Enhancement of CO₂ Affinity in a Polymer of Intrinsic Microporosity by Amine Modification

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ABSTRACT: Nitrile groups in the polymer of intrinsic microporosity PIM-1 were reduced to primary amines using borane complexes. In adsorption experiments, the novel amine−PIM-1 showed higher CO₂ uptake and higher CO₂/N₂ sorption selectivity than the parent polymer, with very evident dual-mode sorption behavior. In gas permeation with six light gases, the individual contributions of solubility and diffusion to the overall permeability was determined via time-lag analysis. The high CO₂ affinity drastically restricts diffusion at low pressures and lowers CO₂ permeability compared to the parent PIM-1. Furthermore, the size-sieving properties of the polymer are increased, which can be attributed to a higher stiffness of the system arising from hydrogen bonding of the amine groups. Thus, for the H₂/CO₂ gas pair, whereas PIM-1 favors CO₂, amine−PIM-1 shows permselectivity toward H₂, breaking the Robeson 2008 upper bound.

INTRODUCTION

Highly selective sorbents and membranes are desired for energy-efficient carbon dioxide capture and other gas separations. Polymeric molecular sieves, such as polymers of intrinsic microporosity (PIMs), offer advantages over inorganic and metal−organic porous materials in terms of processability. PIMs are glassy polymers that exhibit the characteristics of a microporous material (pore size <2 nm, as defined by IUPAC) because their relatively inflexible, contorted backbones cannot pack space efficiently. The archetypal membrane-forming PIM, referred to as PIM-1 (Scheme 1), is comprised of fused ring sequences interrupted by spiro centers and is prepared by a double aromatic nucleophilic substitution reaction between 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane and tetrafluoroterephthalonitrile. PIM-1 is soluble in common volatile solvents such as chloroform and tetrahydrofuran, and can be processed from solution into membranes that exhibit high permeability coupled with selectivity at the 2008 upper bound of performance for gas pairs such as CO₂/N₂. In recent years, there has been intensive effort aimed at achieving even higher performance, either through the synthesis of novel polymers such as Tröger’s base PIMs or through chemical postmodification of PIM-1. The conversion has been reported of the nitrile groups in PIM-1 to carboxylic acid, tetrazole, thioamide, and amidoxime functionality. The amidoxime formation was described as “noninvasive functionalization” on the grounds that it improved carbon dioxide uptake without an adverse effect on physicochemical properties, although neither sorption selectivity nor membrane transport properties have been reported insofar as we are aware.

Scheme 1. Post-Modification of PIM-1 To Give Amine−PIM-1

PIM-1 in solution in THF was reduced using borane−THF complex under reflux. PIM-1 powders and membranes were reduced without dissolution using borane−dimethyl sulfoxide complex in diethyl ether, which swells the polymer to make the reactive sites accessible.

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Amine modification of sorbents is frequently employed to introduce CO$_2$-philic functionality. In principle, the nitrile groups in PIM-1 could be reduced to primary amines using a variety of reagents. However, reactions that work well with low molar mass compounds are not always effective when applied to high molar mass polymers. Initial attempts to carry out the nitrile reduction with lithium aluminum hydride were unsuccessful. Borane complexes have been reported to be effective in reducing nitriles to primary amines with good yield.

Here we show that borane complexes can be used successfully to form amine−PIM-1 (Scheme 1). The incorporation of primary amines enhances CO$_2$ affinity, compared to the parent polymer, as demonstrated by gas adsorption experiments on powder and membrane samples, and by gas permeation studies of membrane samples. For the membrane samples, the reduction was carried out on preformed PIM-1 membranes, since the isolated amine−PIM-1 proved insoluble in common laboratory solvents and could not be cast from solution to form free-standing membranes. Reductions were similarly carried out on PIM-1 powders and on PIM-1 films coated onto glass slides.

## EXPERIMENTAL SECTION

**Materials.** All solvents and reagents were used as purchased without further purification, unless stated otherwise. Methanol, ethanol (≥99.5%), chloroform (≥99.5%), and dimethyl sulfoxide (≥99.5%) were employed. Toluene (≥99.5%) and dimethyl ether (99.5%) were purchased from Sigma-Aldrich. PIM-1 was prepared as described previously.

**PIM-1 Membrane Preparation.** PIM-1 (397 mg) was dissolved in CHCl$_3$ (19.6 mL) and stirred overnight. The membrane was then cast into a 10 cm Petri dish and the solution was allowed to evaporate over a period of 96 h. The membrane was exposed to a mixed ethanol:water (1:1) solution, which helped ease the formation of amine−PIM-1 on the PET film overnight with constant stirring, during which time the reaction mixture was cooled to 0 °C.

**Amine−PIM-1 Synthesis Using Borane−THF Complex.** PIM-1 powder (1 g) was stirred in anhydrous tetrahydrofuran (THF) (65 mL) under an inert atmosphere. Upon dissolution, the mixture was cooled to 0 °C and 1.0 M borane−THF complex (12.24 mmol, 12.24 mL) was added dropwise to the reaction mixture. The reaction was then refluxed overnight with constant stirring, during which time the product precipitated. After cooling, ethanol (40 mL) was added dropwise to remove excess borane. The solid was collected and stirred overnight in 1.0 M methanolic HCl (60 mL), then separated by gravity filtration and stirred in 5% aqueous NaOH solution (100 mL) for 3 h. The solid was washed repeatedly with water until neutral and dried at 120 °C under vacuum overnight. Yield: 846 mg (83%).

**Gas Sorption.** CO$_2$ and N$_2$ adsorption isotherms at a temperature of 0 °C (273.15 K) were obtained using a Micromeritics ASAP 2050 analyzer. Before sorption analysis, the sample was outgassed on the outgas port under vacuum at a temperature of 120 °C for a period of 16 h. Samples then underwent a further manual outgas on the analysis port under high vacuum at 120 °C for a period of 2 h. The measurement is based on determination of the total gas volume absorbed by the material. Helium was used for the free space determination, both at ambient temperature and at 0 °C, after sorption analysis and additional manual outgas for 2 h. The gravimetric adsorption/desorption experiments were carried out using a homemade apparatus equipped with a calibrated McMillan quartz spiral balance (spiral sensitivity 15.253 mg/mm). Experiments were performed at 25 ± 0.1 °C and at absolute pressures ranging from 0 to 17 bar. The detailed experimental procedure and buoyancy testing were described previously.

The sample was appended on the quartz spring by a tiny kanthal wire holder. The glass measuring chamber was evacuated before each measurement to a pressure lower than 10$^{-3}$ mbar by a rotary oil pump (Trivac D4B, Oerlikon Leybold). A Leybold oil-mist filter eliminated (with 99.99% efficiency) contamination of the measuring chamber with oil vapors from the pump. After the exposure of the sample to a particular gas at a known pressure, the elongation of the quartz spiral due to gas sorption by the polymer membrane was monitored by a charge-coupled device (CCD, Sony) until the equilibrium state was reached. The average error of the mass determination reached approximately 30 μg.

Sorption data can be fitted with the well known dual-mode sorption model, describing the gas equilibrium concentration as a function of pressure:

$$ c = k_p p + \frac{C_{hp}}{1 + bp} $$

where $k_p$, $C_{hp}$, and $b$ are the Henry constant, the Henry constant at 1 atm, and the pressure sensitivity, respectively.
where \( c \) is gas concentration, \( p \) is gas pressure, \( k_0 \) is the Henry’s law constant, \( C_g \) is the Langmuir (monolayer) sorption capacity constant, and \( b \) is the Langmuir affinity constant. The gas concentration in the membrane at a given feed pressure is calculated from the gas solubility, \( S \), in the membrane and the gas pressure, \( p \):

\[
c = S \times p
\]  

(2)

If indirect solubility data from permeation measurements are used (see below), then the mean pressure in the membrane must be considered for the calculation of the average permeant concentration:

\[
p = \frac{p_{\text{mean}}}{(p_{\text{feed}} + p_{\text{perv}}} = 2)
\]  

(3)

When applied to permeation data, the above method is only exact if permeability coefficient \( P \), diffusion coefficient \( D \) and solubility coefficient \( S \) are pressure independent, and thus it strictly applies in the case of linear rather than dual-mode sorption. In the case of pressure (or concentration) dependent transport, only complex models that must be solved numerically will give a more robust and correct quantitative description.\(^\text{13,14}\)

**Gas Permeation.** Single gas permeation measurements were carried out at 25 °C and at a feed pressure of 1 bar in a fixed volume pressure increase apparatus (GKSS, Germany) in the time-lag mode.\(^\text{3,15}\) The rotary vacuum pump was equipped with an alumina trap to avoid oil contamination of the membrane. The instrument is equipped with PC controlled pneumatic valves to allow response times of less than 0.5 s.\(^\text{7}\) The gases were tested in the following order: He, H\(_2\), N\(_2\), O\(_2\), CH\(_4\) and CO\(_2\). Before each experiment the membrane sample was carefully evacuated (10\(^{-2}\) mbar) to remove any dissolved gas species. Circular samples with an effective membrane area of 2.14 cm\(^2\) were used. The thickness of the films was determined using a digital micrometer (Mitutoyo, Model IP65). The films were tested as received and after soaking in alcohol overnight and then drying in air at room temperature.

Permeability coefficient, \( P \), and diffusion coefficient, \( D \), were determined as described previously.\(^\text{7}\) The gas permeability is expressed in barrer (1 barrer = 10\(^{-10}\) cm cm\(^2\) s \(^{-1}\) cmHg\(^{-1}\) = 3.35 \times 10\(^{-16}\) mol m\(^{-2}\) s \(^{-1}\) Pa\(^{-1}\)). The solubility coefficient, \( S \), for the gas in the polymer matrix was evaluated indirectly, assuming the validity of the solution-diffusion permeation model:

\[
S = \frac{P}{D}
\]  

(4)

The ideal selectivity for a pair of gases, A and B, was calculated as the ratio of the individual single gas permeabilities. It can be decoupled into solubility-selectivity and diffusivity-selectivity:

\[
\alpha_{A/B} = \frac{P_A}{P_B} = \frac{S_A}{S_B} \times \frac{D_A}{D_B}
\]  

(5)

### RESULTS AND DISCUSSION

**Amine Modification.** Conversion of nitrile to amine was monitored by infrared spectroscopy (Figure 1), which showed loss of the nitrile stretch at 2239 cm\(^{-1}\) and the appearance of peaks at 3360 and 800 cm\(^{-1}\) which may be attributed to N–H stretch and N–H wag, respectively. The presence of nitrogen in the products was confirmed by elemental analysis (e.g., for batch AM1-6: Calc'd for C\(_9\)H\(_9\)N\(_2\)O\(_4\): C, 74.33; H, 6.03; N, 5.98 Found: C, 71.67; H, 6.01; N, 5.13). Solid-state \(^{13}\)C NMR spectra and assignments for PIM-1 and amine–PIM-1 powder prepared using borane–THF complex and borane–dimethyl sulfide complex are shown in Figure 2. On modification, there was a shift in the aromatic peak labeled 11, from 94 ppm in PIM-1 to 118 ppm in amine–PIM-1, and the appearance of a peak at 34 ppm, which may be assigned to the –CH\(_2\)NH\(_2\) carbon. In PIM-1, the CN signal is hidden under the peak for carbons 6 and 9. Both complexes give degrees of conversion >90%, as estimated from IR and NMR data.

Amine modification increased the hydrophilicity of the polymer surface, as evidenced by a decrease in water contact angle from 86° to 66° for thin films on a glass substrate (Figure 3). Amine–PIM-1 membranes were found to be insoluble in chloroform, dichloromethane, hexane, tetrahydrofuran, dimethyl sulfoxide (DMSO), ethyl acetate, acetone, diethyl ether, dimethylacetamide, dimethylformamide, ethanol, 1-propanol, 2-propanol, 1-butanol, n-dodecane, toluene, mesitylene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, m-cresol, pyridine, diethylamine, triethylamine, N,N′,N′-tetramethylthelylenediamine, 1-methyl-2-pyrrrolidinamine, aqueous HCl and aqueous NaOH. They were also insoluble in solvent mixtures such as aqueous HCl/DMSO and aqueous NaOH/DMSO at temperatures up to 60 °C.

Thermogravimetric analysis of amine–PIM-1 showed ca. 7% weight loss in the temperature range 350–450 °C prior to the degradation associated with the PIM-1 backbone (Figure 4). This is consistent with loss of NH\(_3\), although it could also reflect a loss of residual solvent.

Chemical modification of PIM-1, especially with groups that are capable of hydrogen-bonding, frequently results in a reduction in the BET surface area determined from N\(_2\) adsorption at −196 °C (77 K).\(^\text{5,7}\) and in the case of amine–PIM-1, the low temperature N\(_2\) adsorption was so slow that an isotherm could not be obtained. Indeed, gas permeation measurements (below) confirm that amine–PIM-1 is more size-selective than PIM-1, and at lower temperature this will penalize especially the transport of the bulkier N\(_2\) molecules. However, despite this loss of microporosity toward a nitrogen probe at −196 °C, high CO\(_2\) uptake was achieved at 0 and 25 °C, as shown below. A similar loss of BET surface area coupled with enhanced CO\(_2\) affinity was observed for tetrazole-modified PIM-1.\(^\text{6}\)

**Gas Sorption.** Gas sorption results were obtained both at 0 °C, using a volumetric method, and at 25 °C, using a gravimetric method. Isotherms at 0 °C for amine–PIM-1 showed notably higher CO\(_2\) uptake than the parent polymer (Figure 5a) and enhanced CO\(_2\)/N\(_2\) sorption selectivity (Figure 5b). For a membrane sample, the ideal CO\(_2\)/N\(_2\) sorption selectivity at 1 bar was 22 for amine–PIM-1, compared to 16 for the unmodified polymer. Sorption selectivity is especially...
high at low pressure, confirming the much stronger interaction of CO$_2$ with the polymer as compared to N$_2$, as also suggested by the extremely steep start of the CO$_2$ sorption isotherm. From sorption measurements alone one cannot distinguish whether the steep curve is due to strong adsorption of CO$_2$ in very small pores (ultramicropores, <0.7 nm), inaccessible to the slightly larger N$_2$ molecule, or to strong absorption by specific interaction or chemical reaction of the first monolayer of absorbed CO$_2$ in pores of any size.

A repeat adsorption run at 0 °C showed a lower CO$_2$ uptake (Figure 5c). The level of CO$_2$ uptake could be recovered, and even exceeded at high pressure, by repeating the purification procedure used after synthesis (soaking in methanolic HCl, then aqueous NaOH, washing with water and drying). It might be argued that the loss of capacity after the initial run is a consequence of specific binding of CO$_2$, perhaps through formation of carbamic acid or carbamate species, as has been observed for other amine-modified nanoporous materials. However, the gravimetric CO$_2$ adsorption/desorption isotherm up to 17 bar at 25 °C (Figure 5d), while showing a slight hysteresis in the desorption curve, gives a virtually perfect return to the origin (only 0.3% weight change), confirming that there are no changes in the sample due to, for instance, irreversible chemical reaction. An alternative explanation of loss of capacity is rapid physical aging of the polymer in the presence of CO$_2$ at high pressure, as is discussed further in the context of permeation studies below.

Gravimetric sorption data at 25 °C (Figures 5d and 6) compare well with the volumetric data, giving slightly lower uptakes due to the higher temperature. Amine–PIM-1 clearly shows much higher CO$_2$/N$_2$ and CO$_2$/CH$_4$ sorption selectivity than the parent PIM-1. Whereas in PIM-1 and thioamide–PIM-1 the most permeable gas is CO$_2$, for amine–PIM-1 the H$_2$ permeability is higher than that of CO$_2$, evidencing a distinct size-sieving ability of the polymer, as has also been observed for the more rigid PIM-EA-TB. While in the latter the increased...
size-sieving ability derives from the higher rigidity of the EA-TB backbone, in amine−PIM-1 inter- and intrachain hydrogen bond formation between amine groups may be assumed to impart additional stiffness to the system.

Diffusion coefficients calculated from experimental time-lags, and solubility coefficients calculated using eq 4, are given in Table 3 for amine−PIM-1 and thioamide−PIM-1. It is noteworthy that for amine−PIM-1 the values of $D$ for CO$_2$ are lower than those for N$_2$. In polymers the slightly smaller CO$_2$ molecule$^{20}$ is generally expected to diffuse faster than N$_2$, although many examples of the opposite situation exist.$^{21}$ This is consistent with strong immobilizing adsorption of CO$_2$, as demonstrated by Paul and Kemp,$^{22}$ who showed that the incorporation of a strongly adsorbing filler (zeolite 5A) into a polymer (silicone rubber) resulted in much greater time-lags (and hence lower apparent values of $D$) for CO$_2$ than for N$_2$. In the present case, very high affinity of amine−PIM-1 for CO$_2$ is qualitatively visible in Figure 6 as more pronounced dual mode

Figure 5. (a) CO$_2$ (filled symbols) and N$_2$ (open symbols) adsorption isotherms at 0 °C for PIM-1 (○) and amine−PIM-1 (●, ◊) membranes. (b) CO$_2$/N$_2$ ideal sorption selectivity at 0 °C for PIM-1 (○) and amine−PIM-1 (●) membranes. (c) CO$_2$ adsorption isotherms at 0 °C for amine−PIM-1 membrane: First run (●), repeat run (×) and after repurification (◊). (d) CO$_2$ adsorption (●) and desorption (○) isotherms from gravimetric sorption balance at 25 °C, with dual-mode fit, showing uptake in units of g/g (left axis) and mmol/g (right axis).

Figure 6. Gravimetric sorption isotherms (left axis) for CO$_2$ (○), CH$_4$ (Δ), and N$_2$ (□) in (a) methanol-treated amine−PIM-1 membrane (77 μm thickness) and (b) PIM-1 membrane (50 μm thickness). Thin solid lines represent the fit of the data according to the dual mode sorption model and thick solid lines (right axis) represent the corresponding ideal sorption selectivity calculated from the curve fit.
This work and thioamide, but respectively, the affinity is best expressed by the dual mode affinity factor, $b$, and the infinite dilution solubility, $S_0$:

$$S_0 = \lim_{p \to 0} \frac{dc}{dp} = k_d + C_H b$$

(6)

The latter represents the initial slope of the sorption isotherm, which is higher for amine–PIM-1 than for PIM-1 by a factor of nearly three, whereas it is equal for the inert gases methane and nitrogen (Table 4).

The perhaps surprising inversion of the diffusion coefficients of CO$_2$ and N$_2$ by strong affinity between CO$_2$ and the amine groups in the polymer backbone was recently also found for a novel PIM with Tröger’s base units in the backbone, showing unexpectedly low CO$_2$/N$_2$ selectivity and CO$_2$/CH$_4$ selectivity. This principle was previously demonstrated for amine-functionalized polysulfone and has been reviewed by Lin and Freeman. The net effect of increased polymer–penetrant interaction is a delicate balance between increased sorption, favoring transport, and possible “immobilization,” penalizing transport. The result will vary from case to case but will always be negative if interaction is too strong.

For amine–PIM-1, treatment with ethanol increases from two to three times the permeability of most gases, and over four times that of CO$_2$, compared to the as cast membrane (Table 1). After 18 months the permeabilities and the selectivities return to values which are slightly higher than those of the as cast film. The decrease in permeability on aging is more significant for larger gases (O$_2$, N$_2$, CH$_4$, CO$_2$) than for smaller ones (He and H$_2$). The He/N$_2$, H$_2$/CH$_4$ and O$_2$/N$_2$ ideal selectivities, slightly reduced by ethanol soaking, increase upon aging. Glassy polymers typically present a permeability decline over time owing to relaxation of the macromolecular chains, a reduction of the total free volume and a rearrangement of the free volume element size and distribution, and consequent

### Table 1. Gas Permeability Coefficients ($P$, barrer) for Amine–PIM-1 (This Work) and Thioamide–PIM-1 (Ref 7) Membranes with Different Histories at 25 °C

| polymer          | membrane state | He   | H$_2$ | O$_2$ | N$_2$ | CO$_2$ | CH$_4$ |
|------------------|----------------|------|-------|-------|-------|--------|--------|
| amine–PIM-1      | as cast        | 391  | 876   | 216   | 55.7  | 295    | 82.8   |
|                  | ethanol-treated| 863  | 2210  | 662   | 181   | 1230   | 259    |
|                  | aged 18 months | 483  | 1060  | 232   | 55    | 309    | 69     |
|                  | methanol-treated| 1200 | 3070  | 895   | 230   | 1890   | 303    |
| thioamide–PIM-1  | as cast        | 55   | 92    | 19    | 3.9   | 150    | 8.7    |
|                  | ethanol-treated| 270  | 610   | 140   | 37    | 1120   | 56     |

### Table 2. Ideal Selectivity ($\alpha = P/P_i$) for Various Gas Pairs in Amine–PIM-1 (This Work) and Thioamide–PIM-1 (Ref 7) Membranes with Different Histories at 25 °C

| polymer          | membrane state | He/N$_2$ | H$_2$/CH$_4$ | O$_2$/N$_2$ | CO$_2$/N$_2$ | CO$_2$/CH$_4$ |
|------------------|----------------|---------|--------------|-------------|--------------|--------------|
| amine–PIM-1      | as cast        | 0.70    | 1.06         | 3.87        | 5.30         | 3.57         |
|                  | ethanol-treated| 4.77    | 8.54         | 3.66        | 6.81         | 4.76         |
|                  | aged 18 months | 8.81    | 15.4         | 4.31        | 5.65         | 4.48         |
|                  | methanol-treated| 5.22   | 10.1         | 3.90        | 8.24         | 6.24         |
| thioamide–PIM-1  | as cast        | 14.11   | 10.6         | 4.9         | 38.1         | 17.4         |
|                  | ethanol-treated| 7.3     | 10.6         | 3.8         | 30.3         | 19.6         |

### Table 3. Gas Diffusion Coefficients ($D$, 10$^{-8}$ cm$^2$ s$^{-1}$) and Solubility Coefficients ($S$, cm$^3$ [STP] cm$^{-3}$ bar$^{-1}$) in Amine–PIM-1 (This Work) and Thioamide–PIM-1 (Ref 7) Membranes with Different Histories at 25 °C

| polymer          | membrane state | He   | H$_2$ | O$_2$ | N$_2$ | CO$_2$ | CH$_4$ |
|------------------|----------------|------|-------|-------|-------|--------|--------|
| amine–PIM-1      | as cast        | 2290 | 1300  | 48.9  | 14.0  | 7.55   | 4.63   |
|                  | ethanol-treated| 5130 | 2780  | 141   | 40.0  | 25.3   | 12.9   |
|                  | aged 18 months | 2890 | 1790  | 62.6  | 15.8  | 7.0    | 4.52   |
|                  | methanol-treated| 5170 | 3970  | 223   | 59.8  | 39.3   | 17.9   |
| thioamide–PIM-1  | as cast        | 1615 | 590   | 22    | 7.8   | 9.3    | 3.0    |
|                  | ethanol-treated| 1800 | 1250  | 49    | 15    | 21     | 4.4    |
| amine–PIM-1      | as cast        | 0.13 | 0.51  | 3.31  | 2.99  | 29.4   | 13.4   |
|                  | ethanol-treated| 0.13 | 0.60  | 3.51  | 3.39  | 36.5   | 15.1   |
|                  | aged 18 months | 0.125| 0.445 | 2.83  | 2.60  | 33.0   | 11.4   |
|                  | methanol-treated| 0.174| 0.579 | 3.02  | 2.88  | 36.1   | 12.7   |
| thioamide–PIM-1  | as cast        | 0.03 | 0.12  | 0.66  | 0.37  | 12     | 2.2    |
|                  | ethanol-treated| 0.11 | 0.37  | 2.2   | 1.9   | 39     | 9.8    |

sorption behavior and high total sorption of CO$_2$. Quantitatively, the affinity is best expressed by the dual mode affinity factor, $b$, and the infinite dilution solubility, $S_0$:

$$S_0 = \lim_{p \to 0} \frac{dc}{dp} = k_d + C_H b$$

The latter represents the initial slope of the sorption isotherm, which is higher for amine–PIM-1 than for PIM-1 by a factor of nearly three, whereas it is equal for the inert gases methane and nitrogen (Table 4).
increase in polymer density. This can be particularly evident in rigid and highly permeable polymers. Soaking in a lower alcohol reverses the effects of physical aging, as well as removing residues of casting solvent from the films, and allows for a fair comparison of different superglassy polymers by eliminating the casting history. The permeability of the aged sample could thus be fully restored, and even increased, by soaking it in methanol (Table 1). The permeability of CO\(_2\) increases over six times with respect to the as cast film. This confirms the higher effectiveness of methanol compared to ethanol, as observed in PIM-1. The diffusion coefficient is more affected than the solubility by these conditioning procedures (Table 3), giving rise to an increased permeability, along with a slightly reduced selectivity for most gas pairs.

The high H\(_2\) permeability of amine–PIM-1, coupled with good gas selectivities, locates amine–PIM-1 at or above the 2008 Robeson upper bounds for some H\(_2\) separations of technological relevance, such as H\(_2\)/CO\(_2\), H\(_2\)/CH\(_4\) and H\(_2\)/N\(_2\).
(Figure 7), a particularly pronounced effect being observed for H₂/CO₂. For commercial application, higher selectivities would be required, but this work demonstrates the principle that changing a single functional group can lead to a complete reversal of properties.

As discussed above, the incorporation of basic nitrogen functionality enhances the CO₂ capture capacity. Nevertheless, based on pure gas permeation, amine−PIM-1 does not perform better toward CO₂ than PIM-1, and its performance for the CO₂/N₂ and CO₂/CH₄ gas pairs falls below the 2008 upper bounds. The stronger interaction with the polymer matrix reduces the CO₂ diffusion rate, outweighing the relative increase in solubility, giving a net reduction of permeability as compared to other gases and to PIM-1. However, it is not unlikely that this behavior is reverted in mixed gases, where the strong CO₂ sorption is expected to depress permeability of larger molecules, for instance CH₄ in the case of biogas separations. This will be the subject of further studies.

In glassy polymers, gases with a high solubility in the polymer matrix typically show distinct dual-mode sorption behavior, resulting in a pressure dependent permeability. Thus, CO₂ permeation at different pressures revealed a decrease in the gas permeability as the feed pressure increases (Figure 8a), mainly due to a drastic reduction of the CO₂ solubility, whereas the diffusion coefficient increases moderately (Figure 8b). At the lowest pressures, the pressure dependence of the solubility (and permeability) is so high that significant changes occur in the permeate pressure range during a measurement run, manifesting itself as an unusual bend in the permeation curve of CO₂ (Figure 9a). In the same pressure range, nitrogen and methane behave normally (Figure 9b) and have a virtually pressure-independent permeability (Figure 9c), diffusivity, and solubility, and their permeation curves do not show any unusual curvature. Qualitatively, the same kind of behavior was observed in as cast and freshly methanol-soaked membranes.

Swelling, plasticization and/or aging phenomena may further enhance unusual transport behavior in polymer glasses. Figure 8a shows hysteresis in the CO₂ permeation due to notable aging of the freshly methanol-treated membrane during the approximately 10 h of the total measurement cycle. Aging is a well-known phenomenon in PIMs and various approaches have been used to reduce this by chemical modification/cross-linking or by use of mixed matrix materials. The hysteresis is also observed in the diffusion coefficient (Figure 8b), which decreases with time, whereas the solubility is virtually unaffected and independent of time.

Interestingly, it was found that even the indirectly obtained CO₂ solubility data could be fitted fairly well with the dual-mode sorption model (Figure 10). However, there is a discrepancy when this is compared to the directly obtained sorption data. The difference between transport parameters from sorption and permeation is systematic and has recently been reviewed by Robeson et al. In the present case, with very pronounced dual-mode behavior, the discrepancy becomes so strong that in spite of the apparently good qualitative description, the indirect solubility data cannot be used for quantitative analysis.

**CONCLUSIONS**

Borane complexes can be used successfully to reduce the nitrile groups in PIM-1 to primary amines, forming amine−PIM-1. Gas adsorption demonstrates that the incorporation of primary amines enhances the affinity for CO₂ and the CO₂/N₂ and CO₂/CH₄ sorption selectivity, introducing very distinct dual-mode sorption behavior for CO₂ even at low pressures. The affinity is so strong that, in membrane permeation experiments, CO₂ diffusion, and hence permeability, is reduced, but high permeabilities are obtained for small noninteracting gases (H₂ and He). Consequently, for the H₂/CO₂ gas pair, amine modification changes the polymer from being permselective toward CO₂ in PIM-1, to being permselective toward H₂ in amine−PIM-1, breaking the Robeson 2008 upper bound.

The high CO₂ sorption in amine−PIM-1 offers promising perspectives for further improvement in mixed gas permeation, where competitive sorption is expected to favor permeation of CO₂ over other species, and at higher pressures, where swelling and dilation is expected to give a further general increase of permeability. This will be the subject of further studies.

![Figure 10. CO₂ sorption data obtained indirectly from permeability and diffusion coefficients with fit to the dual-mode sorption model (solid line) and the individual contributions of Langmuir sorption (short dashes) and Henry sorption (long dashes).](image-url)
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**ABBREVIATIONS**

NMR, nuclear magnetic resonance; IR, infrared

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