Pure- and mixed-gas carbon dioxide/ethane permeability and diffusivity in a cross-linked poly(ethylene oxide) copolymer

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A B S T R A C T
Pure and mixed-gas CO2 and C2H6 permeability coefficients in a cross-linked poly(ethylene oxide) copolymer were measured at temperatures ranging from –20 to +35 °C. The polymer was prepared by photopolymerization of a solution containing 70 wt% poly(ethylene glycol) methyl ether acrylate (PEGMEA) and 30 wt% poly(ethylene glycol) diacrylate (PEGDA). Four different gas mixtures (10, 25, 50 and 70 mol% CO2) were considered at feed pressures up to 20 atm. Carbon dioxide permeability was not changed by the presence of ethane at T ≥ 25 °C, but it increased with increasing ethane content at lower temperatures. Ethane permeability, in contrast, increased significantly in the presence of carbon dioxide compared to its pure-gas value, an effect whose extent increased with decreasing temperature. Permeability data were combined with pure- and mixed-gas sorption isotherms to calculate pure and mixed-gas effective diffusion coefficients of each gas. For carbon dioxide, there was no significant dependence of the diffusion coefficient on ethane concentration in the feed. On the other hand, the diffusion coefficients of both ethane and carbon dioxide increased with increasing concentration of carbon dioxide in the polymer. A simplified free volume model with two adjustable parameters for each gas was able to correlate the effects of temperature and penetrant concentration on gas permeability, with an average prediction error lower than 8%.

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1. Introduction

After methane, ethane is the second most prevalent hydrocarbon in natural gas, with a typical concentration of 5 mol% [1]. Due to its commercial value as a petrochemical feedstock, ethane is extracted from natural gas. This ethane-rich stream often contains some carbon dioxide, a common impurity in natural gas. These two gases have similar vapor pressures and are notorious for forming highly non-ideal mixtures [2–5]. In fact, the CO2/C2H6 system exhibits a maximum-pressure azeotrope. Traditional separation techniques, including absorption, adsorption, and cryogenic distillation, are currently utilized to break this azeotrope during natural gas treatment. However, such techniques are capital and energy intensive and lead to complex processes [6–8].

Membrane technology could be an interesting alternative for this separation. Early work in this regard was carried out by Saha and Chakma [6], who tested immobilized liquid membranes containing solutions of diethanolamine and poly(ethylene glycol) as the carrier. Cellulose acetate was later tested as a possible membrane material by Gall and Sanders [7], who considered a liquid CO2/C2H6 feed stream, and Nordstad et al. [8], who performed experiments with a ternary gas mixture (C2H6/CO2/CH4). More recently, Kelman et al. [9] explored the use of cross-linked poly(ethylene oxide) (XLPEO) membrane materials to break the CO2/C2H6 azeotrope. Three operating temperatures were considered, and both pure-gas permeability and solubility were measured, which enabled the calculation of the effective diffusion coefficient of each gas in the polymer. Mixed-gas permeation data were also reported for a feed stream containing 45 mol% CO2 and 55 mol% C2H6.

XLPEOs are rubbery materials synthesized from acrylate-functionalized, low molecular-weight oligomers, which can be cross-linked either thermally or by exposure to UV light [10–12]. A substantial amount of pure-gas permeation data for dense XLPEO films prepared from different oligomers is available [10,13–23], but the same is not true for mixed-gas permeation data.

In the present study, we extend the work of Kelman et al. [9] and investigate the performance of an XLPEO film for CO2/C2H6 separation. The polymer was obtained by photopolymerization of a solution containing 30 wt% poly(ethylene glycol) diacrylate (PEGDA) and 70 wt% poly(ethylene glycol) methyl ether acrylate (PEGMEA), and it has high pure-gas CO2 permeabilities and good
pure-gas selectivity values. Permeability and selectivity were measured for four different mixtures (10, 25, 50 and 70 mol% CO₂) at five operating temperatures (−20, −10, 0, 25, and 35 °C) and at feed pressures up to 20 atm. Pure-gas permeation experiments were also performed for comparison. Pure and mixed-gas permeation data were then combined with pure- and mixed-gas solubility data in the polymer to calculate the effective diffusion coefficient of each gas in the membrane at the different operating conditions.

2. Background

2.1. Parameters for membrane performance

Membrane performance is usually characterized in terms of permeability and selectivity values. Permeability (φ) is defined as the thickness and driving-force normalized flux [24]:

\[ \phi_i = \frac{N_i}{P_i - P_j} \]

(1)

where \( N_i \) is the steady-state molar flux of gas i across the membrane, \( l \) is the membrane thickness, \( f_i \) is the fugacity of component i, and the superscripts 0 and l refer to the upstream and downstream faces of the membrane, respectively.

The selectivity of a membrane for penetrant i relative to penetrant j, \( \alpha_{i,j} \), is defined as the ratio of the permeability coefficients of these penetrants [25]:

\[ \alpha_{i,j} = \frac{\phi_i}{\phi_j} \]

(2)

When mixed-gas experiments are performed, a third performance parameter, known as the separation factor, \( \alpha_{i,j}^s \), can be defined [25]:

\[ \alpha_{i,j}^s = \frac{x_i^l/x_j^l}{x_i^0/x_j^0} \]

(3)

where \( x_i \) is the mole fraction of component i in the gas stream in contact with the membrane.

When fluxes are written in terms of partial pressures and the upstream pressure is much greater than the downstream pressure, the selectivity and the separation factor are equal [26]. In this case, differences in membrane performance due to mixed-gas effects are shown, for instance, by differences between separation factor values obtained in mixed-gas permeation experiments and ideal selectivity values calculated from pure-gas permeation results.

However, when fluxes are expressed in terms of fugacity, differences between \( \alpha_{i,j} \) and \( \alpha_{i,j}^s \) can arise simply due to non-ideal effects in the gas phase. For example, at steady-state, the mole fraction of component i on the downstream side of the membrane in contact with a binary feed stream is:

\[ x_i^l = \frac{N_i}{N_i + N_j} \]

(4)

Inserting the definition of permeability (i.e., Eq. (1)) into Eq. (4) and then evaluating \( \alpha_{i,j}^s \) from Eq. (3) when the upstream pressure is much greater than the downstream pressure, one obtains:

\[ \alpha_{i,j}^s = \frac{x_i^l/x_j^l}{x_i^0/x_j^0} = \frac{\hat{f}_i}{\hat{f}_j} \]

(5)

In Eq. (5), \( \hat{f}_i \) is the fugacity of component i in the gas mixture on the upstream side of the membrane. The value of \( \hat{f}_i \) is given by [27]:

\[ \hat{f}_i = x_i \phi_i P \]

(6)

where \( P \) is the total pressure and \( \hat{\phi} \) is the fugacity coefficient of species i in the gas mixture. Substitution of Eq. (6) into Eq. (5) leads to:

\[ \alpha_{i,j}^s = \frac{\hat{\phi}_i}{\hat{\phi}_j} = \alpha_{i,j} \phi_{i,j} \]

(7)

From Eq. (7), when fugacity is used as the driving force to define permeability, the separation factor depends upon both membrane properties (\( \alpha_{i,j} \)) and the non-ideality of the feed mixture (\( \phi_{i,j} \)). Thus, even if pure- and mixed-gas permeability coefficients of two gases in a given polymer are the same and the upstream pressure is much greater than the downstream pressure, the separation factor and selectivity may still be different, and the magnitude of this difference depends on the degree of non-ideality of the feed mixture.

For example, the ratio of fugacity coefficients for different CO₂/C₂H₆ mixtures at 35 °C and −20 °C is plotted as a function of pressure in Fig. 1. All calculations were performed utilizing the virial equation of state truncated to three terms, as detailed elsewhere [28], always keeping total pressure below the mixture dew point [2–4]. For this particular mixture, since the less permeable component, ethane, is also the more non-ideal component, \( \phi_{i,j} \) is greater than one, and its value increases with increasing pressure, increasing ethane content, and decreasing temperature. The opposite situation, that is, \( \phi_{i,j} < 1 \), is observed in the case of n-C₄H₁₀/n-C₄H₈ separation using poly(dimethylsiloxane) (PDMS), since n-C₄H₁₀ has a higher permeability in PDMS and a much higher degree of non-ideality in the mixture than methane [24,29]. From Fig. 1, the difference between \( \alpha_{i,j} \) and \( \alpha_{i,j}^s \) due to non-ideality effects can be as much as 10% at the experimental conditions considered. In this study, membrane separation performance in pure- and mixed-gas experiments is compared in terms of ratios of permeability coefficients, that is, the membrane selectivity given by Eq. (2).

2.2. Effective diffusion coefficients

Penetrant transport across a dense polymeric film is usually modeled using Fick’s law. In a system consisting of a pure gas i permeating through a polymer, if one dimensional transport is assumed, \( N_i \) is given by [25]:

\[ N_i = -\frac{D_{im}}{1 - w_i} \frac{dc_i}{dz} \]

(8)
where $D_{im}$ and $w_i$ are, respectively, the binary mutual diffusion coefficient and the mass fraction of species $i$ in the polymer, $z$ is the spatial coordinate, and $C_i$ is the molar concentration of penetrant $i$ in the polymer.

Upon combining Eqs. (1) and (8) and integrating across the film thickness one obtains [26]:

$$
\phi_i = \frac{D_i (C_i^0 - C_i^1)}{(C_i^0 - f_i^1)}
$$

(9)

where $D_i$ is the concentration-averaged effective diffusion coefficient defined as follows:

$$
\bar{D}_i = \frac{1}{C_i^1 - C_i^0} \int_{C_i^0}^{C_i^1} \frac{D_{im}(C)}{1 - w_i} dC
$$

(10)

If the downstream pressure is kept much lower than the upstream pressure, as it is normally the case during the measurement of pure-gas permeability, Eq. (9) simplifies to:

$$
\phi_i = \frac{D_i C_i^0}{f_i^1} = \bar{D}_i \times S_i^0
$$

(11)

where $S_i^0$ is the solubility coefficient of component $i$ on the upstream face of the membrane.

In the case of multicomponent systems, the definition of an effective diffusion coefficient for each penetrant in the polymer is not as straightforward. In the simplest case, when the feed stream is a binary gas mixture, Fick’s law is written as [30]:

$$
N_1 = -D_{11} \frac{dC_1}{dz} - D_{12} \frac{dC_2}{dz}
$$

(12a)

$$
N_2 = -D_{21} \frac{dC_1}{dz} - D_{22} \frac{dC_2}{dz}
$$

(12b)

where $D_{ij}$ are the multicomponent Fickian diffusion coefficients. These coefficients should not be confused with the binary diffusion coefficients in Eq. (8); they may take positive or negative signs and they are not, in general, symmetric (i.e., $D_{ij} \neq D_{ji}$). Furthermore, the $D_{ij}$ do not reflect the $i$-$j$ interactions. Therefore, the multicomponent $D_{ij}$ do not have the physical significance of the binary Fickian diffusivity [30]. The complexity of the multicomponent Fickian diffusion coefficients arises due to the assumption of concentration gradients, rather than chemical potential gradients, as the driving force for mass transfer. The dependence of $N_i$ on the concentration gradient of all species includes but is not necessarily due to frictional coupling. It reflects the fact that, in a multicomponent system, the chemical potential of species $i$ is generally a function of the concentration of all species. In a forthcoming publication, we shall address the decoupling of these two aspects by the use of the Maxwell–Stefan formulation to describe penetrant transport across polymer films.

To define an effective diffusion coefficient in a ternary system, one assumes that the rate of diffusion of species $i$ depends only on the concentration gradient of that species [30], that is:

$$
N_i = -\bar{D}_i \frac{dC_i}{dz}
$$

(13)

Starting from Eq. (13), one can easily obtain Eq. (11) and therefore estimate effective mixed-gas diffusion coefficients by combining mixed-gas permeation and sorption data, as done in previous studies [24,31–33]. The important aspect to bear in mind is the underlying physical meaning of any diffusion coefficient estimated according to such methodology. Comparison of Eqs. (12) and (13), together with the fact that Eq. (11) implies integration across the film thickness, leads to:

$$
\bar{D}_1 = \frac{1}{C_1 - C_i^1} \int_{C_i^0}^{C_i^1} \left( D_{11} + D_{12} \frac{dC_j}{dz} \right) dC_i
$$

(14a)

$$
\bar{D}_2 = \frac{1}{C_2 - C_i^2} \int_{C_i^0}^{C_i^2} \left( D_{22} + D_{21} \frac{dC_i}{dz} \right) dC_2
$$

(14b)

From Eq. (14), mixed-gas effective diffusion coefficients can lump together many different effects. In particular, a possible dependence of $\bar{D}_i$ on the concentration of component $j$ is intrinsic, not only because the multicomponent Fickian diffusion coefficients are likely to be a function of the total amount of gases dissolved in the polymer, but also because the ratio of concentration gradients of species $i$ and $j$ is involved in the definition.

3. Experimental procedure

Cylinders of ethane (99% purity) and carbon dioxide (99.999% purity) were purchased from Air Gas Southwest Inc. (Corpus Christi, TX). Certified ethane–carbon dioxide mixtures (10, 25, 50 and 70 mol% CO2) were purchased from Praxair Inc. (Danbury, CT). Poly(ethylene glycol) diacrylate (PEGDA; nominal MW = 700 g/mol), poly(ethylene glycol) methyl ether acrylate (PEGMEA; nominal MW = 460 g/mol), and 1-hydroxy-cyclohexyl phenyl ketone (HCPK; 99% purity), the photoinitiator, were obtained from Aldrich Chemical Co. (Milwaukee, WI). All gases and chemicals were used as received.

XLPEO samples were prepared by polymerizing a PEGDA (30 wt%) – PEGMEA (70 wt%) solution containing 0.1 wt% HCPK in a UV-cross-linker (Fisher Scientific, model FB-UVXL-1000), as detailed elsewhere [13,16,34]. The solid films thus obtained were immersed in an ethanol bath for 3 days to remove any residual components or low-molecular-weight species, and then they were dried at room temperature for at least 7 days. The liquid bath was replaced daily with fresh ethanol. The final film thicknesses, measured with a digital micrometer (Mitutoyo, Model ID-C112E) readable to ±1 μm, ranged from 170 to 340 μm. For each sample, thickness was measured at a minimum of 20 different points within the effective permeation area, and the average value was used, whose standard deviation was always less than 3%.

Pure- and mixed-gas permeation properties of XLPEO were determined using the same constant pressure/variable volume apparatus previously described by Raharjo et al. [24], which is basically composed of the permeation cell, a mass flow controller on the upstream side, a soap film flowmeter on the downstream side, and a gas chromatograph (GC) equipped with thermal conductivity (for CO2) and flame ionization (for C2H6) detectors. The polymer samples were partially masked with impermeable aluminum tape on the upstream and downstream faces, as described by Mogri and Paul [35]. The active permeation area was 2.81 cm². On the upstream side, an epoxy resin (Devcon 5 Minute Epoxy) was used to improve the adhesion between the polymer and the masking tape, preventing leakage, which was otherwise observed after operation for a short period of time. The retentate flow rate was set high enough to guarantee a low stage cut (<0.5%) and thereby prevent a significant change in feed concentration due to permeation. Helium was used to sweep the permeate to the GC, in which concentrations of CO2 and C2H6 were measured. The total flow rate on the downstream side was measured with a soap film flowmeter, and its value was set to keep the downstream partial pressure of CO2 and C2H6 at practically zero (<0.06 atm). The permeation cell was immersed in a circulating liquid bath whose temperature was controlled to ±0.1 °C.
The steady-state gas permeability was calculated as follows:

\[ \phi_i = \frac{I_i Q^i}{A P_{i}^{\text{set}} - P_i^j} T^* \]  \hspace{1cm} (15)

where \( Q^i \) is the volumetric flow rate on the downstream side of the membrane, \( T \) is the temperature at which \( Q^i \) was measured, \( A \) is the active membrane area, and \( T^* \) is the standard temperature (273.15 K). Fugacity values were determined as detailed elsewhere [28].

In Eq. (15), \( L \) is normally taken as the thickness of the dry polymer film, whereas, strictly speaking, the actual thickness under the conditions of the permeation experiment should be used. An expression for calculating film thickness during permeation was developed by Paul and Ebra-Lima [36]. Using this expression and our previously reported sorption and dilution data for this system [28,37], one finds that, at the most extreme case (pure CO2, highest pressure, \(-20^\circ\text{C}\)) the increase in thickness due to gas sorption is lower than 5%. Therefore, within the adopted operating conditions, CO2 and ethane permeability coefficients in XLPEO can be estimated based on the thickness of the dry film.

4. Results and discussion

4.1. Pure-gas permeation

Permeability values for pure carbon dioxide and ethane in the XLPEO copolymer are presented in Fig. 2 as a function of upstream gas fugacity and temperature. CO2 permeability is at least five times higher than that of ethane. A significant increase in permeability with increasing upstream fugacity is observed for CO2, especially at low temperatures, which is typical for permeation of highly sorbing penetrants in rubbery polymers [26]. A dependence of permeability on upstream fugacity is also observed for ethane, but the effect is much less pronounced, as shown by a direct comparison between Fig. 2(a) and (b).

Two previous studies [9,16] reported pure-gas permeability data for CO2 and ethane in the XLPEO copolymer considered here. These literature data are included in Fig. 2 for comparison. For carbon dioxide, our permeability values at 35 °C agree well (within 7%) with those reported by Lin et al. [16]. Our values for both CO2 and C2H6 are between 20 and 26% smaller than those reported by Kelman et al. [9]. The data of Lin et al. [16] are also somewhat lower (10–15%) than those of Kelman et al. [9]. Since no other data were available for ethane, additional measurements were made at 35 °C in a constant-volume apparatus (the same one described by Kusuma et al. [18,20]). As shown in Fig. 2(b), these values agree well (within 8–10%) with those obtained in our constant-pressure, mixed-gas permeation system. Moreover, CO2 permeability values measured in this constant-volume set-up (not shown here) agreed within 2% with the data of Lin et al. [16]. At \(-20^\circ\text{C}\), the difference between our permeability values and those reported by Kelman et al. [9] increases to about 50% for ethane. In the case of CO2, a clear increase in the difference between these two data sets with increasing fugacity is shown in Fig. 2(a), with our values being 40–57% smaller than those reported by Kelman et al. [9] at \(-20^\circ\text{C}\).

Apparently, the data of Kelman et al. [9] were obtained without using an epoxy resin to increase the adhesion of the XLPEO copolymer to the masking tape, which could explain this difference. In our experiments, without the epoxy resin, membrane samples would start to leak after operation for some time. At \(-20^\circ\text{C}\), membrane samples started to leak even with the epoxy resin after exposure to high CO2 partial pressures. Such a leak was not always easily spotted, and it could have been mistaken for an increase in permeability due to plasticization, had we not compared values at the same operating conditions obtained with different films (one that had just been placed in the system and another that had been in use for some time). In fact, a special operating procedure was required to obtain reliable data at lower temperatures, fixing the operating pressure and varying the feed composition, in either increasing or decreasing order of CO2 mole fraction, to avoid abrupt changes in membrane dilution caused by gas sorption.

Gas permeability in rubbery polymers is often empirically related to fugacity by an exponential equation [24,38]. In this work, the following expression was adopted:

\[ \varphi_i = \beta_0,i \left[ 1 + \beta_1,i \exp \left( \frac{f_0}{m_i} \right) \right] \]  \hspace{1cm} (16)

where \( \beta_0, \beta_1, \) and \( m_i \) are temperature-dependent adjustable parameters. The reasoning behind the functional form of Eq. (16) is demonstrated in the Supplementary Material. The values of the adjustable parameters were fitted by non-linear regression using the software Origin\textregistered and are listed in Table 1. In the case of CO2, some data from the mixed-gas permeation experiments were also included in the fitting, as detailed in Section 4.3. Values computed with Eq. (16) using the fitted constants are shown as continuous lines in Fig. 2.

With the aid of Eq. (16), one can estimate gas permeability in the limit of infinite dilution, \( \varphi_i^\infty \), by setting \( f_0 = 0 \) (i.e., \( \varphi_i^\infty = \)).
\( \beta_{0,i} + (1 + \beta_{1,i}) \). The effect of temperature on \( \psi^{\infty} \) follows a Van’t Hoff–Arrhenius relation, from which an activation energy of permeation, \( E_p \), can be defined [26]:

\[
\psi^{\infty}_i = \psi_{0,i} \exp \left( -\frac{E_p}{RT} \right)
\]

(17)

From a linear regression of the \( \psi^{\infty} \) values calculated with Eq. (16), the activation energies of permeation for carbon dioxide and ethane in the XLPEO copolymer are \((32 \pm 2)\) kJ/mol and \((45 \pm 2)\) kJ/mol, respectively. These values compare favorably with those reported by Lin and Freeman [15] for a XLPEO prepared from pure PEGDA, that is \((39 \pm 1)\) kJ/mol for CO\(_2\) and \((57 \pm 1)\) kJ/mol for C\(_2\)H\(_6\). Compared to the copolymer used in this study, the XLPEO prepared from pure PEGDA has lower free volume [16], which can increase barriers to diffusion, leading to higher activation energy of permeation for a given penetrant. A larger \( E_p \) value is observed for ethane, which is the larger molecule (\( d = 3.325 \) Å for CO\(_2\) [39] and 4.443 Å for C\(_2\)H\(_6\) [26]).

4.2. Pure-gas diffusivity

Within the range of operating conditions investigated, the pure-gas solubility coefficients of carbon dioxide and ethane in this XLPEO copolymer increase with increasing fugacity [37]. To determine whether this was the sole factor responsible for the influence of upstream fugacity on gas permeability, the data from Fig. 2 were utilized to calculate effective diffusion coefficients with the aid of Eq. (11). The results are presented in Fig. 3. At each operating condition, gas concentration on the upstream side of the membrane was computed using the Flory–Huggins model [28].

At 35 °C, the effective diffusivity coefficient of both gases remains essentially constant as upstream gas concentration in the polymer increases, so any changes in permeability at this temperature are caused by changes in solubility. A slight increase in \( D \) with carbon dioxide concentration in the polymer can be observed at 25 °C in Fig. 3(a), an effect that becomes progressively more evident as temperature is reduced. Therefore, at \( T \leq 25 \) °C, plasticization also plays a role in increasing CO\(_2\) permeability in the polymer. From Fig. 3(a), the concentration of carbon dioxide dissolved in the polymer can be relatively high, leading to rather significant changes in the average diffusion coefficient. For example, at 0 °C, \( D \) increases 55% (from \( 2.0 \times 10^{-7} \) to \( 3.1 \times 10^{-7} \) cm\(^3\)/s) as CO\(_2\) concentration increases from 15 to 64 cm\(^3\)/cm\(^2\)/polym. While, at −20 °C, the effective diffusion coefficient more than doubles (from \( 4.4 \times 10^{-8} \) to \( 8.9 \times 10^{-8} \) cm\(^3\)/s) as CO\(_2\) concentration increases from 41 to 105 cm\(^3\)/cm\(^2\)/polym.

For ethane, there is no appreciable influence of gas concentration on effective diffusivity at either 25 °C or 35 °C. A small degree of plasticization can be seen in the data at 0 °C, which becomes more pronounced at lower temperatures. Although the fugacity axis covers the same range for both gases in Fig. 2, the same is not true for the concentration axis in Fig. 3. At a given upstream fugacity, the equilibrium concentration of ethane dissolved in the polymer is much smaller than that of CO\(_2\) [37]. For instance, at 0 °C, \( D \) increases less than 20% (from \( 5.2 \times 10^{-8} \) to \( 6.2 \times 10^{-8} \) cm\(^3\)/s) as a result of an approximately 6-fold increase in ethane concentration (from 3 to 19 cm\(^3\)/cm\(^2\)/polym). Since diffusivity is a function of penetrant size and ethane is larger than CO\(_2\), \( D \) values for ethane are approximately one third those of carbon dioxide at similar penetrant concentrations.

The effect of temperature on the effective diffusion coefficient in the limit of infinite dilution, \( \bar{D}^{\infty} \), follows an Arrhenius relation, from which an activation energy of diffusion, \( E_D \), can be defined [40]:

\[
\bar{D}^{\infty} = D_{0,i} \exp \left( -\frac{E_D}{RT} \right)
\]

(18)

From the data in Fig. 3, the activation energies of diffusion for carbon dioxide and ethane are \((52 \pm 3)\) kJ/mol and \((58 \pm 3)\) kJ/mol,
respectively. For the same temperature range considered in this work, Lin and Freeman [15] reported an activation energy of diffusion equal to (56 ± 1) kJ/mol for CO₂ and (63 ± 2) kJ/mol for ethane in XLPEO prepared from pure PEGDA. Our slightly lower values are in agreement with the fact that our polymer, prepared from a mixture of PEGDA and PEGMEA, has higher fractional free volume and higher chain mobility (lower glass transition temperature) [16,41], two factors that can reduce barriers to diffusion.

### 4.3. Mixed-gas permeation

At each operating temperature, four different CO₂/C₂H₆ mixtures were used as feed. The permeability values obtained in these experiments are compared in Figs. 4 and 5 as a function of the upstream penetrant fugacity in the mixture, for carbon dioxide and ethane, respectively. Only data at two temperatures are presented to display the general trends. Data at 35, 0 and −20 °C can be found in the Supplementary Material. Uncertainty for each permeability coefficient was computed by applying the rules of uncertainty propagation to Eq. (15), considering the experimental errors in membrane thickness, downstream gas flow rate, and downstream gas composition [42].

From Fig. 4(a) and the data at 35 °C in the Supplementary Material, the presence of ethane has essentially no effect on CO₂ permeability at $T \geq 25$ °C and $x_{CO_2} \geq 0.50$, since the different values agree within the estimated uncertainty. Therefore, these mixed-gas data were used together with pure-gas values to fit the parameters of Eq. (16) at $T \geq 25$ °C. For the two ethane-rich mixtures ($x_{CO_2} = 0.25$ and 0.10), most permeability values also do not differ from the corresponding pure-gas values, even though there seems to be a slight deviation towards higher values in the presence of ethane at sufficiently high operating pressures. This trend becomes more evident at $T \leq 0$ °C, as illustrated by the data at −10 °C in Fig. 4(b). Although the mixed-gas permeability of CO₂ is initially equal to its pure-gas value at low feed pressures, as feed pressure increases, the presence of ethane begins to increase the permeability of carbon dioxide compared to the pure-gas value at the same upstream CO₂ fugacity. The higher the mole fraction of ethane in the feed stream, the smaller the CO₂ fugacity at which the influence of ethane becomes significant. Furthermore, as temperature decreases, the relative difference between CO₂ pure- and mixed-gas permeability at a given CO₂ fugacity increases. For example, at 0 °C, $\varphi_{CO_2} = 110$ Barrier for $f_{CO_2} = 4.74$ atm and $x_{C_2H_6} = 0.25$, a value that is 7.8% higher than the pure-gas permeability at the...
same CO₂ fugacity. On the other hand, at −20 °C, with the same feed composition, CO₂ mixed-gas permeability at \( f_{CO_2} = 3.14 \text{ atm} \), 42 Barrer, is 60% higher than the corresponding pure-gas value. Additionally, for the same ethane content in the feed stream, the lower the operating temperature, the smaller the CO₂ fugacity at which the influence of ethane on CO₂ permeability starts to be seen. From these findings, for \( T < 0 \text{ °C} \), only the point at the smallest feed pressure for each mixture composition was used together with pure-gas values to fit the parameters of Eq. (16).

For ethane, the only case in which pure- and mixed-gas permeability values were the same over the whole range of feed pressures investigated was at 35 °C with \( x_{CO_2} = 0.10 \). At this temperature, for the other mixtures, mixed-gas ethane permeability was only equal to the corresponding pure-gas value at the same ethane fugacity for low feed pressures (<4 atm, see Supplementary Material). As shown in Fig. 5, at \( T \leq 25 \text{ °C} \), differences between pure- and mixed-gas values are observed even at low feed pressures. In fact, for the vast majority of operating conditions investigated, pure-gas values represent, at best, a conservative estimation of the actual ethane permeability obtained when carbon dioxide is present in the feed stream. The higher the CO₂ mole fraction in the gas in contact with the membrane, the larger the increase in ethane permeability at a given ethane fugacity compared to the corresponding pure-gas value. The differences in this case can be rather significant and become progressively more pronounced as the operating temperature is reduced. For instance, at 25 °C, pure-gas ethane permeability equals 33 Barrer at \( f_{C_2H_6} = 5 \text{ atm} \), a value that grows to about 38 Barrer when \( x_{CO_2} = 0.50 \), and reaches 50 Barrer for \( x_{CO_2} = 0.70 \). At −10 °C, on the other hand, the pure-gas permeability is 3.2 Barrer at \( f_{C_2H_6} = 3 \text{ atm} \), but the values in the mixtures with \( x_{CO_2} = 0.50 \) and 0.70 are 4.6 and 9.6 Barrer, respectively (at \( f_{C_2H_6} = 3 \text{ atm} \)). In the most extreme case within our data set, namely, at \( x_{CO_2} = 0.70 \), −20 °C and \( f_{C_2H_6} = 3.6 \text{ atm} \), ethane mixed-gas permeability (6.4 Barrer) is more than 6 times higher than the pure-gas value (1.0 Barrer).

When ethane permeability is plotted as a function of ethane fugacity in the feed, as in Fig. 5, a different curve is obtained for each feed composition. While the differences among pure- and mixed-gas values are less pronounced for CO₂, a single master curve for all feed compositions is not observed at all temperatures when CO₂ permeability is plotted as a function of CO₂ fugacity. Consequently, non-ideal effects in the gas phase are not the main cause of the differences between pure- and mixed-gas permeability values. As an alternative to fugacity, one could use the total amount of gas dissolved in the polymer as the independent parameter. In a recent study, Ribeiro and Freeman [28] measured sorption isotherms for CO₂/C₂H₆ mixtures in the same XLPEO copolymer considered here and found that these could be represented by the multicomponent Flory–Huggins model. Using this model with the parameters given by Ribeiro and Freeman [28,37], the concentration of each gas in the upstream face of the membrane for a given operating condition can be calculated.

Thus, in Figs. 6 and 7, pure- and mixed-gas permeability coefficients of CO₂ and ethane, respectively, are presented as a function of the total amount of gas dissolved in the upstream side of the membrane at 25 and −10 °C. Similar plots for the other temperatures considered in this study are given in the Supplementary Material. At each temperature, pure- and mixed-gas permeability data of a given gas for the different feed streams now lie nearly on a single master curve. Consequently, the key variable affecting gas permeability at a given temperature in this system is the total amount of gas dissolved in the polymer. Since the diffusion coefficient is a function of penetrant concentration, it is not possible to conclude from Figs. 6 and 7 whether the differences between pure- and mixed-gas permeability values at a given fugacity are caused by changes in solubility, diffusivity, or both. To answer this question, the individual contributions of \( S \) and \( D \) must be analyzed, as discussed in Section 4.4.

Mixed-gas selectivities at 25 and −10 °C, plotted as a function of CO₂ fugacity in the feed, are compared in Fig. 8 with selectivity values based on pure-gas measurements. Data related to the other temperatures can be found in the Supplementary Material. Mixed-gas selectivities were computed by substituting experimental CO₂ and C₂H₆ mixed-gas permeability coefficients into Eq. (2). For a given CO₂/C₂H₆ mixture, pure-gas selectivity estimates were also obtained with Eq. (2) using pure-gas permeability values calculated from Eq. (16) at the corresponding upstream fugacities of each gas in the mixture.

For the mixture containing 10 mol% CO₂, the mixed-gas selectivity is either equal to or slightly smaller than the pure-gas prediction at all operating temperatures studied. On the other hand, for the other mixtures, the mixed-gas selectivity at a given CO₂ fugacity is smaller than the pure-gas prediction for most of the operating conditions investigated, except at low feed pressures and \( T \geq 25 \text{ °C} \). Although an increase in selectivity with increasing CO₂ fugacity is expected for \( x_{CO_2} \geq 0.50 \) based on pure-gas data, the experimentally observed trend for mixed-gas selectivity is precisely the opposite, which highlights the importance of performing the mixed-gas experiments.
Fig. 7. Pure- and mixed-gas C₂H₆ permeability in XLPEO copolymer as a function of the total amount of gas dissolved in the upstream side of the membrane. Data are presented at (a) 25.0 and (b) −10.0 °C. All concentrations calculated as a function of operating conditions using the multicomponent Flory–Huggins model [28].

A summary of all mixed-gas permeation data obtained in this work is provided in Fig. 9 as a permeability/selectivity trade-off plot. Interestingly, regardless of feed composition, the system follows a trade-off between permeability and selectivity as temperature decreases.

4.4. Mixed-gas diffusivity

Physical insight into the differences between pure- and mixed-gas permeation data is found by separating permeability into its two components, that is, solubility and diffusivity. As mentioned in Section 4.3, both pure- and mixed-gas sorption in the system under consideration here is well represented by the multicomponent Flory–Huggins model [28], from which the concentration of each gas dissolved in the polymer and the solubility coefficients at a given operating condition can be obtained. These concentrations, in turn, are substituted into Eq. (11) together with the experimental permeabilities to give the effective mixed-gas diffusion coefficient of each gas.

Starting with carbon dioxide, the results for the solubility coefficient on the upstream side of the membrane are presented as a function of fugacity in Fig. 10. The effective diffusion coefficient of CO₂, in turn, is plotted in Fig. 11 as a func-
tion of the upstream concentration of this gas in the polymer film.

From Fig. 10, the presence of ethane increases the carbon dioxide solubility in the XLPEO copolymer at $T \leq 0^\circ$C. Moreover, as ethane content in the gas mixture increases, the mixed-gas CO$_2$ solubility curves deviate from the pure-gas curve in the same way the mixed-gas CO$_2$ permeability curves deviate from the pure-gas permeability values in Fig. 4(b), which suggests that the change in CO$_2$ permeability due to the presence of ethane is a solubility-related effect. This conclusion is corroborated by the effective diffusion coefficient data in Fig. 11, with pure- and mixed-gas values at a given temperature following the same master curve as a function of the upstream concentration of carbon dioxide dissolved in the polymer. At 35 $^\circ$C, the data indicate that $D_{CO_2}$ is constant within the pressure range considered, while a weak linear dependence of $D_{CO_2}$ on CO$_2$ concentration is observed at the other temperatures (the log-scale used in Fig. 11 prevents one from readily seeing this linear trend).

The scenario becomes more complex for the case of the effect of carbon dioxide on ethane permeability. Fig. 12 presents ethane

![Fig. 10](image_url)

**Fig. 10.** Solubility coefficient of carbon dioxide on the upstream side of an XLPEO film contacted with CO$_2$/C$_2$H$_6$ mixtures as a function of the CO$_2$ fugacity in the mixture at different temperatures ($^\circ$C): (a) 35.0, 25.0, 0.0, and (b) −10.0, −20.0. All data calculated with the multicomponent Flory–Huggins model [28] for the experimental conditions of the mixed-gas permeation tests. The lines represent the pure-gas solubility predicted by the multicomponent Flory–Huggins model [28] over the entire range of fugacity covered in each plot.

![Fig. 11](image_url)

**Fig. 11.** Mixed-gas effective diffusion coefficient of carbon dioxide in XLPEO as a function of the upstream concentration of this gas in the polymer at different temperatures. For comparison, pure-gas effective diffusion coefficients are also included.

![Fig. 12](image_url)

**Fig. 12.** Solubility coefficient of ethane on the upstream side of an XLPEO film contacted with CO$_2$/C$_2$H$_6$ mixtures as a function of the C$_2$H$_6$ fugacity in the mixture at (a) 25.0 and (b) −10.0 $^\circ$C. All data calculated with the multicomponent Flory–Huggins model [28] for the experimental conditions of the mixed-gas permeation tests. The lines represent the pure-gas solubility predicted by the multicomponent Flory–Huggins model [28] over the entire range of fugacity covered in each plot.
solubility coefficients on the upstream side of the film as a function of fugacity at 25 and −10 °C. For the same two temperatures, the corresponding effective diffusion coefficients are presented in Fig. 13 as a function of ethane upstream concentration in the film. Similar plots for $D$ and $S$ related to the other temperatures investigated in this work can be found in the Supplementary Material. A detailed discussion of the trends seen in Fig. 12 is given elsewhere [28].

In view of the strong plasticization of the polymer caused by CO$_2$, it is not surprising that the effective diffusion coefficient of ethane increases considerably with carbon dioxide content in the feed stream, as shown in Fig. 13. Even when plotted as a function of the total gas upstream concentration, pure- and mixed-gas $D$ values for ethane do not lie in a single master curve at all temperatures (these plots are given in the Supplementary Material). At $T \geq 25$ °C, the solubility of ethane in the polymer at a given fugacity also increases in the presence of carbon dioxide, as exemplified by the data in Fig. 12(a). Therefore, at these temperatures, the higher mixed-gas permeability of ethane stems from increased solubility and diffusivity of this gas in the polymer induced by the presence of carbon dioxide. In contrast, at $T \leq 0$ °C, the presence of carbon dioxide can actually reduce C$_2$H$_6$ solubility in the polymer (cf. Fig. 12(b)), an effect whose intensity increases as temperature decreases. This decrease in solubility is not directly apparent in the permeability values, as it is overshadowed by a larger increase in the diffusion coefficient. However, the competition between these two opposite effects is particularly evident in the mixed-gas permeability data for $x_{CO_2} = 0.10$, which lie very close to the pure-gas data for ethane fugacities of up to about 9 atm, a fact that would not be expected considering the strong plasticization of the polymer by CO$_2$ at these temperatures. To put these trends into quantitative perspective, at $0$ °C, $f_{C_2H_6} = 6$ atm and $x_{CO_2} = 0.10$, the C$_2$H$_6$ solubility coefficient ($0.98$ cm$^3_{STP}$/cm$^3_{polymer}$ atm) is about 10% smaller than the corresponding pure-gas value ($1.08$ cm$^3_{STP}$/cm$^3_{polymer}$ atm), while the effective diffusion coefficient ($6.1 \times 10^{-8}$ cm$^2$/s) is 17% higher. On the other hand, for the same ethane fugacity at $-20$ °C and $x_{CO_2} = 0.10$, the solubility coefficient ($1.18$ cm$^3_{STP}$/cm$^3_{polymer}$ atm) is 36% smaller, while the effective diffusion coefficient ($8.7 \times 10^{-9}$ cm$^2$/s) is almost twice as large as the pure-gas value ($4.6 \times 10^{-9}$ cm$^2$/s). Consequently, at $T \leq 0$ °C, the higher mixed-gas permeability of ethane is primarily caused by a substantial increase in the diffusion coefficient of this gas in the plasticized polymeric matrix, even though, at sufficiently high fugacities of carbon dioxide in the mixture, an increase in ethane solubility also contributes to increase the mixed-gas permeability.

From the solution-diffusion model, membrane selectivity can be divided into its solubility and diffusivity contributions, the latter being the ratio of diffusion coefficients between the two gases [26]. In Fig. 14, diffusivity selectivity data at 25 and −10 °C are plotted as a function of CO$_2$ concentration on the upstream side of the film. Although the pure-gas prediction is an increase in diffusivity selectivity with increasing CO$_2$ concentration, the actual trend revealed by the mixed-gas data is precisely the opposite. It is somewhat striking, however, that, in spite of the large variation in $D$ for both gases, the value of the diffusivity selectivity remains between 2 and 3 for most of the operating conditions considered in this work.

4.5. Data correlation with a free volume model

Recently, Lin et al. [43] used a simplified free volume model to successfully correlate pure-gas permeability and effective diffusion coefficients of H$_2$, CO$_2$, and CH$_4$ in a series of XLPEO copolymers prepared from PEGA/PEGMEA mixtures. Since the polymer considered in this study is also prepared from PEGA and PEGMEA, an attempt will be made here to employ the same ideas to correlate our data.

Starting with the effective diffusivity, the original model of Lin et al. [43] is written as follows:

$$D_l = A_{D,l} \exp \left( \frac{-B_{D,l}}{FFV} \right)$$

$$FFV = FFV_g + \alpha_l(T - T_g)$$

where $A_{D,l}$ and $B_{D,l}$ are adjustable constants, $T_g$ is the glass transition temperature of the polymer–penetrant mixture, $FFV_g$ is the apparent fractional free volume of the pure polymer at its glass transition, and $\alpha_l$ is the expansion coefficient of the fractional free volume in the rubbery state. For PEGA/PEGMEA copolymers, the values of $FFV_g$ and $\alpha_l$ are (0.055 ± 0.001) and (8.4 ± 2.6) × 10$^{-4}$ K, respectively. These values were determined based on experimental data for glass transition temperature and density of different copolymers [44].

In Eq. (19), the increase in fraction free volume due to gas dissolution in the polymer is accounted for by a depression in the glass transition temperature. This effect of penetrant concentration on
$T_g$ was estimated by Lin et al. [43] with the model of Chow [45], which is based on both classical and statistical thermodynamics:

$$\ln \left( \frac{T_g}{T_{g0}} \right) = \frac{Z R}{M_p \Delta C_{pp}} \left[ (1 - \theta) \ln (1 - \theta) + \theta \ln \theta \right]$$

(21)

where $T_{g0}$ is the glass transition temperature of the pure polymer, $Z$ is the lattice coordination number (equal to 2 for many polymer–penetrant systems, including XLPEO copolymers), $M_p$ is the molecular weight of the polymer repeat unit (which was taken as 44 g/mol, the molecular weight of an ethylene oxide moiety [43]), $\Delta C_{pp}$ is the change in heat capacity of the pure polymer at its glass transition (equal to 0.99 J g$^{-1}$ K$^{-1}$ for our material [43]), and $\theta$ is defined as the ratio of the number of diluent molecules to the number of lattice sites in the polymer–diluent mixture.

In Chow’s original model, $\theta$ was only defined for a single penetrant. In order to use this model for a mixture of $n$ penetrants, we follow the reasoning in Chow’s original work to obtain the following general expression for $\theta$:

$$\theta = \frac{M_p}{Z \left( 1 - \sum_{i=1}^{n} w_i \right)} \sum_{i=1}^{n} \frac{w_i}{M_i}$$

(22)

where $M_i$ and $w_i$ are, respectively, the molecular weight and the mass fraction of penetrant $i$ dissolved in the polymer.

Pure- and mixed-gas effective diffusion coefficients of carbon dioxide and ethane are plotted in Fig. 15 as a function of the fractional free volume estimated with the aid of Eqs. (20)–(22) and using the concentration of each penetrant on the upstream side of the film to evaluate $\theta$. For both gases, the data for different temperatures and feed compositions fall nearly on a single master curve, attesting to the ability of this simplified model to correlate the data. The lines in Fig. 15(a) and (b) represent the prediction of Eq. (19) with the adjustable parameters reported in Table 2, which were fitted by linear regression using pure- and mixed-gas data simultaneously for each gas.

To correlate pure- and mixed-gas H$_2$ permeability in XLPEO copolymers, Lin et al. [43] substituted Eq. (19) into Eq. (11) and then assumed that gas solubility did not vary significantly with fugacity and temperature. A similar approach had been previously used by other authors to correlate polymer free volume and pure-gas permeability. With the assumption of a constant solubility coefficient, only the pre-exponential factor in Eq. (19) would have to be fitted to correlate the permeability data. However, this approach provides a poor correlation of our permeability data, with average prediction errors of 36% and 27% for carbon dioxide and ethane, respectively.

$^2$ In the case of mixed-gas data, H$_2$ concentration in the polymer was neglected in the calculation of $\theta$, which allowed the use of the original expression in Chow’s model.
Table 2
Constants for the estimation of effective diffusion coefficients and permeability coefficients using fraction free volume models.

<table>
<thead>
<tr>
<th>Penetrant</th>
<th>$A_P \times 10^4$ (cm$^2$/s)</th>
<th>$B_0$</th>
<th>$A_P \times 10^{-7}$ (Barrer)</th>
<th>$B_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>6.41 ± 0.64</td>
<td>1.132 ± 0.012</td>
<td>57.1 ± 3.1</td>
<td>0.6891 ± 0.0064</td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>5.89 ± 0.49</td>
<td>1.2298 ± 0.0096</td>
<td>71.6 ± 3.3</td>
<td>0.9689 ± 0.0053</td>
</tr>
</tbody>
</table>

Fig. 16. Pure- and mixed-gas permeability coefficients of (a) carbon dioxide and (b) ethane in XLPEO as a function of fractional free volume. The lines are the prediction of Eq. (23) with the parameters given in Table 2.

From Figs. 10 and 12, the hypothesis of a constant solubility coefficient is too strong for our system. Therefore, to correlate our permeability data, the effect of operating conditions on $S$ must be included. Probably the simplest way to do so is to keep the functional form of Eq. (19) but fit both parameters. In other words, pure- and mixed-gas permeability coefficients are represented by:

$$\psi_i = A_{P,i} \exp \left( -\frac{B_{P,i}}{FFV} \right)$$

with $A_{P,i}$ and $B_{P,i}$ fitted by linear regression of all permeation data for a given gas. The values of these parameters are listed in Table 2.

Pure- and mixed-gas permeability of carbon dioxide and ethane are plotted in Fig. 16 as a function of the fractional free volume estimated with the aid of Eqs. (20)–(22) and using the concentration of each penetrant on the upstream side of the film to evaluate $\theta$. As shown in this figure, Eq. (23) provides a good representation of all permeation data obtained in this work. For carbon dioxide, the average absolute difference between experimental permeability coefficients and values estimated with Eq. (23) is 7.4%, whereas, in the case of ethane, the average difference is 6.5%.

5. Conclusions

Depending on the operating conditions, significant differences between pure- and mixed-gas permeability are found for carbon dioxide and ethane in a cross-linked poly(ethylene oxide) (XLPEO) rubber prepared by photopolymerization of a 30 wt% PEGDA–70 wt% PEGMEA solution. Although the presence of ethane has little effect on carbon dioxide permeability at $T \geq 25{°}C$, mixed-gas carbon dioxide permeability is higher than the corresponding pure-gas value at the same CO$_2$ fugacity at $T \leq 0{°}C$. This difference increases with increasing ethane content in the feed and/or decreasing temperature, and it is caused by an increase in the solubility of carbon dioxide in XLPEO in the presence of ethane. The concentration-averaged effective diffusion coefficient of CO$_2$ does not depend on the amount of ethane dissolved in the polymer, but it increases linearly with CO$_2$ concentration in the polymer at $T \leq 25{°}C$, indicating that CO$_2$ plasticizes the XLPEO film.

Apart from a few exceptions, pure-gas permeability values represent, at best, a conservative estimation of the actual ethane permeability in the XLPEO film when carbon dioxide is present in the feed. The higher the CO$_2$ content in the feed stream, the larger the increase in ethane permeability at a given ethane fugacity compared to the corresponding pure-gas value. This effect is mainly a consequence of the significant increase in the diffusion coefficient of ethane in the polymer brought about by plasticization induced by carbon dioxide. As a result, this effect becomes progressively more pronounced as temperature decreases. On account of this plasticization effect, the effective diffusion coefficient of ethane is a function of the CO$_2$ concentration in the polymer.

For this particular system, the different effects of temperature and penetrant concentration in the polymer on gas permeability can be correlated by a simplified free volume model with two adjustable parameters for each gas, with average prediction errors lower than 8%.

Acknowledgments

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Appendix A. Supplementary data


Nomenclature

- $A$ membrane area (cm$^2$
- $A_P$ pre-exponential factor in Eq. (19) (cm$^2$ s$^{-1}$
- $A_P'$ pre-exponential factor in Eq. (23) (Barrer)
- $B_0$ adjustable parameter in Eq. (19) (dimensionless)
- $B_P$ adjustable parameter in Eq. (23) (dimensionless)
- $C$ gas concentration in the polymer (cm$^3$STP/cm$^3$ polymer)
- $D$ effective diffusion coefficient defined by Eq. (10) for a pure gas and by Eq. (14) for a binary gas mixture (cm$^2$ s$^{-1}$
- $d$ gas kinetic diameter (m)
- $D_0$ pre-exponential factor in Eq. (18)
- $D_f$ multicomponent Fickian diffusion coefficients (cm$^2$ s$^{-1}$
- $D_m$ binary mutual diffusion coefficient in the polymer (cm$^2$ s$^{-1}$
- $E_a$ activation energy of diffusion (kJ mol$^{-1}$
- $E_P$ activation energy of permeation (kJ mol$^{-1}$
- $f$ fugacity (cmHg)
- $FFV$ fractional free volume of the polymer–penetrant mixture (dimensionless)
- $FFV_g$ apparent fractional free volume of the pure polymer at its glass transition (dimensionless)
References