Competitive Permeation of Gas and Water Vapor in High Free Volume Polymeric Membranes

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Abstract

Highly permeable glassy polymeric membranes based on poly (1-trimethylsilyl-1-propyne) (PTMSP) and a polymer of intrinsic porosity (PIM-1) were investigated for water sorption, water permeability and the separation of CO₂ from N₂ under humid mixed gas conditions. The water sorption isotherms for both materials followed behaviour indicative of multilayer adsorption within the microvoids, with PIM-1 registering a significant water uptake at very high water activities. Analysis of the sorption isotherms using a modified dual sorption model which accounts for such multilayer effects gave Langmuir affinity constants more consistent with lighter gases than the use of the standard dual mode approach. The water permeability through PTMSP and PIM-1 was comparable over the water activities studied, and could be successfully modelled through a dual mode sorption model with a concentration dependent diffusivity. The water permeability through both membranes as a function of temperature was also measured, and found to be at a minimum at 80 °C for PTMSP and 70 °C for PIM-1. This temperature dependence is a function of reducing water solubility in both membranes with increasing temperature countered by increasing water diffusivity. The CO₂ - N₂ mixed gas permeabilities through PTMSP and PIM-1 were also measured and modelled through dual mode sorption theory. Introducing water vapour further reduced both the CO₂ and N₂ permeabilities. The plasticization potential of water in PTMSP was determined and indicated water swelled the membrane increasing CO₂ and N₂ diffusivity, while for PIM-1 a negative potential implied that water filling of the micro-voids hampered CO₂ and N₂ diffusion through the membrane.

Keywords: PTMSP, PIM-1, carbon dioxide, water, competitive sorption, plasticization

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1. Introduction

Polymeric membranes for gas separation are attractive because of their low cost and high permselectivity. In particular much emphasis is placed on improving both the permeability and selectivity of the membrane relative to Robeson's upper bound, the criterion denoting current state-of-art performance ¹. However, the majority of measurements are reported under single gas conditions; actual separation performance can deviate greatly within industrial gas mixtures. The presence of other gases and vapours in the feed stream can compete for sorption sites ², reducing solubility and also possibly plasticising the membrane ^{3,4}, increasing diffusivity. If there are significant differences in the hydrophobicity of the vapors and the polymer, the vapour molecules can also form clusters, which block the movement of other species, reducing diffusivity, in a phenomenon often referred to as anti-plasticization ⁵. Importantly, glassy polymers with very high free volume, such as poly (1-trimethylsilyl-1-propyne) (PTMSP) and polymers of intrinsic porosity (PIMs) have been shown to exhibit such blocking behaviour, where large condensable hydrocarbons preferentially sorb into the smaller free volume elements and block the flow of smaller permanent gases ⁶⁻⁹. This leads to significantly different selectivities under mixed gas conditions than for the pure gases.

Water vapour is commonly present in applications such as natural gas processing and post-combustion separation from flue gas ^{2,10}. Water permeability and its influence upon other penetrants have been reported in the literature for polyimides, rubbery polymers and sulfonated polymers ¹¹⁻¹⁷. Water can reduce the solubility of other penetrants through competitive effects, increase free volume and thus diffusivity through plasticization, or alternately reduce diffusivity by clustering or blocking phenomena. However, there is limited information on the influence of water in high free volume membranes, even though there is continuing interest in PTMSP membranes and increasing popularity for PIM based membranes for CO₂ separation ^{18,19}.

Here, we report on the solubility and permeability of water through high free volume membranes based on PTMSP and PIM-1. In addition, the impact of water vapour on the permeability of CO₂ and N₂ under mixed gas conditions is also studied, which simulates a post-combustion carbon capture process. These results are analyzed with a modified dual mode sorption model, coupled with a concentration dependent diffusivity to quantify the change in permselectivity of CO₂/N₂ through PTMSP and PIM-1 in the presence of water. The model enables CO₂ separation performance to be modelled for these membranes under a variety of humid feed gas conditions.

2. Theory

For glassy polymeric membranes, gas sorption is usually modelled by a dual mode approach²⁰, where the concentration in the polymeric matrix is approximated by Henry's law while sorption to the microvoids is by Langmuir adsorption. However, for condensable vapours, strong polymer – vapour and vapour - vapour interactions means that the Langmuir isotherm is too simplistic. This is especially true for vapour sorption isotherms that demonstrate multilayer sorption or clustering. Feng²¹ has developed a more rigorous dual mode sorption model for vapour sorption to polymers:

$$C = \frac{\overline{C_p} k' \frac{f}{f_0}}{1 - k' \frac{f}{f_0}} + \frac{\overline{C_p} (A' - 1) k' \frac{f}{f_0}}{1 + (A' - 1) k' \frac{f}{f_0}} \quad (1)$$

where $\overline{C_p}$ is the weighted mean sorption capacity for a monolayer of penetrant, k' indicates the interaction between the vapour molecule and the polymer molecular segment, and A' measures the interaction of the vapour molecule and the microvoids. f is the fugacity of the vapour penetrant and f_0 is the saturated vapour fugacity at the measurement temperature. This modified dual mode sorption theory can be directly compared to standard dual mode sorption theory, where the Langmuir affinity constant (b) for the vapour is:

$$b = \frac{(A' - 1) k'}{f_0} \quad (2)$$

Paul and Koros²² showed that some of the sorbed gas in the Langmuir microvoids can become trapped or immobilised and thus not contribute to the diffusion through the polymer and account for this through the definition of a mobile concentration (C_m) and an immobilisation factor (F). The effects of competitive sorption can also be addressed through the introduction of a second term in the denominator of the Langmuir sorption term. For gas mixtures that follow the standard dual mode sorption model and assuming a linear concentration gradient, the permeability of gas A (P_A) in the presence of another gas C can then be described by^{23,24}:

$$P_A = \frac{D_A}{f_{A2} - f_{A1}} \left[\left(k_{DA} + \frac{F_A C'_{HA} b_A}{1 + b_A f_{A2} + b_C f_{C2}} \right) f_{A2} - \left(k_{DA} + \frac{F_A C'_{HA} b_A}{1 + b_A f_{A1} + b_C f_{C1}} \right) f_{A1} \right] \quad (3)$$

where k_A is the Henry's Law constant, C'_{HA} the Langmuir capacity, b_A the Langmuir affinity and f_A the fugacity of Gas A. Subscripts 2 and 1 denote the upstream and downstream conditions respectively.

However, when water is present, the diffusion coefficient may become dependent upon the water concentration because of either plasticization or clustering. Consistent with previous work^{4,25}, we assume that the changes in this diffusion coefficient are an exponential function only dependent upon the mobile concentration of water vapour (C_{mB}):

$$D_A = D_{A0} \exp(\beta_B C_{mB}) \quad (4)$$

where β represents the plasticisation potential. A positive value of β reflects membrane swelling (plasticization) and is indicative of a diffusion coefficient that increases with humidity. A negative value indicates blocking behaviour (anti-plasticisation) and a diffusion coefficient that falls with increasing humidity. Hence, the permeability of the mixed gas system can be modelled through²⁶:

$$\begin{aligned} \bar{P}_A = \frac{D_A}{f_{A2}-f_{A1}} & \left\{ \exp \left[\beta_B \left(\frac{\bar{C}_p k' f_{B2}}{f_0} + \frac{F_B \bar{C}_p b_B f_{B2}}{1+b_A f_{A2}+b_B f_{B2}+b_C f_{C2}} \right) \right] \left(k_{DA} + \frac{F_A C'_{HA} b_A}{1+b_A f_{A2}+b_B f_{B2}+b_C f_{C2}} \right) f_{A2} - \right. \\ & \left. \exp \left[\beta_B \left(\frac{\bar{C}_p k' f_{B1}}{f_0} + \frac{F_B \bar{C}_p b_B f_{B1}}{1+b_A f_{A1}+b_B f_{B1}+b_C f_{C1}} \right) \right] \left(k_{DA} + \frac{F_A C'_{HA} b_A}{1+b_A f_{A1}+b_B f_{B1}+b_C f_{C1}} \right) f_{A1} \right\} \end{aligned} \quad (5)$$

When two penetrants can plasticize the membrane, such as CO₂ and H₂O, then the diffusivity coefficient can be expressed as a function of both the plasticization potentials:

$$D_A = D_{A0} \exp(\beta_B C_{mB} + \beta_A C_{mA}) \quad (6)$$

The permeability function is altered accordingly.

3. Experimental

Poly (1-trimethylsilyl-1-propyne) (PTMSP) was purchased from Fluorochem Ltd and used as supplied. PIM-1 is the polycondensation product of ultrahigh purity monomers of 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI) and 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN) and was synthesized following established procedures by Budd and McKeown²⁷. Dense films were cast from solutions of PTMSP in toluene and PIM-1 in dichloromethane respectively and formed through controlled evaporation. The final film thickness was on average 70 μ m and 50 μ m for the two polymers respectively. All films were annealed at 150 °C for 1 day and then cooled to room temperature overnight. To avoid age dependent performance, all PTMSP membranes were measured within two days of heat annealing, and all PIM-1 membranes were washed in methanol before measurement and then allowed

to dry, to reverse any aging effects^{28,29}. Membrane densities were determined through standard procedures³⁰.

Gas sorption measurements of CO₂ and N₂ were undertaken on a Gravimetric sorption analyser (GHP-FS, VTI Instruments), operating at 35 °C and in static mode. The pressure was changed incrementally between 0 – 20 bar, with helium used for buoyancy correction. Vapour sorption measurements of water in both membranes was undertaken on the same sorption analyser, operating in flow mode, with helium as the carrier gas. Detailed experimental procedures for both gas and vapour measurements have been previously reported³¹. Single gas permeabilities were undertaken on a variable pressure constant volume apparatus as previously described²⁵, with feed pressures between 1 – 15 bar and 35 °C. Mixed gas permeability measurements were undertaken on constant pressure variable volume instruments which have also been previously reported³². For water permeability measurements, water was added to the feed gas through an upstream bubbler arrangement¹², with the humid feed gas at 4 bar. Mixed gas permeability for CO₂ and N₂ were undertaken on the same apparatus at 4 bar and 35 °C, with a feed of variable humidity achieved through variation of temperature in the bubbler. To ensure concentration polarization did not occur on both sides of the membranes it was established that the feed flowrate had to be greater than 1.5 L/min and the argon sweep gas greater than 100 mL/min¹². Pure CO₂ (Industrial grade), pure N₂ (High purity) and 10% CO₂ in N₂ mixtures were obtained from BOC Ltd.

Modelling of the data was undertaken using a nonlinear regression approach based on the Levenberg-Marquardt algorithm in Mathematica.

4. Results and Discussion

4.1 Gas Solubility

The CO₂ concentration isotherms for PTMSP and PIM-1 demonstrate standard dual mode sorption behaviour (Figure 1a). At low pressures there is substantial sorption into both membranes as CO₂ sorbs predominately into the micro-voids of the membrane. As the pressure rises the increase in CO₂ concentration is reduced as the micro-voids become saturated and CO₂ sorption is limited to the polymeric matrix. The PTMSP CO₂ sorption isotherm is comparable to that reported by Merkel *et al.*³³ and in good agreement with other CO₂ isotherms reported in the literature given the sensitivity to film preparation and history. The PIM-1 isotherm demonstrates that more CO₂ is sorbed at low pressures

than for PTMSP, indicative of stronger affinity for the micro-voids. The CO₂ sorption profile for PIM-1 is comparable in shape to that reported by Li *et al.*³⁴, Mason *et al.*³⁵ and Du *et al.*³⁶. However the magnitude of CO₂ sorbed differs from the literature because of the different temperatures of these studies, as well as the sensitivity of the films to their preparation protocols and history.

The N₂ concentration isotherms for PTMSP and PIM-1 are provided in Figure 1b, and clearly indicate that PIM-1 absorbs N₂ more strongly than PTMSP. As expected, both membranes absorb more CO₂ than N₂. The N₂ sorption isotherm in PTMSP closely correspond to the literature^{37,38}, while the PIM-1 N₂ isotherm profile is also comparable to that reported by Li *et al.*³⁴.

Figure 1

Modelling of the concentration isotherms enables the dual mode sorption parameters of CO₂ and N₂ in both polymeric membranes to be determined. Merkel *et al.*³³ reported parameters for CO₂ and N₂ in PTMSP, which within error can successfully model the sorption profiles reported here, and as such these values are utilised in all further analysis (Table 1). However, there is considerable discrepancy in the literature on these parameters. For example, Ichiraku and Stern³⁸ reports k_D and b values for both gases that are higher than those by Merkel *et al.*³³, while the C'_H values are less. In contrast, Srinivasan *et al.*³⁹ has reported a higher C'_H for CO₂ and a lower C'_H for N₂, while Plate *et al.*⁴⁰, reports a C'_H that is a third of the Merkel value, and k_D and b values that are higher than those reported. Merkel *et al.*³³ provides a good theoretical analysis of the dual sorption parameters of various gases in PTMSP and their correlation with physical properties.

The dual mode sorption parameters determined for PIM-1 (Table 1) indicate that the micro-voids accommodate less CO₂ and N₂ than in PTMSP (lower C'_H values), but sorption to these regions is stronger, highlighted by the greater Langmuir affinity values (b). This accounts for the substantial sorption of CO₂ into PIM-1 at low pressures. The Henry's law constant for CO₂ is similar between PTMSP and PIM-1, while for N₂, the Henry's law constant for PIM-1 is an order of magnitude greater than that reported for PTMSP. Li *et al.*³⁴ reports parameters that are reasonably consistent with those determined here, although the k_D and C'_H values for CO₂ are significant higher. This probably reflects the lower

measurement temperature of 25 °C which would lead to greater sorption into both the Henry's and Langmuir domains.

Table 1

4.2 Water Solubility

The water concentration within PTMSP and PIM-1 is provided in Figure 2 and 3 respectively, both as functions of water activity and temperature. The convex isotherm shape is indicative of multilayer sorption^{11,12}. Interestingly, there is significant difference in the profiles at very high activities, with a substantial increase in water uptake observed for PIM-1, relative to PTMSP. The key difference probably relates to the chemical structure of PIM-1, which can sorb significant amounts of water because of hydrogen bonding with the ether and nitrile groups present⁴¹. Interestingly, the sorption profile for water vapour in PIM-1 presented by Minelli *et al.*⁴² does not report this substantial increase at high water activity. This may be due to morphology differences or aging effects, or it may reflect these authors allowing insufficient time for their membranes to reach equilibrium sorption levels. For both PTMSP and PIM-1, increasing temperature reduces the amount of water sorbed into the membrane.

Figure 2

Figure 3

The heat of sorption can be determined from the solubility data in Figures 2 and 3 at each humidity value by applying the van't Hoff relationship. For PTMSP, the average heat of sorption is calculated as -66 kJ/mol and for PIM-1 it is -52 kJ/mol. These heats of sorption are greater than those determined for water sorption to hydrophilic SPEEK and Nafion membranes, -33 and -44 kJ/mol respectively⁴³. Indeed, the magnitude is consistent with strong hydrogen bonding^{44,45}, which may imply that the majority of water sorption is actually water clustering within the polymer micro-voids rather than direct intermolecular bonding between the water molecule and the hydrophobic polymers.

The isotherms can be fitted to the modified dual mode sorption model (Equation 1). The water interactions with the micro-void region (A') and polymer matrix (k') do not vary significantly with temperature for either polymer and hence the average values are provided in Table 2. The interaction between water and the PIM-1 polymer (k') is greater than that with PTMSP, highlighting the hydrogen bonding between water and PIM-1 as described above. The affinity of water for the micro-void regions (A') is similar for both polymers and comparable to other hydrophobic glassy polymeric membranes²⁶, but considerably lower than that observed for hydrophilic Nafion^{11,13}.

The corresponding Langmuir affinity constants (Equation 2) for water in both polymers are also reported in Table 2. In both systems the Langmuir affinity constants are lower than would be predicted based on the standard dual mode sorption model (see Figure 4). However, as first noted by Chen²⁶ the values determined from the modified model are consistent with a linear extrapolation of the affinity constant for gases of lower critical temperature. This suggests that such a modified model is more appropriate for gases of higher critical temperature than the Langmuir model, as it more correctly accounts for multilayer sorption and allows the constants for all gases and vapors to be fitted to a single line.

Table 2

Figure 4

The weighted mean sorption capacity (Figure 5) again demonstrates that PIM-1 can sorb more water in the first monolayer than PTMSP. In addition, the sorption capacity clearly decreases with temperature, which is characteristic of all physisorption processes. Interestingly, the sorption capacities for both membranes are an order of magnitude lower than water in hydrophobic Matrimid and 6FDA-TMPDA²⁶. This difference may be associated with differences in the hydrophobicity of the respective polymers.

Figure 5

4.3 Dry Gas Permeability

The pure gas CO₂ permeability data (Figure 6 and Table 3) highlights the very large free volumes within PTMSP and PIM-1. The measured CO₂ permeability corresponds well with the literature^{28,29,33,39,46}, as does the trend of decreasing permeability with increasing feed pressure. This trend is due to falling solubility with increasing pressure as the micro-voids fill with CO₂ (Figure 1a). For both membranes, the N₂ permeability does not deviate with pressure within experimental error (Table 3) as the sorption isotherm is more linear with respect to pressure over the range studied (Figure 1b). PTMSP has an ideal CO₂/N₂ selectivity of 4 - 6 over the pressure range studied while PIM-1 is from 15 – 24 (Figure 7). This result highlights the trade-off between permeability and selectivity.

Figure 6

Figure 7

Table 3

The permeability model (Equation 3) enables the immobilisation factor (F) to be determined from the pure gas permeability and concentration data, using the diffusivity of CO₂ and N₂ through PTMSP reported by Merkel *et al.*³³ and similar diffusivity data through PIM-1 reported by Staiger *et al.*⁴⁷ (Table 4). All values are high, particularly for CO₂, relative to other polymeric membranes^{25,26,48}. This probably relates to the high free volume within these membranes. It implies that the micro-void regions are well connected throughout the membrane and there are relatively few micro-void regions that can be considered dead end.

Table 4

The CO₂ and N₂ permeabilities in a 10% CO₂ in N₂ mixture at a feed pressure of 4 bar are also provided in Table 3. For both membranes the N₂ permeability falls under mixed gas conditions, reflecting

competitive sorption effects. The CO₂ permeability is relatively unchanged, reflecting the combined effects of competitive sorption and plasticisation.

These competitive sorption and plasticization effects can also be modelled through Equation 3, using the dual mode sorption and diffusivity parameters provided in Table 1 and 4, but with a recalculation of the immobilization factor (F). This is necessary, since the presence of condensed CO₂ within the micro-voids could block the migration of either gas through some micro-void channels. The mixed gas immobilization factors determined in this manner are provided in Table 5. To minimise the number of fitting parameters in the model, it is assumed for PTMSP that plasticization does not occur. For PTMSP, under mixed gas conditions the immobilization factors for CO₂ and N₂ are essentially the same, and are reduced compared to the pure gas factors (Table 4). For PIM-1, the CO₂ immobilization factor is also reduced by a similar magnitude. However, the N₂ permeability under mixed gas conditions through PIM-1 can only be modelled if it is assumed that CO₂ plasticizes the membrane, as the observed permeability is greater than can be accounted for through competitive sorption. It is possible for CO₂ to plasticize a glassy polymer^{48,49}, and this is more likely to occur for PIM-1 with a CO₂ concentration of 3.3 cm³/cm³ in the polymer, than PTMSP with a CO₂ concentration of 1.9 cm³/cm³ at these feed gas conditions. The CO₂ plasticization potential is determined to be 0.07 cm³ polymer/cm³.

Table 5

4.4 Water Permeability

The permeability of water in PTMSP and PIM-1 is provided in Figure 8 as a function of water activity. The water permeability data through PTMSP corresponds well with that reported by Sato *et al.*⁵⁰. The permeability of water through PIM-1 is slightly lower across all water activities. The increase in water permeability with water activity is consistent with the observations of other researchers in glassy polymeric membranes^{15,51}. This increase is thought to mainly relate to the increase in water solubility at higher activities. Based on this data, the H₂O/CO₂ selectivity of PTMSP is around unity and PIM-1 around 5, while the H₂O/N₂ selectivity of PTMSP ranges from 4 to 6.1 and PIM-1 from 100 – 130.

Figure 8

These water permeabilities can be modelled by Equation 5, including the competitive sorption from the nitrogen carrier gas. This enables the infinite dilution diffusivity ($D_{H_2O,0}$) of water vapour, the immobilization factor (F) of water and the plasticization potential of water (β_{H_2O}) to be estimated (Table 6). Sato *et al.*⁵⁰ has reported the infinite dilution diffusivity of water in PTMSP and this value is used here. The estimated water immobilization factor in PTMSP is low at 0.1 ± 0.05 , implying the majority of the water sorbed within the micro-voids region of PTMSP is immobile. This may reflect blocking of these voids by water clusters. As described in the Introduction, such blocking behaviour is common in these systems. The plasticization potential of water on PTMSP was determined to be $\beta = 3.1 \pm 1.0 \text{ cm}^3 \text{ polymer/cm}^3$. A positive potential is indicative of water swelling the PTMSP structure and the large value implies that there is significant plasticization. Sato *et al.*⁵⁰ also obtain a positive value for this polymer, although they define the plasticization potential on a different basis. For comparison, the plasticization coefficient obtained here based on the Sato *et al.* definition is 1.3 ± 0.4 , which is comparable to that reported by Sato *et al.* of 0.79.

The infinite dilution diffusivity for PIM-1 is a third of that reported for PTMSP, reflective of the lower fractional free volume of this polymer. This diffusivity is similar in magnitude to that reported for PMMA and PVP⁵². However, the plasticization potential of water in PIM-1 is negative which is indicative of water clustering hindering diffusion through this polymer, rather than a swelling mechanism. This may reflect the lower water concentrations within the polymer at these water activities, relative to PTMSP. That is, there may be sufficient water present to form clusters, but these clusters are only present in the microvoids; they are insufficient in number to occupy and swell the polymer matrix.

Table 6

The temperature dependence of the water permeability through PTMSP and PIM-1 is provided in Figure 9 at a constant water activity of 0.3. For both membranes the water permeability initially decreases with temperature as the solubility of water within both polymeric structures is reduced (Figures 2 and 3).

However, the permeability reaches a minimum and then increases. The minimum permeability occurs at $\sim 70^\circ\text{C}$ for PIM-1 and $\sim 80^\circ\text{C}$ for PTMSP. The most likely cause of this behaviour is the break-up of water clusters within both membranes at the higher temperature due to the lower water concentrations in the membrane. Individual water molecules have higher diffusivities than water clusters through polymeric membranes⁵², which results in the increase in permeability at higher temperature, and overcomes the decrease in water solubility with temperature.

Figure 9

4.6 Mixed Gas Permeability with Water Vapour

The permeabilities of PTMSP in a humid gas mixture of 10% CO_2 in N_2 are provided in Figure 10. It is important to note that above a water activity of 0.4 it was difficult to achieve steady state results. This is because at the high feed flowrate necessary to avoid concentration polarisation, the water within the upstream bubbler quickly ran out. This is reflected in the larger error bars under these conditions. As the water activity in the feed gas increases there is a decrease in the permeability of both gases. The CO_2 permeability reaches a relatively constant value of ~ 28300 barrer, while N_2 permeability decreases below 3000 barrer as water activity increases. This is a decrease of 12 % for CO_2 and over 20% for N_2 . The changes can relate to a combination of competitive sorption of water in the micro-cavities reducing both CO_2 and N_2 solubility, coupled with swelling of the polymer by water (which increases diffusivity) or water clustering and blocking (which reduces diffusivity). The ideal CO_2/N_2 selectivity increases slightly to 9, indicative of the stronger impact of competitive water sorption on N_2 relative to CO_2 (Figure 12). This data can be modelled through Equations 5 and 6, based on the parameters in Tables 1, 4 and 5. The resulting average calculated plasticization potential of water on CO_2 and N_2 in PTMSP is $0.08 \pm 0.06 \text{ cm}^3 \text{ polymer/cm}^3$ (Table 7).

Figure 10

Table 7

The CO₂ and N₂ permeabilities through PIM-1 in a humid 10% CO₂ in N₂ mixture are provided in Figure 11. Similar to the PTMSP result, there is a decrease in both CO₂ and N₂ permeability through PIM-1. The permeability declines to ~3800 Barrer for CO₂ and ~120 barrer N₂ for a water activity of 0.71; corresponding to a decrease of 38% for CO₂ and 39% for N₂. In the humid feed, the ideal CO₂/N₂ selectivity remains relatively constant (Figure 12); because of the similar impact of water on both CO₂ and N₂ in this case. Modelling, based on parameters in Tables 1, 4 and 5, again enables the averaged plasticization constant of water on CO₂ and N₂ in PIM-1 to be determined (Table 7). Importantly, the plasticization constant for PIM-1 is negative, indicative that water is filling the microvoids and limiting the diffusivity of both CO₂ and N₂ through the PIM-1 membrane. This is opposite to the water swelling effect observed for PTMSP, but supports the negative plasticization potential observed for water permeability in PIM-1.

Figure 11

Figure 12

5. Conclusion

Sorption of CO₂, N₂ and water into PTMSP and PIM-1 membranes was successfully modelled using a modified dual mode sorption theory that accounts for multilayer sorption. This approach allows a single correlation to be provided for the Langmuir constant of all penetrants. The permeability of these gases, both individually and in mixtures could also be successfully modelled through permeability theory, with the mobility factor and plasticization potential as adjustable parameters. The change in immobilization factors for both gases highlighted a reduction in the transport of CO₂ and N₂ through the micro-voids regions of the membranes under mixed gas conditions. The modelling suggested that water plasticized the PTMSP membrane and increased the diffusivity of CO₂ and N₂, while water reduced the diffusivity of CO₂ and N₂ in PIM-1, indicative of water filling of the micro-voids.

Also measured was the change in water solubility and permeability with temperature. While the solubility declined with temperature as expected, the permeability through both membranes went

through a minimum at 80 °C for PTMSP and 70 °C for PIM-1. Above this temperature water diffusivity dominated the permeability while below this temperature water solubility behaviour dominated.

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References

1. Robeson, L. M. J. *Membr. Sci.* 2008, 320, 390-400.
2. Scholes, C. A.; Kentish, S. E.; Stevens, G. W. *Sep. Purif. Reviews* 2009, 38, 1-44.
3. Huang, J.; Cranford, R. J.; Matsuura, T.; Roy, C. J. *Membr. Sci.* 2004, 241, 187-196.
4. Stern, S. A.; Saxena, V. J. *Membr. Sci.* 1980, 7, 47-59.
5. Nguyen, Q. T.; Favre, E.; Ping, Z. H.; Néel, J. *Journal of Membrane Science* 1996, 113, 137-150.
6. Thomas, S.; Pinnau, I.; Du, N.; Guiver, M. D. J. *Membr. Sci.* 2009, 338, 1-4.
7. Teplyakov, V. V.; Roizard, D.; Favre, E.; Khotimskii, V. S. J. *Membr. Sci.* 2003, 220, 165-175.
8. Pinnau, I.; Toy, L. G. *Journal of Membrane Science* 1996, 116, 199-209.
9. Pinnau, I.; Casillas, C. G.; Morisato, A.; Freeman, B. D. *Journal of Polymer Science Part B: Polymer Physics* 1996, 34, 2613-2621.
10. Steeneveldt, R.; Berger, B.; Torp, T. A. *Chem. Eng. Res. Des.* 2006, 84(A9), 739-763.
11. Azher, H.; Scholes, C. A.; Stevens, G. W.; Kentish, S. E. J. *Membr. Sci.* 2014, 459, 104-113.
12. Chen, G. Q.; Scholes, C. A.; Qiao, G. G.; Kentish, S. E. J. *Membr. Sci.* 2011, 379, 479-487.
13. Li, Y.; Nguyen, Q. T.; Buquet, C. L.; Langevin, D.; Legras, M.; Marais, S. J. *Membr. Sci.* 2013, 439, 1-11.
14. Potreck, J.; Uyar, F.; Sijbesma, H.; Nijmeijer, K.; Stamatialis, D.; Wessling, M. *Phys. Chem. Chem. Phys.* 2009, 11, 298-308.
15. Reijerkerk, S. R.; Jordana, R.; Nijmeijer, K.; Wessling, M. *Int. J. Greenhouse Gas Control* 2011, 5, 26-36.
16. Potreck, J.; Nijmeijer, K.; Kosinski, T.; Wessling, M. J. *Membr. Sci.* 2009, 338, 11-16.
17. Metz, S. J.; van de Ven, W. J. C.; Potreck, J.; Mulder, M. H. V.; Wessling, M. J. *Membr. Sci.* 2005, 251, 29-41.
18. Guiver, M. D.; Lee, Y. M. *Science* 2013, 339, 284-285.
19. Lau, C. H.; Nguyen, P. T.; Hill, M. R.; Thornton, A. W.; Konstas, K.; Doherty, C. M.; Mulder, R. J.; Bourgeois, L.; Liu, A. C. Y.; Sprouster, D. J.; Sullivan, J. P.; Bastow, T. J.; Hill, A. J.; Gin, D. L.; Noble, R. D. *Angew. Chem.* 2014, 126, 5426-5430.
20. Petropoulos, J. H. In *Polymeric gas separation membranes*; Paul, D. R.; Yampolskii, Y., Eds.; CRC Press: Boca Raton, 1994, p 17-81.
21. Feng, H. *Polymer* 2007, 48, 2988-3002.
22. Paul, D. R.; Koros, W. J. J. *Polym. Sci. Part B: Polym. Phys.* 1976, 14, 675-685.
23. Koros, W. J. J. *Polym. Sci. Part B: Polym. Phys.* 1980, 18, 981-992.

24. Koros, W. J.; Chern, R. T.; Stannett, V.; Hopfenberg, H. B. J. *Polym. Sci. Part B: Polym. Phys.* 1981, 19, 1513-1530.
25. Duthie, X.; Kentish, S. E.; Powell, C.; Nagai, K.; Qiao, G. G.; Stevens, G. W. J. *Membr. Sci.* 2007, 294, 40-49.
26. Chen, G. Q.; Scholes, C. A.; Doherty, C. M.; Hill, A. J.; Qiao, G. G.; Kentish, S. E. J. *Membr. Sci.* 2012, 409-410, 96-104.
27. Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. *Chem. Commun.* 2004, 230-231.
28. Budd, P. M.; McKeown, N. B.; Ghanem, B. S.; Msayib, K. J.; Fritsch, D.; Starannikova, L.; Belov, N.; Sanfirova, O.; Yampolskii, Y. J. *Membr. Sci.* 2008, 325, 851.
29. Thomas, S.; Pinnau, I.; Du, N.; Guiver, M. D. J. *Membr. Sci.* 2009, 333, 125-131.
30. ASTM. Standard test methods for density and specific gravity (relative density) of plastics by displacement; ASTM International: West Conshohocken, 1993.
31. Scholes, C. A.; Tao, W. X.; Stevens, G. W.; Kentish, S. E. J. *Applied. Polym. Sci.* 2010, 117, 2284-2289.
32. Anderson, C. J.; Tao, W.; Scholes, C. A.; Stevens, G. W.; Kentish, S. E. J. *Membrane Sci.* 2011, 378, 117-127.
33. Merkel, T. C.; Bondar, V.; Nagai, K.; Freeman, B. D. J. *Polym. Sci. Part B: Polym. Phys.* 2000, 38, 273-296.
34. Li, P.; Chung, T. S.; Paul, D. R. J. *Membr. Sci.* 2013, 432, 50-57.
35. Mason, C. R.; Maynard-Atem, L.; Heard, K. W.; Satilmis, B.; Budd, P. M.; Friess, K.; Lanc, M.; Bernardo, P.; Clarizia, G.; Jansen, J. C. *Macromolecules* 2014, 47, 1021-1029.
36. Du, N.; Park, H. B.; Robertson, G. P.; Dal-Cin, M. M.; Visser, T.; Scoles, L.; Guiver, M. D. *Nature Materials* 2011, 10, 372-375.
37. Prabhakar, R. S.; Merkel, T. C.; Freeman, B. D.; Imizu, T.; Higuchi, A. *Macromolecules* 2005, 38, 1899-1910.
38. Ichiraku, Y.; Stern, S. A.; Nakagawa, T. J. *Membr. Sci.* 1987, 34, 5-18.
39. Srinivasan, R.; Auvel, S. R.; Burban, P. M. J. *Membr. Sci.* 1994, 86, 67-86.
40. Plate, N. A.; Bokarev, A. K.; Kaliuzhnyi, N. E.; Litvinova, E. G.; Khotimskii, V. S.; Volkov, V. V.; Yampolskii, Y. J. *Membr. Sci.* 1991, 60, 13-24.
41. Chaukura, N. In Faculty of Engineering and Physical Sciences; University of Manchester: Manchester, 2011.
42. Minelli, M.; Friess, K.; Vopicka, O.; de Angelis, M. G. *Fluid Phase Equilibria* 2013, 347, 35-44.
43. Azher, H. In Department of Chemical and Biomolecular Engineering; University of Melbourne: Melbourne, 2014.
44. Emsley, J. *Chem. Soc. Rev.* 1980, 9, 91-124.
45. Suresh, S. J.; Naik, V. M. J. *Chem. Phys.* 2000, 113, 9727-9732.
46. Budd, P. M.; Msayib, K. J.; Tattershall, C. E.; Ghanem, B. S.; Reynolds, K. J.; McKeown, N. B.; Fritsch, D. J. *Membr. Sci.* 2005, 251, 263-269.
47. Staiger, C. L.; Pas, S. J.; Hill, A. J.; Cornelius, C. J. *Chem. Mater.* 2008, 20, 2606-2608.
48. Scholes, C. A.; Chen, G. Q.; Stevens, G. W.; Kentish, S. E. J. *Membr. Sci.* 2010, 346, 208-214.
49. Bos, A.; Punt, I. G. M.; Wessling, M.; Strathmann, H. J. *Membrane Sci.* 1999, 155, 67-78.
50. Sato, S.; Suzuki, M.; Kanehashi, S.; Nagai, K. J. *Membr. Sci.* 2010, 360, 352-362.
51. Sijbesma, H.; Nijmeijer, K.; van Marwijk, R.; Heijboer, R.; Potreck, J.; Wessling, M. J. *Membr. Sci.* 2008, 313, 263-276.
52. Davis, E. M.; Elabd, Y. A. J. *Phys. Chem. B.* 2013, 117, 10629-10640.

Table Captions

Table 1: Dual mode sorption parameters for CO₂ and N₂ sorption into PTMSP and PIM-1 at 35 °C, including data from relevant references.

Table 2: Average water sorption parameters (A' and k') for PTMSP and PIM-1, determined by fitting the water sorption isotherms to Equation 3.

Table 3: CO₂ and N₂ permeability data for single gases and a mixture of 10% CO₂ in N₂ at 35°C. The CO₂ pressure for the single gas experiment is 1 Bar, while the data for pure N₂ is the average across the 1 -15 bar pressure range. The mixed gas data is for a total pressure of 4 Bar.

Table 4: Diffusivity (cm²/s) of CO₂ and N₂, and the immobilization fraction (F), for PTMSP and PIM-1, as determined from permeability and solubility data. Data taken from Merkel *et al.*³³ and Staiger *et al.*⁴⁷.

Table 5: Mixed gas immobilization factor (F) and plasticization constant of CO₂ for PTMSP and PIM-1, based on mixed gas permeability data at 4 bar total pressure and 35°C.

Table 6: H₂O permeability model parameters for PTMSP and PIM-1 at 35 °C, determined from Equation 5. (*) indicates values taken from Sato *et al.*⁵⁰.

Table 7: Plasticization constant for water (β_{H_2O}), for PTMSP and PIM-1, based on mixed gas permeability data.

Figure Captions

Figure 1: (a) CO₂ concentration isotherms and (b) N₂ concentration isotherms of PTMSP (•) and PIM-1 (□) as a function of pressure (bar) at 35 °C. The lines represent fits to a standard dual mode sorption model.

Figure 2: Water sorption (cm³/cm³ polymer) in PTMSP as a function of water activity and temperature. The lines represent fits to Equation 1.

Figure 3: Water sorption (cm³/cm³ polymer) in PIM-1 as a function of water activity and temperature, with insert graph highlighting the sorption at low water activities. The lines represent fits to Equation 1.

Figure 4: Langmuir affinity constants (b) for a range of gases/vapors in various polymeric membranes at 35°C relative to the gas/vapor critical temperature^{2,26}. The filled symbols represent data fitted from the dual mode sorption model, while the hollow symbols represent the data fitted from the modified dual mode sorption model (Equations 1 and 2).

Figure 5: $\overline{C_{BP}}$ (cm³/cm³ polymer) of water in PTMSP and PIM-1 as a function of temperature. The line is for guidance only.

Figure 6: (a) CO₂ permeability (barrer) in PTMSP (•) and PIM-1 (□) as a function of pressure (bar) at 35 °C. The line represents the fits to Equation 3.

Figure 7: CO₂/ N₂ selectivity in PTMSP (•) and PIM-1 (□) as a function of pressure (bar) at 35 °C. The lines are for guidance only.

Figure 8: Water permeability (Barrer) in PTMSP and PIM-1 as a function of water activity, at 35 °C. The line represents the model fits to Equation 5.

Figure 9: Water Permeability (Barrer) in PTMSP and PIM-1 as a function of temperature (°C), at water activity of 0.3. The line is for guidance only.

Figure 10: (a) CO₂ Permeability (barrer) under N₂ mixed gas conditions with water present in PTMSP, (b) N₂ Permeability (barrer) under mixed gas conditions with water present in PTMSP. Also displayed are fits to the model (Equations 5 and 6).

Figure 11: (a) CO₂ Permeability (barrer) under N₂ mixed gas conditions with water present in PIM-1, (b) N₂ Permeability (barrer) under mixed gas conditions with water present in PIM-1. Also displayed are fits to the model (Equations 5 and 6).

Figure 12: CO₂/ N₂ selectivity in PTMSP (•) and PIM-1 (□) under mixed gas conditions in the presence of water vapor at various activities. The lines are for guidance only.

Tables

Table 1

PTMSP			PIM-1			
	CO ₂ ³³	N ₂ ³³	CO ₂	CO ₂ ³⁴ , 25°C	N ₂	N ₂ ³⁴ , 25°C
			this work, 35°C		this work, 35°C	
k _D (cm ³ /cm ³ atm)	1.05	0.08	1.3 ± 0.2	2.35	0.60 ± 0.07	0.49
C' _H (cm ³ /cm ³ polymer)	130	74	57 ± 6	107	26 ± 3	31
b (atm ⁻¹)	0.04	0.014	0.52 ± 0.06	0.42	0.06 ± 0.01	0.076

Table 2

	PTMSP	PIM-1
k'	0.71 ± 0.13	1.01 ± 0.19
A'	1.40 ± 0.22	1.45 ± 0.24
b (atm ⁻¹)	5.1 ± 0.8	8.2 ± 1.2

Table 3

	PTMSP			PIM-1		
	CO ₂	N ₂	CO ₂ /N ₂	CO ₂	N ₂	CO ₂ /N ₂
	Barrer	Barrer		Barrer	Barrer	
Pure Gas	31100 ± 400	5200 ± 100	6	7640 ± 90	235 ± 13	33
10% CO ₂ in N ₂	32200 ± 300	3890 ± 50	8	6100 ± 100	190 ± 20	32

Table 4

	CO ₂		N ₂	
	D (cm ² /s)	F	D (cm ² /s)	F
PTMSP	$5.0 \times 10^{-5.33}$	0.7 ± 0.3	$6.4 \times 10^{-5.33}$	0.6 ± 0.2
PIM-1	$5.5 \times 10^{-6.47}$	0.9 ± 0.2	$1.2 \times 10^{-6.47}$	0.7 ± 0.2

Table 5

	F	β_{CO_2} cm ³ (polymer)/cm ³ (STP)
PTMSP	0.46 ± 0.26	-
PIM-1	0.5 ± 0.3	0.07 ± 0.02

Table 6

	PTMSP	PIM-1
D _{H₂O,0} (cm ² /s)	$68 \times 10^{-8} (*)$	21×10^{-8}
F _{H₂O}	0.1 ± 0.05	0.7 ± 0.2
$\beta_{\text{H}_2\text{O}}$ (cm ³ polymer/cm ³)	3.1 ± 1.0	-0.047 ± 0.014

Table 7

	$\beta_{\text{H}_2\text{O}}$
PTMSP	0.08 ± 0.06
PIM-1	-0.09 ± 0.04

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

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