solute diffusion,
diffusion coefficient of Na$^+$ was increased and diffusion coefficient of Ca$^{2+}$ was decreased on double solute diffusion (Table 4). It was due to higher affinity between Na$^+$ and PVA/PAAm membrane and smaller size of NaCl molecules that led to higher rejection of Ca$^{2+}$ ions. While Ca$^{2+}$ ions were rejected, Na$^+$ ions moved more easily, thus coefficient diffusion of Na$^+$ was increased. Moreover, diffusion coefficient was also affected by solute concentration. By using lower concentration of NaCl and CaCl$_2$, diffusion coefficient of Na$^+$ was increased while diffusion coefficient of Ca$^{2+}$ was decreased. When the amount of Na$^+$ and Ca$^{2+}$ ions were low, the interaction of ions and membrane charge decreased that led to the decrease of Ca$^{2+}$ rejection and Na$^+$ mobility.

**CONCLUSION**

In this work, PVA membrane was prepared by phase inversion method with the addition of PAAm to increase its hydrophilicity and glutaraldehyde as crosslinking agent to control the membrane swelling. The results showed that the increase of PAAm concentration led to increase of membrane swelling degree. The addition of PAAm with concentration of 4%, 8%, and 12% produced membrane with swelling degree 4.577, 5.337, and 6.614, respectively. Meanwhile, the swelling degree was almost constant for all crosslinking ratios. For both single and double solutes, diffusion of Na$^+$ and Ca$^{2+}$ were slightly decreased with the increase of swelling degree. However, in double solute diffusion, there was interaction between Na$^+$, Ca$^{2+}$, and membrane that made Na$^+$ ions moved faster and Ca$^{2+}$ ions moved slower compared to single solute diffusion. In addition, diffusion coefficient of Na$^+$ was increased while diffusion coefficient of Ca$^{2+}$ was decreased with the increase of solute concentration.

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