Water permeability and competitive permeation with CO₂ and CH₄ in perfluorinated polymeric membranes

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Abstract

The permeability of water through polymeric membranes is of particular interest in gas separation, because of the high water vapor content found in many industrial applications. Polymeric membranes that are resistant to competitive sorption and plasticization by water are especially attractive, since they can reduce the need for gas pretreatment in many membrane applications. The perfluorinated polymers Teflon AF1600 and Hyflon AD60 are studied here for this purpose because of their strong hydrophobicity and unusual solvent properties. It was observed that water permeability through both perfluorinated polymers was of the same magnitude as CO₂. Indeed, under the conditions studied, Teflon AF1600 was selective for CO₂ over water. Such reverse selectivity for the CO₂ – H₂O gas pair has not been reported before for glassy polymeric membranes and reflects the very low solubility of water in the polymer. The water permeability through Hyflon AD60 was greater than that for CO₂ with a minimum at 55 °C. The change in both CO₂ and CH₄ permeability through Teflon AF1600 and Hyflon AD60 was investigated as a function of water activity in the feed gas to investigate the effects of competitive permeation. It was observed that CO₂ and CH₄ permeability in both membranes reduced with water activity. For both Teflon AF1600 and Hyflon AD60, the decrease in permeability of both gases with water activity was interpreted as water clusters blocking the diffusion of both CO₂ and CH₄ through the membrane.

Keywords: Teflon AF1600, Hyflon AD60, water, CO₂, permeability

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1. Introduction

Polymeric membranes are attractive for a range of gas separation applications, because of their permselectivity and ability to be fabricated economically. In particular, there is considerable interest in glassy polymeric membranes for CO₂ separation applications, such as natural gas sweetening, post-combustion capture, biogas processing as well as syngas processing [1]. In all of these applications, the feed gas has water vapor present, often at near saturation conditions, which is known to reduce membrane separation performance because of competitive sorption and plasticization [2-4]. Water permeability is generally orders of magnitude greater than other gases present [5, 6] and hence water will concentrate in the permeate stream. If the water vapor concentration in the permeate passes the dew point, then condensation will occur on the membrane or in the support layer, which can lead to further reduction in separation performance. In addition, if the permeate water vapor pressure cycles above and below the dew point, then capillary pressure caused by evaporating and reforming water droplets can collapse micro-voids and pores within the membrane and support layer, which is detrimental to membrane performance. Hence, for many membrane applications pretreatment processing to remove the majority of the water present is required [7]. As such, membranes that are resistant to the impact of water are of particular interest because of the potential to reduce pretreatment processing and to handle wet feed gas.

Amorphous glassy perfluoropolymers are an interesting class of polymers, because the perfluorinated structure makes these polymers insoluble in both water and in many organic solvents [8, 9]. Hence, they do not tend to swell or plasticize in the presence of condensable vapors [10]. They are also known for their thermal and chemical stability because of the very stable carbon – fluorine bond [11]. Importantly, the bulky substituted dioxole moiety in the Teflon AF and Hyflon AD series of perfluoropolymers reduces chain mobility and limits crystallinity, producing amorphous polymeric films with poor packing and high fractional free volume [11, 12]. Both these series of perfluoropolymers have been studied for CO₂ separation [11, 13-15], as well as organic vapor separation, because of their solvent resistance [16-21]. However, the water permeability and the impact of water on other feed gases has not been characterized. Hence, this investigation characterizes the water permeability in Teflon AF1600 and Hyflon AD60 as a function of water activity and temperature; as well as the impact of a humid feed gas on CO₂ and CH₄ permeation through both perfluorinated polymers. This provides important insight into the behavior of water within these perfluorinated polymers, as well as their suitability as CO₂ separation membranes in a range of industrial applications.

The permeability of gases through glassy polymeric membranes is dependent on the concentration of penetrant within the membrane. Gas sorption can be associated with two distinct regions, the polymeric matrix (C_{XA}) and the free volume or micro-void region (C_{VA}). Therefore, the total gas concentration is defined as:

$$C_A = C_{XA} + C_{VA} \quad (1)$$

For non condensable gases, the standard dual sorption theory more than adequately models the gas concentration in the polymeric membrane, where sorption to the polymeric matrix is described by Henry's law and sorption to the micro-voids through Langmuir adsorption [22]:

$$C_A = k_A f_A + \frac{C'_{HA} b_A f_A}{1 + b_A f_A} \quad (2)$$

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.

Paul and Koros [23] determined that permeability through the micro-void region can be impeded relative to movement through the Henry's law region, and hence only a fraction (F) of the micro-void concentration is mobile. Further, the presence of another gas will compete for sorption to the micro-voids region. Koros [24] accounted for this competition in the Langmuir adsorption term. Combining these parameters with Fick's Law leads to the following equation for the permeability of a gas A in the presence of gas B:

$$P_A = \frac{D_A}{f_{A2} - f_{A1}} \left[\left(k_{DA} + \frac{F_A C'_{HA} b_A}{1 + b_A f_{A2} + b_B f_{B2}} \right) f_{A2} - \left(k_{DA} + \frac{F_A C'_{HA} b_A}{1 + b_A f_{A1} + b_B f_{B1}} \right) f_{A1} \right] \quad (3)$$

2. Experimental

Amorphous Teflon AF1600 (copolymer of 65 mol% 2,2-bis-trifluoromethyl-4,5-difluoro-1,3-dioxole and 35 mol% tetrafluoroethylene) was purchased from DuPont (USA), Hyflon AD60 (copolymer of 60 mol% 2,2-bis(trifluoromethyl)-4-fluoro-5-trifluoromethoxy-1,3-dioxole with 40 mol% tetrafluoroethylene) was purchased from Solexis (Japan) and both were used as supplied. The chemical structures are provided in Figure 1. Dense films were prepared from both polymers through controlled evaporation from the fluorinated solvent PF5060 (3M, Australia). The final film thickness of both polymeric membranes was

on average 120 μm . All films were dried under vacuum at 40 $^{\circ}\text{C}$ for 3 days [13]. To minimize any age dependent behavior, all membranes were used within 5 days of drying.

Figure 1

Membrane densities were determined through standard procedures [25]. Gas sorption measurements of CO_2 , N_2 and CH_4 were undertaken on a Gravimetric sorption analyzer (GHP-FS, VTI Instruments), operating at 35 $^{\circ}\text{C}$ and in static mode where the pressure was changed incrementally between 0 and 20 bar. Detailed experimental procedures have been previously reported [26]. Water sorption was determined in flow mode using the same instrument [2].

Single gas permeabilities were undertaken on a variable pressure constant volume apparatus as previously reported [27]. These measurements were undertaken with a feed pressure between 1 to 15 bar at 35 $^{\circ}\text{C}$. Mixed gas permeability measurements were undertaken on a constant pressure variable volume instrument, as also previously reported [2, 28]. For humid gas measurements, water was added to a dry feed gas through a bubbler arrangement, and water permeability was measured through humidity probes (HMT, Probe type 334 Vaisala Oyj, Finland) on the feed and permeate side, with the humid feed gas at 400 kPa. The water activity of the feed gas was varied by varying the water bubbler temperature relative to that of the membrane cell. Concentration polarization was not observed for these polymeric membrane systems, but to ensure good flow conditions the feed flowrate was at 1 L/min and the Helium sweep gas was at 24 mL/min, which are comparable flow conditions to our previous work [2]. Pure CO_2 (Industrial grade), pure N_2 (High purity) and pure CH_4 (High purity) were obtained from Coregas (Australia). The gas permeate flowrate was measured through a universal flowmeter (Agilent Technologies ADM3000) and composition through gas chromatography (Varian CP-3800, with Molecular sieve and PORAPAK Q columns).

3. Results and Discussion

3.1 Density and Fractional Free Volume

The density and corresponding fractional free volumes for Teflon AF1600 and Hyflon AD60 are provided in Table 1, where fractional free volume was calculated through the group contribution method [29-32]. Our measurements for Teflon AF1600 are comparable to literature reports [19, 33], and correspond well with molecular simulations of polymer packing density [34]. The density of Hyflon AD60 is also comparable with that reported by Markhloufi *et al.* [35]; and indicates that Hyflon AD60 achieves a much denser morphology and correspondingly a lower FFV than Teflon AF1600.

Table 1

3.1 Gas Sorption

The concentration profiles of CO₂, N₂ and CH₄ in Teflon AF1600 are provided in Figure 2. The convex shape to the pressure axis arises because of sorption at low pressures to the micro-voids within the membrane, at higher pressures the micro-voids become saturated and sorption is limited to the polymeric matrix, resulting in the tapering off of the isotherm. Importantly, CO₂ has a significantly higher concentration in Teflon AF1600 at pressure than both CH₄ and N₂, indicative of a CO₂ selective membrane. The sorption isotherms for all three gases are comparable to those reported in the literature [21, 36], and the CH₄ isotherm is also similar to that reported by Merkel *et al.* [13]. The dual-sorption parameters determined by Alentiev *et al.* [21] for the three gases in Teflon AF1600 fit to the experimental data here, within error (Table 2).

Figure 2

All three gases are less soluble in Hyflon AD60 at any given pressure (Figure 3). To the best of the authors' knowledge, no sorption isotherms for CO₂, N₂ and CH₄ for Hyflon AD60 have previously been reported in the literature to enable comparison. However, sorption isotherms for these gases in Hyflon AD80 has been reported by Prabhakar *et al.* [14]. Those isotherms have the same shape but higher

sorbed amounts, believed to be associated with the greater fractional free volume in Hyflon AD80 compared to AD60. The solubility (C/f) of the three gases in Hyflon AD60 is comparable to that reported by Merkel *et al.* [11] over the pressure range studied. Similar, CO_2 solubility is comparable to that reported by Jansen *et al.* [37] over the pressure range studied. The dual-sorption parameters for CO_2 , N_2 and CH_4 in Hyflon AD60 determined from Equation 2 are provided in Table 2. The Langmuir capacity (C'_H) for all three gases is greater in Teflon AF1600, reflecting the greater FFV of this polymer, which provides more micro-void volume for gas sorption (Table 1). The Langmuir affinity values (b) are consistent with the literature for these penetrants [5].

Figure 3

Table 2

The sorption of water into both Teflon AF1600 and Hyflon AD60 membranes was too small to be detected using the gravimetric sorption analyser. Indeed, soaking both membranes in water for over 6 hours at 35 °C failed to indicate any detectable water uptake, indicative that the amount of water sorbed into both membranes is very small. This would be expected given the extreme hydrophobicity of both polymers and the correspondingly high water contact angles observed upon their films [38, 39]. Correspondingly, very low water sorption has been reported for the base Teflon polymer [40].

3.2 Gas Permeability

The single dry gas permeability through Teflon AF1600 is provided in Figure 4, and for Hyflon AD60 in Figure 5, over the pressure range 1 – 15 bar. The permeability through both membranes is clearly in the order of $\text{CH}_4 < \text{N}_2 < \text{CO}_2$, with Teflon AF1600 having higher permeabilities than Hyflon AD60 because of the greater FFV (Table 1). The Teflon AF1600 CO_2 permeabilities are comparable with literature [17, 33, 35], but those of CH_4 and N_2 are half that reported by Alentiev *et al.* [21]. This discrepancy may be a

product of film casting techniques which is known to impact the performance of fluorinated polymers [37]. For Hyflon AD60, the permeabilities are comparable to those reported by Jansen *et al.* [17], however Makhoul *et al.* [35] report lower CO₂ and N₂ permeabilities, which could correspond to the lower temperature of their measurement, 21 °C.

Figure 4

Figure 5

Modeling the single gas permeability of the gases in Teflon AF1600 and Hyflon AD60 using Equation 4 enables the diffusivity and immobilization factor (F) to be estimated (Table 3). The diffusivities for Teflon AF1600 are comparable to Alentiev *et al.* [21] For Hyflon AD60, the diffusivity of CO₂ and CH₄ are comparable to those obtained from time lag measurements by Jansen *et al.* [37], while the N₂ diffusivity reported here is lower. Alternatively, the later paper by Jansen *et al.* [17] reports diffusivities that are systematically lower than those determined here for both polymers. The cause of these discrepancies can be attributed to experimental method and the systematic difference between effective diffusivity and apparent diffusivity [41], as well as differences in membrane fabrication and annealing.

Table 3

The immobilization factors for both membranes indicate the fraction of micro-void volume that contributes to the permeance of gases through the membrane. For the three gases studied, these voids are less available to Teflon AF1600 than Hyflon AD60. This indicates that Teflon AF1600 has fewer connections between micro-voids within the membrane than Hyflon AD60. This is interesting, given Teflon AF1600 has a higher FFV than Hyflon AD60 (Table 1) and is highly permeable to some organic vapors, which is believed to be based on the interconnectivity between micro-voids [17]. Hyflon AD60 mobility factors are comparable to other glassy polymeric membranes [4, 42].

3.3 Water Permeability

The water permeability through Teflon AF1600 and Hyflon AD60 as a function of water activity in nitrogen is provided in Figure 6. The increase in permeability with water activity is common and is generally attributed to increasing water solubility in the polymer [2].

DuPont quote a single gas water permeability in Teflon AF1600 of 1142 barrer [39], which is three times greater than the average permeability measured here. They also quote a N₂ permeability of 130 barrer, which is double that observed here, and a lower density (1.78). This indicates a greater fractional free volume in their membrane, most likely associated with film casting and annealing history. The reference also does not state the temperature or pressure conditions of their measurement and these may also contribute to the discrepancy.

Interestingly, the water permeability in Hyflon AD60 is double that observed for Teflon AF1600 under similar water activities. This is contrary to the dry gas permeability behavior (Figures 4 and 5) and the higher FFV of Teflon AF1600 (Table 1). To the best of the authors' knowledge, no water permeability for Hyflon AD60 has been reported in the literature. Further, for both membranes the water permeability is of a comparable magnitude to the CO₂ permeability. Indeed, in the case of Teflon AF1600, the dry CO₂ permeability is greater than that of H₂O across the full range of humidities tested (0.2 to 0.9).

It is interesting to compare this permeability data with that of other polymers for the H₂O-CO₂ gas pair. Figure 7 provides such a comparison in the form of a Robeson plot[43]. The upper bound gradient ($\lambda_{A/B}$) in this plot is based on the kinetic diameters (d) of the respective gas pair[44]:

$$\lambda_{A/B} = (d_B/d_A)^2 - 1 \quad (4)$$

The data for other polymers within this plot is based on literature values for both pure gas and gas mixtures across a wide range of water activities. Thus, while not under identical test conditions, the data still provides an order of magnitude comparison. It is clear that a selectivity of less than unity is highly unusual. However, the result is consistent with the very low solubility of water in Teflon AF1600.

Similar reverse selectivity for the NH₃/CO₂ gas pair has been reported by Makhloufi *et al.* [35] for Teflon AF1600 and Hyflon AD60 and was attributed to the strong contrast between the interactions of NH₃ with the fluorinated moieties relative to CO₂. Unfavorable NH₃ – fluorinated moiety interactions similarly

decreased NH_3 solubility giving rise to this reverse selectivity. It is likely that similar behavior is impacting water solubility and hence permeability within the perfluorinated polymers here, since covalently bound fluorine is a poor hydrogen acceptor [45].

Figure 6

Figure 7

The water permeability through both fluorinated polymeric membranes as a function of temperature is provided in Figure 8, and they demonstrate significantly different behavior. Teflon AF1600 water permeability increases exponentially with temperature, which is usually associated with a diffusivity dominated permeability mechanism. The corresponding activation energy of permeation for water in Teflon AF1600 was determined to be 67 kJ/mol. Alentiev *et al.* [21] reports much low permeation activation energies for CO_2 and N_2 of -1.8 and 4.6 kJ/mol respectively for Teflon AF1600. This behavior is possibly associated with the combined effects of a large activation energy for diffusion and a positive heat of sorption. Conversely, the permeation of water through Hyflon AD60 water reaches a shallow minimum at 55 °C. Below this temperature the permeability falls as temperature increases, presumably reflecting the declining solubility of water. Above this temperature, the increase in permeability indicates diffusivity is the dominating mechanism.

Figure 8

Figure 9 clearly demonstrates that at a relative humidity of 30%, Teflon AF1600 is selective for CO_2 over H_2O below ~ 45 °C. Above this temperature, the permeability increase with temperature is more substantial for H_2O than CO_2 . Conversely, over the temperature range studied, Hyflon AD60 always remains a H_2O selective membrane. A minimum in selectivity is observed at 55 °C, which corresponds to the minimum H_2O permeability observed at this temperature (Figure 8).

Figure 9

3.3 Water impact on CO_2 and CH_4 Permeability

For both Teflon AF1600 and Hyflon AD60 membranes, there is a reduction in both CO_2 and CH_4 permeability as the water activity increases (Figures 10 and 11). For Teflon AF1600, CO_2 permeability reduces consistently with increasing water activity, while for Hyflon AD60, the CO_2 permeability

reduction starts to plateau at higher water activities. At a water vapor activity of 0.75, the CO₂ and CH₄ permeability has fallen by 8% and 13% respectively, while for Hyflon AD60, the reductions are 4% and 2%. These decreases in permeability, especially for Hyflon AD60, are considerably less than that observed in other polymeric membranes. For polyimides upon exposure to humid feed, the CO₂ and CH₄ permeability can reduce by 50%, dependent on pressure and water activity, similarly PTMSP and PIM-1 CO₂ permeability can reduce by almost 40%, again dependent on pressure and water activity [4, 42]. As a consequence of the negligible impact of humid feeds, the CO₂/CH₄ ideal selectivity of both membranes is constant, within error, for the water activities studied (Figure 12). This highlights the resilience of these perfluorinated polymers to water vapor sorption.

Figure 10

Figure 11

Figure 12

For most polymeric membranes, such behavior corresponds to a combination of competitive sorption, where water competes with CO₂ or CH₄ for space within the micro-void region; and hindered diffusivity, where large clusters of water obstruct the movement of other species. Given the water sorption in both perfluorinated polymers was below the limit of detection, the decrease in permeability in this case is believed to be associated with water clustering. This is particularly likely given the poor interaction between water and the fluorinated moieties, and would explain the high permeation activation energy for Teflon AF1600. Hence, the water molecules that do manage to penetrate the membrane structure will prefer to associate with each other than with the polymer chains. It has been shown in Teflon AF2400 that methanol and ethanol also cluster because of the hydrophobic conditions [46].

Conclusion

The water permeability within Teflon AF1600 and Hyflon AD60 in a nitrogen feed gas was measured and indicated that water had a lower permeability through Teflon AD1600 than Hyflon AD60. This is opposite to that observed for CO₂, N₂ and CH₄ permeabilities in these membranes, and is counterintuitive based on the greater fractional free volume in Teflon AF1600. This behavior was attributed to the very low solubility of water in these polymers, reflective of their strong hydrophobicity. The water permeability increased exponentially with temperature for Teflon AD1600, reflecting a diffusivity dependent

mechanism. Conversely Hyflon AD60 exhibited a minimum water permeability at around 55°C. The low water permeability in Teflon AF1600 meant that it was selective for CO₂ over H₂O, which is unlike any other glassy polymeric membrane that has been reported in the literature. In all systems, the CO₂ and CH₄ permeability decreased when exposed to a humid feed gas. This was associated with water clusters blocking the pathways needed for gas permeation through the membrane. Importantly, the loss of permeability was minor relative to other polymeric membranes, reflecting the low solubility of water in these systems. These features mean that both perfluorinated polymeric membranes can be utilized in applications where gas pretreatment to remove water is difficult.

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Table Caption

Table 1: Density (g/cm^3) and Fractional free volume (FFV) in Teflon AF1600 and Hyflon AD60 membranes.

Table 2: Dual sorption parameters for CO_2 , CH_4 and N_2 in Teflon AD1600 and Hyflon AD60. Teflon AF1600 values are taken from Alentiev *et al.* [21]

Table 3: Diffusivity (cm^2/s) and immobilization factor (F) for CO_2 , N_2 and CH_4 in Teflon AF1600 and Hyflon AD60.

Figure Caption

Figure 1: Chemical structures of Teflon AF1600 and Hyflon AD60.

Figure 2: CO₂, CH₄ and N₂ sorption isotherms in Teflon AF1600 at 35 °C.

Figure 3: CO₂, CH₄ and N₂ sorption isotherms in Hyflon AD60 at 35 °C.

Figure 4: CO₂, N₂ and CH₄ single gas permeabilities in Teflon AF1600 as a function of feed pressure at 35 °C.

Figure 5: CO₂, N₂ and CH₄ single gas permeabilities in Hyflon AD60 as a function of feed pressure at 35 °C.

Figure 6: Water permeability (barrer) in Teflon AF1600 and Hyflon AD60 as a function of feed gas water activity at 35 °C. The dashed line is added to guide the eye.

Figure 7: The permeability of water versus H₂O – CO₂ permselectivity for a range of polymeric membranes. The gradient of the upper bound line is determined according to theory [44]. Highlighted are Teflon AF1600 and Hyflon AD60 at water activity of 0.3. Also shown is the reported performance for some common polymeric materials, although it should be noted that the gas testing conditions including the water activity vary for this literature data.

Figure 8: Water permeability (barrer) in Teflon AF1600 and Hyflon AD60 as a function of temperature (°C) at 30% relative humidity.

Figure 9: H₂O/CO₂ selectivity of Teflon AF1600 and Hyflon AD60 as a function of temperature, with the transition from CO₂ to H₂O selectivity marked.

Figure 10: CO₂ permeability in (a) Teflon AF1600 and (b) Hyflon AD60 exposed to humid feed gas, at 35 °C.

Figure 11: CH₄ permeability in (a) Teflon AF1600 and (b) Hyflon AD60 exposed to humid feed gas, at 35 °C.

Figure 12: CO₂/CH₄ selectivity of Teflon AF1600 and Hyflon AD60 as a function of water activity in the feed gas, at 35 °C.

Tables

Table 1

	Density (g/cm ³)	FFV
Teflon AF1600	1.84	0.29
Hyflon AD60	1.91	0.17

Table 2

	Teflon AF1600			Hyflon AD60		
	CO ₂	CH ₄	N ₂	CO ₂	CH ₄	N ₂
k_D (cm ³ (STP)/cm ³ atm)	1.22	0.42	0.20	0.78	0.31	0.22
C'_H (cm ³ (STP)/cm ³ polymer)	15.4	8.1	14.8	9.11	2.95	4.48
b (atm ⁻¹)	0.10	0.07	0.03	0.13	0.08	0.03

Table 3

D (cm ² /s x 10 ⁶)	Teflon AF1600			Hyflon AD60		
	CO ₂	N ₂	CH ₄	CO ₂	N ₂	CH ₄
This work	2.9 ± 0.4	2.0 ± 0.3	0.57 ± 0.21	0.79 ± 0.09	0.47 ± 0.10	0.17 ± 0.10
Jansen [37]				0.75	0.73	0.25
Jansen [17]	1.29	1.16	0.38	0.48	0.47	0.11
Alientev [21]	0.95 – 2.5	1 - 3	0.35 – 1.8			
F (this work)	0.17 ± 0.03	0.25 ± 0.05	0.30 ± 0.06	0.50 ± 0.11	0.85 ± 0.18	0.85 ± 0.19

Figure 1
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Teflon AF1600

Hyflon AD60

Figure 2
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Figure 3
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Figure 12

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