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Mohsin Mukaddam, Eric Litwiller, Ingo. Pinnau

PII: S0376-7388(16)30270-8
DOI: <http://dx.doi.org/10.1016/j.memsci.2016.04.042>
Reference: MEMSCI14442

To appear in: *Journal of Membrane Science*

Received date: 16 February 2016

Revised date: 15 April 2016

Accepted date: 17 April 2016

Cite this article as: Mohsin Mukaddam, Eric Litwiller and Ingo. Pinnau Pressure-dependent pure- and mixed-gas permeation properties of Nafion® *Journal of Membrane Science*, <http://dx.doi.org/10.1016/j.memsci.2016.04.042>

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Pressure-dependent pure- and mixed-gas permeation properties of Nafion[®]

Mohsin Mukaddam, Eric Litwiller, Ingo Pinnau*

King Abdullah University of Science and Technology (KAUST), Advanced Membranes and Porous Materials Center (AMPMC), Physical Sciences and Engineering Division and Chemical and Biological Engineering Program, Al-Jazri Building 4, Thuwal, 23955-6900, Kingdom of Saudi Arabia

*Corresponding author: King Abdullah University of Science and Technology, Advanced Membranes and Porous Materials Center, Division of Physical Sciences and Engineering, Al-Jazri Bldg. 4, Thuwal 23955-6900, Saudi Arabia, Tel: +966-12-808-2406

E-mail address: ingo.pinnau@kaust.edu.sa (I. Pinnau)

Abstract

The permeation properties of Nafion[®] at 35 °C are presented for pure gases H₂, N₂, O₂, CH₄, CO₂, C₂H₆ and C₃H₈, as a function of pressure between 2 and 20 atm. The effect of pressure on permeability and selectivity is analyzed to understand two observed phenomena: compression and plasticization. In pure-gas experiments, at increasing feed pressure, compression of the

polymer matrix reduced the permeability of low-sorbing penetrants H_2 , N_2 , O_2 , and CH_4 . In contrast, permeabilities of more soluble penetrants CO_2 and C_2H_6 increased by 18 and 46% respectively, as plasticization effects overcame compression effects. Permeability of C_3H_8 decreased slightly with increasing pressure up to 4.6 atm as a result of compression, then increased by 3-fold at 9 atm as a result of plasticization associated with high C_3H_8 solubility. Binary CO_2/CH_4 (50:50) mixed-gas experiments at total feed pressures up to 36 atm quantified the effect of CO_2 plasticization on separation performance. At 10 atm CO_2 partial pressure, CH_4 permeability increased by 23% relative to its pure-gas value of 0.078 Barrer, while CO_2 permeability decreased by 28%. Consequently, CO_2/CH_4 selectivity decreased to 19, i.e., 42% below its pure-gas value of 32.

Keywords: Nafion[®], gas separation, plasticization, polymer compression, mixed-gas permeation.

1. Introduction

The importance of natural gas (NG) as a fuel source and chemical feedstock has grown in tandem with advances in technologies for its bulk removal and purification [1, 2]. Separation of contaminants such as CO_2 and H_2S from raw NG streams, traditionally accomplished using large amine absorption towers, is now often done using membrane systems – particularly on offshore

platforms where space is at a premium [2-4]. The most common commercial membrane material in this application is cellulose acetate (CA), which can provide CO₂/CH₄ selectivity of 10-15 under high-pressure mixed-gas conditions [5]. Polyimide-based membranes are viewed as an alternative to CA membranes and also have a share of the market [2, 4-6].

Plasticization limits real-world membrane performance primarily by reducing selectivity, resulting in methane loss [5-7]. Plasticization occurs when large quantities of condensable gases such as CO₂, ethane, propane, butane and C₅₊ hydrocarbons sorb into the polymer matrix, increasing polymer chain mobility [8-11]. Macroscopic effects of plasticization include volume dilation, reduced mechanical stability, and depression of glass transition temperature [9, 10, 12-14]. The effects of CO₂ plasticization on gas transport include: (i) higher CO₂ permeability, (ii) even higher relative increase in mixed-gas CH₄ permeability, (iii) lower mixed-gas selectivity and (iv) time-dependent increases in CO₂ permeability (conditioning) [8-11, 15, 16]. These observations stem from the fact that polymers undergo reorganization of local segmental chains upon significant CO₂ sorption [8]. It has been shown for several glassy polymers that a CO₂ concentration of about 38 cm³(STP)/cm³ inside the polymer matrix is high enough to induce plasticization [2, 11].

Several strategies have been employed to reduce plasticization, including cross-linking of polymers, polymer blending, and thermal treatment [17-19]. These approaches have been more successful in delaying the onset of plasticization than in treating its underlying cause, i.e., the high solubility of plasticizing components. An alternative approach to counter the effect of plasticization may be to identify polymers that have *lower solubility* for plasticizing penetrants [20, 21].

Nafion's[®] polytetrafluoroethylene (PTFE) backbone places this ionomer in the class of perfluoropolymers (**Fig. 1**). Materials in this class have already found important commercial applications in chemical, electronic and medical industries [22-26], owing in large part to their exceptional chemical and mechanical stability. Semi-crystalline PTFE shows low gas permeability [27] and cannot be solvent cast into thin films [21], but newer amorphous glassy perfluoropolymers such as Teflon[®] AF (Du Pont), Hyflon[®] AD (Solvay), Cytop[®] (Asahi Glass) and others have shown promise in several gas separation applications [20, 21, 28-35]. These polymers are soluble in perfluorinated solvents and thus can be fabricated into thin-film composite membranes. Their unique ability to combine restricted, efficient chain packing with low gas solubilities has allowed permeability-selectivity combinations to surpass 2008 Robeson upper bound curves for several gas pairs: He/CH₄, He/H₂, N₂/CH₄, and H₂/CH₄ [21, 30-32, 36, 37]. Nafion[®] is unusual in that its phase-separated microstructure exhibits two glass transition temperatures: one from its rubbery PTFE phase and another from its ionic sulfonic acid clusters. In our previous work, we suggested that Nafion[®] may hold promise as a membrane material for CO₂ removal from *dehydrated* NG [38]. In this earlier study, solubility measurements revealed CO₂ uptake in Nafion[®] of about 8 cm³(STP)/cm³ at 10 atm – 3-fold lower than CA [39] and almost 2-fold lower than perfluorinated Cytop[®] [21]. Moreover, C₃H₈ uptake in Nafion[®] was about 1 cm³(STP)/cm³ at 2 atm – 25-fold lower than polyimide 6FDA-6FpDA [40] and 5-fold lower than Cytop[®] [21]. These results motivated further research to determine Nafion's[®] permeation properties under high-pressure mixed-gas conditions.

In this work we report pure-gas permeation properties of Nafion[®] for H₂, O₂, N₂, CH₄, CO₂, C₂H₆, and C₃H₈ as a function of pressure at 35 °C. The coupling effects of penetrant sorption and diffusion in mixed-gas experiments often result in reduced selectivity. Accordingly, binary

(50:50) CO₂/CH₄ mixed-gas permeation experiments were conducted to evaluate the potential effectiveness of Nafion[®] in separating CO₂/CH₄ mixtures.

Fig. 1. Chemical structure of Nafion[®] EW 1100.

2. Experimental

2.1. Materials

Isotropic, dispersion-cast, 25 µm thick Nafion[®] NRE 211 (1100 g/equiv) films were obtained from Ion Power, Inc. in the H⁺ form. To ensure data accuracy and minimize possible errors due to sample variation, the exact same film drying protocol was applied for all permeation and sorption (reported in [38]) experiments. The thermogravimetric analysis (TGA) curve in **Fig. S1** showed that 300 minutes at 80 °C was sufficient to dehydrate these films. All films tested were pre-dried at 80 °C under vacuum for 2 days, and then degassed under vacuum for at least 24 hours in the permeation test apparatus. Pure gases H₂, N₂, O₂, CH₄, CO₂, C₂H₆, and C₃H₈, and mixtures of CO₂/CH₄ (50:50) were purchased from Abdullah Hashim Group (AHG), KSA with purity of at least 99.99%.

2.2. Gas permeation experiments

2.2.1. Pure-gas permeation experiments

Pure-gas permeabilities in Nafion[®] were determined by the variable pressure/constant volume method at 35 °C [41, 42]. Permeabilities of condensable gases CO₂, C₂H₆ and C₃H₈ were each measured on different films, whereas the low-solubility gases were measured on the same film in the following order: N₂, H₂, N₂, O₂, N₂, CH₄. The repeated N₂ measurements gave permeabilities that were within $\pm 5\%$ of each other, verifying that exposure to other gases did not change film properties. Permeabilities for H₂, N₂, O₂, CH₄, CO₂, and C₂H₆, were determined between 2 and 20 atm, and for C₃H₈ between 2 and 9 atm. Permeabilities were calculated by:

$$P = D S = 10^{10} \frac{V_d l}{p_{up} A R T} \frac{dp}{dt}$$

where P is the permeability in Barrers (1 Barrer = 10^{-10} cm³ (STP) cm/cm² s cmHg), p_{up} is the upstream pressure (cmHg), dp/dt is the steady-state permeate-side pressure increase (cmHg/s), V_d is the calibrated permeate volume (cm³), l is the membrane thickness (cm), A is the effective membrane area (cm²), T is the operating temperature (K), and R is the gas constant (0.278 cm³ cmHg /cm³ (STP) K). The ideal selectivity for a gas pair is given by the following relationship:

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

2.2.2. Mixed-gas permeation experiments

Binary mixed-gas permeation properties were measured using a CO₂/CH₄ (50:50) feed at 35 °C using the technique of O'Brien et al. [43]. Prior to mixed-gas testing, a pure-gas N₂ permeability test at 2 atm was carried out to ensure sample reproducibility, as described above.

Samples were tested at total pressures of 4, 10, 20, 24, 30, and 36 atm. The stage cut (permeate flow/feed flow) was maintained below 1%. Mixed-gas permeabilities were calculated by:

$$P_{CO_2} = 10^{10} \frac{y_{CO_2} V_d l}{x_{CO_2} p_{up} ART} \frac{dp}{dt}$$

$$P_{CH_4} = 10^{10} \frac{y_{CH_4} V_d l}{x_{CH_4} p_{up} ART} \frac{dp}{dt}$$

where x and y are the mole fractions in the feed and permeate, respectively. Because the downstream pressure was negligible, the mixed-gas CO_2/CH_4 selectivity was obtained from:

$$\alpha_{CO_2/CH_4} = \frac{y_{CO_2}/y_{CH_4}}{x_{CO_2}/x_{CH_4}}$$

3. Results and discussion

3.1. Pressure-dependent pure-gas permeability

Fig. 2 shows permeability of low sorbing gases: (a) N_2 , CH_4 and (b) H_2 , O_2 , in Nafion[®] as a function of pressure at 35 °C. In all cases, permeability decreased slightly with increasing pressure. Gas permeabilities at 2 atm, tabulated in [38], were in reasonably good agreement with those reported by Chiou and Paul [44]. Solubilities of H_2 , O_2 , N_2 , and CH_4 in Nafion[®] reported in our previous study were constant up to 20 atm and followed Henry's law, indicating rubber-like behavior [38]. Because permeability is the product of diffusivity and solubility, the constant solubility values indicate that the decrease in permeability was caused by a decrease in gas diffusivity. If polymer chain compression narrows gas transport pathways, larger penetrant molecules should display greater permeability decreases. Subsequently, as pressure increased from 2 to 20 atm, permeability of the largest gas CH_4 decreased by 13%, N_2 and O_2 decreased by

8%, and the much smaller H_2 by only 1%. Permeability reduction resulting from compression has been reported for several gases in rubbery polymers where the decrease in permeability was associated with a compression-induced decrease in diffusivity with increase in pressure [45-47]. For example, in poly(dimethylsiloxane) (PDMS) non-interacting gases such as He and N_2 showed permeability decreases of 27 and 24%, respectively, between 3 and 30 atm [45]. Similarly, in poly(octylmethylsiloxane) (POMS), CH_4 and *n*-butane permeability dropped by 75 and 77%, respectively, between 2 and 10 atm [47]. Nafion[®] shows rubber-like behavior similar to PDMS and POMS with low Young's modulus and ~250% elongation at break at 35 °C (see Fig. S2).

Fig. 2. Permeabilities of low sorbing penetrants in Nafion[®] for (a) N_2 , CH_4 ; and (b) H_2 , O_2 , as a function of pressure at 35 °C.

Permeabilities of more condensable gases CO_2 and C_2H_6 increased with pressure, as shown in Figs. 3(a) and (b). Permeabilities are plotted with their pressure-dependent diffusivities derived from $D=P/S$, using solubility values obtained from our previous study [38]. CO_2 and C_2H_6 permeabilities increased by 18 and 46%, respectively, as pressure increased from 2 to 20

atm. Also, the permeability of CO₂ was considerably higher than that of C₂H₆ across the investigated pressure range. The increase in permeability with pressure can be explained as follows: the solubility coefficients of CO₂ and C₂H₆ measured in our previous study were essentially constant between 1 and 20 atm, so the observed permeability increase can be attributed solely to increases in diffusivities. Presumably, plasticization enhances polymer chain mobility and thereby increases the gas diffusivity in the polymer. The higher permeability of CO₂ relative to C₂H₆ results from its smaller molecular diameter combined with enhanced solubility due to its quadrupolar nature that enables strong specific (polar-quadrupolar) interaction with the polar sulfonate groups in Nafion[®] [48].

Fig. 3. Pressure dependence of pure-gas permeability (P) and diffusivity (D) for high sorbing penetrants (a) CO_2 ; (b) C_2H_6 ; and (c) C_3H_8 in Nafion[®] at 35 °C. Solubility (S) data were extracted from [38] and diffusivities were obtained from $D = P/S$. Open points: pure-gas diffusivity. Closed points: pure-gas permeability.

Fig. 3(c) shows C_3H_8 permeability as a function of pressure combined with diffusivities obtained as described above. Permeability decreased slightly as pressure increased from 2 to 4.6 atm, and then increased dramatically. The slight permeability decrease can be explained by analyzing individual contributions from solubility and diffusivity to the overall gas permeability. Solubility increased by 25% between 2 and 4.6 atm. As $P = DS$, the observed 22% decrease in permeability results from comparatively larger (~40%) decrease in diffusivity due to pressure-induced chain compression. As dissolved C_3H_8 concentration increases, the polymer matrix of Nafion[®] becomes softer which enhances chain mobility. As a result, a ~64% increase in C_3H_8 permeability was observed between 4.6 and 9 atm due to a dominant ~59% increase in solubility combined with ~43% increase in diffusivity. Plots of C_3H_8 permeability versus time are included in **Fig. S3** to show that sufficient time was provided to reach steady state.

3.2. Mixed-gas CO_2/CH_4 (50:50) permeation properties

Fig. 4 compares permeabilities of pure CH_4 (also shown in **Fig. 2(a)**) and CO_2 (**Fig. 3(a)**) with those of a 50:50 feed mixture as a function of pressure at 35 °C. It is well known that mixtures containing CO_2 tend to introduce non-ideal effects such as plasticization and competitive sorption, often resulting in different permeation behavior compared to pure-gas measurements. Thus, we conducted mixture experiments over a range of CO_2 partial pressures between 2 and 18 atm to assess the effect of plasticization on membrane separation performance. **Fig. 4(a)** plots pure- and mixed-gas CO_2 permeabilities with respect to both pressure and fugacity. Fugacity values were calculated for each pressure point using the Soave-Redlich-Kwong (SRK) equation of state [49]. Across the entire pressure range investigated, mixed-gas CO_2 permeability was lower than pure-gas. For example, at 18 atm CO_2 partial pressure, CO_2 permeability was about 35% lower than its pure-gas value. Competitive sorption explains the

difference: when CH_4 is added to the feed, it competes with CO_2 for sorption sites in the polymer, reducing CO_2 solubility. When plotted with respect to fugacity, mixed-gas CO_2 permeability increases with increasing pressure, but less steeply than in the pure-gas case. Under mixed-gas conditions, the permeability increase caused by plasticization is partially offset by the decrease caused by additional compression from CH_4 . These offsetting effects of plasticization and compression were first highlighted by Jordan and Koros for rubbery PDMS in their mixed-gas study of CO_2/CH_4 and CO_2/N_2 [45].

Fig. 4. Pure- and mixed-gas (50:50) permeability of (a) CO_2 and (b) CH_4 in Nafion[®] as a function of partial pressure or fugacity at 35 °C. Open points: mixed-gas permeability. Closed points: pure-gas permeability.

As shown in **Fig. 4(b)**, at lower pressures (up to 5 atm), mixed-gas CH_4 permeability was slightly lower than its pure-gas value. As discussed above, competitive sorption and compression can explain this decrease. At pressures above 5 atm, permeability increased linearly and markedly. CH_4 mixed-gas permeability with respect to fugacity was slightly higher; however, the general trend was the same. At 18 atm CO_2 partial pressure, mixed-gas CH_4 permeability was

almost 70% higher than its pure-gas value. The polar sulfonate group in Nafion[®] allows specific interaction with CO₂ molecules, which increases segmental mobility. Thus, the significant increase in CH₄ permeability is a direct consequence of CO₂-induced plasticization that facilitates the diffusion of CH₄ molecules under mixed-gas conditions.

Fig. 5. Pure- and mixed-gas (50:50) CO₂/CH₄ selectivity in Nafion[®] as a function of CO₂ partial pressure at 35 °C. Open points: mixed-gas selectivity. Closed points: pure-gas selectivity.

Given the decrease in mixed-gas CO₂ permeability coupled with comparatively larger increase in CH₄ permeability, overall mixed-gas CO₂/CH₄ selectivities were lower than pure-gas ideal selectivities over the entire pressure range investigated, as illustrated in **Fig. 5**. At CO₂ partial pressure of 10 atm, typical in natural gas applications [5, 7], Nafion[®] mixed-gas selectivity dropped by ~42% relative to its pure-gas value, from 32 to 19.

4. Conclusions

In summary, the pressure-dependent permeability results obtained for Nafion[®] highlighted two divergent phenomena: gas compression and plasticization. In pure-gas experiments, permeability of permanent gases H₂, O₂, N₂ and CH₄ decreased due to polymer compression, whereas the permeability of more condensable gases CO₂, C₂H₆ and C₃H₈ increased due to solubility-induced plasticization. Mixed-gas CO₂/CH₄ experiments showed reduced performance as a result of dominant CO₂ plasticization effects. At typical NG partial CO₂ pressure of 10 atm, Nafion[®] exhibited CO₂/CH₄ selectivity of 19, similar to standard industrial CA membranes.

The market for using Nafion[®] membranes as the primary separation unit in NG processing may not look promising owing to its low CO₂ permeability, moderate mixed-gas CO₂/CH₄ selectivity (**Fig. S4**) and high cost. However, its unique ability to preferentially permeate CO₂ and N₂ while retaining CH₄ and C₂₊ hydrocarbons in the product stream may offer significant advantages compared to glassy polymeric membranes such as CA. Nafion[®] offers high N₂/CH₄ selectivity of 2.9, in contrast to commercially available polymers like CA (0.8), polysulfone (0.6), and polycarbonate (0.8) [50]. Considering that 14% of U.S. gas wells are contaminated with unacceptably high concentrations of N₂ [51], removing N₂ and CO₂ simultaneously is commercially valuable. In addition, NG is the world's major source of helium, typically containing 0.4-0.5%, which is usually recovered alongside N₂ [4, 52]. Nafion[®] could be a candidate membrane material for this application as it exhibits He/CH₄ selectivity of 440 owing largely to its extraordinarily high diffusivity selectivity, and He permeability of 37 Barrer – 3-fold higher than CA.

Acknowledgments

The research reported in this publication was supported by funding from King Abdullah University of Science and Technology (KAUST).

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Highlights

- Gas transport in Nafion[®] revealed two divergent phenomena: compression and plasticization.
- Low sorbing gases show decrease in permeability due to chain compaction by compression.

- High sorbing gases show increase in permeability due to solubility-induced chain plasticization effect.
- Binary mixed-gas CO₂/CH₄ experiments showed decrease in selectivity induced by CO₂ plasticization.

Accepted manuscript