

Effect of addition of Proline, ionic liquid [Choline][Pro] on CO₂ separation properties of poly(amidoamine) dendrimer / poly(ethylene glycol) hybrid membranes

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Abstract. Poly(amidoamine) (PAMAM) dendrimers were incorporated into cross-linked poly(ethylene glycol) (PEGDMA) matrix to improve carbon dioxide (CO₂) separation performance at elevated pressures. In our previous studies, PAMAM/PEGDMA hybrid membranes showed high CO₂ separation properties from CO₂/H₂ mixed gases. In this study, proline, choline and ionic liquid [Choline][Pro] compounds were selected as rate promoters that were used to prepare PAMAM/ PEGDMA hybrid membranes. The effect of addition of proline, choline, IL [Choline][Pro] on separation performance of PAMAM/PEGDMA) hybrid membranes for CO₂/H₂ separation was investigated. Amino acid proline, choline, and IL [Choline][Pro] were used to promote CO₂ and amine reaction. With the addition of [Choline][Pro] into PAMAM/PEG membrane, CO₂ permeance of PAMAM/PEG hybrid membranes are increased up to 46% without any change of selectivity of membrane for CO₂.

1. Introduction

A major reason of global warming is the emissions of CO₂ into the atmosphere, sea level change and extreme weather conditions [1]. CO₂ emission level in the atmosphere will still increase according to the current status of energy supply and demand such in industrial activity and energy though solar and nuclear energy increased. Therefore, reducing the emissions of CO₂ is crucial [2]. Many technologies are currently employed for separation and capture of CO₂ from gas streams [3], with membrane separation is being one of the promising solutions because of its energy efficiency and operation simplicity. Membrane based separation affords CO₂ separation from a pressurized gas stream, for example through the integrated coal gasification combined cycle (IGCC) process. The high-pressure difference between the feed and permeate sides of the membrane provides sufficient driving force to conduct membrane separation in the absence of additional compressors and vacuum pumps, thus affording reduced CO₂ separation costs [4]. In our research group, various CO₂ separation membranes containing PAMAM dendrimers have been developed for CO₂/H₂ separation [5]. Especially, the dendrimer can be readily immobilized in a crosslinked PEG by photopolymerization of PEGDMA in the presence of the dendrimer. The resulting polymeric PAMAM/PEGDMA/4GMAP membrane exhibits excellent CO₂ separation performance over H₂ under humidified conditions [6]. However,



permeability of CO₂ should be enhanced for practical use. A change in gas permeance with PAMAM/PEGDMA/4GMAP as a function of the membrane thickness was studied. It was found that thinner membranes give higher CO₂ permeation properties as expected, but the selectivity was decreased.

PAMAM dendrimer includes 4 primary amine groups at the terminal end is shown in figure 1. It is widely believed that carbamates could be formed by the reaction between primary/secondary amine and CO₂ in the absence of water [7]. The proposed reaction mechanism is as follows:



where R^1 and R^2 represent functional groups including H or alkyl groups. The overall reaction is represented by the equation below.

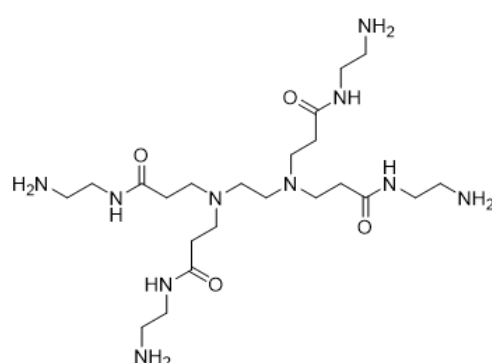


Figure 1. Polyamindoamine (PAMAM) dendrimer (G = 0), MW: 516.7.

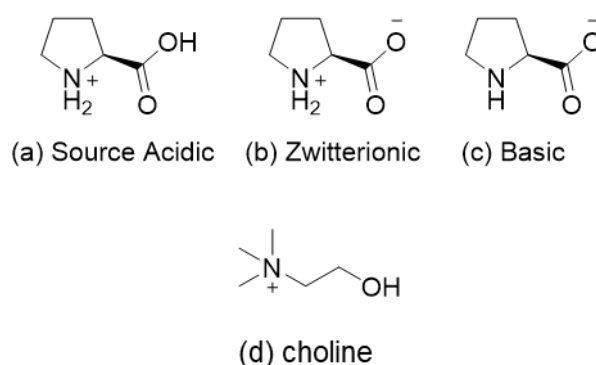
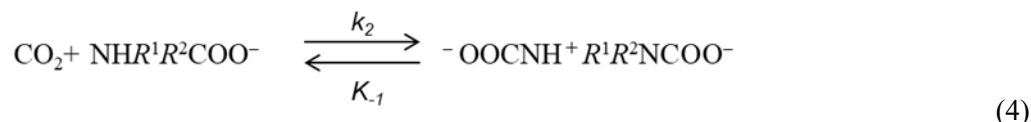


Figure 2. (a-c) Structures and pK of proline (d) Choline.

Proline is used as rate promoter in the reaction of primary amine with CO₂ reaction. With the addition of proline, the reaction mechanism can be different. Aqueous amino acid proline exist in three states: acidic, zwitterionic and basic or deprotonated (figure 2. (a ~ c)). The acidic state and zwitterionic state of the amino acids are much less reactive towards CO₂ than the deprotonated state (basic). Proline promotion mechanism can be summarized by equation (4). This reaction is followed by the removal of a proton from the zwitterionic carbamate by base, PAMAM, to form a neutral carbamate, changing chemical equilibrium of reaction of PAMAM and CO₂ shown in equation 3. It is resulting promotion of reaction of PAMAM and CO₂. Reaction between CO₂ and proline is represented by the equation below.



In this work, proline, choline and IL [Choline][Pro] were added to PAMAM/PEG membrane to promote CO₂ and amine reaction. This addition can lead to high CO₂ flux transfer into membrane, as a result high CO₂ permeance Q_{CO_2} and high selectivity will achieve. This way we can develop cost-effective technologies for CO₂ capture[8].

2. Experimental

2.1. Synthesis of [Choline] [Pro]

According to references of [9, 10], the route to prepare IL (2-hydroxyethyl)-trimethyl-ammonium (S)-2-pyrrolidinecarboxylic acid salt ([Choline][Pro]) is shown in figure 3. Choline chloride was first converted to choline hydroxide methanol solution. The solution was filtrated to remove KCl salt. The resulting solution was neutralized with equivalent amount of proline. After reaction complete, the evaporation of methanol was done at 40 °C under vacuum 10 mmHg to obtain the IL [Choline][Pro] - which is a light-yellow oil at room temperature.

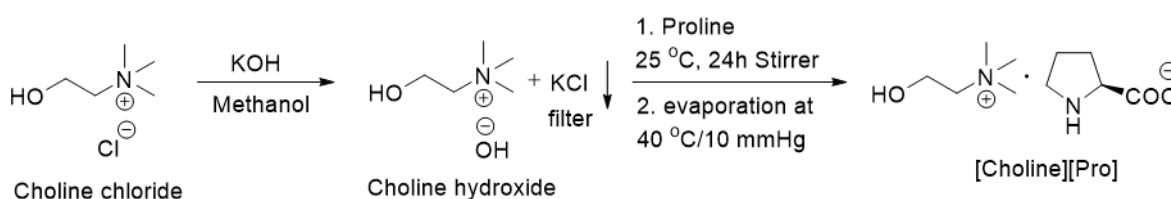


Figure 3. Schematic illustration to synthesized the IL [Choline][Pro]

2.2. Membrane preparation and SEM observation

A polymeric membrane was fabricated by photopolymerization of PEGDMA in the presence of PAMAM dendrimer in water [5]. The compositions of precursor solutions are (1) PAMAM (50 wt.%), PEGDMA (42.5 wt.%) and 4GMAP (7.5 wt.%) and addition (2) proline, (3) choline, (4) [Choline][Pro] with various mixture ratios (2) PAMAM/ proline/ PEGDMA/ 4GMAP = 47.5/2.5/42.5/7.5 (wt%), (3) PAMAM/ choline/ PEGDMA/ 4GMAP = 47.5/2.5/42.5/7.5 (wt%) and (4) PAMAM/ [Choline][Pro]/ PEGDMA/ 4GMAP = 47.5/2.5/42.5/7.5 (wt%) in water. The membrane thickness is controlled by sandwiching the reaction mixture with quartz plates and stainless steel spacers (50µm in thick) followed by the UV curing and transferred onto PES substrate membrane.

The morphologic analysis of composite membrane was performed using scanning electron microscopy (SEM, HitachiS-4800), at an accelerating voltage of 1.0 kV. Cross-sections of the composite membrane were obtained by fracturing the membrane in liquid N₂, and these sections were made conductive by coating with Pt/Pd.

2.2.1. Gas separation test

Test of gas membrane separation diagram setup used herein was provided in reference [5]. A CO₂/H₂ (80/20 by vol.) gas mixture was humidified at 80 % of relative humidity and then fed to a flat-type membrane cell at a flow rate of 100 ml/min. The CO₂ partial pressure under atmospheric condition was 80 kPa, while it was 560 kPa when the total pressure was 700 kPa. 80 % of relative humidity He was supplied to the permeate side of the cell as a sweep gas at a flow rate of 10 ml/min to collect the permeate gas. Operating temperature was 40 °C. CO₂ and H₂ concentration in both feed and permeate gas was measured by a gas chromatography with a pulsed discharge detector (GC-4000, GL Sciences Inc., Tokyo, Japan). In this experimental condition, the pressure ratio of the feed to the permeate side was sufficiently large, and the separation factor was thus accounted as an ideal separation factor (selectivity). Permeance, Q, and selectivity, α_{CO₂/H₂} were calculated according to equations (5) and (6):

$$\alpha(\text{CO}_2/\text{H}_2) = \frac{y_{\text{CO}_2}/y_{\text{H}_2}}{x_{\text{CO}_2}/x_{\text{H}_2}} \quad (5)$$

$$Q_i = \frac{N_i}{A \cdot \Delta p_i \cdot t} \quad (6)$$

Qi: permeance of gas I (m³(STP)/(m² s Pa)); α_{CO₂/H₂}: CO₂/H₂ separation factor (selectivity); Ni: total flow rate of sweep gas (m³ (STP)/s); x and y: mole fraction of feed and permeate side,

respectively; Pf and Pp: Pressure of feed (Pf) and permeate side (Pa) respectively; A: Effective membrane area (m^2).

3. Results and discussion

3.1. Membrane characterization via photos and SEM images

The photographs of PAMAM/PEG hybrid membranes with various PAMAM dendrimer concentration were shown in figure 4. The solutions for prepared membranes became yellow with addition of choline and [Choline][Pro]. The resulting membranes were transparent as seen in figure 4. Membrane thickness was measured by scanning electron microscope (SEM).

SEM images of PAMAM/PVA hybrid membrane and PES substrate are shown in figure 5. From surfaces image of SEM, there were a lot of pores on the surface of PES substrate. On the other hand, there were no pores on surface of PAMAM/PEGDMA/4GMAP hybrid composite membrane in figure 5. (a), (b). PAMAM/PEGDMA/4GMAP hybrid membrane layer was observed formed uniformly onto PES substrate and the thickness of about $23.5\ \mu\text{m}$ from cross-sectional images in figure 5. (c), (d).

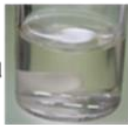

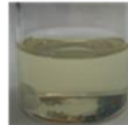



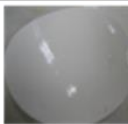
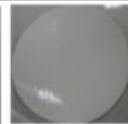
Additive	(1) without	(2) proline	(3) choline	(4) [choline][Pro]
Solution for prepared membrane				
Composite membrane				
Thickness	$23.5\ \mu\text{m}$	$20.4\ \mu\text{m}$	$25\ \mu\text{m}$	$25\ \mu\text{m}$

Figure 4. Preparation of solutions, membranes and membrane thickness.

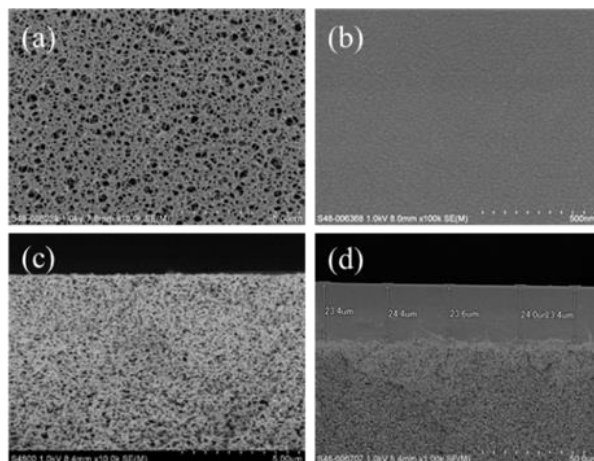


Figure 5. SEM images of (a) PES surface (b) PES cross-section (c) surface of membrane and (d) of PAMAM/PEGDMA/4GMAP = 50.0/42.5/7.5 (wt%) on PES substrate

3.2. Effect of CO_2 partial pressure in feed on CO_2 separation performance

Change in CO_2 separation properties as a function of CO_2 partial pressure were studied with (1)~(4) hybrid membranes and the results were shown in figure 6. As observed, Q_{CO_2} decreased with increasing CO_2 partial pressures in the feed gas. Conversely, H_2 permeance was relatively constant and only decreased slightly as CO_2 partial pressure increased. A decrease in the permeance of CO_2 as pressure increases is typically observed when gas separation takes place via an improved transport mechanism process [11], as indicated by the CO_2 chemical sorption i.e., CO_2 sorption might reach near saturation at relatively low CO_2 partial pressure as indicated in (1) PAMAM/PEGDMA/4GMAP = 50.0/42.5/7.5 (wt%) hybrid membrane showed great decrease in Q_{CO_2} at high applied CO_2 high

pressure. Choline addition showed little decrease in Q_{CO_2} at high applied CO_2 high pressure because of its space inhibitor as much reaction-inhibiting PAMAM with CO_2 . [Choline][Pro] addition exhibited little decrease in Q_{CO_2} and showed high Q_{CO_2} at high applied CO_2 high pressure. [Choline][Pro] was found to absorb CO_2 by both chemical and physical sorption occurring at high applied CO_2 pressure [12]. Physical absorption was dominated by Van der Waals forces, and exhibit an easier desorption process resulting in transported CO_2 desorption fast from permeate side of membrane, so [Choline][Pro] addition membrane showed high Q_{CO_2} .

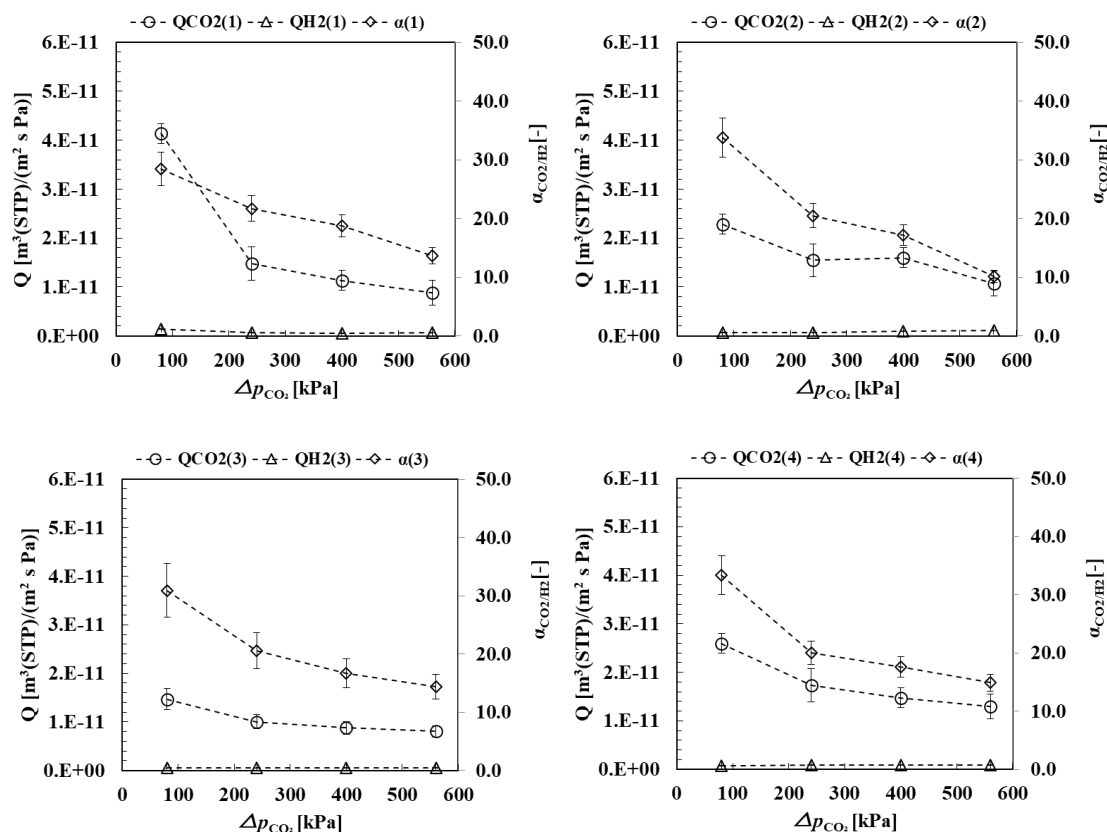


Figure 6. CO_2 separation properties of membranes as a function of CO_2 partial pressure.

3.3. Additive effect on CO_2 separation performance

The effect of various additive on CO_2 separation properties of membrane were shown in figure 7 at 0.56KPa of CO_2 partial pressure in feed. The membrane with addition [Choline][Pro] exhibit high CO_2 separation performance under higher pressurized conditions. The $\alpha(CO_2/H_2)$ and $Q(CO_2)$ are 14.9 and $1.30 \times 10^{-11} m^3(STP) m^{-2} s^{-1} Pa^{-1}$, respectively, at 0.56 MPa of $\Delta p(CO_2)$ and 0.70 MPa of total pressure. As result, addition of [Choline][Pro] into PAMAM/PEG membrane, Q_{CO_2} of PAMAM/PEG hybrid membranes increased 46% without change of selectivity of membrane for CO_2 . Addition of [Choline][Pro] in PAMAM/PEG membrane could enhance the rates of absorption and desorption of CO_2 [10] shown in figure 8. [Choline][Pro] are able to absorb CO_2 at low CO_2 partial pressure through a chemical reaction or chemical bonding. If the partial pressure of CO_2 is further increased, there will be a steady increasing as loading with an increase in pressure, providing evidence that both chemical and physical sorption are occurring at high applied CO_2 pressure with [Choline][Pro] [8, 12]. Choline[Pro] shows the effect facilitated transport of CO_2 though membrane by chemical and physical sorption.

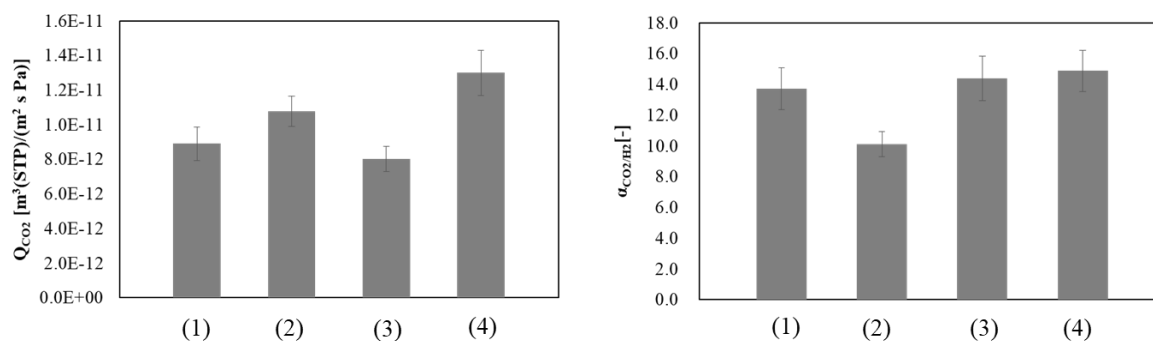


Figure 7. Various additive effect on CO₂ separation properties of membranes.

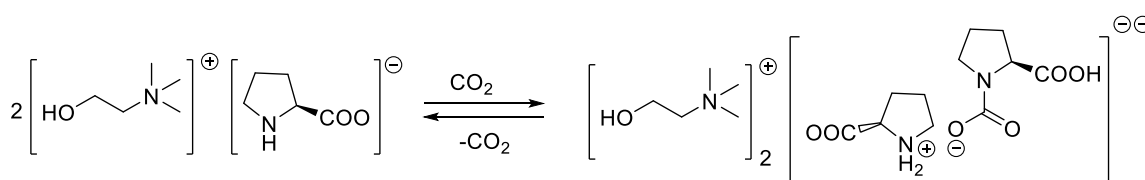


Figure 8. Schematic illustration of absorption and desorption of CO₂ by the IL [Choline][Pro]

4. Conclusions

The effect of addition of proline, choline, [Choline][Pro] on CO₂ separation properties of membrane were studied. The membrane with addition 2.5wt% [Choline][Pro] exhibits high CO₂ separation performance under higher pressurized conditions. The reason is addition of [Choline][Pro] in PAMAM/PEG membrane could enhance the rates of absorption and desorption of CO₂. The PAMAM dendrimer/PEG with addition of [Choline][Pro] shows a potential for CO₂ separation from H₂ at an elevated pressure such as IGCC practical use.

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References

- [1] Liu A, H Liang 2011 Strategy for promoting low-carbon technology transfer to developing countries: The case of CCS *Energy Policy* **39** 3106–3116
- [2] Hegerl G, Stott P 2014 Atmospheric science. From past to future warming *Science* **343** 844–845.
- [3] Nagumo R, Kazama S and Fujioka Y 2009 Techno-economic evaluation of the coal-based integrated gasification combined cycle with CO₂ capture and storage technology *Energy Procedia* **1** 4089–4093
- [4] Chu S, Majumdar A 2012 Opportunities and challenges for a sustainable energy future *Nature* **488** 294–303.
- [5] Taniguchi I, Duan S, Kazama S and Fujioka Y 2008 Facile fabrication of a novel high performance CO₂ separation membrane: immobilization of poly(amidoamine) dendrimers in poly(ethyleneglycol) networks *Journal of Membrane Science* **322** 277–280
- [6] Taniguchi I, Kai T, Duan S and Kazama S 2013 PAMAM Dendrimer Containing Polymeric Membrane for Preferential CO₂ Separation Over H₂—Interplay between CO₂ Separation Properties and Morphology *Energy Procedia* **37** 1067–1075

- [7] Kovvali A S, Chen H and Sirkar K K 2000 Dendrimer membranes: A CO₂-selective molecular gate *Journal of the American Chemical Society* **122** 7594–7595
- [8] Hu G P, Smith K, Wu Y, Kentish S and Stevens G 2017 Recent progress on the performance of different rate promoters in potassium carbonate solvents for CO₂ capture *Energy Procedia* **114** 2279 – 2286
- [9] Hu S Q, Jiang T, Zhang Z F, Zhu A L, Han B X, Song J L, Xie Y and Li W J 2007 Functional ionic liquid from biorenewable materials: synthesis as a and application catalyst in direct aldol reactions *Tetrahedron Letters* **48** 5613-5617
- [10] Li X Y, Hou M Q, Zhang Z F, Han B X, Yang G Y, Wang X L and Zou L Z 2008 Absorption of CO₂ by ionic liquid/polyethylene glycol mixture and the thermodynamic parameters, *Green Chemistry* **10** 879 – 884
- [11] Zou J, Ho W S W 2006 CO₂-selective polymeric membranes containing amines in crosslinked poly(vinylalcohol) *Journal of Membrane Science* **286** 310–321
- [12] Wang C M, Lou H M, Jiang D E, Li H R and Dai S 2010 Carbon dioxide capture by superbase-derived protic ionic liquids *Angewandte Chemie International Edition* **49** 5978–5981