Materials dependence of mixed gas plasticization behavior in asymmetric membranes

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Abstract

The mass transport of asymmetric membranes for the separation of carbon dioxide/methane mixtures is determined by competitive sorption and plasticization. With increasing feed pressure in mixed gas experiments, the selectivity decreases due to both effects. Distinction whether one or the other mechanism is responsible for the selectivity loss is important since competitive sorption is related to intrinsic material properties and cannot be tailored, whereas plasticization can be suppressed by various chemical means. This paper describes the systematic analysis for five different asymmetric membranes with respect to the balance between competitive sorption and plasticization. Four asymmetric membranes where prepared for this study, one membrane was based on a commercial precursor. Of these membranes, three are based on the polyimide Matrimid: pure Matrimid, and blends of Matrimid with polyethersulfone as well as Matrimid with a polyimide P84. These membranes are compared with two other ones: cellulose acetate and polyphenyleneoxide PPO. The blend of Matrimid with P84 shows the highest mixed gas selectivity and is very resistant against plasticization without any further chemical modification.
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1. Introduction

There exists a huge amount of experimental data focusing on the understanding of mass transport in glassy polymers. Many of the journal papers report values of sorption, diffusion and permeation of gases in films. Prime motivation of these research activities has been to understand the underlying physics of transport through polymers as well as to establish a structure–property relationship: how does the chemistry of the material influence the polymer structure and the transport properties [1]. A second motivation is the quest for a material that passes the so-called upper bound [2,3]. All these experiments were carried out for single gasses and thick films. Even though an uncountable number of polymers have been synthesized, only eight are currently commercially used [4].

Much less experimental work was carried out with gas mixtures. Also, most experiments were carried out with thick films where the thickness is larger than 10 μm. Such measurements were normally carried out at low feed gas pressures. Very little experimental evidence exists on the mass transport in thin glassy films where the film thickness is significantly smaller than 5 μm. Hardly any mixed gas experiments are carried out for such thin films. Although industrial reality, glassy polymer based asymmetric membranes are seldom subject to extensive mass transport characterization. Such membranes have frequently a skin thickness of less than 1 μm, its morphology is very difficult to elucidate and a structure–property relationship is difficult to establish at all.

We feel that the industrial progress of asymmetric gas separation membranes needs to be accompanied by a fundamental understanding of the transport properties of such membranes under real process conditions—as opposed to the significantly different transport behavior in thick films. Recently, we have systematically investigated the mass transport behavior of asymmetric hollow fiber membranes based on a blend of Matrimid and polyethersulfone [5]. These membranes show comparable transport performance as industrial membranes [6]. We described the observation of a subtle balance between plasticization and competitive sorption both determining the permeability and selectivity for CO_2/CH_4 mixtures. The next important step

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towards a better understanding is to investigate whether or not the same balance can be observed as well for asymmetric membranes based on other polymers.

2. Background

In natural gas sweeting, i.e. the removal of sour gasses such as CO_2 and H_2S, glassy polymer gas separation membranes are often preferred over rubbery polymer membranes due to their higher CO_2/CH_4-selectivity. However, glassy polymers generally show a decreasing selectivity with increasing feed pressure due to gas induced plasticization of the polymer matrix and competitive sorption [5,7]. With respect to plasticization, sorption of CO_2 into the polymer causes an enhanced polymer chain segmental mobility, resulting in enhanced mass transport of all components to separate, but in particular the less permeating methane [8]. Staudt-Bickel and Koros [9] reported an almost complete loss of selectivity in the separation of a 50/50 vol.% CO_2/CH_4-mixture with dense films of a typical 6FDA-polyimide. This dramatic loss has stimulated the suggestion that polyethyleneoxide based rubbery polymers might be viable materials for high pressure natural gas separation: even though PEO based polymer show a low intrinsic selectivity of CO_2/CH_4, however, they show very little selectivity loss with increasing feed pressure [10].

Generally, plasticization phenomena observed in glassy polymer gas separation membranes are complex due to the non-equilibrium state of the polymer glass. The extent of plasticization may vary depending on factors like the membrane material, the membrane morphology (integrally skinned asymmetric or dense membranes), the thickness of the membrane [11], the feed composition, pressure and temperature [12] and the types of penetrants permeating. Recent gravimetric sorption studies suggest that there exists a critical volume dilation threshold above which relaxational sorption occurs indicating, what is frequently coined, the phenomenon of plasticization [13]. Most recent research focuses on gaining more insights concerning the complex transport behavior in the presence of strong plasticizing components. Strong plasticizing penetrants are for example present in the separation of natural gas with high CO_2-concentrations and traces of higher hydrocarbons [14] or the separation of higher hydrocarbons itself (e.g. C_3H_6/C_3H_8). Especially in these areas a large market potential is predicted for polymer gas separation membranes [4].

Next to plasticization, there exists a second phenomenon complicating the understanding of transport: competitive sorption due to the glassy state of the polymer matrix. The presence of a second component typically causes the permeability of the first component to reduce in glassy polymer membranes [15]. This may be explained in terms a simple dual mode sorption model: penetrants compete for sorption sites which are associated with the non-equilibrium free volume in glassy polymers [15]. Chern et al. [16] showed that by adding small amounts of water vapor the CO_2-permeance in Kapton polyimide was significantly suppressed due to competitive sorption. Furthermore, Sada et al. [17], Lee et al. [18] and Donohue et al. [19] demonstrated that the addition of CH_4 to the feed

suppressed the CO_2-permeability in cellulose acetate membranes.

Competitive sorption effects cause the permeability of penetrants to decrease with increasing feed pressure, while plasticization effects cause a permeability increase with increasing feed pressure. An increasing permeability reduction is obtained with increasing CH_4-feed concentration (more competition, less plasticization), while a larger permeability increase can be observed with increasing CO_2-feed concentration (less competition, more plasticization). It is important to point out that the decrease in the separation factor due to these effects is difficult to attribute to one of these effects only because in most cases both plasticization and competitive sorption reduce the separation factor. Cellulose acetate is a good example: it is known that asymmetric cellulose acetate membranes are very susceptible to CO_2-plasticization resulting in strongly decreasing CO_2/CH_4-selectivities with increasing CO_2-feed content. More importantly, with increasing CO_2 partial pressure the methane permeability increases to a larger extent than CO_2 [18].

However, the presence of CO_2-plasticization does not always result in lower separation performances [5]. PES/Matrimid asymmetric hollow fiber membranes show higher CO_2/CH_4-selectivities with increasing CO_2-feed concentrations due to the effect of competitive sorption. These two examples indicate the complexity arising from the superposition of competitive sorption and plasticization effects. For this reason it is desirable to investigate the balance between competitive sorption and plasticization effects in other membrane materials in more detail and to identify which effect is the most dominating.

This paper reports the transport properties of five different asymmetric membranes and their characterization using three different CO_2/CH_4-feed compositions over large range of feed pressures. Four of the membranes (Matrimid, P84/Matrimid, PES/Matrimid and CA) were specifically developed for this purpose, the PPO hollow fiber is a commercial fiber from Parker Gas (Etten-Leur, The Netherlands).

3. Experimental

3.1. Materials

The polyimides, Matrimid 5218 (BTDA-AAPTMI) and P84 (BTDA-TDI/MDI), were purchased from Vantico AG (Switzerland) and HP Polymer GmbH (Austria), respectively, while PES (Sumikaexcel) was purchased from Sumitomo (Belgium). Blending of Matrimid with PES, or with the co-polyimide P84 can be an effective way to suppress CO_2-induced plasticization effects in dense thick films for CO_2/CH_4-separation [20]. Besides, P84/Matrimid membranes intrinsically have a much higher CO_2/CH_4-selectivity and may therefore be more interesting for these kinds of separations. Therefore, P84/Matrimid (50/50) hollow fiber membranes were produced to make a comparison with hollow fiber membranes consisting of a PES/Matrimid (20/80) blend and pure Matrimid. A mixture of 50/50 wt.% was chosen for P84/Matrimid to have the ben-

efit of the high selectivity of P84 and the high permeability of Matrimid. The ratio 20/80 wt.% was chosen for PES/Matrimid because our previous work on this polymer blend. For both blends, variations of the blend composition will strongly affect the transport behavior.

To obtain a more comprehensive overview, the mixed gas permeation behavior of cellulose acetate (CA) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) asymmetric membranes was investigated as well. PPO is known for its extremely high permeability at fairly low selectivity [21,22], while cellulose acetate is the most commonly used material in natural gas membrane separations [4]. The flat sheet cellulose acetate asymmetric membranes were prepared in house to guarantee consistency of the permeation experiments. Cellulose acetate, (CA-398-3) with a molecular weight M_w of 100,000 g/mol and an acetyl content of 39.8%, was purchased from Eastman Company (the Netherlands). Integrally skinned asymmetric poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) hollow fibers were kindly provided by Parker Gas Separation (the Netherlands).

All solvents N-methylpyrrolidon (NMP), acetone, ethanol, methanol and *n*-hexane, analytical grade) were purchased from Acros (the Netherlands) and were used as received. Pure gases (purity > 99.5%) and pre-calibrated gas mixtures were obtained from Praxair (the Netherlands) and used without further purification.

3.2. Membrane preparation

3.2.1. Preparation of asymmetric flat sheet membranes

Integrally skinned asymmetric cellulose acetate flat sheet membranes were prepared by dry/wet phase inversion following a recipe using acetone and methanol as the solvent and non-solvent [23]. After filtration of the polymer solution (0.15 μm metal filter), wet films were cast on glass plates at room temperature using 0.3 and 0.5 mm casting knifes. After an evaporation step of 20 s, the membranes were immersed into a methanol coagulation bath. After coagulation the membranes were rinsed for 24 h with fresh methanol. Subsequently the membranes were solvent exchanged in *n*-hexane for at least 4 h and slowly dried in air (in a nearly closed container). Finally the membranes were dried in a 100 °C vacuum oven for at least for 24 h to remove residual solvent. Critical in the reproducible preparation of asymmetric CA membranes appeared to be the drying procedure, as too fast drying resulted in excessive shrinkage and poor mechanical stability.

3.2.2. Preparation of asymmetric hollow fiber membranes

Integrally skinned asymmetric hollow fibers were prepared by dry/wet spinning following recipes described in literature [24,25]. Table 1 shows the compositions of the polymer dopes and bore liquids used in the spinning process. Acetone was added to the spinning dope to enhance the formation of a defect-free top layer [24]. In both cases, the spinning process was carried out a temperature of 50 °C and a tube-in-orifice spinneret with an outer diameter of 0.5 mm and an inner diameter of 0.2 mm was used.

Table 1
Dope and bore liquid compositions used in spinning process

	P84/Matrimid	Matrimid
Polymer (wt.%)	30	25
Solvent (NMP, wt.%)	60	45
Additive (acetone, wt.%)	10	30
Bore liquid (NMP/H_2O, wt.%)	80/20	70/30

3.3. Membrane structure analysis

The geometry and morphology of the prepared membranes were determined using scanning electron microscopy (SEM, Jeol JSM-T220). Samples were prepared by freeze fracturing pieces of film and fiber using liquid nitrogen and subsequently covered with a thin layer of gold using a Balzer Union SCD 040 sputtering device.

3.4. Pure gas permeation characteristics

All permeation characteristics were determined by using the variable pressure method as described by Kapantaidakis and Koops [6]. In the case of hollow fiber membranes, five fibers of 20 cm long were potted into $3/8 \times 2.54$ cm (3/8 in.) stainless steel holders, while sealing the other side with an epoxy resin. The hollow fiber membrane modules were pressurized from the shell side. In the case of flat sheet membranes, films were cut in circles (surface area of 11.95 cm^2) and pressurized from the dense (skin) side.

Single gas permeance values of N_2 and O_2 were determined at a pressure of 4×10^5 Pa (4 bar) and a temperature of 35 °C and were calculated from the steady-state pressure increase in time in a calibrated volume at the permeate side. The thickness of the asymmetric skin was calculated from the of intrinsic permeability coefficient for a certain gas and its permeance for the asymmetric membrane. The ideal separation factor (the ratio of the pure gas permeances) was used to determine whether the prepared membranes were defect-free. If needed, defects and pinholes were plugged by dip coating the membranes with a 5 wt.% PDMS-solution in *n*-hexane [26].

Besides the ideal O_2/N_2-separation performance, the pure gas CO_2-permeance was measured as a function of pressure to observe the difference in strength of CO_2-plasticization for the used materials. Permeance values were always recorded after 3 h of measuring.

3.5. Mixed gas separation performance

Mixed gas separation experiments were always conducted using membrane modules without permeation history [27,28]. Consequently, the mixed gas separation performance may fluctuate slightly from module to module. Four different CO_2/CH_4-compositions (20/80, 50/50, 80/20 and 98/2 vol.% CO_2/CH_4) were investigated at a temperature of 35 °C. In every gas separation experiment two similar membrane modules were measured simultaneously. The gas separation performance was determined according to the following protocol:

- determination of permeance properties with successively N_2 and O_2 at 4×10^5 Pa (4 bar) to check quality of membranes;
- degassing for at least half an hour;
- determination of separation performance of CO_2/CH_4 gas mixture at 4×10^5 Pa (4 bar) for approximately 6 h;
- tracing residual conditioning by measuring N_2-permeance decay overnight (16 h);
- degassing and evacuation for 30 min;
- increasing mixed gas pressure;
- repeating steps 5, 6 and 7 up to the maximum pressure (depending on the mechanical stability of the membranes).

Feed and permeate compositions were analyzed using a Perkin-Elmer gas chromatograph (GC) equipped with a HayeSep Q column. The GC was calibrated with the pre-calibrated feed mixtures. In principle, low stage-cuts (ratio of permeate to feed flow, Q_p/Q_f) are preferred in mixed gas permeation experiments. However, low stage-cuts could not be maintained in experiments with high-flux membranes (P84/Matrimid and PPO). Therefore, a linear cross-flow model was used to define the CO_2- and CH_4-permeabilities [29]. The model assumes a linear profile for the feed concentration. Accordingly, the permeability 'P' of component 'i' is defined as:

$$P_i = \frac{y_i Q_p}{A(p_f \bar{x}_i - p_p y_i)} \quad (1)$$

where

$$\bar{x}_i = \frac{Q_f x_f - Q_r x_r}{Q_f + Q_r} \quad (2)$$

where x and y are the feed and permeate concentrations, respectively, A the surface area, p_f and p_p the feed and permeate pressure (Pa), and Q_f, Q_r and Q_p the feed, retentate and permeate flow (ml/min). The mixed gas selectivity is defined as the ratio of permeance values:

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad (3)$$

The permeation driving force is expressed in terms of fugacity to take into account non-ideal behavior of gas mixtures at elevated pressures. Fugacities were calculated using the Peng-Robinson equation-of-state [5]. To take into account the time dependency of conditioning and to guarantee the consistency of the permeance data, permeance values were collected in all cases after six hours measuring time [28]. CO_2-conditioning causes subtle packing alterations in the non-equilibrium polymer matrix. Within the relative short time scales of the experiments the polymer chains cannot relax back into their original state [28]. Therefore, an additional indication for plasticization can be obtained by measuring the N_2-permeance decay in time directly after a CO_2-mixed gas experiment. When plasticization has occurred, the N_2-permeance will be significantly higher than its original value and will decrease very slowly in time [5,30].

4. Results and discussion

4.1. Asymmetric membrane structure analysis

Fig. 1a–e shows the cross-sections of the asymmetric membranes used in the gas permeation experiments. All hollow fiber membranes (Fig. 1a–d) have a typical asymmetric structure; a dense thin top layer at the outside supported by a spongy porous substructure. The P84/Matrimid and Matrimid hollow fiber membranes show large amounts of fingerlike macrovoids that are oriented from outside to inside, whereas the PES/Matrimid and PPO membranes have not. The CA asymmetric membranes (Fig. 1e) have a more symmetric geometry with a macrovoid-free
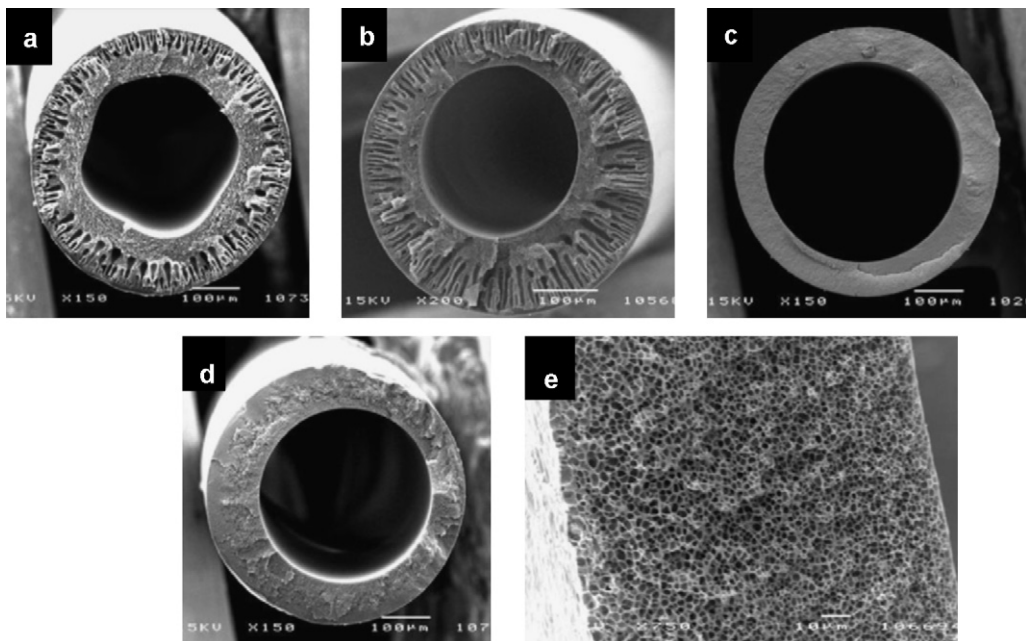

Fig. 1. Cross-sections of prepared asymmetric membranes: (a) Matrimid, (b) P84/Matrimid, (c) PES/Matrimid, (d) PPO and (e) CA.

Table 2
Pure gas permeation characteristics of the asymmetric membranes used in the mixed gas permeation experiments

	P/l (N_2) (GPU)	P/l (O_2) (GPU)	α (O_2/N_2)	l (N_2) (μm)
CA	0.32	1.7	5.2	0.43
P84/Matrimid	0.61	4.9	7.9	0.09
Matrimid	0.42	2.8	6.8	0.35
PES/Matrimid	0.38	2.6	6.7	0.27
PPO	4.8	20	4.1	0.43

Table 3
Pure gas permeation characteristics of the asymmetric membranes used in the mixed gas permeation experiments

	P/l (N_2) (GPU)	P/l (O_2) (GPU)	P/l (CH_4) (GPU)	α (O_2/N_2)	l (N_2) (μm)
CA	0.32	1.7	–	5.2	0.43
P84/Matrimid	0.61	4.9	0.43	7.9	0.09
Matrimid	0.42	2.8	–	6.8	0.35
PES/Matrimid	0.38	2.6	0.32	6.7	0.27
PPO	4.8	20	–	4.1	0.43

morphology. The presence of macrovoids is not detrimental as it will not influence the separation performance but only decrease the mechanical resistance of the membrane. Since we are after a fundamental understanding of the mass transport behavior of the skin, we feel comfortable in neglecting a mechanically optimized support membrane morphology. Also the concentricity is far from optimal. For industrial high-pressure gas separation processes however, macrovoids should not be present in support structure and wall thickness must be equal.

4.2. Pure gas permeation characteristics

Table 2 shows the pure gas permeation characteristics of the different membranes. The permeance values (1 GPU (gas permeation unit) is 1×10^{-6} cm^3 (STP)/cm^2 s cmHg or 7.6×10^{-12} m^3 (STP)/m^2 s Pa) are an average of three to four different membranes. The standard deviation in the gas permeation measurements was less than 10% for PPO and the Matrimid-based hollow fiber membranes. However, the CA membranes were very difficult to reproduce, which resulted in a significantly larger standard deviation ($\sim$25%). Furthermore, the developed P84/Matrimid membranes have much thinner separating layer compared to the other four materials, which have a more or less equal top layer thickness.

Except for the PES/Matrimid membranes, all membranes were post-treated by applying a PDMS coating to recover the intrinsic selectivity of the material. P84/Matrimid possesses the

highest ideal O_2/N_2-selectivity, PPO the lowest. After coating with PDMS, the selectivity for the PPO-based hollow fibers does not completely correspond to the intrinsic selectivity of $\alpha = 4.7$ as measured for the thick film prepared from the same high molecular weight polymer from, The original fibers had a low selectivity scattering around 2 for O_2/N_2. The PDMS pushed the selectivity towards the intrinsic value of PPO (Table 3).

Fig. 2a and b shows the absolute and normalized pure gas CO_2-permeance as a function of pressure for the used membranes. CA and Matrimid membranes show the strongest increase in CO_2-permeance, which stands for the strongest effect of plasticization. PPO membranes seem to experience the smallest effect of plasticization.

4.3. Mixed gas separation performance

The results will be discussed in terms of the CO_2-permeance (absolute and normalized values), the N_2-permeance decay (tracing the residual conditioning), the mixed gas CO_2/CH_4-separation factor and the normalized CH_4-permeance. The normalized CO_2-and CH_4-permeances are the ratio of the permeance at each pressure (P_{CO_2} and P_{CH_4}) to the permeance at a feed pressure of 4×10^5 Pa (4 bar) (P_0) and gives the opportunity to compare the separation performance of the different membrane materials. The dotted lines presented in figures are only used to guide the eye. The results shown of PES/Matrimid membranes have been recently reported [5], but are added to the
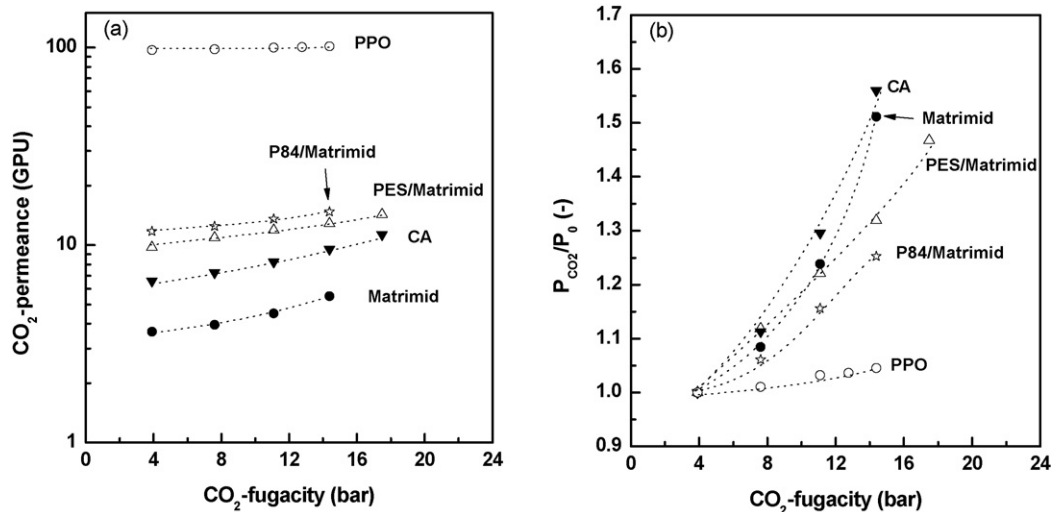

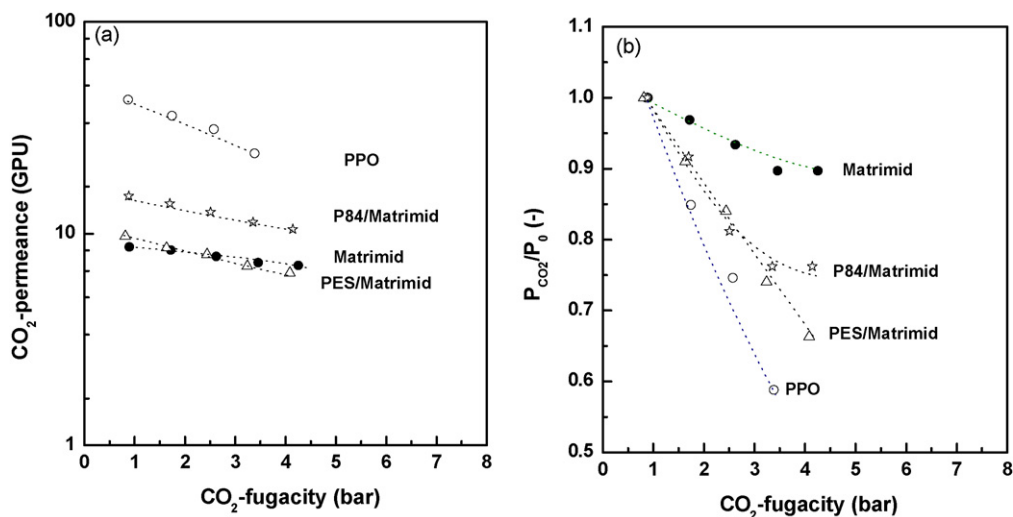Fig. 2. (a) Absolute (in GPU) and (b) normalized pure gas CO_2-permeance as function of CO_2-fugacity.

Fig. 3. (a) Absolute (in GPU) and (b) normalized CO_2-permeance as a function of the CO_2-fugacity using a 20/80 vol.% CO_2/CH_4-feed gas mixture.

other results in order to make a more comprehensive comparison.

4.3.1. 20/80 vol.% CO_2/CH_4-separation

Fig. 3a and b shows the absolute and the normalized CO_2-permeance, respectively, as a function of CO_2-fugacity for the different membranes using a feed gas of 20/80 vol.% CO_2/CH_4. All membranes show a continuous decrease in the CO_2-permeance with increasing fugacity. The largest total permeance reduction is observed for PPO and the smallest for Matrimid (Fig. 3b). This can be explained by stronger competitive sorption effects or smaller plasticization effects.

The amount of residual conditioning is determined from the N_2-permeance decay in time (Fig. 4). Fig. 4 shows that almost no (PPO and the Matrimid blends) or only minor residual con-

Fig. 4. N_2-permeance decay after 20/80 vol.% CO_2/CH_4-separation at a feed pressure of 16×10^5 Pa (16 bar) (CO_2-fugacity of 3.3×10^5 Pa (3.3 bar)).

ditioning (Matrimid) has occurred for all membranes. Of all membranes, Matrimid shows the largest effect of conditioning which correlates with the smaller reduction in CO_2-permeance with increasing fugacity observed in Fig. 3b. While the CO_2-permeance reduction for PPO, P84/Matrimid and PES/Matrimid is only caused by competition effects, plasticization effects have slightly counterbalanced these competition effects in the case of Matrimid.

Fig. 5a and b shows the obtained mixed gas CO_2/CH_4-separation factors and normalized CH_4-permeance as a function of CO_2-fugacity. All membranes exhibit a continuous decrease in separation factor with increasing fugacity. This is a result of a stronger decrease in the CO_2-permeance compared to the CH_4-permeance which is a typical behavior of glassy polymer membranes [31]. However, the decreasing separation factor of Matrimid membranes may be slightly influenced by plasticization effects which were already observed in Fig. 4. Al-Juaied and Koros [14] observed no plasticization effects using a feed composition of 10/90 CO_2/CH_4 up to a fugacity of $\sim 14 \times 10^5$ Pa (~ 14 bar) in similar Matrimid hollow fiber membranes. The obtained results for Matrimid show that at 20 vol.% CO_2 plasticization effects are present, but have only a minor effect of the mixed gas separation performance. It may be suggested that at this CO_2-feed gas concentration (20 vol.%) a threshold value for CO_2 sorption is reached, sufficient to induce plasticization effects.

PPO membranes give a low mixed gas selectivity below 10. Very different values for the ideal CO_2/CH_4-separation factor are reported ranging from 12 to more than 20 [21,32]. We have tested the intrinsic property in single gas experiments and obtained 13.7. The lower selectivity for the asymmetric fibers may be caused by strong competition effects, which generally decrease mixed gas selectivity compared to ideal (pure gas) selectivity. The asymmetric Matrimid-based membranes have significant higher mixed gas selectivity than PPO. Blending Matrimid with P84 gives higher separation factors compared to pure Matrimid, while blending with PES results in less selective membranes.
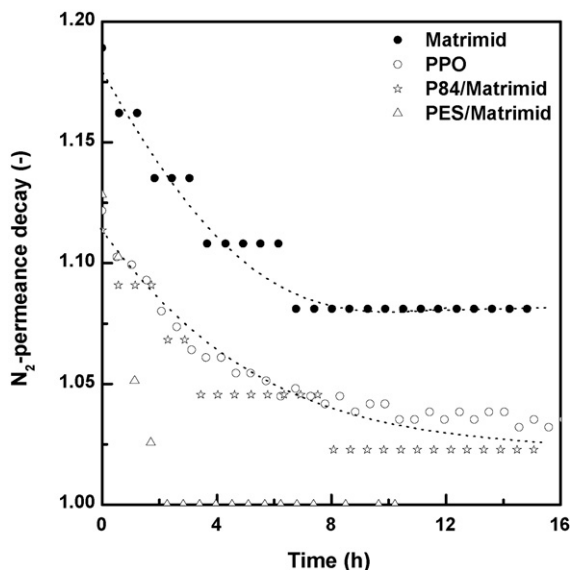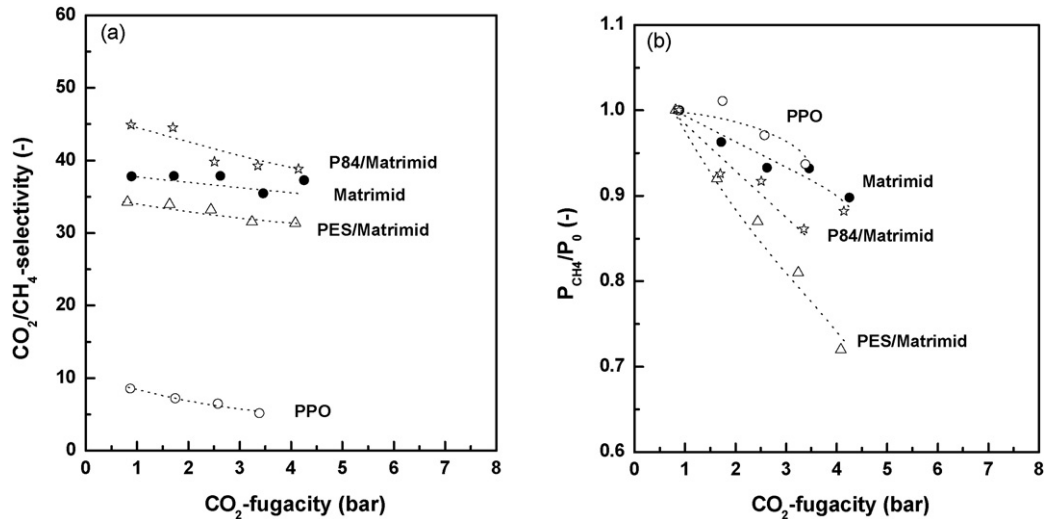
Fig. 5. (a) CO_2/CH_4-selectivity and (b) normalized CH_4-permeance as a function of CO_2-fugacity using a 20/80 vol.% CO_2/CH_4-feed gas mixture.

Summarizing, the separation performance of all membrane materials investigated is fully determined by competitive sorption effects because plasticization effects are (almost) absent. The CO_2-permeance and the separation factor decrease with increasing feed fugacity for all membranes investigated, which is consistent with the effects expected upon competitive sorption.

4.3.2. 50/50 vol.% CO_2/CH_4-separation

Fig. 6 shows (a) the absolute and (b) the normalized CO_2-permeance as a function of the CO_2-fugacity for CA, P84/Matrimid and PES/Matrimid membranes in the separation of a 50/50 vol.% CO_2/CH_4-gas mixture. All three-membrane materials show a continuous decrease in the CO_2-permeance with increasing CO_2-fugacity, with the strongest permeance reduction for PES/Matrimid (Fig. 6b).

However, the N_2-permeance decay measurements (Fig. 7) show that P84/Matrimid and PES/Matrimid membranes exhibit the largest extent of residual conditioning. CA membranes seem to recover considerably faster to their original N_2-permeance

(before the permeation experiment), while PES/Matrimid and P84/Matrimid membranes end up with ∼15% residual conditioning.

Donohue et al. [19] reported that plasticization induced changes in CA membranes seem to recover relative fast after the separation of CO_2/CH_4-mixtures. The polymer chains of CA apparently relax very fast back to a compactly dense packed state upon release of the CO_2-mixture. This can be interpreted in terms of the fact that CA has the lowest T_g of all membranes investigated [8]. As the magnitude of the T_g is a measure for chain stiffness, CA will have the highest polymer chain mobility to relax.

Fig. 8 shows (a) the CO_2/CH_4-separation factor and (b) the normalized CH_4-permeance as a function of CO_2-fugacity. All membrane materials show a relative strong decrease in separation factor with increasing CO_2-fugacity. The CH_4-permeance shows a significant increase in fugacity for CA membranes, while it is more or less unchanged for PES/Matrimid and P84/Matrimid membranes.
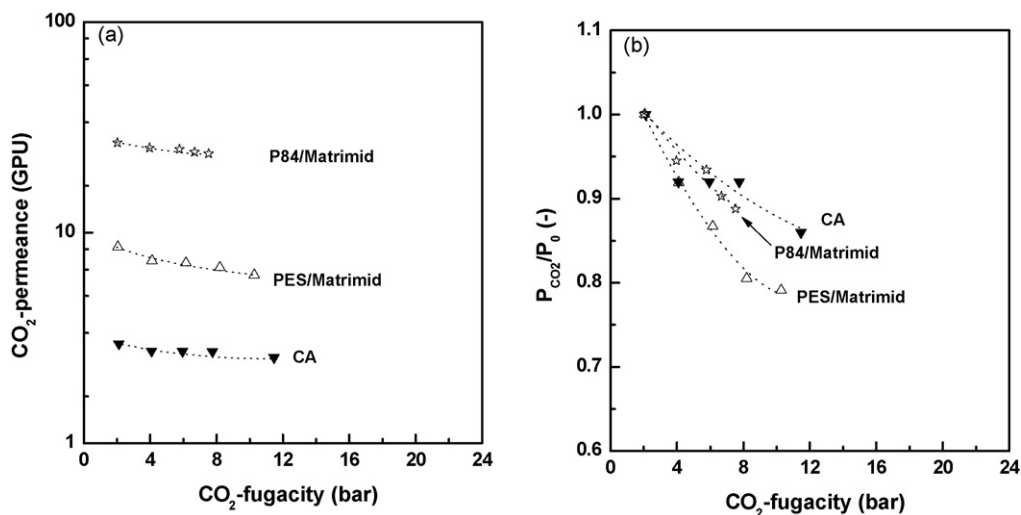

Fig. 6. (a) Absolute (in GPU) and (b) normalized CO_2-permeance as a function of CO_2-fugacity using a 50/50 vol.% CO_2/CH_4-feed gas mixture.
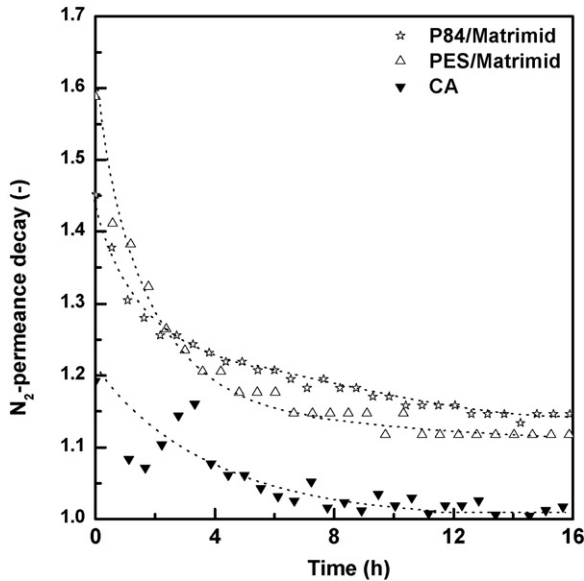
Fig. 7. N_2-permeance decay after 50/50 vol.% CO_2/CH_4-separation at a feed pressure of 16×10^5 Pa (16 bar) (CO_2-fugacity of 8.2×10^5 Pa (8.2 bar)).

The strong increase in CH_4-permeance and consequently decreasing separation factor for CA membranes is caused by plasticization effects. Therefore, it can be concluded that plasticization effects dominate the mixed gas transport behavior of CA membranes. As the CH_4-permeance does not change much with increasing fugacity, the decrease in mixed gas selectivity for PES/Matrimid and P84/Matrimid membranes can be attributed to competition effects. It can be concluded that the mixed gas transport behavior for PES/Matrimid and P84/Matrimid membranes is dominated by competition effects using a 50/50 vol.% CO_2/CH_4-feed gas mixture.

Summarizing, CA, PES/Matrimid and P84/Matrimid membranes show a *decreasing* CO_2-permeance with increasing fugacity. Nevertheless, plasticization effects dominate the separation performance of CA membranes. The CH_4-permeance

increases with increasing fugacity, which gives a strong decrease in separation factor. On the other hand, the separation performance of PES/Matrimid and P84/Matrimid membranes is dominated by competition effects, although plasticization effects are not completely absent as was shown by the N_2-permeance decay measurements.

4.3.3. 80/20 vol.% CO_2/CH_4-separation

Fig. 9 shows (a) the absolute and (b) the normalized CO_2-permeance as a function of the CO_2-fugacity for all membranes in the separation of a 80/20 vol.% CO_2/CH_4-feed gas mixture. The absolute CO_2-permeances (in GPU) are somewhat higher for all membranes compared to the previous described gas mixtures (20/80 and 50/50). Because the CH_4-feed gas concentration is decreased, competition effects will be smaller. On the other hand, plasticization effects will be stronger due to a higher CO_2-feed gas concentration. Both effects will result in a higher (absolute) CO_2-permeance.

Fig. 9b shows that the normalized CO_2-permeance increases significantly with increasing CO_2-fugacity for Matrimid and CA, suggesting a much stronger plasticization effect compared to the previous described gas mixtures. P84/Matrimid and PPO membranes show a slight decrease in CO_2-permeance with increasing fugacity. On the other hand, a continuous decrease in CO_2-permeance with increasing fugacity is still observed for PES/Matrimid membranes, suggesting relative strong competition effects.

Fig. 10 shows the N_2-permeance decay measurements for all membranes after the separation of a 80/20 vol.% CO_2/CH_4-feed gas mixture. Again, the N_2-permeance decay for CA membranes show a relative fast decrease towards the initial N_2-permeance, although the increase in the normalized CO_2-permeance with increasing CO_2-fugacity (Fig. 9b) suggested a large effect of plasticization. This was explained in the previous section (50/50 vol.%) by the larger polymer chain mobility of CA compared to the other membrane materials. On the other hand, the CO_2-permeance behavior of PPO and
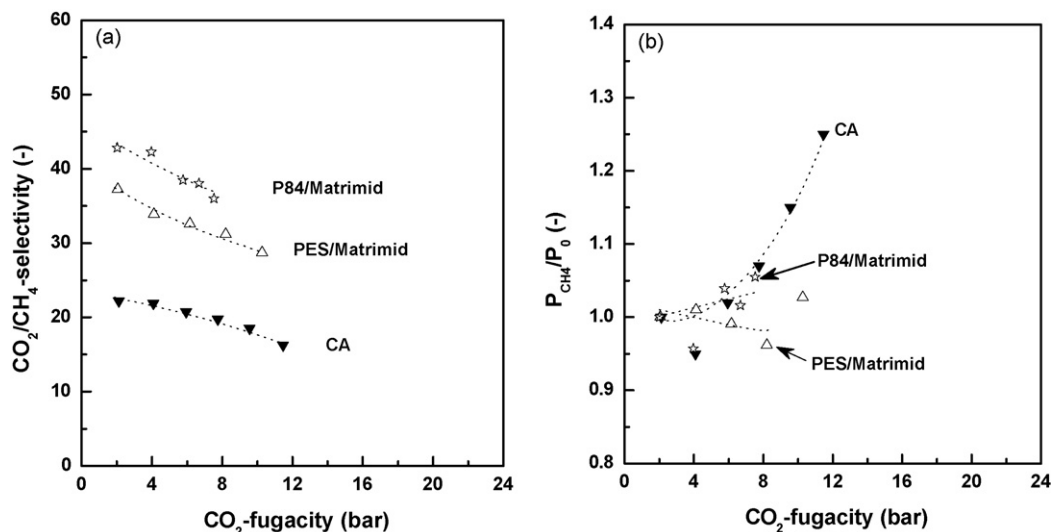

Fig. 8. (a) CO_2/CH_4-selectivity and (b) normalized CH_4-permeance as a function of CO_2-fugacity using a 50/50 vol.% CO_2/CH_4-feed gas mixture.
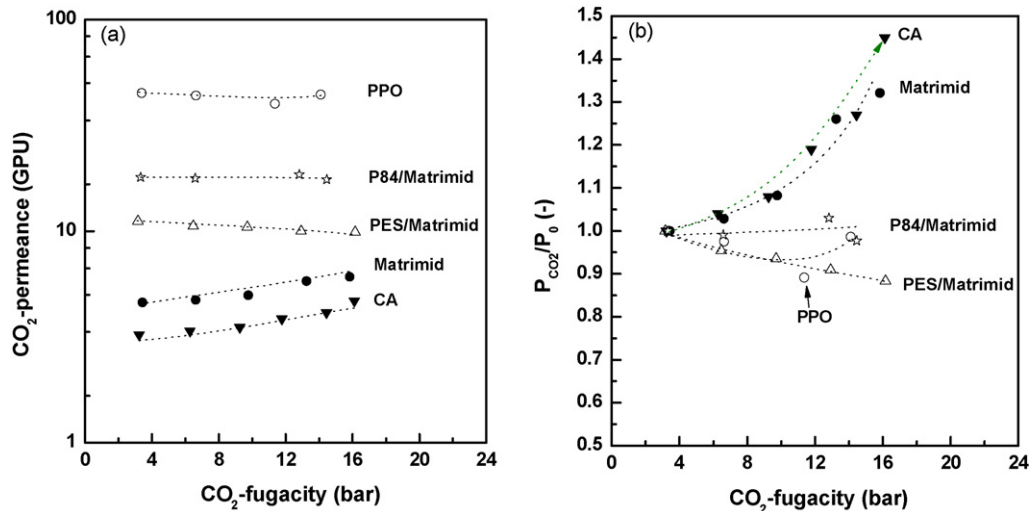
Fig. 9. (a) Absolute (in GPU) and (b) normalized CO_2-permeance as a function of the CO_2-fugacity using a 80/20 vol.% CO_2/CH_4-feed gas mixture.

the Matrimid-based membranes are confirmed by these experiments (Fig. 10). Matrimid membranes show the highest amount of CO_2-induced residual conditioning (>40%) and thus the strongest effect of plasticization. The other materials appeared to be less susceptible to plasticization looking at the trends in CO_2-permeance. They show significantly less residual conditioning after the mixed gas permeation experiment (~20%). Furthermore, the two polyimide blends experience a similar extent of residual conditioning, suggesting a similar magnitude of CO_2-induced plasticization effects. This was also observed in the permeation experiments with pure CO_2 (Fig. 2). However, the mixed gas CO_2-permeance shows a permeance reduction for PES/Matrimid membranes and a permeance increase for P84/Matrimid membranes with increasing fugacity. Probably, the observed difference in the CO_2-permeance behavior may be attributed to a more pronounced competitive sorption effect
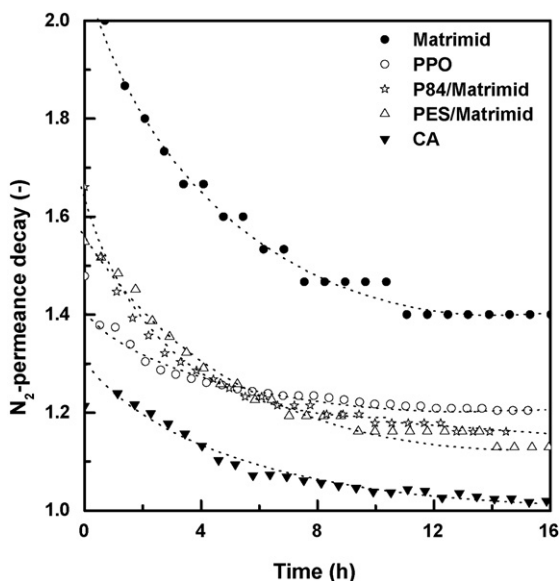
in PES/Matrimid membranes compared to P84/Matrimid membranes.

Fig. 11 shows the (a) mixed gas CO_2/CH_4-separation factors and (b) normalized CH_4-permeance as a function of CO_2-fugacity for the different membranes investigated. Plasticization has a much stronger effect on the separation performance due to the higher CO_2-feed concentration compared to the previously described gas mixtures, as was shown by N_2-permeance decay measurements (Fig. 10). Therefore, decreases in selectivity are not only caused by competitive sorption effects, but by plasticization effects as well. For example, for cellulose acetate it is reported that plasticization is the most dominating effect [17]. This is verified by looking at the CO_2/CH_4-separation factors in Fig. 10. CA membranes show the largest loss in selectivity as a function of fugacity of all used materials, which is confirmed by looking at the normalized CH_4-permeance. The increase in normalized CH_4-permeance with increasing fugacity is the strongest for CA membranes.

For the other membranes (Matrimid, P84/Matrimid, PES/Matrimid and PPO) plasticization effects are pronounced as well, as the CH_4-permeance increases with increasing fugacity as well. However, in the case of CA membranes, the selectivity as a function of fugacity was lower at this CO_2-feed gas concentration compared to the previous described feed gas mixtures, while it increased for PPO, PES/Matrimid and P84/Matrimid membranes. It suggests that plasticization is not as dominant in these latter membranes compared to CA membranes. For Matrimid membranes similar selectivities were obtained compared to the 20/80 vol.% CO_2/CH_4-feed gas mixture, suggesting stronger plasticization effects than for PPO and the Matrimid-based blends, but weaker than for CA membranes. Typically, in the absence of plasticization, the mixed gas selectivity increases with increasing CO_2-feed gas concentration due to competition effects. Since the selectivity is higher with increasing CO_2-feed gas concentration, it can be concluded that competition effects still dominate the mixed gas separation performance of P84/Matrimid, PES/Matrimid and PPO membranes. Plasticization effects are clearly present but do not significantly influence
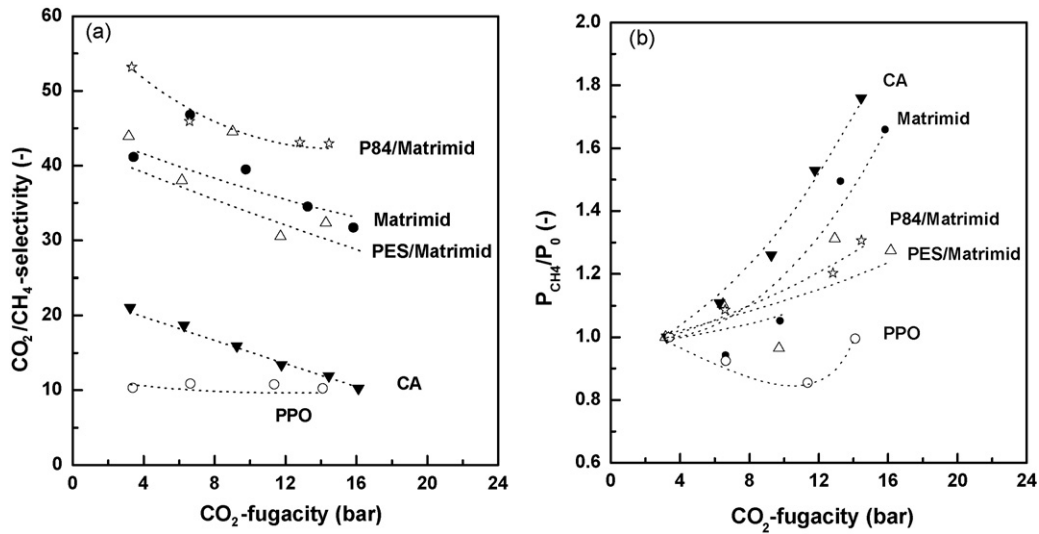

Fig. 10. N_2-permeance decay after 80/20 vol.% CO_2/CH_4-separation at a feed pressure of 16×10^5 Pa (16 bar) (CO_2-fugacity of 13.3×10^5 Pa (13.3 bar)).

Fig. 11. CO_2/CH_4-selectivity as a function of CO_2-fugacity using a 80/20 vol.% CO_2/CH_4-mixture.

the separation performance of these membranes, while they do for CA and Matrimid membranes.

Summarizing, at a CO_2-feed gas concentration of 80 vol.% plasticization effects start to dominate the separation performance of Matrimid membranes. CA membranes experience a stronger effect of plasticization compared to the previous mixture, causing a decrease in selectivity with increasing CO_2-feed concentration. Competition effects are dominating the separation performance of P84/Matrimid, PPO and PES/Matrimid membranes, although plasticization effects are clearly visible.

4.3.4. 98/2 vol.% CO_2/CH_4-separation

The trends that can be observed in the absolute and normalized CO_2-permeance (Fig. 12) using a 98/2 vol.% feed gas mixture are similar to those observed using a 80/20 vol.% feed gas mixture (Fig. 9). The absolute CO_2-permeances for the different materials are higher due to a decrease in competitive sorption effects (decreasing concentration of second component CH_4). Furthermore, the normalized CO_2-permeance increases with increasing fugacity for CA, Matrimid and P84/Matrimid membranes. For PES/Matrimid membranes still a slight decrease in the CO_2-permeance with increasing fugacity is observed. Due to smaller competition effects and a higher degree of plasticization at this feed gas composition, the increase in CO_2-permeance is stronger for P84/Matrimid compared to the 80/20 vol.% feed gas mixture. For the same reasons, the decrease in CO_2-permeance with increasing fugacity is less strong for PES/Matrimid membranes.

A stronger increase in CO_2-permeance with increasing fugacity is not observed for CA membranes. The total increase in CO_2-permeance seems to be more or less unchanged. As all used membranes were completely aged before performing any mixed gas permeation experiment, a difference in the level of physical aging can be excluded as the reason for this effect. Furthermore, membranes without CO_2-permeation history were always used for a mixed gas experiment. The exact reason for the devia-
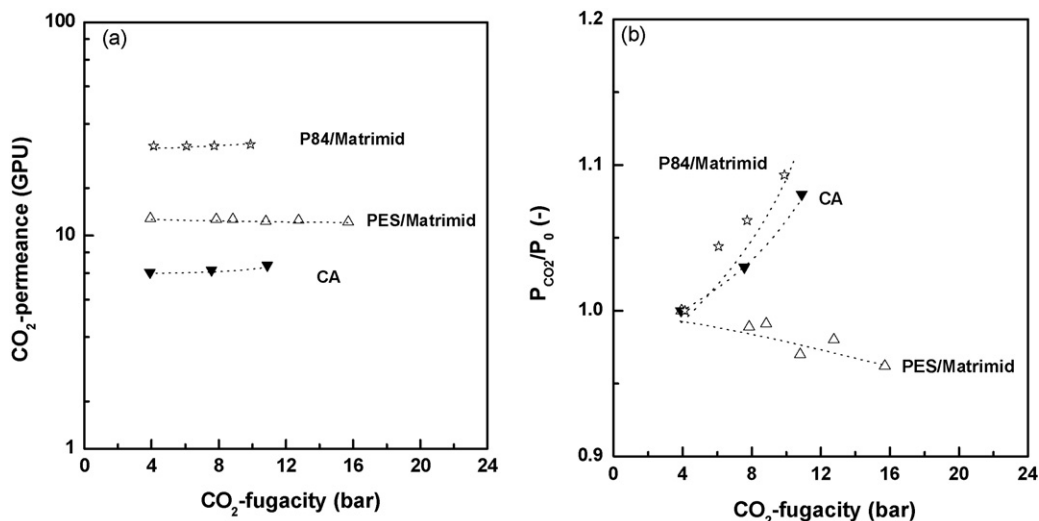

Fig. 12. (a) Absolute (in GPU) and (b) normalized CO_2-permeance as a function of CO_2-fugacity using a 98/2 vol.% CO_2/CH_4-feed gas mixture.
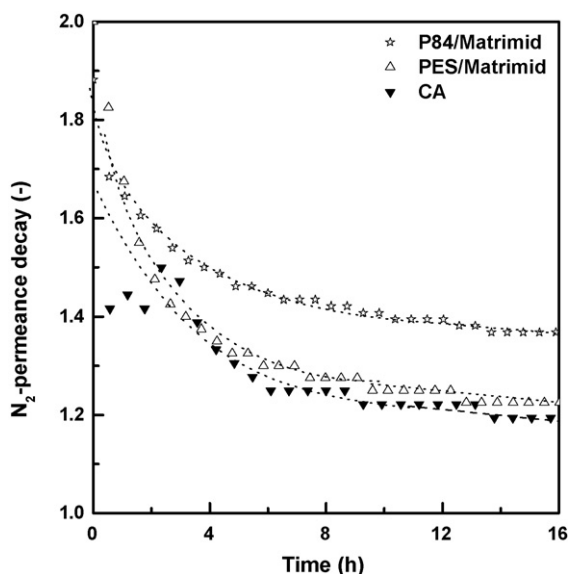
Fig. 13. N_2-permeance decay after 98/2 vol.% CO_2/CH_4 separation at a feed pressure of 16×10^5 Pa (16 bar) (CO_2-fugacity of 13.3×10^5 Pa (13.3 bar)).

tion in the CO_2-permeance behavior of CA membranes remains unclear.

Nonetheless, the extent of residual conditioning measured by the N_2-permeance decay (Fig. 13) is significantly higher for CA membranes at this feed gas concentration compared to the 80/20 vol.% feed gas mixture.

The degree of plasticization is that high that the initial N_2-permeance is not recovered anymore as was observed in the previously described feed gas mixtures (50/50 and 80/20 vol.% CO_2/CH_4). For the other membranes (PES/Matrimid and P84/Matrimid), a higher extent of residual conditioning is observed at this CO_2-feed concentration. The effects of plasticization appeared to be stronger for P84/Matrimid membranes compared to PES/Matrimid membranes, while the difference in pure gas CO_2-permeation behavior was very small.

Fig. 14 shows (a) the mixed gas separation factor and (b) the normalized CH_4-permeance as a function of CO_2-fugacity in the separation of a 98/2 vol.% CO_2/CH_4-feed gas mixture. The separation factor of CA membranes is lower compared to the separation of the 80/20 vol.% CO_2/CH_4-feed gas mixture, which is due to strong and dominating plasticization effects. This causes also a strong increase in the normalized CH_4-permeance with increasing CO_2-fugacity. Plasticization is clearly more pronounced for P84/Matrimid membranes at a 98/2 vol.% feed gas concentration because a relative strong decrease in separation factor with increasing CO_2-fugacity is observed, while the values of the CO_2/CH_4-selectivity are lower compared to those in the separation of a 80/20 vol.% CO_2/CH_4-feed gas mixture. Besides, a large increase in the normalized CH_4-permeance with increasing fugacity is observed (Fig. 14b). Therefore, it can be concluded that plasticization is dominating the separation performance of P84/Matrimid membranes at a 98/2 vol.% CO_2/CH_4-feed gas composition.

Plasticization has also a significant effect on the separation performance of PES/Matrimid membranes as the normalized CH_4-permeance is increasing with increasing CO_2-fugacity (Fig. 14b). However, competitive sorption still seems to be the dominant effect, as the mixed gas selectivity values increased with increasing CO_2-feed concentration (from 80 to 98 vol.%) as a result of less competition effects.

Summarizing, plasticization effects are significantly stronger at a CO_2-feed concentration of 98% vol.%, as is shown by the N_2-permeance decay measurements. Furthermore, plasticization effects start to dominate the separation performance of P84/Matrimid membranes, because the mixed gas selectivity decreases with increasing CO_2-feed gas concentration (80–98 vol.%) and the CH_4-permeance shows a relative strong increase with increasing fugacity. Although plasticization effects are also more pronounced for PES/Matrimid membranes, the mixed gas selectivity still increases by increasing the CO_2-feed gas concentration from 80 to 98 vol.%, which suggests the mixed gas separation performance is not significantly influenced
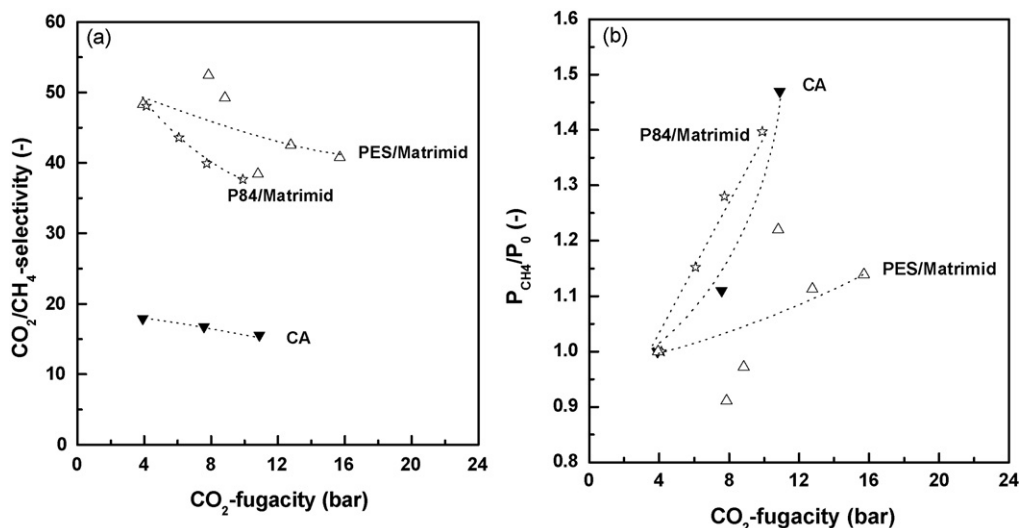

Fig. 14. CO_2/CH_4-selectivity as a function of CO_2-fugacity in the separation of a 98/2 vol.% CO_2/CH_4-feed gas mixture.

by plasticization effects over the complete concentration range investigated.

4.4. Discussion

Overall it can be concluded that a subtle balance between competition and plasticization effects exists in all asymmetric membranes investigated. However, depending on the material studied, plasticization or competition dominates the mixed gas transport behavior. For Matrimid membranes plasticization is dominant at high CO_2-feed gas concentrations (80 vol.% CO_2), while competition effects are dominant at low CO_2-feed gas concentrations (20 vol.% CO_2). For CA membranes, plasticization appears to be always the dominant effect (with the used feed gas compositions). Especially in the case of CA, plasticization effects can cause significant losses in selectivity with increasing CO_2-level, as was also observed by others [17–19]. PPO appeared to less susceptible to plasticization, but showed poor mixed gas selectivities probably caused by strong competition effects. Furthermore, the PPO membranes still contained some surface defects, which logically lowered the maximum achievable selectivity.

Of all asymmetric membranes investigated, PES/Matrimid and P84/Matrimid membranes have the most promising CO_2/CH_4-separation properties. The separation properties improve with decreasing CH_4-fugacity, which was interpreted as a result of strong competitive sorption effects in PES/Matrimid membranes. Plasticization effects seem not to influence the mixed gas separation performance much. A similar trend was observed for P84/Matrimid membranes; the separation properties became better with decreasing CH_4-fugacity. However, at the lowest CH_4-fugacity and higher CO_2-fugacity (high CO_2-feed gas concentrations) the separation properties start to decline due to significant plasticization. Blending Matrimid with PES or P84 positively influences the plasticization resistance and thus the mixed gas separation performance, although it appears to be more effective at high CO_2-feed gas concentrations for PES/Matrimid membranes. Unless the fact that P84/Matrimid membranes seem to be slightly more susceptible to plasticization effects, they have much higher mixed gas selectivities compared to PES/Matrimid membranes.

It should be pointed out that plasticization phenomena are highly dependent on the conditions of the experiment. To allow a fair comparison, it was attempted to use membranes with a more or less similar skin thicknesses. However, the P84/Matrimid membranes possessed a thinner skin than the other four membranes. Typically, plasticization effects are more pronounced with decreasing thickness of the separation layer [11]. Furthermore, we were unable to obtain defect-free PPO membranes, which obviously influenced the maximum obtainable selectivity, while the reproducibility of the CA membranes was poor. Nevertheless, the observed trends to our opinion give a reliable view on the effects occurring in the mixed gas permeation behavior of different membrane materials based on glassy polymers.

Competitive sorption and especially plasticization effects can result in significant lower mixed gas selectivities for glassy polymer membranes. However, glassy polymer membranes may still
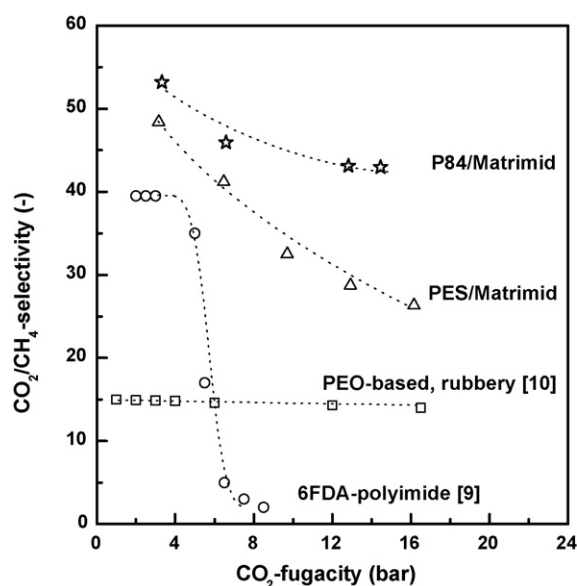

Fig. 15. Mixed gas CO_2/CH_4-selectivity as a function of the CO_2-fugacity for two Matrimid-based glassy polymer membranes using a 80/20 vol.% CO_2/CH_4-feed gas mixture and a PEO-based rubbery membrane [10].

show a much better separation performance than for example rubbery membranes which do not experience competitive sorption effects [10]. Fig. 15 shows the mixed gas CO_2/CH_4-selectivity as a function of CO_2-fugacity of PES/Matrimid, P84/Matrimid membranes using a 80/20 vol.% CO_2/CH_4-feed gas mixture and a PEO-based rubbery membrane [10]. The two Matrimid-based membranes exhibit much higher CO_2/CH_4-selectivities, mainly due to high diffusion selectivities. Although for other glassy polymer membranes (6FDA-polyimide in Fig. 15) the diffusion selectivity is often completely lost due to CO_2-plasticization [9], Fig. 15 shows that a stable separation performance is obtained for PES/Matrimid and P84/Matrimid membranes up to at least 14×10^5 Pa (14 bar) CO_2. This partial pressure is in the range of typical CO_2-fugacities in natural gas.

5. Conclusions

The results show that a subtle balance exists between competitive sorption and plasticization effects for all asymmetric membranes investigated. The magnitude of competition or plasticization effects varies depending on the materials investigated. Different levels of CO_2-concentration are required to reach the point where plasticization starts to dominate the separation performance of a certain material. The mixed gas permeation results showed that plasticization effects dominated the mixed gas separation performance of asymmetric Matrimid and CA membranes, resulting in a relative large loss of selectivity. PPO membranes appeared to be less susceptible to plasticization, but gave low mixed gas CO_2/CH_4-selectivities. The mixed gas separation performance of asymmetric PES/Matrimid membranes was not very sensitive for CO_2-plasticization due to relative strong competitive sorption effects. Although it enhanced the plasticization resistance, blending PES with Matrimid resulted in membranes with a lower selectivity compared to pure

Matrimid membranes. On the other hand, the addition of P84 to a Matrimid-based blend resulted in higher selectivity and increased plasticization resistance. However, this was only valid for CO_2-feed gas concentrations below 80 vol.%. Above this CO_2-feed gas concentration plasticization effects started to dominate the mixed gas separation performance of P84/Matrimid membranes above this CO_2-feed gas concentration.

Acknowledgements

References

[1] S.A. Stern, Polymers for gas separations—the next decade, J. Membr. Sci. 94 (1994) 1–65.

[2] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, J. Membr. Sci. 62 (2) (1991) 165–185.

[3] W.J. Koros, R. Mahajan, Pushing the limits on possibilities for large scale gas separation: which strategies? J. Membr. Sci. 175 (2) (2000) 181–196.

[4] R.W. Baker, Future directions of membrane gas separation technology, Ind. Eng. Chem. Res. 41 (2002) 1393–1411.

[5] T. Visser, G.H. Koops, M. Wessling, On the subtle balance between competitive sorption and plasticization effects in asymmetric hollow fiber gas separation membranes, J. Membr. Sci. 252 (1–2) (2005) 265–277.

[6] G.C. Kapantaidakis, G.H. Koops, High flux polyethersulfone-polyimide blend hollow fiber membranes for gas separation, J. Membr. Sci. 204 (2002) 153–171.

[7] M. Wessling, S. Schoeman, T.v.d. Boomgaard, C.A. Smolders, Plasticization of gas separation membranes, Gas Sep. Purif. 5 (4) (1991) 222–228.

[8] A. Bos, I.G.M. Pünt, M. Wessling, H. Strathmann, CO_2-induced plasticization phenomena in glassy polymers, J. Membr. Sci. 155 (1) (1999) 67–78.

[9] C. Staudt-Bickel, W.J. Koros, Improvement of CO_2/CH_4 separation characteristics of polyimides by chemical crosslinking, J. Membr. Sci. 155 (1) (1999) 145–154.

[10] H. Lin, E. Van Wagner, R. Raharjo, B.D. Freeman, I. Roman, High-performance polymer membranes for natural-gas sweetening, Adv. Mater. 18 (1) (2006) 39–44.

[11] M. Wessling, M. Lidon Lopez, H. Strathmann, Accelerated plasticization of thin-film composite membranes used in gas separation, Sep. Purif. Technol. 24 (1–2) (2001) 223–233.

[12] X. Duthie, S. Kentish, C. Powell, K. Nagai, G. Qiao, G. Stevens, Operating temperature effects on the plasticization of polyimide gas separation membranes, J. Membr. Sci. 294 (1–2) (2007) 40–49.

[13] T. Visser, M. Wessling, Sorption-induced relaxation phenomena in a glassy polyimide, Macromolecules, submitted for publication.

[14] M. Al-Juaied, W.J. Koros, Performance of natural gas membranes in the presence of heavy hydrocarbons, J. Membr. Sci. 274 (1–2) (2006) 227–243.

[15] W.J. Koros, R.T. Chern, V. Stannett, H.B. Hopfenberg, Model for permeation of mixed gases and vapors in glassy polymers, J. Polym. Sci. Polym. Phys. Ed. 19 (10) (1981) 1513–1530.

[16] R.T. Chern, W.J. Koros, E.S. Sanders, R. Yui, Second component effects in sorption and permeation of gases in glassy polymers, J. Membr. Sci. 15 (1983) 157–169.

[17] E. Sada, H. Kumazawa, P. Xu, S.T. Wang, Permeation of pure carbon-dioxide and methane and binary-mixtures through cellulose-acetate membranes, J. Polym. Sci., Part B: Polym. Phys. 28 (1) (1990) 113–125.

[18] S.Y. Lee, B.S. Minhas, M.D. Donohue, Effect of gas composition and pressure on permeation through cellulose acetate membranes, AiChE Symp. Ser. 84 (261) (1989) 93–99.

[19] M.D. Donohue, B.S. Minhas, S.Y. Lee, Permeation behaviour of carbon dioxide-methane mixtures in cellulose acetate membranes, J. Membr. Sci. 42 (1989) 197–214.

[20] A. Bos, I.G.M. Pünt, M. Wessling, H. Strathmann, Suppression of gas separation membrane plasticization by homogeneous polymer blending, AIChE J. 47 (5) (2001) 1088–1093.

[21] S. Gagne, G. Chowdhury, T. Matsuura, B. Laverty, Optimization of CO_2/CH_4-separation performance of integrally skinned assymetric membranes prepared from poly (2,6-dimethyl-1,4-phenylene oxide) by factorial design, J. Appl. Polym. Sci. 72 (12) (1999) 1601–1610.

[22] J. Smid, J.H.M. Albers, A.P.M. Kusters, The formation of asymmetric hollow fibre membranes for gas separation, using PPE of different intrinsic viscosities, J. Membr. Sci. 64 (1–2) (1991) 121–127.

[23] J.H. Hao, S. Wang, Influence of quench medium on the structure and gas permeation properties of cellulose acetate membranes, J. Appl. Polym. Sci. 68 (8) (1998) 1269–1276.

[24] J.J. Krol, M. Boerrigter, G.H. Koops, Polyimide hollow fiber gas separation membranes: preparation and the suppression of plasticization in propane/propylene environments, J. Membr. Sci. 184 (2) (2001) 275–286.

[25] T. Visser, M. Wessling, High-flux integrally skinned P84/Matrimid asymmetric hollow fiber membranes for gas separation, in press.

[26] M.K. Murphy, E.R. Beaver, A.W. Rice, Post-treatment of asymmetric membranes for gas application, AIChE Symp. Ser. 85 (272) (1989) 34–40.

[27] P.H. Pfromm, I. Pinnau, W.J. Koros, Gas-transport through integral-asymmetric membranes—a comparison to isotropic film transport-properties, J. Appl. Polym. Sci. 48 (12) (1993) 2161–2171.

[28] M. Wessling, I. Huisman, T. Vanderboomgaard, C.A. Smolders, Time-dependent permeation of carbon-dioxide through a polyimide membrane above the plasticization pressure, J. Appl. Polym. Sci. 58 (11) (1995) 1959–1966.

[29] H.M. Ettouney, O. Majeed, Transport and permeation properties of a ternary gas mixture in a medium-size polysulfone hollow fiber permeator, Sep. Sci. Technol. 31 (11) (1996) 1573–1596.

[30] J.N. Barsema, G.C. Kapantaidakis, N.F.A. van der Vegt, G.H. Koops, M. Wessling, Preparation and characterization of highly selective dense and hollow fiber asymmetric membranes based on BTDA-TDI/MDI co-polyimide, J. Membr. Sci. 216 (1–2) (2003) 195–205.

[31] W.R. Vieth, J.M. Howell, J.H. Hsieh, Dual sorption theory, J. Membr. Sci. 1 (1976) 177.

[32] G. Chowdhury, R. Vujosevic, T. Matsuura, B. Laverty, Effects of polymer molecular weight and chemical modification on the gas transport properties of poly (2,6-dimethyl-1,4-phenylene oxide), J. Appl. Polym. Sci. 77 (5) (2000) 1137–1143.