



Piperazine-immobilized polymeric membranes for CO₂ capture: mechanism of preferential CO₂ permeation

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Abstract

Amines are incorporated into various membranes to improve their CO₂ separation performance. With amine-containing polymeric membranes, gas transport properties are often enhanced under humidity, where CO₂ migrates through the membranes in the form of bicarbonate ions. Piperazine (Pz) and its derivatives are known to catalyze the conversion of CO₂ to bicarbonate ions and have been used in liquid amine scrubbing technology. Piperazines were immobilized in poly(vinyl alcohol) (PVA), and the resulting polymeric membranes showed high CO₂ separation performance over H₂ and CH₄. The gas transport properties were dependent on the chemical structure of the amines. In particular, 3-(1-piperazinyl)-1,2-propanediol (PzPD)-containing polymeric membranes gave excellent CO₂ separation performance, and the CO₂ permeability and CO₂ selectivity over CH₄ were 1060 Barrer and 370, respectively, at 50 °C and 90% relative humidity with a transmembrane CO₂ pressure of 11 kPa. The interaction between PzPD and CO₂ was quantitatively studied by inverse-gate decoupling ¹³C NMR spectroscopy. CO₂ interacted with the secondary amino group on the Pz ring to form a carbamate, which was readily hydrolyzed to produce bicarbonate ions. The hydroxyl group on the C2 carbon of PzPD facilitated the interaction between CO₂ and the amine through hydrogen bonding, resulting in enhanced diffusivity of CO₂ in the membranes.

Introduction

In addition to promoting renewable energy and innovating energy-saving technologies, CO₂ capture and utilization/storage (CCUS) is one of the most plausible options to mitigate CO₂ emissions causing climate change issues [1–3]. Approximately 20 full-scale CCS demonstrations are currently ongoing worldwide to validate the approach. For example, the Sleipner project in the North Sea has been

operating since 1996, and 0.9 MMt of captured CO₂ from natural gas sweetening has been injected annually into an aquifer under a seabed [4]. However, CCUS technologies have not been commercialized due to the high capital and operational cost, in which the CO₂ capture cost accounts for ~60 % [5]. Current CO₂ capturing has been carried out by liquid amine scrubbing at the demonstration scale [4]. CO₂ at the mass emission source is separated over other gaseous species by passing the target gas through an aqueous amine solution, followed by CO₂ regeneration by heating. Even with CO₂ capture at thermal power stations, the heating process is energy intensive and results in high energy consumption and cost. Thus, lower-energy alternative CO₂ capture technologies are required for the implementation of CCUS, and membrane separation is one of the potential technologies [6].

In gas separation by membranes, the separation proceeds spontaneously based on the transmembrane pressure difference of a gaseous species of interest, and additional energies, such as heating, are not required. A number of membranes, including organic, inorganic, and hybrid membranes such as mixed matrix membranes, have been developed for CO₂ separation [6–11]. Among these

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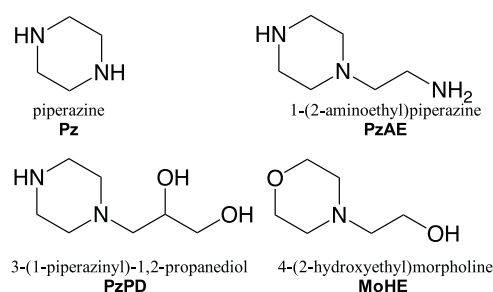
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Fig. 1 Chemical structure of amines used in this study and a typical amine-containing polymeric membrane (PzPD: 50 wt%, 5.8 μm)



membranes, organic or polymeric membranes hold potential due to their synthetic feasibility, scalability and processability as well as cost effectiveness, although inorganic membranes show higher CO_2 separation performance than that of organic membranes. For example, a comb copolymer poly(vinyl chloride)-graft-poly(oxyethylene methacrylate) can be readily synthesized by atom transfer radical polymerization and holds potential in various applications, including CO_2 capture [12]. However, only a few polymeric membranes, such as the Polaris® by Membrane Research Technology Inc. (MTR) for post-combustion CO_2 capture at the National Carbon Capture Center in the USA, have reached pilot-scale demonstration [13, 14].

While MTR's membranes display a benchmark in CO_2 capture by membranes, their separation performance is still insufficient for commercialization [15]. To improve gas transport properties, amines have been incorporated into polymeric membranes as CO_2 carriers, and CO_2 diffusion in the membranes increased by facilitated transport, as represented by Ho's work [16–19]. With amine-containing membranes, several research groups reported a significant increase in CO_2 permeability under highly humidified conditions [20]. The authors found that a part of the sorbed CO_2 in the membranes became bicarbonate ions under humidity and that this ionic form was the major migrating species across the membranes [21, 22]. Enhancement of bicarbonate ion formation is a key to elevating CO_2 permeability for amine-containing polymeric membranes.

Pz and its derivatives, which are known to accelerate CO_2 absorption in chemisorbents, have been used as additives in liquid amine scrubbing, i.e., aqueous mixtures of various amines [23–29]. In the sorbent, CO_2 first reacts with Pz to form a carbamate, which is readily hydrolyzed to produce bicarbonate ions under basic conditions. Thus, Pz would be effective in elevating the CO_2 permeability of amine-containing polymeric membranes. Herein, Pz and its derivatives in Fig. 1 were incorporated into PVA membranes, and CO_2 separation of the resulting membranes was examined to investigate the interaction between the chemical structure of the amines and the gas transport properties of the membranes. The mechanism of preferential CO_2 permeation was also studied.

Experimental

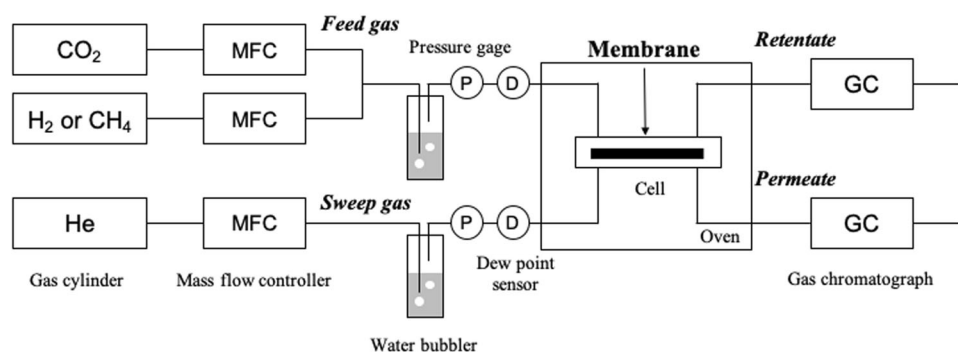
Materials

Pz and PVA (M_w : 60,000; saponification: $\geq 98\%$) were purchased from Wako (Osaka, Japan) and Merck Millipore (Darmstadt, Germany), respectively. PzPD, 1-(2-aminoethyl)piperazine (PzAE), and 4-(2-hydroxyethyl)morpholine (MoHE) were kindly gifted by Tosoh Corp. (Tokyo, Japan), and other chemicals were of reagent grade and used without further purification. High-purity gases ($<99.99\%$) were used for the CO_2 separation experiment.

Gas permeation experiment

Polymeric membranes were prepared by casting an aqueous mixture of amines and PVA with predetermined mixing ratios. Typically, PVA (5.0 g) was added to 95 g of deionized water, and the mixture was refluxed at 90°C for at least 12 h to dissolve PVA in water completely. A 0.50 g aliquot of Pz (58 mmol) was added to 10 g of the PVA solution obtained. The resulting mixture was filtered with a membrane filter (nominal pore size: $0.1\ \mu\text{m}$) to remove dust particles, cast on a plastic Petri dish (ϕ : 5.5 cm), and dried at ambient temperature for 2 days. The obtained membranes were further dried 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 a transparent, self-standing membrane with a thickness of $3\text{--}10\ \mu\text{m}$ was used in this study, as shown in Fig. 1.

The gas separation properties of the obtained amine-containing polymeric membranes were determined under isobaric conditions. The polymeric membranes were placed on a porous poly(vinylidene difluoride) support with a nominal pore size of $0.45\ \mu\text{m}$ (Durapore® membrane filter, HVLP02500, Merck Millipore), and the thin-film composite (TFC) membrane was set in a custom-made flat sheet membrane cell, in which the effective membrane area was $2.27 \times 10^{-4}\ \text{m}^2$ [30]. A CO_2 /gas mixture was humidified by passing through a water bath and fed to the membrane cell, while humidified He was supplied to the permeate side of the cell as a sweep gas. Here, the relative humidity on both

Fig. 2 The gas separation system used in this study

sides was identical to avoid the effect of water vapor transportation across the membranes. Gaseous species in both the retentate and permeate were quantified on an Agilent 7890 A gas chromatograph with a thermal conductivity detector and a pulsed discharge helium ionization detector, respectively (Agilent Technologies, Tokyo, Japan). The gas separation system used is schematically drawn in Fig. 2. The gas permeability coefficient P_i and permeance Q_i of gas i were defined by the following Eqs. 1 and 2.

$$P_i = N_i(\text{STP}) \cdot l/A \cdot t \cdot \Delta p_i, \quad (1)$$

$$Q_i = P_i/l = N_i(\text{STP}) \cdot l/A \cdot t \cdot \Delta p_i, \quad (2)$$

where $N(\text{STP})$, l , A , t , and Δp are the gas flux at standard temperature and pressure, membrane thickness of the thin film, effective membrane area, transmission time, and transmembrane pressure difference, respectively.

Molar fraction ratios in retentate x and permeate y gave a gas selectivity of $\alpha(i/j)$. In the gas separation experiments, the stage-cut (permeate/feed $\times 100$) was less than 3%, and the selectivity was thus able to be approximated as a ratio of permeability coefficients of gases i and j in Eq. 3.

$$\alpha(i/j) = (y_i/y_j)/(x_i/x_j) \doteq P_i/P_j. \quad (3)$$

Membrane swelling under humidity

A PzPD-containing PVA membrane with an amine content of 60 wt% was kept at 40 °C under saturated water vapor in a vacuum oven, and the weight increase was monitored as a function of time. The swelling ratio S was calculated as follows.

$$S = (W_t - W_0)/W_0 \times 100, \quad (4)$$

where W_0 and W_t were the initial dry weight (ca. 0.3 g each) and the weight at time t of the membranes, respectively. The ratio was averaged and is expressed with standard errors ($n = 3$).

NMR study

The interaction between PzPD and CO₂ in D₂O was quantitatively investigated by inverse-gate decoupling ¹³C NMR. A 600 μL aliquot of a PzPD/D₂O mixture with a molar ratio of 8.9×10^{-2} was put into an NMR tube that was sealed with a silicone rubber septum. Humidified CO₂/H₂ (20/80 by vol.) was introduced into the NMR tube through a syringe for 24 h at ambient temperature, which allowed for CO₂ absorption equilibrium to be reached. Prior to conducting the ¹³C NMR experiments, T_1 values of carbons were determined, and the largest value was 5.1 s at 162.6 ppm. Thus, the ¹³C NMR spectrum was obtained by the accumulation of 1024 resonances with a pulse interval of 30 s, by which the nuclear Overhauser effect was minimized. Benzene-*d*₆ in a capillary was used as an internal standard.

Results and discussion

CO₂ separation performance of Pz-containing TFC membranes

Various amine-containing polymeric membranes were successfully prepared by a simple solution casting of aqueous amine and PVA mixtures. The resulting membranes were placed on a porous PVDF support for the gas permeation experiment, in which the thin-film dense PVA layer, or a CO₂-selective layer, determined the gas transport properties. Figure 3 represents the CO₂ separation performance of the TFC membranes over CH₄ at 313 K under 90% relative humidity and $\Delta p(\text{CO}_2)$ of 11 kPa. In comparison to Pz and its derivatives, a MoHE-containing TFC membrane displayed very low CO₂ selectivity over CH₄, with a CO₂ permeability coefficient $P(\text{CO}_2)$ of 28.8 Barrer (1 Barrer = $7.5 \times 10^{-18} \text{ m}^3(\text{STP})\text{m}/(\text{m}^2\text{sPa})$) and a CO₂ selectivity $\alpha(\text{CO}_2/\text{CH}_4)$ of 5.5. The tertiary amino group of MoHE was not efficient at raising the CO₂ solubility of the dense polymeric layer or working as a CO₂ carrier in the thin-film layer, while the immobilized-Pz TFC membranes

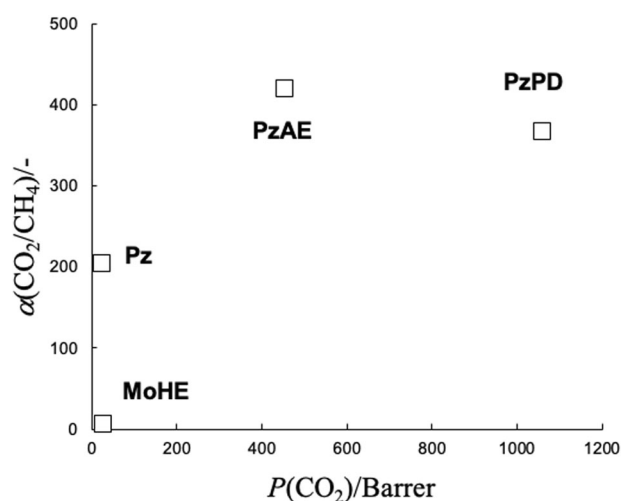


Fig. 3 CO_2 separation properties of various amine-containing polymeric membranes over CH_4 at 313 K under 90% relative humidity and a $\Delta p(\text{CO}_2)$ of 11 kPa

displayed preferential CO_2 permeation over CH_4 under the operating conditions.

The gas transport properties were strongly dependent on the amines, and the PzAE-containing membrane showed much higher CO_2 separation performance than that of the Pz-containing membrane. The primary amino group of PzAE interacts with CO_2 more readily than the secondary amino group of the Pz ring due to lower steric hindrance and a higher electron density on the nitrogen atom, resulting in elevated CO_2 solubility in the membrane. However, the PzPD-containing membrane exhibited a further enhanced $P(\text{CO}_2)$ of 1060 Barrer with a slightly lower $\alpha(\text{CO}_2/\text{CH}_4)$ of 370 in comparison to those of the PzAE-containing membrane: 460 Barrer for the $P(\text{CO}_2)$ and 420 for $\alpha(\text{CO}_2/\text{CH}_4)$. Although the Pz derivatives have similar carbon skeletons, PzPD, bearing two hydroxyl groups, gave higher CO_2 permeability than that of PzAE, which has a primary amino group. Hereafter, we focused on CO_2 separation by PzPD-containing membranes, and the details of the CO_2 transport mechanism are discussed later.

Effect of amine content on gas transport properties

To investigate the mechanism of preferential CO_2 permeation, the effect of the amine content of a CO_2 -selective layer was first examined. The amine-containing polymeric membranes were prepared by solution casting, and self-standing membranes were obtained when the amine content was up to 80 wt%. Figure 4 displays the CO_2 separation properties over H_2 as a function of the amine content at 323 K under a relative humidity of 90% and a $\Delta p(\text{CO}_2)$ of 45 kPa. The gas transportation was strongly dependent on the amine content in the thin-film layer, and preferential CO_2 permeation was achieved over H_2 . The $P(\text{CO}_2)$ increased in

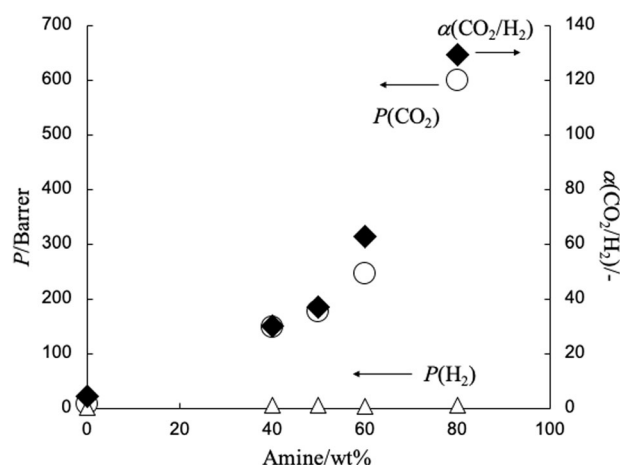


Fig. 4 Effect of PzPD content on the CO_2 separation performance of amine-containing TFC membranes (PzPD: 60 wt%) at 323 K under relative humidity of 90% and a $\Delta p(\text{CO}_2)$ of 45 kPa

proportion to the amine content, while the $P(\text{H}_2)$ was almost constant over the amine contents examined. Thus, the $\alpha(\text{CO}_2/\text{H}_2)$ increased with increasing amine content. The CO_2 permeability coefficient and the selectivity reached 600 Barrer and 130, respectively, with an amine content of 80 wt%. The obtained results can be explained by typical carrier-mediated CO_2 transportation.

With the thin-film layer containing 80 wt% PzPD, trace amine leakage was found from the TFC membrane under highly humidified conditions, although it did not cause a serious reduction in the gas separation performance. The amine content was then fixed at 50 or 60 wt% in the following investigations.

Effect of relative humidity on gas transport properties

The CO_2 separation performance of amine-containing membranes is often significantly influenced by humidity [20], although few reports discussed the details [22]. A time course of the gas transport properties under humidity is illustrated in Fig. 5a. The polymer matrix PVA is known to represent the nature of gas barriers [31, 32] and has been used for rapping films in various fields [33]. The TFC membrane was first in a dry state and exhibited very low gas permeability, and the permeability increased gradually with the introduction of a humidified gas. PVA and amines are highly hygroscopic, and the selective layer swelled by water vapor absorption in the gas separation experiments. This would result in an increased fractional free volume in the membranes, and the gaseous species could readily penetrate through the membrane. The water uptake was also verified by measuring the weight of the membrane under saturated water vapor at 40 °C, as shown in Fig. 5b. An increase in the membrane weight was observed for the first 6 h, and

Fig. 5 Change in CO₂ separation properties of PzPD-containing TFC membranes (PzPD: 50 wt %) as a function of time at 313 K under relative humidity of 90% and a $\Delta p(\text{CO}_2)$ of 40 kPa (upper) and change in weight of the TFC membranes as a function of time under saturated water vapor at 313 K

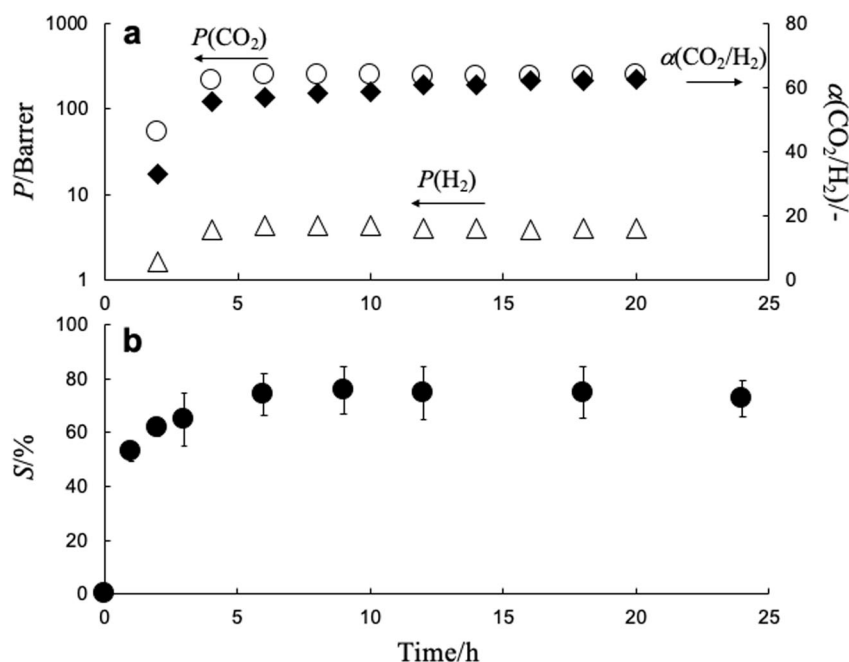
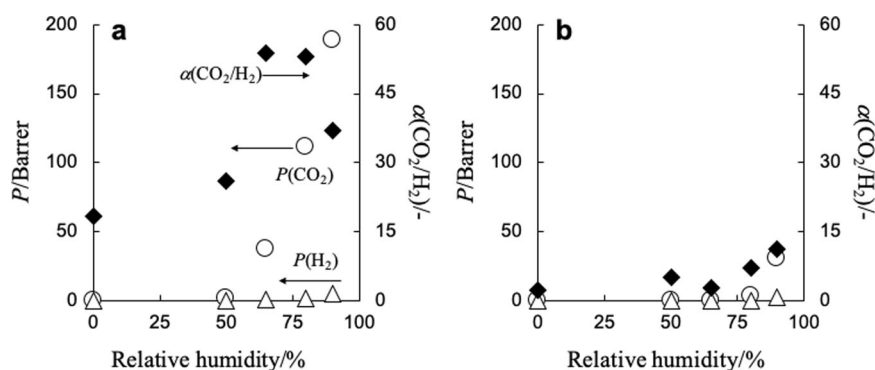


Fig. 6 Effect of relative humidity on CO₂ separation properties of TFC membranes at 313 K and a $\Delta p(\text{CO}_2)$ of 40 kPa: **a** with PzPD (50 wt %); **b** without PzPD



thereafter, the water uptake reached equilibrium with a 72 wt% increase in the membrane weight. The uptake profile was substantially in agreement with the change in gas permeabilities shown in Fig. 5a. In comparison to the increase in H₂ permeation, CO₂ permeability was further elevated upon humidification, which triggered a significant increase in $\alpha(\text{CO}_2/\text{H}_2)$ in the first 6 h. It should be noted that while the $P(\text{CO}_2)$ became constant at 250 Barrer after 6 h, the $P(\text{H}_2)$ slightly decreased by 2.8×10^{-2} Barrer/h. A gradual increase in the CO₂ selectivity was thus confirmed from 57 to 63 over 14 h even in an equilibrium state of water uptake.

Humidity is one of the crucial factors impacting the CO₂ separation properties of amine-containing TFC membranes, and the effect of relative humidity was validated in Fig. 6a. While the gases hardly penetrated the membranes under dry conditions, gas permeation was found under humidified conditions. With the amine-containing TFC membrane, the

$P(\text{CO}_2)$ was very low, i.e., 2.5×10^{-2} and 2.0 Barrer under a relative humidity of 0% and 50, respectively. However, the values showed exponential growth and reached 190 Barrer at a relative humidity of 90%. On the other hand, $P(\text{H}_2)$ also increased from 2.5×10^{-2} to 5.0 Barrer upon humidification. A significant, 7600-fold increase in $P(\text{CO}_2)$ was found, while the $P(\text{H}_2)$ increased 380-fold. As a consequence, the CO₂ selectivity was elevated under humidified conditions. A decrease in the selectivity under higher relative humidity, from 80 to 90%, was due to a further increase in the fractional free volume, which would help nonspecific permeation of H₂, which is smaller than CO₂. In contrast, a pristine PVA TFC membrane displayed much lower gas permeabilities, as shown in Fig. 6b. Even the polymer matrix exhibited CO₂-selective permeation over H₂ under humidified conditions. The CO₂ selectivity under a relative humidity of 90% was 11, which could be explained by the difference in gas solubility of the absorbed water but not of

Fig. 7 Inverse-gate decoupling ^{13}C NMR spectra of PzPD/ D_2O before (bottom) and after (upper) equilibrium under humidified CO_2/H_2 at 298 K

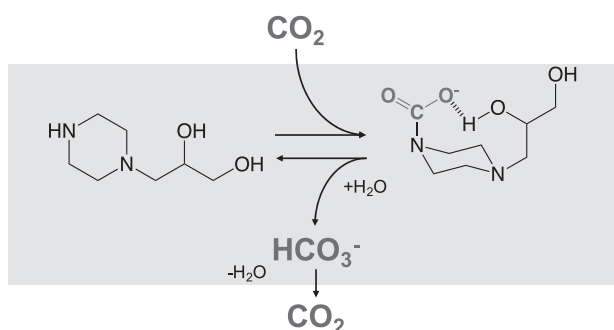
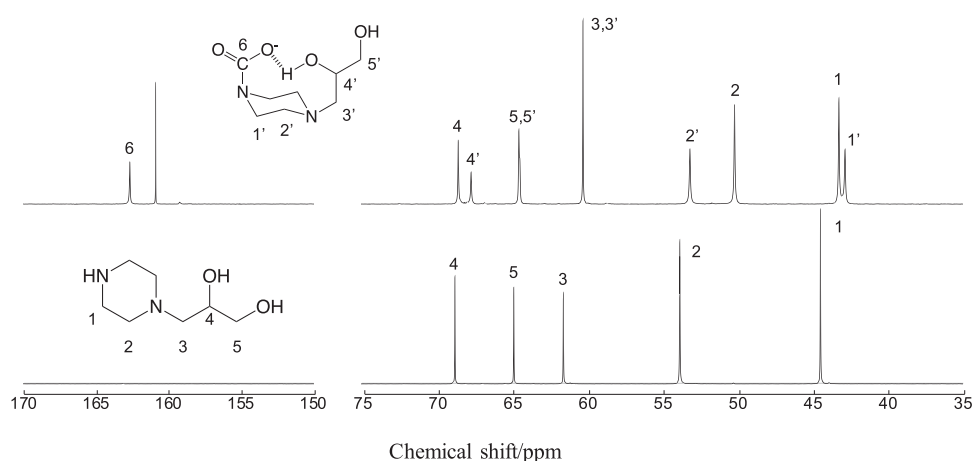


Fig. 8 A schematic drawing of CO_2 permeation through a PzPD-containing PVA membrane

the polymer matrix. According to the reference values, the gas solubilities of CO_2 and H_2 in water at 40°C and 1 atm are 0.53 and $0.016\text{ cm}^3(\text{STP})/\text{cm}^3\text{-H}_2\text{O}$, respectively [34]. The composition of CO_2 and H_2 in the feed gas was 20/80 by vol. and thus the volume ratio of CO_2/H_2 dissolved in water could be 8.3 under these conditions. These results suggested that the enhanced CO_2 permeation was brought about by the amine and the absorbed water in the thin-film layer. In addition, the PVA was negligible in the preferential permeation of CO_2 .

Interaction between Pz derivatives and CO_2

The PzPD-containing PVA membranes swelled during water vapor absorption under humidity. After reaching equilibrium, the weight ratio of PVA:PzPD:water was calculated as 23:34:43 by weight and thus the molar ratio of PzPD/water was 8.9×10^{-2} . The interaction between PzPD and CO_2 was studied by inverse-gate decoupling ^{13}C NMR. A PzPD/heavy water mixture (8.9×10^{-2} by mol) was equilibrated under humidified CO_2/H_2 (20/80 by vol.). The ^{13}C NMR spectra before and after equilibrium are shown in Fig. 7. After introducing CO_2 , new peaks were observed at

160.9 and 162.6 ppm and were assigned as carbons of the bicarbonate ion and carbamate, respectively [25]. Bicarbonate ions can be formed only in the presence of water. With the results obtained above, it could be concluded that CO_2 would permeate through the membranes in the form of bicarbonate ions.

On the other hand, the peaks of carbons of a Pz ring at 44.5 and 53.8 ppm were split into two peaks at 42.9 and 43.3 ppm and 50.3 and 53.2 ppm, respectively. CO_2 interacted with the secondary amino group during the formation of a carbamate. Here, the peak of a methylene carbon at 61.6 ppm adjacent to the tertiary amino group was not split, which suggested that the tertiary amino group was not involved in the interaction with CO_2 . This was supported by the much lower CO_2 separation properties of a MoHE-containing TFC membrane than those of the Pz membranes in Fig. 3.

In addition to the peak shifts relating to carbamate formation between the secondary amino group and CO_2 , another peak splitting of the C2 carbon was found. An integral value of the peak at 67.8 ppm was half of those at 42.9 and 53.2 ppm (carbons of Pz) and identical to that at 162.6 ppm (a carbon of carbamate), which suggested that the hydroxyl group on the C2 carbon also participated in the interaction with CO_2 . A plausible chemical structure is given in Fig. 7 by taking into consideration suitable bond angles. Hydrogen bonds formed between the carbamate and hydroxyl groups, which were also reported when alkanolamines interacted with CO_2 [35, 36]. This facilitated the interaction between the amines and CO_2 , and the PzPD membrane exhibited higher CO_2 separation performance than the PzAE membrane, even though PzPD did not have a primary amino group. In addition, the ^{13}C NMR spectrum indicated that 40% of PzPD in the selective layer interacted with CO_2 , while the rest stayed intact in an equilibrium state and that CO_2 existed as bicarbonate ions and carbamate at a molar ratio of 43/57.

A CO₂ transport mechanism was determined from the obtained experimental results, as shown in Fig. 8. CO₂ solubility in the selective layer was increased by the incorporation of the amine into the PVA matrix. CO₂ first interacted with the secondary amino group of Pz with the formation of a carbamate, which was further facilitated by forming a hydrogen bond with an adjacent hydroxyl group in the case of PzPD. The carbamate was then readily hydrolyzed to produce bicarbonate ions under relatively high humidified conditions, while a carbamate with primary amino groups was hardly hydrolyzed. Since CO₂ was converted to ionic species in the membrane, the increased ionic strength reduced the solubility of nonpolar H₂, leading to suppression of the gas permeation by enhancing CO₂ selectivity. While the CO₂ permeability became constant after reaching an equilibrium swelling state, a continuous and slight decrease in H₂ permeability in Fig. 5a was explained by this salting out effect, leading to a slight increase in CO₂ selectivity.

Conclusion

Increased CO₂ permeation under humidity through amine-containing polymeric membranes has been reported and was explained by the formation of bicarbonate ions in the presence of water, a major migrating species [22]. The effect of Pz incorporation into polymeric membranes on the CO₂ separation performance was investigated under various operating conditions. The separation performance was strongly dependent on the chemical structure of the amines, and PzPD gave the highest gas transport properties among the four amines examined. With PzPD-containing membranes, a drastic enhancement in CO₂ permeability was confirmed due to the efficient formation of bicarbonate ions under humidified conditions. The developed amine-containing TFC membranes expressed much higher CO₂ separation performance than that of PAMAM membranes and similar CO₂ separation performance to monoethanolamine-containing TFC membranes in a previous study, although the operating conditions were not exactly the same [37]. Some simulation results revealed the role of hydroxyl groups of alkanolamines in facilitating carbamate formation and subsequent bicarbonate ion production upon hydrolysis [35, 36]. Solid or direct experimental results were not obtained to validate hydrogen bonding between the hydroxyl group and carbamate except for the ¹³C NMR result. However, the alkanolamine PzPD provided a greater CO₂ permeability than that of PzAE with a slightly lower CO₂ selectivity, as they have similar carbon skeletons.

Pz is known as an additive for the catalysis of bicarbonate ion formation from CO₂ in chemisorbents for post-combustion CO₂ capture. Further improvement of CO₂ separation

performance could be achieved by the addition of Pz to amines in CO₂-selective membranes.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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