Effect of amine structure on CO₂ capture by polymeric membranes

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ABSTRACT
Poly(amidoamine)s (PAMAMs) incorporated into a cross-linked poly(ethylene glycol) exhibited excellent CO₂ separation properties over H₂. However, the CO₂ permeability should be increased for practical applications. Monoethanolamine (MEA) used as a CO₂ determining agent in the current CO₂ capture technology at demonstration scale was readily immobilized in poly(vinyl alcohol) (PVA) matrix by solvent casting of aqueous mixture of PVA and the amine. The resulting polymeric membranes can be self-standing with the thickness above 3 μm and the amine fraction less than 80 wt%. The gas permeation properties were examined at 40 °C and under 80% relative humidity. The CO₂ separation performance increased with increase of the amine content in the polymeric membranes. When the amine fraction was 80 wt%, the CO₂ permeability coefficient of MEA containing membrane was 604 barrer with CO₂ selectivity of 58.5 over H₂, which was much higher than the PAMAM membrane (83.7 barrer and 51.8, respectively) under the same operation conditions. On the other hand, ethylamine (EA) was also incorporated into PVA matrix to form a thin membrane. However, the resulting polymeric membranes exhibited slight CO₂-selective gas permeation properties. The hydroxyl group of MEA was crucial for high CO₂ separation performance.

1. Introduction
CO₂ is the major component of greenhouse gases (GHGs), which cause the global warming and climate change. Addressing the GHG issue, the Paris agreement has warned to limit a global temperature rise to 1.5 °C [1], and mitigation of the GHG emission is an urgent task to be tackled. Carbon capture and storage (CCS) has been approved as one of the effective solutions toward the issue, and about 20 full-scale CCS demonstrations have been planned or carried out all over the world [2]. In the CCS, CO₂ is captured at the mass emission sources without exhausting to atmosphere, such as thermal power plants and steel works, and then injected into the aquifer of certain geological structures underground or under seabed [3]. However, for implementation of the CCS, the cost reduction is inevitable, in which the CO₂ capture dominates of the total. Liquid amine scrubbing is the most widely investigated CO₂ capture method [4,5] and adopted in the large-scale demonstrations [2]. For example, CO₂ in the flue gas from a coal-fired plant was captured by aqueous amine over other gaseous species, and then recovered by heating. The heating process is energy intensive even at the thermal power stations, which resulted in high cost. Thus, alternate low-energy CO₂ capture technologies have to be developed for the implementation of CCS. Among various CO₂ capture
membranes and MMMs are not CO2 selective because amines have been incorporated greater than S preferential CO2 permeation. For the CO2 capture, CO2 (3.30 Å) is separated over smaller H2, and porous inorganic membranes and MMMs are not CO2 selective because the separation proceeds by molecular sieving mechanism. Polymeric membranes are dense and non-porous, and the gas permeability is explained by the following expression (Equation (1)). Ideal gas selectivity for gas i over j \(a_{ij}\) is then given by the ratio of permeabilities as Equation (2).

\[
P = S \times D
\]

\[
a_{ij} = \frac{P_i}{P_j} = \frac{S_i}{S_j} \times \frac{D_i}{D_j}
\]

where S and D are solubility to the polymer matrix and diffusivity in the polymer, respectively [9]. Because the kinetic diameter of H2 (2.89 Å) is smaller than that of CO2 (3.30 Å), \(D_{CO2}/D(H2)\) is smaller than one. For preferential CO2 permeation, \(S_{CO2}\) should be much greater than \(S(H2)\). Amines have been incorporated physically or chemically into the polymeric membranes to enhance CO2 solubility in the membranes [10–15], where the amines also work as a CO2 carrier to facilitate the gas permeation through the membranes. PAMAM exhibits excellent CO2 separation performance [10,16], and the CO2 separation properties of PAMAM immobilized poly(ethylene glycol) (PEG) membranes have been extensively investigated in this research group [17–20]. The resulting mixture was cast on a plastic petri dish and exposed to UV light (365 nm, 12 mW/cm2, UVP B-100AP, CA, USA) for 3 min to polymerize PEGDMA [17]. The resulting polymeric membranes were dried under vacuum overnight. On the other hand, with amine-containing PVA membranes, 5 wt% of aqueous PVA was prepared by dissolving pre-determined amount of PVA in deionized water at 90 °C overnight under stirring. Amines were then added to the aqueous PVA, where the weight fraction of them was varied from 10 to 90 wt% relative to the polymer. The resulting mixture was cast on a plastic petri dish and dried at ambient temperature for 2 days and then under vacuum at 40 °C for at least 6 h until no weight change was recorded. The membrane thickness was controlled by varying the casting amount and less than 50 μm. The membrane thickness was determined by a Mitutoyo digimatic micrometer (Tokyo, Japan).

2.2. Membrane preparation process

For amine-containing PEG membranes, PEGDMA and amines were dissolved in ethanol, where the amine:PEGDMA:solvent ratio was kept to 6:4:5 by weight, and the monomer to initiator ratio was also kept by the molar ratio of 60. The reaction mixture was sandwiched with quartz plates with stainless spacers (50 μm in thickness) and exposed to UV light (365 nm, 12 mW/cm2, UVP B-100AP, CA, USA) for 3 min to polymerize PEGDMA [17]. The resulting polymeric membranes were dried under vacuum overnight. On the other hand, with amine-containing PVA membranes, 5 wt% of aqueous PVA was prepared by dissolving pre-determined amount of PVA in deionized water at 90 °C overnight under stirring. Amines were then added to the aqueous PVA, where the weight fraction of them was varied from 10 to 90 wt% relative to the polymer. The resulting mixture was cast on a plastic petri dish and dried at ambient temperature for 2 days and then under vacuum at 40 °C for at least 6 h until no weight change was recorded. The membrane thickness was controlled by varying the casting amount and less than 50 μm. The membrane thickness was determined by a Mitutoyo digimatic micrometer (Tokyo, Japan).

2.3. Membrane characterizations

The thermal properties of amine-containing membranes were examined by differential scanning calorimetry (DSC) on a Netzsch DCS 204 F1 Phoenix (Netzsch,
3. Results and discussion

CO₂ separation by amine-containing polymeric membranes has been studied in this research group. Amines were readily immobilized in a cross-linked PEG by UV curing of PEGDMA in the presence of the amines [17]. However, poor compatibility between amines and PEG resulted in forming opaque or translucent membranes, which was due to macrophase separation on a couple of microns scale between amines and the matrix [18]. Thus, when the membrane thickness was reduced less than a few tens microns, leakage of amines were found. As a result, the membrane lost the CO₂ separation performance. In comparison to the translucent PEG membranes, the amine-containing PVA membranes were transparent as shown in Figure 1. The better compatibility between amines and the matrix would reduce the phase separation.

One approach to examine the macrophase separation was expected to see thermal properties on DSC. The properties of the amine-containing PVA membranes would be different from pristine PVA due to change in the heat capacity upon phase mixing. Figure 2 displayed the DSC profiles of various amine-containing polymeric membranes. While pristine PVA membrane showed the glass transition temperature (T_g) at 55 °C in Figure 2(e), the thermal transition of the amine-containing PVA membranes became ambiguous (Figure 2(a)–(c)). The glassy PVA became rubbery upon complexation with the amines. On the contrary, the amine-containing PEG membranes showed a clear thermal transition between −60 and −50 °C in Figure 2(d) and (e), which was corresponded to the T_g of PEG of the polymer matrix. Due to poor miscibility between the amines and PEG, a PEG-rich domain was formed, and the PEG matrix thus kept the inherent thermal properties even after the amine loading. An exothermic and endothermic peaks at −30 and 3 °C indicated crystallization and melting of MEA in Figure 2(d). The melting peak of PAMAM overlapped with the T_g of PEG and was not clear in Figure 2(e).

The macrophase separation was also studied by eluting out the incorporated amines in ethanol [25], which was a poor solvent for the polymer matrices. When the amine-containing PEG and PVA membranes were immersed in ethanol, physically immobilized amines came out into the solvent. For the PAMAM-containing
membranes, the solutes were collected and determined as the incorporated amines in the matrices by $^1$H NMR as shown in Figure 3. This result suggested that the amines stayed intact in the polymer matrices even during the photopolymerization process to fabricate PEG membranes. In other words, Michael addition reaction between amines and vinyl compounds were negligible in the UV curing conditions. With the PAMAM-containing PEG membrane in Figure 3 (top spectrum), a peak was found at 3.6 ppm, which was the resonance of methylene protons of PEG. Oligomeric PEG would be released from the matrix. Because peaks of allyl protons of PEGDMA at 6.2–5.5 ppm were not seen, the monomer conversion would be completed.
also confirmed after the ethanol immersion, and a flat and smooth surface was seen in Figure 4(a) and (b). When the entrapped amines formed the rich phase upon macrophase separation similar to the PEG membranes, a porous structure would be found because PVA was insoluble in the solvent and in a grassy state ($T_g$: 55 °C in Figure 2(f)) in the experimental conditions. Thus, combined with the DSC results, it could be concluded that the amines and PVA were miscible on a micron scale, and a thinner membrane preparation was expected to be possible without amine leakage for the PVA matrix.

Gas permeation properties of amine-containing membranes were then investigated under isobaric conditions at 40 °C. The gas permeabilities changed with time by absorbing water under humidity and mostly reached equilibrium after 12 to 20 h incubation at the operation conditions as shown in Figure 5. Table 1 described a comparison of CO$_2$ separation properties of MEA-containing PVA and PEG membranes over H$_2$. The membrane thickness was measured immediately after the gas permeation test under humidified conditions. The PEG membranes were 52.7 μm in thickness, which was the minimum to prevent the amine leakage from the PEG matrix, and much thicker than the PVA ones (5.7 μm). The CO$_2$ permeance of the PEG membranes was 7.9 GPU and lower than that of the PVA membranes (16.2 GPU). The higher CO$_2$ selectivity of the PEG membranes was explained by higher amount of the amines, which worked as a CO$_2$ carrier to facilitate the gas transportation through the membranes. On the other hand, the PVA membranes retained the CO$_2$ separation properties over H$_2$ by reducing the thickness to ca. 6 μm to give higher CO$_2$ permeance.

In the PVA membrane preparation process, the amine content was varied from 10 to 90 wt% relative to PVA matrix, and self-standing membranes were obtained

On the other hand, with the MEA-containing membranes, MEA was found in ethanol by $^1$H NMR: 3.57 and 2.71 ppm for O–CH$_2$ and N–CH$_3$, respectively, in deuterated methanol. However, the amine was evaporated with ethanol during dry process, and the recovery was thus not precisely determined. In the PEG membranes, it was confirmed that the matrices were quantitatively recovered or physically entrapped amines were completely eluted out by the amine leaching experiment. On the contrary, while the amine fraction was 60 wt%, the weight reductions were 41 and 44% for the MEA- and PAMAM-containing PVA membranes. Better compatibility of the matrix to the amines suppressed the leakage from the membranes.

The resulting matrices after the amine leaching were observed by SEM, and the obtained cross-section images were displayed in Figure 4. With the amine-containing PEG membranes, porous structures were found in the resulting matrix in Figure 4(b) and (d). The $T_g$ of PEG was −60 ºC and would be flexible during the amine leaching experiment at ambient conditions. However, cross-linking reaction confined the rearrangement of PEG chains, and the PEG-rich phase was fixed. As a result, the monolith like structure with micron-sized pores was remained, and the pore was originally filled with the amines immobilized in the UV curing of PEGDMA. The macrophase separated structures on a couple of microns scale resulted in the translucent membranes.

On the other hand, the amine-containing PVA membranes were transparent. Here, when the amines and PVA would be incompatible and have a similar photorefractive index, diffused reflection of light would be suppressed at the interface, and the resulting mixture would be transparent. In the case of the PVA membranes, quantitative recovery of the amines from the membranes was also confirmed after the ethanol immersion, and a flat and smooth surface was seen in Figure 4(a) and (b). When the entrapped amines formed the rich phase upon macrophase separation similar to the PEG membranes, a porous structure would be found because PVA was insoluble in the solvent and in a grassy state ($T_g$: 55 °C in Figure 2(f)) in the experimental conditions. Thus, combined with the DSC results, it could be concluded that the amines and PVA were miscible on a micron scale, and a thinner membrane preparation was expected to be possible without amine leakage for the PVA matrix.

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the CO2 transport properties was then investigated with self-standing membranes, and the results were shown in Figure 6. Because the membrane thicknesses of the specimens were from 3 to 43 μm depending on the amines and the contents, the gas permeability was expressed by permeability coefficient \( P \), which was permeance normalized by the membrane thickness, 1 barrer corresponded to 1 GPU when the thickness was 1 μm.

For MEA- and PAMAM-containing PVA membranes, the CO2 permeance and separation factor increased with increase of the amine content, which indicated that the preferential CO2 permeation was based on facilitated transportation by the amines. The CO2 transport mechanism was different from those of the PEG membranes [17]. In the case of PAMAM-containing PEG membranes, the CO2 permeability slightly increased with increase of PAMAM content in the similar operation conditions. On the other hand, the H2 permeability significantly decreased, and as a result, the separation factor increased drastically with increase of the amine content. In the PEG membranes, the PAMAM-rich phase was formed upon microphase separation [18,25], and CO2 migrated the amine-rich phase rather than the PEG-rich phase due to difference in the CO2 solubility. When CO2 was fed to the membranes, dissolved CO2 reacted to the primary amines of PAMAM with the formation of carbamate as illustrated in Figure 7. PAMAM was crosslinked by the resulting carbamate ion pairs, and the amine leakage was negligible under the gas permeation operation conditions. Effect of amine loading on the CO2 transport properties was then investigated with self-standing membranes, and the results were shown in Figure 6. Because the membrane thicknesses of the specimens were from 3 to 43 μm depending on the amines and the contents, the gas permeability was expressed by permeability coefficient \( P \), which was permeance normalized by the membrane thickness, 1 barrer corresponded to 1 GPU when the thickness was 1 μm.

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3.6 to 604 barrer and from 3.3 to 59, respectively. EA had the same carbon skeleton as MEA but no hydroxyl group, and the amine-containing membranes did not have effective CO\textsubscript{2} separation performance. Thus, hydroxyl group of the alkanolamine would be a key to exhibit preferential CO\textsubscript{2} permeation properties. The CO\textsubscript{2} separation performance of the MEA-containing PVA membranes was actually higher than that of the PAMAM membranes. The CO\textsubscript{2} permeability of the PAMAM membranes was less than 100 barrer and far below of that of the MEA membranes, while the separation factor was relatively smaller at the same amine weight fraction. A hydroxyl group in β-carbon adjacent to amino group helped to form a seven-membered ring when CO\textsubscript{2} interacted to the amino group in the polymeric membranes [27,28]. The ring formation reduced the activation energy of the interaction and facilitated both of the association and dissociation between CO\textsubscript{2} and the amino group, resulting in enhancing CO\textsubscript{2} diffusion in the membranes.

quasi-crosslinks restricted the H\textsubscript{2} permeation to provide a quite high CO\textsubscript{2} selectivity by a CO\textsubscript{2}-selective molecular gate function [16,19].

On the contrary, the amines were compatible to PVA and did not form such amine-rich phase in the membranes confirmed by the SEM observations in Figure 4. The amines were diffused homogeneously through the PVA membranes and worked as a CO\textsubscript{2} carrier to provide higher gas permeability, which was more preferable rather than the higher selectivity for practical CO\textsubscript{2} capture [26].

\[2R - \text{NH}_2 + \text{CO}_2 \rightleftharpoons R - \text{NH} - \text{COO}^- + \text{N}^+\text{H}_3 - R\]

Chemical structure of the amines was one of the crucial factors to characterize the CO\textsubscript{2} separation performance in the PVA membranes. As depicted in Figure 6, MEA gave the highest CO\textsubscript{2} permeation properties among the amines tested in the same weight fraction. With increase of MEA content from 10 to 80 wt%, the CO\textsubscript{2} permeance and separation factor went up from 3.6 to 604 barrer and from 3.3 to 59, respectively. EA had the same carbon skeleton as MEA but no hydroxyl group, and the amine-containing membranes did not have effective CO\textsubscript{2} separation performance. Thus, hydroxyl group of the alkanolamine would be a key to exhibit preferential CO\textsubscript{2} permeation properties. The CO\textsubscript{2} separation performance of the MEA-containing PVA membranes was actually higher than that of the PAMAM membranes. The CO\textsubscript{2} permeability of the PAMAM membranes was less than 100 barrer and far below of that of the MEA membranes, while the separation factor was relatively smaller at the same amine weight fraction. A hydroxyl group in β-carbon adjacent to amino group helped to form a seven-membered ring when CO\textsubscript{2} interacted to the amino group in the polymeric membranes [27,28]. The ring formation reduced the activation energy of the interaction and facilitated both of the association and dissociation between CO\textsubscript{2} and the amino group, resulting in enhancing CO\textsubscript{2} diffusion in the membranes.
4. Conclusions

The PAMAM-containing membranes have been studied for effective CO₂ separation over H₂. To reduce macrophase separation between the amine and the matrix, PVA was employed to improve compatibility to the amine. The resulting PVA membranes were transparent, and the DSC and the amine elution experiments clarified suppression of the macrophase separation. A thinner membrane formation was then possible with PVA matrix by reducing the phase separation, and an increase in CO₂ permeability was confirmed. Furthermore, it was suggested that MEA exhibited higher CO₂ permeability and selectivity than PAMAM in the polymer matrices. Hydroxyl group adjacent to the amino group would be a key to enhance the CO₂ separation performance.

In this research, the CO₂ separation properties over H₂ was investigated under isobaric conditions, which was lower than the CO₂ partial pressure of syngas after water-gas shift reaction at an IGCC. Thus, the separation performance under pressure was not clear. On the other hand, this membrane would hold potential to capture CO₂ in the industrial H₂ production process by steam reforming of light hydrocarbons. For example, H₂ is generated from CH₄ by the steam reforming followed by the shift reaction, and then purified over CO₂ by pressure-swing adsorption (PSA). The PSA off-gas comes out at ambient pressure and contains certain amount of H₂, which is used as fuel to keep the reformer at elevated temperature, and CO₂ is in the off-gas eventually emitted. A feasibility study revealed that the CO₂ separation properties observed could meet the required values to separate CO₂ in the off-gas [29] and that the amine-containing PVA membranes would be applicable to make the current H₂ process carbon-free.

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Disclosure statement

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