A study of gas transport through interfacially formed poly(*N,N*-dimethylaminoethyl methacrylate) membranes

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ARTICLE INFO

ABSTRACT

Gas transport through interfacially formed poly(*N,N*-dimethylaminoethyl methacrylate) membranes was investigated. The membrane performance for the separation of binary CO_2/N_2, CO_2/CH_4 and CO_2/H_2 mixtures was studied, and the coupling effects between the permeating species were evaluated by comparing the permeance of individual components in the mixture with their pure gas permeance. For the permeation of these binary gas mixtures, the presence of CO_2 was shown to influence the permeation of the other components (i.e., N_2, H_2 and CH_4), whereas the permeation of CO_2 was not affected by these components. In consideration that water vapor is often encountered in applications involving CO_2 separation, the presence of water vapor on the membrane permselectivity was also studied. When hydrated, the membrane was shown to be more permeable to CO_2, while the membrane selectivity did not change significantly. Unlike membranes based on size-sieving of penetrant molecules, the present membranes exploit the favorable interactions between the hydrophilic quaternary amines in the membrane and CO_2, especially in the presence of water vapor in the feed.

1. Introduction

There is a great need for membrane-based CO_2 separation in many industrial applications, including flue gas separation for greenhouse gas emission control, landfill gas upgrading, natural gas sweetening, and hydrogen production by water shift reaction. For selective separation of CO_2 from the gas mixtures, membranes with such functional groups as amino groups which can interact with CO_2 strongly are expected to yield a high permselectivity for CO_2 permeation. In our previous work [1], a polyamine (e.g., poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA)) was coated on a microporous polysulfone (PSF) substrate, followed by a solid–liquid interface crosslinking, thereby forming a thin film composite membrane. The weak acid–base interactions between CO_2 molecules and the amine moieties in PDMAEMA enhance the selective solubility of CO_2, and the interfacial crosslinking can induce an asymmetric structure in the skin layer in terms of the crosslinking density. The crosslinking initially occurred at the outer surface of the coating layer and the crosslinked surface restrained further diffusion of the crosslinking molecules to the interior part of the coating layer. As a result, the outer surface of the coating layer was highly crosslinked, and interior region was less crosslinked. The highly crosslinked outer surface dominated the permselectivity,

and the less crosslinked interior region offered low resistance to permeation. Consequently, the PDMAEMA composite membranes showed a high gas permeation rate. When tested with pure gases, the membrane exhibited a CO_2 permeance of 80 GPU and a CO_2/N_2 permeance ratio of 50 at 23 °C and 308 kPa. Recently, Zhao et al. [2] studied a series of PDMAEMA–poly(ethylene oxide) copolymer membranes, which showed good permselectivity for CO_2/N_2 and CO_2/H_2 separation.

For many gas separation applications involving CO_2, the gas mixture is often moist or sometimes even saturated with water vapor. The presence of water vapor is expected to affect gas permeation through membranes especially for hydrophilic membranes. Gas diffusion in a membrane depends on the free volume and the mobility of the polymer chains. In a dry membrane, the free volume is relatively small and the mobility of the polymer segments is limited. When the membrane is hydrated, however, both the free volume and the polymer chain mobility will increase due to membrane swelling induced by water, and the resistance to gas diffusion is thus decreased. On the other hand, the solubility of CO_2 in the membrane can be enhanced by hydration because of the favourable solubility of CO_2 in water. Therefore, the presence of water is expected to increase both the solubility and diffusivity of the gas in the membrane. If the water content in the membrane is high enough, the water molecules may form clusters [3] which can function as a passageway for gas permeation as well. As such, gas transport in a water-swollen membrane can be considered to consist of transport in the polymer matrix and the transport in the

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Nomenclature

A	effective area of membrane
J	permeance
J^0	pure gas permeance
N	permeation flux
N^0	ideal permeation flux without coupling effect
N^*	limiting value of permeation flux at zero stage cut
p_h	feed gas pressure
p_l	permeate gas pressure
Δp	transmembrane pressure difference
Q	permeation rate
X	feed concentration (mol fraction)
Y	permeate concentration (mol fraction)
Y^*	limiting value of permeate concentration at zero stage cut
θ	permeation ratio

Subscripts

i and j	permeating species i and j

water phase. Because the gas solubility and diffusivity in water are usually higher than those in a polymer matrix, the permeability of a hydrated membrane is expected to be higher than a dry membrane. Therefore, the gas permeability in hydrophilic membranes can be improved significantly by incorporation of water, although the thickness of the resulting membrane may increase due to membrane swelling by water. Higuchi et al. [4] showed that the permeability of O_2 in a water-wet cellophane membrane was about 10^4 times higher than that in a dry membrane. Park and Lee [5] also showed that for gas permeation through a water-swollen membrane, the gas molecules pass mainly through the free volume which was filled by water, resulting in an enhancement in the gas permeability. In this work, the effects of water on the transport of CO_2 and N_2 through PDMAEMA membranes were investigated.

For gas mixtures, the presence of one component may affect the permeation of the other component, and such a coupling effect arises from the interactions between the permeants in the mixture or with the polymer. In comparison with pure gas permeation, the coupling effect may facilitate or impede the permeation of a given species. Positive coupling effect is often caused by membrane swelling or plasticization. When the sorbed amount of a permeant (e.g., strongly sorptive permeant CO_2, H_2O) in a polymer matrix is high enough, the local segmental motion of the polymer chains increases, leading to an increased diffusion coefficient [6,7]. The negative coupling effect, on the other hand, is often due to the competitive sorption and/or diffusion between the permeating components in a membrane. In principle, there are fixed amounts of sorption sites and transport passageways in the membrane, for which the competition among the permeating components tends to cause a reduction in the permeability [8,9]. As far as permeability is concerned, the effects of membrane swelling and plasticization counteract with competitive sorption and diffusion. Therefore, in comparison to pure gas permeability, the permeability of a component in a mixture may increase or decrease due to the presence of the other component, depending on the nature of the coupling effect [10–12].

In this work, the effects of feed composition and pressure on the permeation and separation behaviour of three CO_2-containing gas mixtures (i.e., CO_2/N_2, CO_2/CH_4, and CO_2/H_2) were studied and the permeabilities of individual components were compared with pure gas permeability in order to determine the coupling effect in the gas mixture permeation.

2. Experimental

2.1. Materials

Poly(*N,N*-dimethylaminoethyl methacrylate) was synthesized by free radical bulk polymerization in our lab [13]. Polysulfone (PSF) (P-1700) was obtained from Amoco Performance Products. Polyvinylpyrrolidone (PVP) (K30, molecular weight ~40,000) was supplied by Fluka Chemika. *p*-Xylylene dichloride (XDC) supplied by Sigma–Aldrich was used as the crosslinking agent. *N,N*-Dimethylacetamide (DMAc) (Acros Organics), ethanol (Fisher Scientific), heptane (Sigma–Aldrich) were used as solvents; they were all reagent grade and used without further purification. The gases used for the gas permeation experiments were of research grade (99.0–99.998% pure), and they were supplied by Praxair Specialty Gases and Equipment.

2.2. Membrane preparation

The polysulfone substrate membrane was prepared by the phase inversion technique. DMAc and PVP were used as the additive and the solvent, respectively, and water was used as the non-solvent. The detailed procedure has been described elsewhere [13]. The interfacially formed PDMAEMA/PSF composite membrane was prepared by coating a thin layer of PDMAEMA on the PSF substrate, followed by crosslinking with *p*-xylylene dichloride in a heptane solution [1]. Specifically, a PDMAEMA–ethanol solution at a concentration of 15 g/L was brought into contact with the surface of the polysulfone substrate for 15 min, and then the excess coating solution was removed, followed by air drying in a fume hood. The coated PDMAEMA surface was allowed to contact with a solution of *p*-xylylene dichloride dissolved in heptane at a concentration of 10 g/L so that alkylation reaction took place at the solid–liquid interface. After 5 h, the excess crosslinking solution was removed and the membrane surface was washed at least three times with heptane to remove the residual unreacted *p*-xylylene dichloride on the membrane surface. Finally, the membrane was air dried.

2.3. Gas permeation measurement

A schematic diagram of the apparatus for binary gas mixture permeation experiments is shown in Fig. 1. The PDMAEMA/PSF composite membrane was mounted in the permeation cell, and the effective area for permeation is 16.6 cm^2. The feed gas was humidified before admission to the feed side of the membrane, and the residue flow was controlled by a mass flow controller. The permeate gas exited at atmospheric pressure. The humidifier was removed
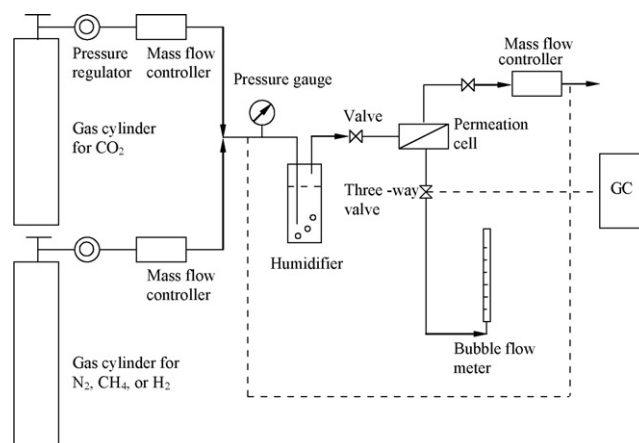

Fig. 1. Schematic diagram of experimental setup for gas permeation.

when measuring the gas permeability of dry membranes. The operating temperature was maintained at 23 °C. The binary feed gas mixtures were prepared using a dynamic gas blending system comprised of two Matheson mass flow controllers (Model 8270). When evaluating the effects of feed pressure and composition, a relatively high residue flow rate (about 60 cm³ (STP)/min) was used to minimize concentration polarization. The flow rates of the permeate and residue streams were measured by bubble flow meters. The compositions of the feed, residue and permeate streams were determined by an Agilent gas chromatograph (Model 6890N) equipped with a Supelco packed column (Carboxen-1000, 60/80) and a thermal conductivity detector. Quantitative evaluation was carried out by external calibration using standard samples of known concentrations. The permeance (J_i) of an individual component in the gas mixture through the membrane was determined by

$$J_i = \frac{Y_i Q}{A \Delta p_i} \tag{1}$$

where Q is the permeate flow rate, Y_i is the mole fraction of gas i in the permeate, A is the effective area of the membrane for permeation, and Δp_i is the partial pressure difference of gas i across the membrane. The permeation tests were repeated several times with replicate membrane samples from different batches, and the deviations in the reproducibility were found to be within 10%.

3. Results and discussion

3.1. Pure gas permeation

Fig. 2 shows the permeation fluxes of pure CO_2 and N_2 through the composite membrane with and without the presence of water vapor. The permeance of CO_2 and N_2 and the CO_2/N_2 permeance ratio are presented in Fig. 3. It was shown that the permeation
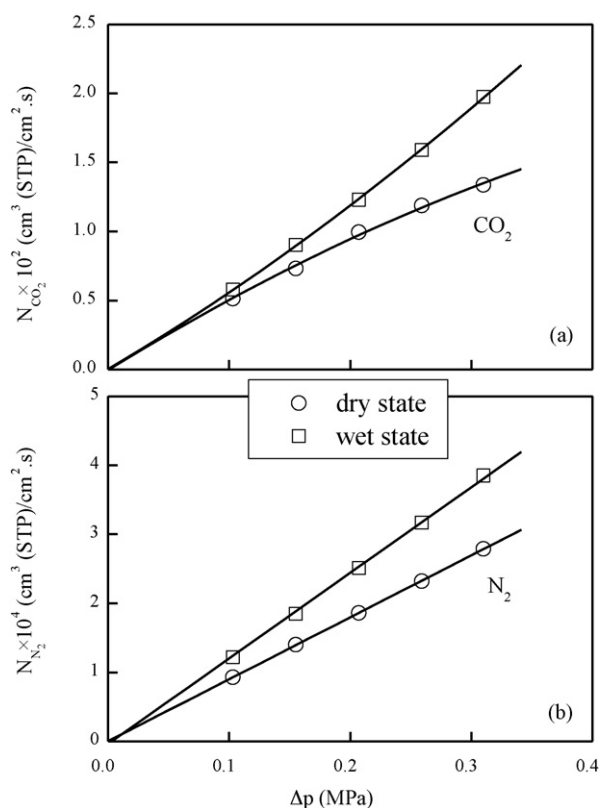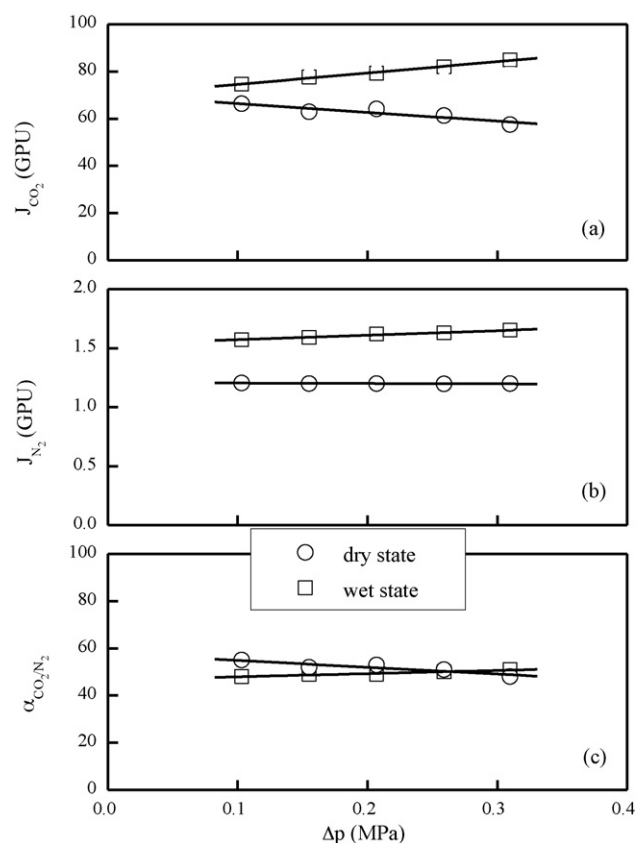

Fig. 3. A comparison of permeance and selectivity between hydrated and dry membranes.

flux of N_2 in the dry membrane was proportional to the transmembrane pressure difference, and thus the N_2 permeance was a constant under the experimental conditions tested. N_2 transport in the membrane occurs presumably by the simple solution–diffusion mechanism based on molecular diffusion. It is not surprising that CO_2 permeation does not follow the same trend because of the interactions between CO_2 molecules and the polymer. It may be postulated that the amino groups in the membrane act as fixed carriers for CO_2 transport, and there are two modes of transport occurring simultaneously in the membrane: free molecular diffusion and carrier-mediated transport. When the CO_2 pressure increases, the carriers in the membrane will be gradually saturated with CO_2 molecules, and the CO_2 flux due to carrier-mediated transport will approach constant. As a result, the overall CO_2 flux will increase with an increase in CO_2 pressure, but the rate of the increase in CO_2 will gradually diminish. Consequently, the CO_2 permeance gradually decreases as the pressure increases. This is typical of carrier-mediate transport.

When the membrane is hydrated, the permeance of a gas through a water-swollen membrane J can be considered to comprise of two parts: one through polymer matrix and the other through water passageways. The solubilities, diffusivities and the permeabilities of CO_2 and N_2 in water at 25 °C are shown in Table 1. The CO_2/N_2 selectivity based on permeation in water is 49.7, which is close to the CO_2/N_2 selectivity in the dry membrane. The high permselectivity of PDMAEMA to CO_2/N_2 is attributed to the amino groups in the polymer, which interact with CO_2 favorably. For many other hydrophilic membranes (e.g., poly(vinyl alcohol), chitosan and carboxyl methyl cellulose), the polymer matrixes themselves do not exhibit good CO_2/N_2 selectivities, and the overall permselectivity of the hydrogel membranes derives primarily from the contribution of water in the membrane [15].

Fig. 2. Permeation flux of pure CO_2 and N_2 through hydrated and dry membranes at different pressures.

Table 1
Solubility, diffusivity and permeability of gases in water (25 °C).

	S (cm^3 (STP)/cm^3 cmHg)[a]	D (cm^2/s)[a]	P (Barrer)[b]
CO_2	1.01×10^{-2}	1.91×10^{-5}	1923
N_2	1.94×10^{-4}	2.00×10^{-5}	38.7
H_2	2.31×10^{-4}	5.11×10^{-5}	118.1
CH_4	4.18×10^{-4}	1.49×10^{-5}	62.3

[a] From Ref. [14].
[b] The permeability was estimated from the solubility and the diffusivity data using $P = DS$.

It is worth noting that CO_2 molecules can interact with water to form ionic HCO_3^-. Zhang et al. [16] investigated a hydrolyzed polyvinylpyrrolidone membrane and confirmed that there exist complexes of CO_2 with active groups (i.e., secondary amine and carboxyl groups) as well as complexes of CO_2 with H_2O (i.e., HCO_3^-) when the membrane is humidified. PDMAEMA is also subjected to hydration and dissociation in water to form quaternary ammonium cations [13]. Matsuyama et al. [17] proposed that such a membrane should be called a fixed reaction site membrane or a catalytic membrane because the quaternary ammonium cations or tertiary amino groups can act as a weak base catalyst for CO_2 hydration.

Therefore, in humidified PDMAEMA membranes, facilitated transport of CO_2 through the functional groups in the membrane matrix and the water passageways take place simultaneously. The transport of CO_2 in water passageways is enhanced by the amino groups in the membrane, and the transport of CO_2 facilitated by the amino group carriers is improved by the hydration of CO_2. These interactions are expected to be more significant for CO_2 permeation at higher concentrations.

It should be pointed out that unlike other hydrophilic membranes mentioned before, the permeance of both CO_2 and N_2 through the hydrated PDMAEMA membranes was not substantially higher than that of the dry membrane. When hydrated, the membrane structure becomes "loose", which tends to increase the permeability, but the overall thickness of the membrane also increases due to membrane swelling. The enhanced permeability needs to compensate for the opposing effect of increased membrane thickness, and thus the permeance (that is, the permeability normalized by the membrane thickness) increased less significantly by the hydration. As far as the membrane selectivity is concerned, the CO_2/N_2 permeance ratio in the hydrated membrane is lower than that in the dry membrane at low pressures, and it gradually increases to exceed the dry membrane selectivity when the pressure is high enough. In general, the membrane hydration does not seem to affect the membrane selectivity significantly.

3.2. Binary gas permeation

When a gas mixture passes along the surface of a membrane, the driving force for the fast permeating component decreases gradually due to selective permeation through the membrane. Fig. 4 shows the CO_2 concentration in permeate and the total permeation flux at different stage cuts. Stage cut is the ratio of the permeate flow rate to the feed flow rate, representing the fractional amount of feed permeated through the membrane. A high CO_2 concentration in permeate was accompanied with a high permeation flux. With an increase in the stage cut, the permeation flux and concentration of CO_2 in permeate decrease. For a given feed composition, the flux and permeate CO_2 concentration reach maximum at the limit of zero stage cut. The permeation flux and permeate concentration relative to their maximum obtainable values (which are denoted by N* and Y*, respectively) are shown in Fig. 5. It is clear that at a given stage cut, the feed concentration does not significantly affect the relative permeate concentration, but the relative permeation flux decreased remarkably with an increase in the CO_2 concentration in
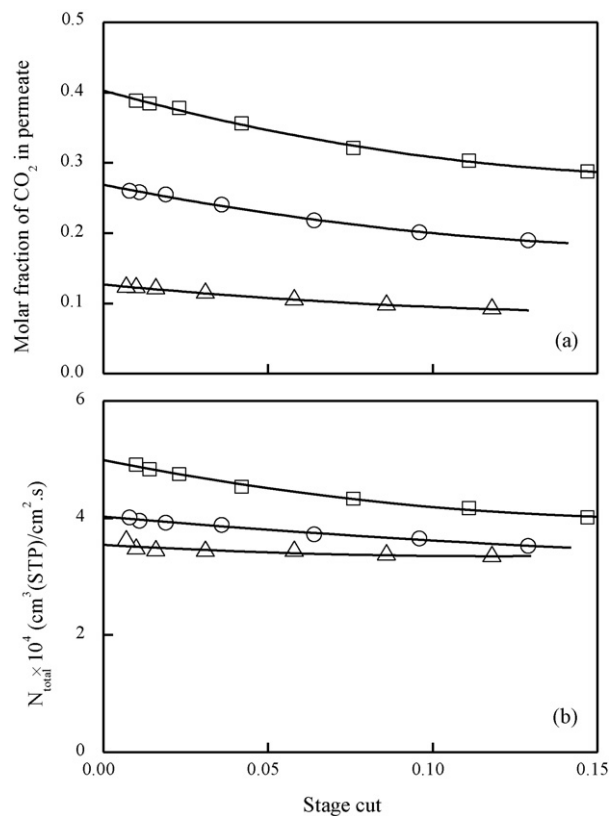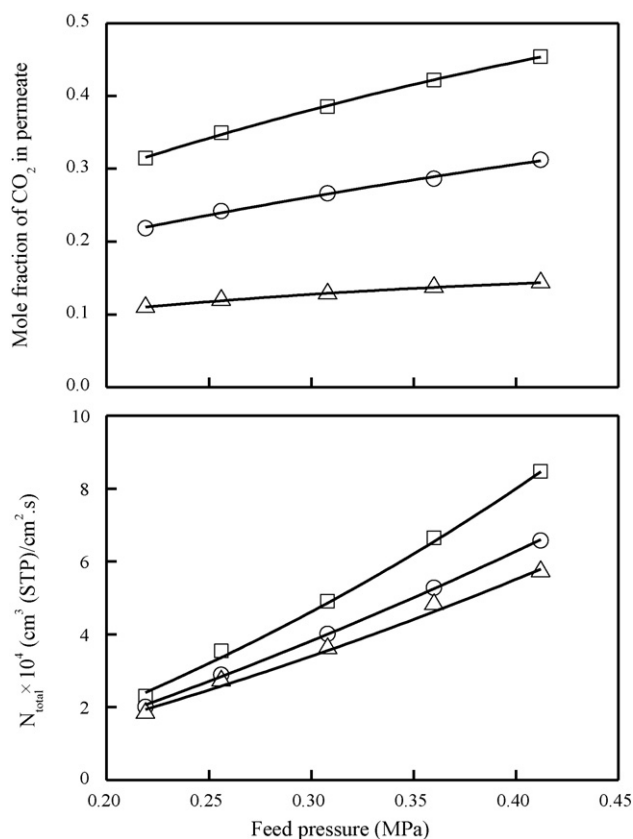

Fig. 4. Effects of stage cut on permeation flux and permeate concentration. Feed pressure, 308 kPa; temperature, 23 °C. Feed concentration: (□) 15% CO_2; (○) 10% CO_2; (△) 5% CO_2.
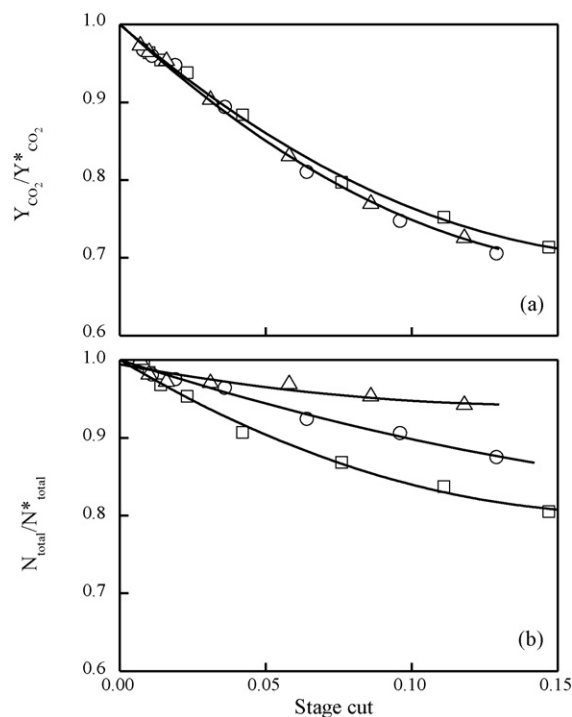
Fig. 5. The permeation flux and permeate concentration relative to their maximum obtainable values. Operating conditions same as those in Fig. 4.

Fig. 6. Effects of feed pressure on permeation flux and permeate concentration for the separation of binary CO_2/N_2 mixtures. Feed pressure, 308 kPa; temperature, 23 °C. Feed concentration: (□) 15% CO_2; (○) 10% CO_2; (△) 5% CO_2.

the feed. This is easy to understand because the permeation flux is determined to a large extent by partial pressure difference of CO_2 across the membrane, and a higher CO_2 concentration in the feed means a greater driving force for CO_2 permeation and thus a higher rate of depletion in CO_2 on the feed side of the membrane.

When determining the membrane permeance to individual components in gas mixture permeation at given feed pressures and concentrations, a relatively high feed flow rate corresponding to a small stage cut (~0.01) was used so as to minimize the variation in the feed concentration during the measurements. Fig. 6 shows the permeation flux of CO_2/N_2 binary mixtures through the PDMAEMA/PSF membrane at different feed pressures (205–412 kPa). A higher feed pressure appears to be more favourable for the separation of CO_2 from N_2 from a separation performance point of view. Similar results on poly(dimethyl siloxane) membrane was reported by Wu et al. [18]. Figs. 7 and 8 show the individual permeance of CO_2 and N_2 as a function of their partial pressure differences across the membrane. It was shown that at a given partial pressure difference, the permeance of CO_2 in the mixture increases as CO_2 concentration in the feed increases, while there is no significant change in the permeance of N_2. In addition, the N_2 permeance increases slightly with its partial pressure difference, but the CO_2 permeance decreases quickly with an increase in the CO_2 partial pressure difference and then gradually levels off. In comparison with pure gas permeation, the permeance of N_2 in gas mixture permeation is higher. The CO_2 permeance is shown to decreases as the concentration of N_2 in the feed increases. Based on these observations, one may perceive that the transport of CO_2 (the fast gas) is slowed down by the presence of N_2 (the slow gas) and the transport of the slow-permeating N_2 is enhanced by CO_2. However, for given operating conditions (i.e., feed and permeate
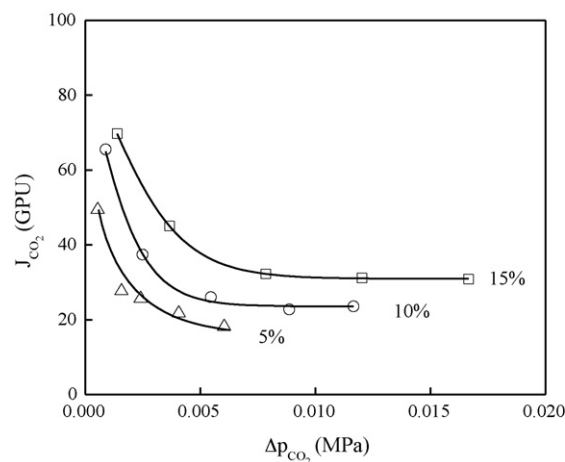
Fig. 7. Permeance of CO_2 in CO_2/N_2 mixtures vs partial pressure difference of CO_2 across the membrane. Operating conditions same as those in Fig. 6.

pressures, feed composition), an increase in the permeance of a component due to the coupling effect will increase its concentration in the permeate, resulting in a decrease in its partial pressure difference across the membrane. As a result, there will be a compromise between the two opposing effects as far as the permeation rate is concerned.

To further illustrate this point, the permeation of three binary mixtures (i.e., CO_2/N_2, CO_2/CH_4, and CO_2/H_2) with different feed compositions was carried out at a feed pressure of 308 kPa, and the partial permeation fluxes for individual components in the gas mixtures as a function of the feed composition are plotted in Figs. 9 and 10. The dotted lines represent the ideal permeation flux that would be obtained if there were no coupling effects between the permeating components; the ideal permeation flux is determined from
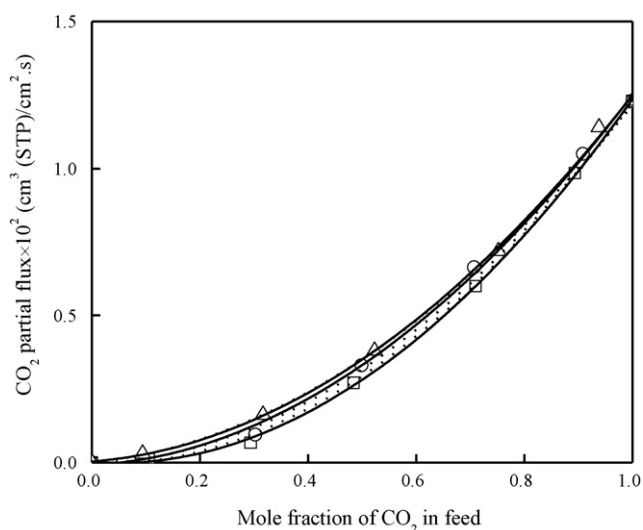
$$N_i^0 = J_i^0(p_h X_i - p_l Y_i') \tag{2}$$

$$N_j^0 = J_j^0[p_h(1 - X_i) - p_l(1 - Y_i')] \tag{3}$$

$$Y_i' = \frac{N_i^0}{N_i^0 + N_j^0} \tag{4}$$
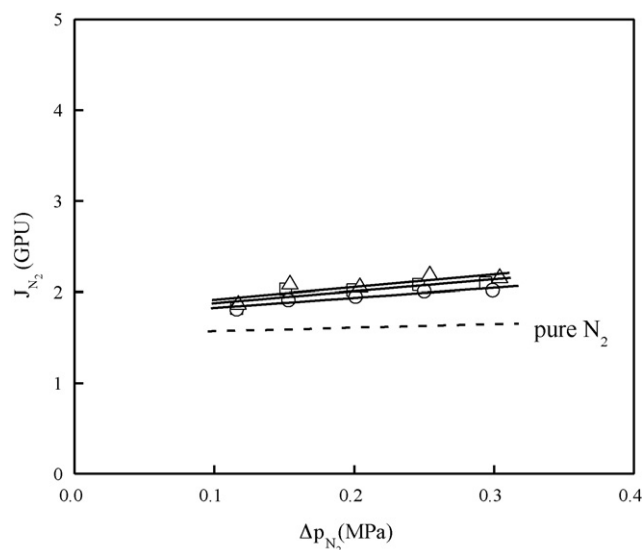
Fig. 8. Permeance of N_2 in CO_2/N_2 mixtures vs partial pressure difference of N_2 across the membrane. Operating conditions same as those in Fig. 6.

**Fig. 9.** Partial permeation flux of CO_2 vs concentration of CO_2 in feed for permeation of binary gas mixtures. (□) CO_2/N_2, (○) CO_2/CH_4 and (△) CO_2/H_2. Feed pressure, 308 kPa. Dotted line represents the ideal permeation flux.

where subscripts i and j denote the fast component (i.e., CO_2 in the present work) and the slow component in the binary mixture, respectively, J^0 is the pure component permeance, and N^0 is the ideal permeation flux. For the three pairs of binary gas mixtures studied, the partial permeation flux of CO_2 is close to its corresponding ideal permeation flux (see Fig. 9). This suggests that the presence of the slow permeating components (i.e., N_2, CH_4 and H_2) in the mixture has little effect on the permeation rate of CO_2, presumably due to the strong interactions between CO_2 and the membrane. On the other hand, the partial permeation fluxes of N_2 and CH_4 are shown to be higher than their ideal permeation fluxes, while the opposite is observed for the permeation flux of H_2 (Fig. 10). Huang and Lin [19] used a permeation ratio, θ, to quantitatively measure the deviation of the actual permeation from the ideal permeation for pervaporation separations. The same concept can be used for gas permeation as well. The permeation ratio for an individual component i can be expressed as

$$\theta_i = \frac{N_i}{N_i^0} \tag{5}$$
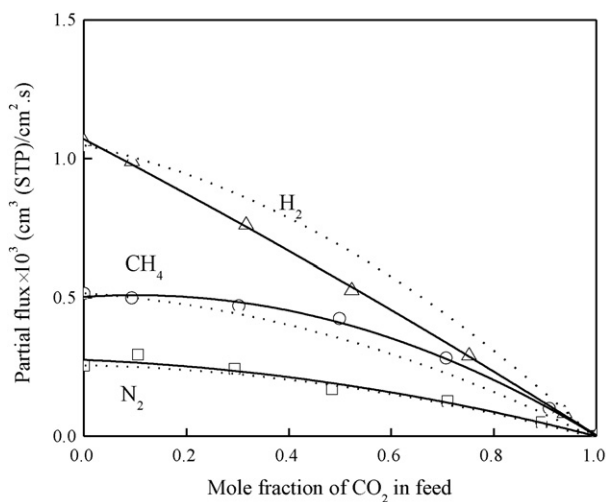
Fig. 10. Partial permeation fluxes of N_2, CH_4 and H_2 vs feed concentration for permeation of binary gas mixtures. (□) CO_2/N_2, (○) CO_2/CH_4 and (△) CO_2/H_2 mixtures. Feed pressure, 308 kPa. Dotted lines represent the ideal permeation flux.
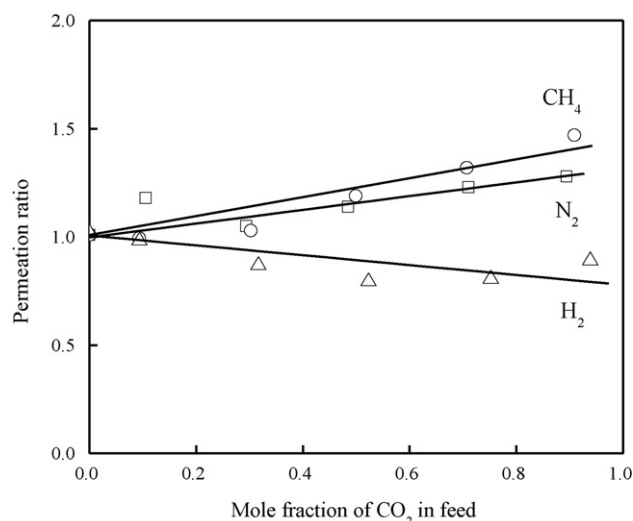
Fig. 11. Permeation ratio of N_2, CH_4 and H_2 for the permeation of binary CO_2/N_2, CO_2/CH_4 and CO_2/H_2 mixtures at different CO_2 concentrations in feed. Feed pressure, 308 kPa.

Fig. 11 shows the permeation ratio for H_2, N_2 and CH_4 at various CO_2 concentrations in binary CO_2/N_2, CO_2/CH_4 and CO_2/H_2 feed mixtures. In general, the deviation from the ideal permeation becomes more significant as the feed CO_2 concentration increases. The presence of CO_2 appears to have a positive impact on the permeation of both CH_4 and, to a lesser extent, N_2, whereas the permeation of H_2 is affected negatively. These trends can be explained from the aspects of solubility and diffusivity of the penetrants. On the one hand, carbon dioxide molecules can interact with water in the membrane to form bicarbonate (i.e., ionic HCO_3^-), and this will reduce the solubility of the other components (i.e., H_2, N_2 and CH_4) in the membrane due to the "salting out" effects [20], which tends to lower their permeability and cause a negative deviation from ideal permeation. On the other hand, the CO_2 dissolved in the membrane will make the polymer chains more flexible, which enables the permeant to diffuse through the membrane more easily. Recall that the membrane studied here is weak in size-sieving of the gas components, and the permselectivity is largely derived from the relative solubility. Studies on gas diffusion in weakly size-sieving polymers such as silicone rubbers show that the diffusivities of larger gas penetrants are more sensitive to the molecular structure of the membrane [21,22] because larger penetrant molecules interact with more segments of the surrounding polymer chains during molecular jumps in the membrane. The permeation ratios of the three gases considered here appear to be consistent with the above physical reasoning in consideration of their kinetic diameters (which are 0.38, 0.364 and 0.289 nm for CH_4, N_2 and H_2, respectively).

4. Conclusions

Gas permeation through PDMAEMA/PSF composite membranes was investigated. The membranes were prepared by solid–liquid interfacial crosslinking. The permeation of CO_2 and N_2 was studied with and without the presence of water vapor. When hydrated the membrane tended to be more permeable than the dry membrane, the change in the permeance was not drastic. The performance of the membrane for the separation of binary CO_2/N_2, CO_2/CH_4 and CO_2/H_2 mixtures was determined, and the effects of feed pressure and composition on the permselectivity of the membrane were studied. The permeance of the membrane for binary mixture permeation and pure gas permeation was compared to evaluate the

coupling effect. It was shown that the presence of CO_2 influenced the permeation of the other permeating components (e.g., N_2, CH_4 and H_2), while the permeation of CO_2 was not significantly affected by these components.

Acknowledgement

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