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Mixed-gas sorption in polymers via a new barometric test system: sorption and diffusion of CO₂-CH₄ mixtures in polydimethylsiloxane (PDMS)

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ABSTRACT

Mixed-gas sorption of CO₂-CH₄ mixtures in rubbery polydimethylsiloxane (PDMS) at 35 °C demonstrated that the presence of CH₄ changed the behavior of CO₂ sorption and vice versa. This mutual interaction indicated that gases in mixtures do not sorb independently in rubbery membranes. Moreover, we observed that at increasing pressures the interaction between PDMS and CO₂-CH₄ mixtures enhanced the solubility selectivity of PDMS. Mixed-gas solubility coefficients of CH₄ in PDMS were lower than 0.5 cm³(STP) cm⁻³ atm⁻¹. To accurately measure these values, a new sorption system was designed, constructed, and optimized for low solubility coefficients; an operator-friendly approach to mixed-gas sorption experiments is also discussed in this work. CO₂-CH₄ mixed-gas diffusivity trends were evaluated from Maxwell-Stefan model fitting of mixed-gas permeation and sorption data. The analysis of both mixed-gas diffusion and sorption data demonstrated that CO₂/CH₄ mixed-gas permselectivity of PDMS was mainly influenced by CO₂ sorption. In mixtures, CH₄ diffusion coefficients increased with higher volumetric CO₂ concentration, whereas CO₂ diffusion coefficients were essentially concentration independent in both pure- and mixed-gas environments.

Graphical abstract:

Keywords: mixed-gas sorption; mixed-gas permeation; mixed-gas diffusion; polydimethylsiloxane; barometric mixed-gas sorption system.

1. Introduction

The solution-diffusion theory [1] is a pillar in the description of gas permeation through *dense* polymer membranes [2-5]. For polymers, the diffusion coefficient of gas mixtures can be estimated from Fick's or Maxwell-Stefan's based models by fitting of experimental pure- and mixed-gas permeabilities once the mixed-gas sorption behavior of those gases is correctly described — which requires experimental observation of pure- and mixed-gas solubilities. Because mixed-gas sorption systems are difficult to design and operate, only a few mixture sorption studies have been performed to date on a limited number of polymers. While mixed-gas permeation data are frequently reported, the inability of producing mixed-gas sorption data also limits the generation of mixed-gas diffusion data. Consequently, diffusion- and

sorption related phenomena, such competitive sorption and plasticization, are typically discussed in a speculative manner.

Mixed-gas sorption experiments are *essential* for fundamental understanding of the effects of: (i) competitive sorption on gas permeability and permselectivity; (ii) penetrant-induced swelling/plasticization on diffusion coefficients during permeation of mixtures; (iii) polymer design for structure/property relationships, thus allowing optimal synthesis/selection of materials for industrial applications. The present study focuses on mixed-gas sorption using the barometric pressure decay system technique [6, 7]. To perform pure- and mixed-gas barometric sorption experiments, the unit must have at least two volumes, *i.e.*, V_A and V_B (**Fig. 1**). The feed volume (V_B) is monitored by a pressure transducer (TR_B), which allows controlling the amount of the *i*-gas ($n_i^{V_B - V_A}$) sent to the sample chamber (V_A). At equilibrium, the transducer TR_A mounted on V_A is used for estimating the amount of gas in the sample chamber, *i.e.* the amount of *i*-gas not sorbed (n_i^{eq, V_A}). Therefore, the amount sorbed in the polymer, $n_i^{eq, pol.} = n_i^{V_B - V_A} - n_i^{eq, V_A}$, can quickly be calculated. In order to use this equation for mixed-gas sorption, one must characterize the concentration of the feed mixture in V_B and the equilibrium mixture in V_A , typically performed *via* gas chromatography.

While mixed-gas permeability experiments are a common practice in membranes studies [8], the number of published data on mixed-gas sorption is limited and restricted to few polymers (*i.e.*, PEO, PDMS, PPO/CPPO, PMMA, PIM-1, PTMSP, 6FDA-TADPO, TZPIM, AO-PIM-1 and polynonene) [6, 9-19]. The reason is that constructing and maintaining these systems as well as data analysis are very tedious and time consuming. For example: (i) data scattering is minimized only by proper system design [6, 9]; (ii) the unit must be properly integrated with a gas concentration analysis system; (iii) volumes calibration and transducer accuracy are critical and potential leaks of the volumes should be continuously monitored to avoid introducing experimental errors; (iv) experiments are slow and the time scale to obtain a single data point can be several days.

Fig. 1. Schematic of the barometric two-volumes gas sorption system.

This work proposes an efficient methodology to analyze mixed-gas transport of gases in polymeric membranes from experimental data. Because the bottleneck of the gas transport analysis is the accurate measurement of mixed-gas sorption data, the literature covering barometric mixed-gas sorption units is reviewed in the first part of this paper. Some effective features of these early units that are amenable to designing and constructing a new mixed-gas system were assessed. Second, construction details of the new unit and approaches to optimization of its volumes are discussed in detail. CO_2 and CH_4 pure-gas sorption uptakes in rubbery polydimethylsiloxane (PDMS) at 35 °C are compared with those in the literature to confirm the capability of the new unit in terms of data quality (*e.g.*, level of scattering, sensibility, accuracy). Third, CO_2 - CH_4 mixed-gas sorption in PDMS at 35 °C are reported for the first time. Finally, mixed-gas diffusion coefficients were estimated from Maxwell-Stefan model fitting of mixed-gas permeability data obtained in-house. To date only a few reports dealt with experimental mixed-gas diffusivity in polymeric membranes [20-24].

2. Experimental

2.1. PDMS film preparation

To confirm the accuracy of the instrument and to discuss a typical mixed-gas experiment, first CO_2 - CH_4 pure- and mixed-gas sorption in PDMS were performed. A PDMS film was made using a mixture of a

10:1 solution of Sylgard 184[®] A and B (Dow Corning[™]). The solution was poured into a Teflon petri dish. After 2 h evaporation under ambient conditions, the pre-dried film was placed in an oven under vacuum at 50 °C. After two days, the temperature was increased to 100 °C, maintained for one day, and finally kept at 150 °C for four days. The membrane was washed with *n*-heptane (HPLC grade Fisher Chemical) and then dried in an oven at 150 °C. To ensure that any unreacted crosslinker and/or solvent were removed, the weight of the film was monitored until no change was observed. The average value of density obtained from seven PDMS film samples, derived from weight, area and thickness measurements, was $0.97 \pm 0.02 \text{ g cm}^{-3}$, which is consistent with values previously reported in the literature [12, 25, 26].

2.2. Pure- and mixed-gas sorption

Pure-gas CH₄ sorption in PDMS at 35 °C was performed with a sample weight of 1.40 g. Prior to the sorption experiment, the sample was degassed overnight. V_B was initially charged with a known amount of gas that was then expanded into V_A. At steady state, additional gas was injected into V_A. The S-R-K (Soave-Redlich-Kwong) equation of state [27] was used to estimate compressibility factor and fugacity with CO₂ and CH₄ parameters reported by Vopička et al. [16].

After pure-gas methane sorption, CO₂-CH₄ mixtures were sorbed in the same sample. These experiments were carried out following the *constant feed concentration* method; *i.e.*, mixtures were first injected in V_B and then expanded V_A that was previously evacuated (the valve separating V_A from V_B is opened and then quickly closed). Gas mixtures of certified concentrations (*i.e.*, 25/75, 50/50 and 75/25% CO₂-CH₄ molar concentration) were purchased from AHG Specialty Gases (Saudi Arabia). Finally, CO₂ pure-gas sorption runs were performed similarly to CH₄ pure-gas experiments.

The Flory-Huggins [28] model was fitted to the mixed-gas sorption uptake data. For pure gases, the model has the following equation:

$$\ln \frac{f_i}{f_i^{sat}} = \ln \phi_i + (1 - \phi_i) + \chi_{i,p} \cdot (1 - \phi_i)^2 \quad (1)$$

where f_i^{sat} is the saturation fugacity of the penetrant, $\chi_{i,p}$ is the Flory-Huggins (F-H) interaction parameter, and ϕ_i is the penetrant volume fraction that can be calculated as follows (note: the subscript “ p ” refers to the polymer and “ i ” to the penetrants):

$$\phi_i = \frac{(C_i/22414) \cdot \bar{V}_i}{1 + (C_i/22414) \cdot \bar{V}_i} \quad (2)$$

where C_i is the pure-gas concentration in the polymer with units [$\text{cm}^3(\text{STP}) \text{ cm}^{-3}$] and $\bar{V}_i$ is partial molar volume of the sorbed gas. As discussed by De Angelis et al. [29], CO_2 and CH_4 partial molar volumes in PDMS are nearly concentration independent (volume additivity applies); *i.e.*, CO_2 and CH_4 partial molar volumes are equal to their infinite dilution values. For CH_4 and CO_2 , the average values of partial molar volumes at infinite dilution used in this work were $56.7 \text{ cm}^3 \text{ mol}^{-1}$ [12, 29, 30] and $49 \text{ cm}^3 \text{ mol}^{-1}$, respectively [29, 30].

Gas solubility coefficients at infinite dilution were also obtained from the F-H model for fugacities approaching zero:

$$S_i^\infty = \lim_{f_i \rightarrow 0} \frac{C_i}{f_i} = \frac{22414}{f_i^{sat} \cdot \bar{V}_{i,\infty}} \cdot \exp(-1 - \chi_{i,p}^\infty) \quad (3)$$

where $\chi_{i,p}^\infty$ is the F-H interaction parameter at infinite dilution.

The solubility coefficient at infinite dilution was also directly estimated from the intercept of the linear interpolation of experimental solubility coefficient vs. fugacity data [31]:

$$S_i^\infty = S_i - (\Delta S_i / \Delta f_i) \cdot f_i = \text{constant} \quad (4)$$

where, $\Delta S_i / \Delta f_i$ is the slope of this linear interpolation.

Mixed-gas sorption data were interpolated with the F-H model for a ternary system (polymer-gas1-gas2) [32]. Because macromolecules substantially exceed the gas penetrants molecular weight, the simplification $\bar{V}_i / \bar{V}_p \rightarrow 0$ and $\bar{V}_j / \bar{V}_p \rightarrow 0$ is reasonable [14] (“j” refers to the second penetrant of the mixture). The F-H equations for a ternary system are:

$$\ln \frac{f_i}{f_i^{\text{sat}}} = \ln \phi_i + (1 - \phi_i) - \phi_j \cdot \frac{\bar{V}_i}{\bar{V}_j} + (\chi_{ij} \cdot \phi_j + \chi_{i,p} \cdot \phi_p) \cdot (\phi_j + \phi_p) - \chi_{j,p} \cdot \frac{\bar{V}_i}{\bar{V}_j} \phi_j \cdot \phi_p \quad (5a)$$

$$\ln \frac{f_j}{f_j^{\text{sat}}} = \ln \phi_j + (1 - \phi_j) - \phi_i \cdot \frac{\bar{V}_j}{\bar{V}_i} + \left(\chi_{ij} \cdot \phi_i \cdot \frac{\bar{V}_j}{\bar{V}_i} + \chi_{j,p} \cdot \phi_p \right) \cdot (\phi_i + \phi_p) - \chi_{i,p} \cdot \frac{\bar{V}_j}{\bar{V}_i} \phi_i \cdot \phi_p \quad (5b)$$

2.3. Pure- and mixed-gas permeation

CO₂-CH₄ pure- and mixed-gas permeability behavior in PDMS film was observed via the constant-volume/variable-pressure technique [8]. Changes in permeate pressure per unit time were monitored and recorded from the signal of a 100 Torr MKS Baratron transducer. CO₂ and CH₄ pure- and mixed-gas permeabilities were estimated by:

$$P_i = 10^{10} \frac{y_i \cdot V_{perm} \cdot l}{x_i \cdot p_{feed} \cdot T \cdot R \cdot A} \cdot \frac{dp}{dt} \quad (6)$$

where P is the gas permeability in [Barrers] (1 Barrer = 10^{-10} cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹), x_i and y_i are mol fraction in the feed and permeate, respectively (compositions were characterized by a Agilent 3000A Micro GC), V_{perm} is the permeate volume [cm³], l is the thickness of the membrane [cm], p_{feed} is the feed pressure [cmHg], R is the universal gas constant, A is the area of the membrane [cm²], and dp/dt is the variation of permeate pressure with time [cmHg s⁻¹]. In the case of pure-gas permeation x_i and y_i were equal to 1.

Pure- and mixed-gas permeabilities were fitted with a modified version of the Maxwell-Stefan (MS) transport model based on volume fractions instead of mass fractions [3, 33, 34]. As described in detail elsewhere [3], the pure-gas Maxwell-Stefan model — that integrates the F-H sorption behavior — predicts permeability with the following equation:

$$P_i = \frac{D_{i,p}^{\infty}}{f_i^0 \cdot \bar{V}_i} \cdot \left\{ \left(\frac{\gamma_i + 2 \cdot \bar{V}_i \cdot B_{i,p}}{\gamma_i^2} \right) \cdot [\exp(\gamma_i \cdot \phi_i^0) - 1] - \frac{2 \cdot \bar{V}_i \cdot B_{i,p}}{\gamma_i} \cdot \phi_i^0 \cdot \exp(\gamma_i \cdot \phi_i^0) \right\} \quad (7)$$

where the subscript “ i ” can be either CO₂ and CH₄, the superscript “0” indicates the feed side of the membrane, $B_{i,p} = \chi_{i,p}/\bar{V}_i$ is the polymer-gas dimensional parameter defined by Ribeiro et al. [3] and $D_{i,p}^{\infty}$ is the infinite dilution diffusion coefficient. γ_i derives from the use of the exponential function:

$$D_i = D_{i,p}^{\infty} \cdot \exp(\gamma_i \cdot \phi_i). \quad (8)$$

This function correlates the i -gas pure-gas diffusion coefficient with its own volumetric concentration and is commonly applied in the literature [3]. The parameters $D_{i,p}^{\infty}$ and γ_i were fitted via a solver developed

in-house and based on the *lsqcurvefit* and *fsolve* functions of MATLAB R2016B computer program. In particular, the *lsqcurvefit* function determines the parameters ($D_{i,p}^{\infty}$ and γ_i) that minimize the sum of squares of the difference between permeability predictions (estimated via eq. (7) implemented into the *fsolve* function) and experimental values.

For a binary gas mixture, the Maxwell-Stefan model integrating the F-H sorption equations has the following dimensionless matrix formulation (details on the derivation of the mixed-gas M-S/F-H system of equations can be found elsewhere [3]):

$$\dot{Y} = M^{-1} \cdot F(Y) \quad (9a)$$

$$\dot{Y} = \begin{bmatrix} \frac{d\phi_i}{d\eta} \\ \frac{d\phi_j}{d\eta} \end{bmatrix} \quad (9b)$$

$$M = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} \quad (9c)$$

$$F(Y) = \begin{bmatrix} \frac{1}{\phi_i} \cdot \left(\zeta_j \cdot \frac{\phi_i \cdot \bar{V}_j}{\psi_{ij} \cdot \bar{V}_i} - \zeta_i \cdot \left(\frac{\phi_j}{\psi_{ij}} + \frac{\phi_p}{\psi_{i,p}} \right) \right) \\ \frac{\bar{V}_j}{\bar{V}_i \cdot \phi_j} \cdot \left(\zeta_i \cdot \frac{\phi_j}{\psi_{ij}} - \zeta_j \cdot \left(\frac{\phi_i \cdot \bar{V}_j}{\psi_{ij} \cdot \bar{V}_i} + \frac{\phi_p}{\psi_{j,p}} \right) \right) \end{bmatrix} \quad (9e)$$

$$\eta = \frac{z}{l} \quad (9f)$$

$$\zeta_i = \frac{P_i \cdot f_i^0 \cdot \bar{V}_{CH_4}}{D_{CH_4,p}^\infty}, \quad \zeta_j = \frac{P_j \cdot f_j^0 \cdot \bar{V}_{CH_4}}{D_{CH_4,p}^\infty} \quad (9g)$$

$$\psi_{i,p} = \frac{D_{i,p}}{D_{CH_4,p}^\infty}, \quad \psi_{j,p} = \frac{D_{j,p}}{D_{CH_4,p}^\infty}, \quad \psi_{ij} = \frac{D_{ij}}{D_{CH_4,p}^\infty} \quad (9h)$$

where z is the local thickness of the film and varies from 0 to l , and D_{ij} is the MS coupled diffusion coefficient. The formulation of each of the components of the matrix “ M ” depends on the form the F-H interaction parameters. In this work, PDMS sorption interaction parameters were found concentration independent (see the Results and Discussion section). Hence, in this case the matrix “ M ” is:

$$m_{11} = \bar{V}_i \cdot \left(\frac{1}{\bar{V}_i} \cdot \left(\frac{1}{\phi_i} - 1 \right) - B_{i,p} \cdot (\phi_j + 2 \cdot \phi_p) - \phi_j \cdot (B_{ij} - B_{j,p}) \right) \quad (10a)$$

$$m_{12} = \bar{V}_i \cdot \left(-\frac{1}{\bar{V}_j} + (\phi_j + \phi_p) \cdot (B_{ij} - B_{i,p}) + (\phi_j - \phi_p) \cdot B_{j,p} \right) \quad (10b)$$

$$m_{21} = \bar{V}_j \cdot \left(-\frac{1}{\bar{V}_i} + (\phi_i + \phi_p) \cdot (B_{ij} - B_{j,p}) + (\phi_i - \phi_p) \cdot B_{i,p} \right) \quad (10c)$$

$$m_{22} = \bar{V}_j \cdot \left(\frac{1}{\bar{V}_j} \cdot \left(\frac{1}{\phi_j} - 1 \right) - B_{j,p} \cdot (\phi_i + 2 \cdot \phi_p) - \phi_i \cdot (B_{ij} - B_{i,p}) \right) \quad (10d)$$

This dimensionless system (Eq. (9-10)) was fitted to the experimental mixed-gas permeation data in MATLAB R2016b via the *lsqcurvefit* function that determined the parameters of $D_{i,p}$, $D_{j,p}$, and D_{ij} by minimizing the sum of squares of the difference between permeability predictions and experimental values. Permeability predictions were estimated by an *fsolve* based function that minimizes the difference

between the penetrants volumetric concentration at the feed side predicted by the F-H model and the result of the integration of eq. (9a) at the feed side of the film — the *ODE15s* routine of MATLAB computer program was used to perform all numerical integrations. Eq. (9a) was integrated imposing the following boundary condition:

$$\phi_i = \phi_j = 0 \quad \text{if } \eta = 1. \quad (11)$$

3. Results and discussion

3.1. Design and experimental procedures for the new barometric mixed-gas sorption system

Koros' and Paul's [6] detailed description of the barometric pressure decay technique demonstrated how an incorrect volume choice might lead to data scattering. They reported that this scattering could be reduced if the *active-volumes ratio* $AVR = (V_A - V_P)/V_B$ is close to or higher than 1 and $V_B/V_A \leq 1$ (V_A is the sample volume, V_B is the service volume, and V_P is the volume of the polymer). These parameters were applied for the design of the first barometric mixed-gas system (design-0 in **Fig. 2a**) and used to

evaluate sorption of $\text{CO}_2/\text{C}_2\text{H}_4$ at 35°C in poly (methyl methacrylate). Here, V_D collects samples for gas chromatography (GC) analysis.

As shown in **Fig. 2b**, design-1 consisting of three volumes and three transducers was later proposed by Raharjo et al. [13, 14]. In V_A gases are mixed with the help of V_B , while gas sampling for GC characterization relies on V_C . The workload is well distributed (*i.e.*, V_B and V_C have different functions), resulting in an AVR higher than 1 and therefore data scattering is minimal.

Design-2, published a few years later [16], is shown in **Fig. 2b**. Here, V_B connects to a GC, two transducers (high- and low-pressure range), and four valves. Hence, if compared with design-0 and design-1, V_B is substantially larger than V_A in design-2. The larger V_B results in greater amount of gas that can be expanded into V_A and, therefore, a wider region of equilibrium partial pressure can be explored. However, a $V_B > V_A$ produces an $\text{AVR} < 1$, thus increasing the risk of data scattering.

Fig. 2. Designs of barometric mixed-gas sorption systems reported in the literature. (a) first historical design (design-0) [6, 9]. Later proposed simplifications are design-1 (b) [13, 14] and design-2 (c) [16].

Fig. 3. (a) Design of the new three-volumes mixed-gas gas sorption system; (b) schematic of the technique adopted to minimize non-active volumes; and (c) simple two-volumes unit.

Table 1

Volumes and Standard Deviation of the New Three-Volumes Sorption Unit.

Volume	[cm ³]
V_A	9.00±0.03
V_B	7.77±0.03
V_C	10.44±0.04

We applied the most effective features of the designs shown in **Fig. 2** in our new design (**Fig. 3a**). The system consists of three volumes, four transducers (Honeywell™ Super TJE, three 35 atm and one 6.8 atm operating range), and five manual valves (type SS-4UW-V51 from Swagelok™). The 6.8 atm transducer mounted on V_C enables more precise readings of the pressure (if needed). Data of pressure and

temperature were acquired via an OM-USB-TEMP-AI board (OMEGA™, Manchester UK) and recorded by in-house developed software (running in LabVIEW®). Valves, sensors and sample chamber were connected by Swagelok VCR ¼-inch tubes welded to VCR heads. Our target was to obtain accurate data from samples with small amount of high free volume glassy polymer samples (< 300 mg) or from large amount (> 1 g) of low-sorbing polymers to sense very low gas solubilities — that is the case of this study, as discussed below. Therefore, non-active volumes were minimized via the technique shown schematically in **Fig. 3b**; *i.e.*, stainless steel rods and metallic elements were inserted into all tubes and transducers, respectively. Table 1 lists all volumes of the unit estimated via Burnett's expansion technique [9, 35]. The uncertainty was determined by the error propagation theory [36]. The concentration of gas mixtures was characterized by an Agilent 490 Micro GC Natural Gas Analyzer.

As in design-1 (**Fig. 2b**), the AVR of the new unit is always close to unity for minimal data scattering. When V_P varies from zero to the maximum value allowed by the sample cell, AVR ranges between 1.2 and 0.9. Moreover, as in design-2 (**Fig. 2c**), the new unit may explore regions of high partial fugacities of both gases in a mixture. For this scope, V_B can be enlarged such that the valve that connects V_B with V_C is left open. Also, additional volume can be installed in the VCR port of V_B . Because of its rational design, our mixed-gas unit can perform various types of experiments (as design-2) to obtain different data outcomes (see Supporting Information) — *e.g.*, experiments at: (i) *constant equilibrium partial pressure/fugacity* [9, 11-13], (ii) *constant equilibrium concentration* [15-17], or (iii) *constant feed concentration* [14]. To study the sorption of CO₂-CH₄ mixed-gases in PDMS, we followed the *constant feed concentration procedure*. As described in the supporting information (**Fig. S1**), this procedure allowed acquiring data points directly after reaching equilibrium. Hence, the time needed to test a polymer sample was minimized. Moreover, when certified gas mixtures are available, the *constant feed concentration procedure* can be run in a simple two-volume unit (**Fig. 3c**), where V_B feeds gas mixtures to the sample chamber, and after degassing, it receives gases for GC analysis.

3.2. Gas sorption of pure-components and mixed CO₂-CH₄ in PDMS

Pure- and CO₂-CH₄ mixed-gas sorption was studied in PDMS as a reference material in the new unit by following the *constant feed concentration* procedure. When a sorption experiment reached equilibrium, the sample was degassed for at least 18 h. The low range transducer mounted on V_C confirmed that desorption phenomena did not occur prior to the subsequent sorption step. In pure-gas sorption experiments, the polymer was not degassed between two different experiments; *i.e.*, gas was added cumulatively to V_A.

As shown in **Fig. 4a**, pure-gas CH₄ sorption data in PDMS were essentially in perfect agreement with the data reported by Raharjo et al. [12]. Furthermore, pure-gas CO₂ and CH₄ sorption (**Fig. 4a** and **4b**) was also in good agreement with the data reported by Merkel et al. [25], Shah et al. [31], and Pope et al. [37]. Our rational design minimized data scattering and errors (note that the error bars lie under the markers). The pure-gas Flory-Huggins (F-H) model Eq. (1-2) along with concentration independent CH₄-polymer and CO₂-polymer F-H interaction parameters ($\bar{\chi}_{CH_4,p} = 0.16 \pm 0.02$ and $\bar{\chi}_{CO_2,p} = 1.05 \pm 0.02$) provided an excellent prediction of pure-gas uptakes; the average prediction error ($\bar{\epsilon} = 1/n \cdot \sum_i^n |C_i^{exp} - C_i^{pred}| / C_i^{exp}$ being n the number of data points) was lower than 2.1%. Table 2 shows that F-H interaction parameters and infinite dilution solubilities (Eq. (3)) retrieved from in-house sorption data and from literature sorption data of PDMS samples of density close to 0.97 g/cm³ (that is the value of density also observed in this work for PDMS) are in excellent agreement.

Fig. 4. Pure-gas (a) CH₄ and (b) CO₂ sorption uptakes in PDMS. Literature values are included for comparison [12, 25, 37]. (c) CH₄ and CO₂ solubilities vs. gas fugacity. The S-R-K equation of state was used for calculation of fugacity coefficients. Curves represent interpolation via the Flory-Huggins (F-H) model.

Table 2

Concentration averaged Flory-Huggins interaction parameters ($\bar{\chi}_{i,p}$), and solubility coefficient at infinite dilution (S^∞_i) of CH₄ and CO₂ in PDMS at 35 °C and comparison with literature data; PDMS density (ρ) data are also reported.

ρ	$\bar{\chi}_{CH_4,p}$	$\bar{\chi}_{CO_2,p}$	$S^\infty_{CH_4}$	$S^\infty_{CO_2}$	Reference
[g/cm ³]	[-]	[-]	[cm ³ (STP) cm ⁻³ _{polym} atm ⁻¹]	[cm ³ (STP) cm ⁻³ _{polym} atm ⁻¹]	
0.97±0.02	-	-	0.47±0.01	1.15±0.01	This work - Eq. (4)
	0.16±0.02	1.05±0.02	0.45±0.01	1.13±0.03	This work - F-H model
0.97	0.16±0.02*	0.99±0.02*	0.45±0.01*	1.20±0.02*	Shah et al. [31]
0.98	0.15±0.01*	-	0.45±0.01*	-	Raharjo et al. [12]

* Values re-calculated using the Flory-Huggins model from literature sorption data using the average experimental value of partial molar volume at infinite dilution of 56.7 cm³/mol [12, 29, 30] and 49 cm³/mol [29, 30], respectively for CH₄ and CO₂; the hypothetical vapor pressures of CH₄ and CO₂ were estimated from the Wagner equation [38] (*i.e.*, $P_{CH_4}^{sat} = 359$ atm and $f_{CO_2}^{sat} = 81.9$ atm) and converted into fugacities via the S-R-K equation of state (*i.e.*, $f_{CH_4}^{sat} = 277.9$ atm and $f_{CO_2}^{sat} = 52.2$ atm).

By means of custom made and certified feed concentrations, we populated the 3D graphs of CH₄ and CO₂ mixed-gas uptakes (shown respectively in **Fig. 5a** and **5b**). The sorption surfaces were estimated via the multicomponent F-H model reported in eq. (5). We could not find a clear correlation between the χ_{ij} and the volumetric gas concentration in the polymer; hence, we assumed the χ_{ij} to be concentration independent ($\bar{\chi}_{ij}$), and we analyzed the multicomponent F-H prediction in terms of average prediction error (calculated from $\bar{\epsilon} = 1/n \cdot \sum_i^n |C_i^{exp} - C_i^{pred}|/C_i^{exp}$, being n the number of experimental data). As better described in **Fig. S3**, the lowest prediction error of about 5.3% could be obtained for $\bar{\chi}_{ij}$ equal to about 17.8 — for $\bar{\chi}_{ij}$ ranging between 6 and 20, $\bar{\epsilon}$ was always below 10%. This high value of $\bar{\chi}_{ij}$ depicts a condition of some kind of competitive interaction that CH₄ and CO₂ experience in PDMS at 35 °C. The multicomponent F-H uptake surfaces for CH₄ and CO₂ uptake are shown in **Fig. 6a** and **6b**, respectively. Experimental mixed-gas data accuracy and consistency was confirmed by the following procedure: after all pure- and mixed-gas data point were recorded, the mixed-gas system was dismantled and meticulously remounted; volumes and GC were recalibrated and the series of data points obtained from

50% CO₂ molar feed concentration was repeated obtaining very consistent mixed-gas uptake data (see Fig. S3).

Fig. 5. Mixed-gas sorption data for (a) CH₄ and (b) CO₂ in PDMS at 35 °C. The surfaces are prediction of the multicomponent Flory-Huggins model.

Fig. 6. Comparison between experimental and predicted (via the Flory-Huggins model) pure- and mixed-gas uptakes.

Because **Fig. 5** is not of simple interpretation, pure- and mixed-gas uptake data were plotted in 2D graphs (**Fig. 7**). At 35 °C, gas uptakes measured with CO₂-CH₄ mixtures in PDMS were *mostly* equal or lower

than those obtained with pure gases, and this deviation was increasing with the concentration of the mixture, as shown in **Fig. 7a** and **7b**. At all explored feed concentrations and pressures, the estimated error of CO₂ sorption uptake was small. On the other hand, at low CH₄ feed pressures and concentrations, the sensibility of the sorption system reached its lowest level and, therefore, the estimated error of the values of uptake of CH₄ was notable (see **Table S1**). This limit depends on the accuracy of the transducers, volume calibration, and the GC system. However, in this study the highest detected values of CH₄ solubility coefficient were a minimum of 1.5 times lower than the lowest value of CH₄ solubility coefficient obtained for PTMSP [16], PPO [11], and PIM-1 [15] during similar mixed-gas sorption experiments at 35 °C. Sorption of CO₂-CH₄ mixtures at 35 °C in PDMS was quite challenging because of the low solubility of these two gases — specifically CH₄. The reduction of non-active volumes in the system and the use of 1.40 g of PDMS made it possible to sense such low solubility coefficients.

Fig. 7. Pure- and mixed-gas sorption uptake vs. gas fugacity for (a) CH₄ and (b) CO₂. Dashed curves represent interpolation of pure-gas data via the Flory-Huggins model. All experimental values are listed in Table S1 of the supporting information.

Owing to the excellent prediction of pure- and mixed-gas uptakes by the F-H model (**Fig. 6**), we applied this model to the analysis of mixing effects on CO₂ and CH₄ solubilities. This analysis is shown in **Fig. 8** where CO₂ mixed-gas solubility coefficients are plotted against the corresponding CH₄ uptakes in PDMS and, conversely, CH₄ mixed-gas solubility coefficients are plotted vs. CO₂ uptakes. The blue and the red

bands represent respectively the regions of methane and carbon dioxide pure-gas solubility coefficients (in the pressure ranges of **Fig. 4a** and **b**). As CO₂ uptake increases CH₄ mixed-gas solubility coefficient reduces almost independently from the concentration of the gas phase in equilibrium with PDMS. The effect of methane uptake on CO₂ mixed-gas solubility coefficient is more complex. If at equilibrium the gas phase contains more CH₄ than CO₂ (*i.e.*, equilibrium concentrations < 50% molar CO₂-CH₄), CO₂ mixed-gas solubility coefficient is depressed by a kind of competitive sorption phenomenon. Differently, for gas phase equilibrium concentration > than 50% molar CO₂ in CH₄, CO₂ solubility coefficient follows the pure gas-trend — *i.e.*, CO₂ mixed-gas solubility coefficient increases with the total pressure. To the best of our knowledge this is the first report of a competitive sorption effect for both sorbants in a rubbery polymer. The literature has already shown the possibility of enhancement or depression of gas solubility due to mixture interactions. For example, Raharjo et al. [12] observed enhanced CH₄ solubility in PDMS in the presence of *n*-C₄H₁₀ relative to the pure-gas CH₄ values because the presence of *n*-C₄H₁₀ created a more favorable environment for CH₄ sorption. Similarly, Ribeiro et al. [14] reported that CO₂ solubility coefficient in a crosslinked poly(ethylene oxide) was enhanced in mixtures with ethane; moreover, they also found that at temperatures < 0 °C and for low CO₂ uptakes, ethane solubility coefficient was lower than the corresponding pure-gas values. Further analysis of this CO₂-C₂H₆-XLPEO mixed-gas system via model calculations by Minelli et al. [39] showed that depending on the operative conditions, CO₂ can exhibit solubilities higher or lower than the pure-gas values.

Fig. 8. Solubility coefficient behavior of one gas vs. the gas uptake of the other gas of the mixture for equilibrium concentrations of 25, 50, and 75% molar CO_2 in CH_4 . In this figure, the range 0 to 12 atm total fugacity was explored. The blue and the red bands mark the regions of pure-gas solubility coefficients of CH_4 and CO_2 , respectively.

The CO_2/CH_4 solubility selectivity vs. CO_2 partial fugacity in PDMS is shown in **Fig. 9**. For pure-gas CO_2 or at infinite dilution of CH_4 , the CO_2/CH_4 solubility selectivity was in the range of 2.4-2.8. Because the variation of CO_2 solubility coefficient was lower than that of CH_4 between pure-gas and mixed-gas sorption values, the CO_2/CH_4 solubility selectivity increased with pressure. Previous work also showed that the solubility selectivity was enhanced in gas mixtures by $\text{CO}_2\text{-C}_2\text{H}_6$ sorption in crosslinked poly(ethylene oxide) [14] at low CO_2 concentrations in the polymer. Also, solubility selectivity was enhanced by $\text{CO}_2\text{-CH}_4$ sorption in glassy poly(1-trimethylsilyl-1-propyne) [16] and in PIM-1 [15, 17] due to competitive interactions between the two gases.

Fig. 9. Experimental solubility selectivity vs. CO₂ partial fugacity at 35 °C.

3.3. Permeabilities and diffusivities of pure- and mixed CO₂-CH₄ in PDMS at 35 °C

The discussion is now extended to the permeability and diffusivity of CO₂-CH₄ mixed-gas in PDMS at 35 °C. Gas permeability data were obtained in-house. CO₂ and CH₄ pure-gas permeability data are shown in **Fig. 10** in the range of 2-30 atm fugacity; CH₄ pure-gas permeability was in agreement with data reported by Raharjo *et al.* [24] and Merkel *et al.* [25]. The Maxwell-Stefan model was fitted to the pure-gas permeation data with a maximal average prediction error of 1.6%. Interestingly, both CH₄ and CO₂ diffusion coefficients were found independent from their respective volumetric concentration because the value of the γ_{CH_4} and γ_{CO_2} parameters (Eq. (8)) were small and lower than the respective standard deviations (in this case, a parameter is statistically non-significant and can be set equal to zero). Hence, the pure-gas M-S diffusivities were: $D_{\text{CH}_4,p} = D_{\text{CH}_4,p}^{\infty} = (2.09 \pm 0.07) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{CO}_2,p} = D_{\text{CO}_2,p}^{\infty} = (2.92 \pm 0.14) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

Fig. 10. Comparison of pure-gas CO₂ and CH₄ permeability data in PDMS. Filled-symbols are data from this work. Unfilled symbols were digitalized from [24, 25]. The data published by Merkel et al. [25] were corrected with Soave-Redlich-Kwong [27] fugacity coefficients. Curves were predicted via the Maxwell-Stefan pure-gas permeation model (Eq. (7)).

We studied the mixed-gas pressure range limited to about 12 atm total fugacity that is roughly the range covered by our mixed-gas sorption data. In this range, the CO₂ mixed-gas permeability (red circles in **Fig. 11a**) was essentially equal to the pure-gas values (black solid to curve in **Fig. 11a**); instead, methane permeability was enhanced by mixture phenomena (blue squares in **Fig. 11a**). What is responsible for this increase of methane permeability and decrease in the CO₂/CH₄ permselectivity of PDMS?

At first we studied the kinetic of permeation in terms of pure- and mixed-gas concentration-averaged effective (C.A.E.) diffusion coefficients that were calculated from $\bar{D}_i = P_i/S_i^{up}$ where, S_i^{up} is the solubility coefficient of the i-gas at the upstream pressure and P_i is the gas permeability at negligible permeate pressure (as done previously elsewhere [13, 21, 23, 24, 40]). If the C.A.E. diffusion coefficients are averaged in the range 0-12 atm total fugacity, CH₄ and CO₂ mixed-gas values appear coinciding (**Table 3**); *i.e.*, mixture effects enhance methane C.A.E.-diffusion coefficient. However, this same approach also indicates that CO₂ mixed-gas C.A.E.-diffusion coefficient are on average clearly higher than the corresponding pure-gas values (**Table 3**); that is indeed a result of difficult interpretation.

Table 3

CO₂ and CH₄ pure- and mixed-gas concentration-averaged-effective diffusion coefficients (PDMS at 35 °C).

	Pure-gas [cm ² s ⁻¹]	Mixed-gas [cm ² s ⁻¹]
CH ₄	(2.10±0.03) x 10 ⁻⁵	(2.89±0.10) x 10 ⁻⁵
CO ₂	(2.87±0.06) x 10 ⁻⁵	(3.14±0.06) x 10 ⁻⁵

To an unambiguous insight about the CO₂-CH₄ mixed-gas kinetic behavior during permeation through PDMS, we fitted the Maxwell-Stefan (M-S) transport model Eq. (9-10) to our mixed-gas permeability data. Data fitting this model can be quite tedious that is why Krishna [5] proposed some model simplifications. In our case, the fact that pure- and mixed-gas CO₂ permeabilities (**Fig. 11a**) coincide simplified the M-S mixed-gas data fitting; in fact, we first fitted the mixed-gas permeability data assuming that both CO₂ and CH₄ mixed-gas diffusion coefficients were not influenced by mixture effects (*i.e.*, that they are independent from the concentration of the *other* component of the mixture). **Fig. 11a** shows that this assumption works for CO₂ but not for methane whose mixed-gas permeability prediction is represented in this case by the dashed blue curve (1). By this first fitting, we obtained a value for the coupled diffusion coefficient — *i.e.*, $D_{ij} = (1.57 \pm 0.26) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Hence, we fixed D_{ij} , and we fitted the mixed-gas permeability data imposing the following empirical correlation of CH₄ diffusion coefficient vs. CO₂ volumetric concentration: $D_{CH_4,p} = D_{CH_4,p}^{\infty} \cdot (1 + \xi_{ij} \cdot \sqrt{\phi_{CO_2}})$; the rationale for this function is given in the Supporting Information (**Fig. S5**). A value of $\xi_{ij} = 4.0 \pm 1.3$ was found, and it allowed an adequate prediction of the CH₄ mixed-gas permeability data (see curve (2) in **Fig. 11a**); in this case, the average prediction was lower than 4% (**Fig. S4**).

Fig. 11. (a) Permeabilities and (b) diffusivities vs. fugacity for the two cases of pure-gas and 50/50 mol% mixture concentration at equilibrium. Diffusion coefficients were obtained from Maxwell-Stefan model (derived elsewhere [3]) fitting of in-house pure- and mixed-gas permeability data. In (a): black solid line are M-S predictions of pure-gas permeabilities (**Fig. 10**); the red solid line is the M-S prediction of the CO₂ mixed-gas permeability data (red circles); blue lines represent the M-S prediction of methane mixed-gas permeability data (blue squares) for the CH₄ diffusion coefficient being independent (dashed curve) and dependent (solid curve) from the CO₂ volumetric concentration. Note: the CH₄ mixed-gas diffusion coefficient curve in (b) was estimated from CO₂ volumetric concentrations constant and equal to that at the feed-side of the film.

Based on the findings of Assink [41], Jordan and Koros [42] suggested that methane and carbon dioxide induce opposite trends in PDMS; that is, methane tends to compress the flexible polymer under pressure whereas CO₂ swells the polymer. Our findings suggest that swelling is predominant. Ribeiro et al. [21] showed that CO₂ induced swelling in XLPEO rubber, thus increasing the diffusivity of C₂H₆ under mixed-gas conditions and lowering the CO₂/C₂H₆ permselectivity. Similarly, the enhanced mobility of the

PDMS chains due to CO₂ swelling increases the diffusivity of CH₄ — as indicated by curve **Fig. 11b**. Note: the trend curve of CH₄ mixed-gas diffusion coefficient shown in **Fig. 11b** (solid curve in blue) was calculated when the CO₂ volumetric concentration in PDMS was fixed to the feed-side value and assumed constant throughout the film thickness; as discussed previously, mixed-gas $D_{CH_4,p}$ depends on ϕ_{CO_2} that varies with the local thickness (*i.e.*, **Fig. 11b** simply shows the approximate behavior of mixed-gas $D_{CH_4,p}$). Although the permeation environment of glassy polymers differs from that of rubbers, another interesting analogy can be found comparing the CO₂-CH₄-PDMS and the CO₂-CH₄-Matrimid [43] permeation systems. In fact, Ricci et al. [43] showed how the CO₂ concentration averaged diffusion coefficient of a 55/45 mol% CO₂-CH₄ mixture was not affected by mixture effects, whereas methane diffusion coefficient was strongly enhanced by the presence of CO₂; this behavior is qualitatively very similar to the one shown in **Fig. 11**.

4. Conclusions

When permeating gas mixtures, the separation performance of membranes can deviate from that obtained in pure-gas experiments. To quantitatively study this behavior, mixed-gas sorption data must be measured experimentally. Inspired by other systems reported in the literature, this study describes the design and operation of a new mixed-gas barometric gas sorption unit. Volumes were optimized to minimize data scattering and to increase the accuracy of the system. The pure-gas solubility of CO₂ and CH₄ in PDMS (measured at 35 °C) was in excellent agreement with reported data in the literature.

Gas sorption of CO₂ and CH₄ at 35 °C was also performed with custom-made commercial mixtures. In this way, points of *constant feed concentration* were recorded (as also done elsewhere [14]). With this procedure, backflow between sample chamber and feed chamber was not an issue and adjustment of the pressure in the sample chamber was not necessary. Moreover, the isothermal surfaces of sorption of each gas of a binary mixture can be populated directly after pressure equilibration.

Consistent with the literature, we found that gases in mixtures do not sorb independently. When exposed to CO₂-CH₄ mixtures, PDMS exhibited mostly lower or equal gas uptake than when tested with pure gases. A modeling analysis of the mixed-gas solubility behavior revealed that for equilibrium concentration <50% molar CO₂ in CH₄, both methane and CO₂ suffer of a kind of competitive behavior. Equilibrium gas phases containing CO₂ more than CH₄ are accompanied by CO₂ solubilities that increase with pressure, whereas CH₄ solubility keeps being depressed by the presence of carbon dioxide in the PDMS film. In mixtures at 35 °C, our results show that CO₂ induced strong swelling of PDMS, which exceeded the effect of polymer matrix compression. As a result of mixture effects, CO₂/CH₄ permeability selectivity of PDMS decreased because methane diffusion coefficient was enhanced by the presence of CO₂.

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Highlights

- A new mixed-gas sorption system with optimized volumes for low-solubility detection
- CO₂-CH₄ mixed-gas sorption in rubbery PDMS deviates from pure-gas trends
- Enhanced CO₂/CH₄ solubility selectivity was caused by mixture effects and pressure
- CO₂ induced phenomena increased CH₄ diffusion coefficient