



High-pressure CO₂/CH₄ separation of Zr-MOFs based mixed matrix membranes

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ABSTRACT

The gas separation properties of 6FDA-DAM mixed matrix membranes (MMMs) with three types of zirconium-based metal organic framework nanoparticles (MOF NPs, ca. 40 nm) have been investigated up to 20 bar. Both NPs preparation and MMMs development were presented in an earlier publication that reported outstanding CO₂/CH₄ separation performances (50:50 vol% CO₂/CH₄ feed at 2 bar pressure difference, 35 °C) and this subsequent study is to demonstrate its usefulness to the natural gas separation application. In the current work, CO₂/CH₄ separation has been investigated at high pressure (2–20 bar feed pressure) with different CO₂ content in the feed (10–50 vol%) in the temperature range 35–55 °C. Moreover, the plasticization, competitive sorption effects, and separation of the acid gas hydrogen sulfide (H₂S) have been investigated in a ternary feed mixture of CO₂:H₂S:CH₄ (vol% ratio of 30:5:65) at 20 bar and 35 °C. The incorporation of the Zr-MOFs in 6FDA-DAM enhances both CO₂ permeability and CO₂/CH₄ selectivity of this polymer. These MMMs exhibit high stability under separation conditions relevant to an actual natural gas sweetening process. The presence of H₂S does not induce plasticization but increases the total acid gas permeability, acid gas/CH₄ selectivity and only causes reversible competitive sorption. The overall study suggests a large potential for 6FDA-DAM Zr-MOF MMMs to be applied in natural gas sweetening, with good performance and stability under the relevant process conditions.

1. Introduction

The acid gas content (carbon dioxide, CO₂; hydrogen sulfide, H₂S) in raw natural gas varies accordingly to the hydrocarbon geo-origins [1,2] and is commonly in the range of 25–55 mol.% for CO₂ and below 2 mol.% for H₂S (≥ 5 mol.% in several regions) [3,4]. CO₂, the most undesirable diluent aside from H₂S, is essential to be discarded from the gas stream as it corrodes transmission pipelines in the presence of water [5,6]. Additionally, CO₂ lowers the natural gas caloric value and causes atmospheric pollution [2,3,5]. Consequently, the content of these impurities must be reduced to meet the industrial processing and pipeline distribution requirements, e.g., maximum allowable contents of 2–3 mol.% CO₂ and 0.0004–0.0005 mol.% (4.3–5.0 ppm) H₂S (see Table S1) [7]. In the last decades, the advances in gas separation

membranes have allowed the technology to increase its share of the total membrane market, comprising over 1000–1500 million US dollar per year [8] and appear to be the most viable alternative to substitute the conventional highly energy consuming processes, including the solvent-based adsorption processes [5]. However, due to challenges such as plasticization especially at high-pressure operation and degradation, membrane processes only represents < 5% of the natural gas sweetening market [9,10].

Both plasticization and degradation effects can be suppressed by polymer blending and cross-linking [11–15], but a more promising method is the combination of polymeric and inorganic materials as mixed matrix membranes (MMMs) [16–20]. Yong et al. [16] reported the effectiveness of 2 wt% POSS (polyhedral oligomeric silsesquioxane) nanoparticles into the highly permeable PIM-1 to suppress the neat

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polymer CO₂-induced plasticization pressure of 15 bar in the range of tested pressure (30 bar) with 50:50 vol% CO₂:CH₄ feed mixture, at 35 °C. Additionally, the MMM presented 40.8% CO₂ permeability and 11.4% CO₂/CH₄ selectivity improvements. Adams et al. [17] reported a more than five times increase of CO₂ partial pressure needed to plasticize PVAc-50 wt% zeolite 4A at 30 bar, also measured with 50:50 vol % CO₂:CH₄ feed mixture, at 35 °C. Both Shahid and Nijmeijer [18] and Samadi and Navarchian [19] reported higher CO₂-plasticization pressures of Matrimid® 5218 (neat P_{plasticization} of ~10 bar) by incorporating 30 wt% mesoporous Fe-BTC [18], 5 wt% MgO [19] and 10 wt% modified clay mineral with polyaniline [19], up to 21, 15 and 30 bar, respectively.

Permeation of a mixture of gases through a membrane can depend strongly on the operating parameters, for example, the feed pressure and temperature, amongst others due to the gases' non-ideal behavior [21–23] and their competitive sorption [21,23–25]. Moreover, in a MMM system, the presence of a porous filler and the new filler-polymer interfacial phase created need to be understood as they further influence the gas mobility and sorption through the membrane. Metal organic frameworks (MOFs), formed with metal-based clusters linked by organic ligands [26] in three-dimensional crystalline frameworks with permanent porosity, are an emerging class of porous fillers [27]. They have gained substantial attention due to their high CO₂ uptake (i.e., HKUST-1 of 7.2 mmol·g⁻¹ [28], MOF-74 of 4.9 mmol·g⁻¹ [29], at 1 bar, 273–298 K), large surface areas up to 7000 m²·g⁻¹ [30], well-defined selective pores due to their crystallinity, amongst other features. Many researchers observed that the incorporation of a MOF into the polymer continuous phase improved not only its separation properties but also its physical properties [16,31–33], due to interfacial interactions between the polymer and the MOFs. The polymer, in some cases, penetrates the MOF open pores or rigidifies and forms microvoids at the interface [34,35], thereby affecting the membrane's physical properties and gas separation performance.

Zr-based MOF UiO-66 is a highly stable new material and has recently been applied as part of a MMM [31,36,37]. The synthesis of three types of Zr-MOFs, namely UiO-66 and its functionalized derivatives, UiO-66-NH₂ and UiO-66-NH-COCH₃, as well as MMM fabrication with 6FDA-DAM have been presented earlier [31,34]. In the current paper, we present the gas separation performance of the neat 6FDA-DAM membranes and their derived Zr-MOF MMMs as a function of feed pressure between 2 and 20 bar. At the highest pressure, the effects of CO₂ content in the feed mixture on membrane performance have been investigated, at various temperatures (35–55 °C). Finally, the presence of H₂S to the separation performances has been studied.

2. Experimental

2.1. Materials and membrane fabrications

The UiO-66 and UiO-66-NH₂ NPs (ca. 40 nm in size) were synthesized accordingly to Hou et al. [38], at 1 to 1 M ratio of zirconium (IV) chloride (ZrCl₄, ≥99.5% trace metal basis) to 1,4-benzenedicarboxylic acid (BDC, 98%) or 2-amino-1,4-benzenedicarboxylic acid (NH₂-BDC, 99%), in *N,N*-dimethylformamide (DMF, ≥99.9%), through a solvothermal process in a pre-heated oven at 120 °C/24 h for UiO-66 and at 80 °C/14 h for UiO-66-NH₂. A second heating step was conducted for UiO-66-NH₂ at 100 °C for 24 h. UiO-66 was activated by thermal treatment in a furnace at 300 °C for 3 h, with a heating rate of 15 °C·min⁻¹, whereas chemical activation was conducted for UiO-66-NH₂, where the precipitated NPs were washed in an absolute ethanol bath at 60 °C, three times in three days (ethanol was changed daily). After the complete cycle, the NPs were dried at room temperature. A covalent post-synthetic modification (PSM) was conducted onto UiO-66-NH₂ to produce UiO-66-NH-COCH₃ in chloroform (CHCl₃, anhydrous ≥99%) and acetic anhydride (AcO₂, ACS Reagent, ≥98.0%) solution, under reflux at 55 °C/24 h. Once completed, the colloidal

solution was centrifuged, rinsed with fresh CHCl₃ (15 mL, 3x) and dried overnight at 150 °C before characterization and use. The conversion yield was determined by the percentage of amide groups present in the modified NPs using proton nuclear magnetic resonance (¹H NMR), and the digestion method was presented elsewhere [38,39]. All reactants applied in the NP synthesis were supplied by Sigma-Aldrich.

6FDA-DAM (Mw = 418 kDa) was purchased from Akron Polymer Systems, Inc. and dried overnight at 100 °C before use. Pure polymer membranes (“neat”) and MMMs were fabricated by dissolving the corresponding amount of 6FDA-DAM in chloroform, making a dope solution of 10 wt%. In the case of MMM, a priming step was conducted with 10–15 wt% of the total polymer weight that proves to improve the inorganic filler dispersion in the continuous polymer phase [40–42]. The final dope solutions were casted in a Petri dish and covered for controlled solvent evaporation overnight before being treated at 110 °C before subsequent characterization and permeation measurements. The flat sheet membranes were in the thickness range of 100–150 μm.

2.2. Standard permeation measurement

To assess the gas separation performance of the membranes, a 25/25 cm³(STP)·min⁻¹ CO₂/CH₄ binary feed mixture was used at a pressure difference of 2 bar at 35 °C applying He as sweep gas at 1 cm³ (STP)·min⁻¹. The permeate composition was analyzed online by an Agilent 3000A micro-GC equipped with a thermal conductivity detector (TCD) at the Institute Nanoscience of Aragon (INA), University of Zaragoza. The membrane module is as described elsewhere [43]. The permeability was calculated as the penetrated gas flux, normalized for the membrane thickness and the partial pressure drop across the membrane, and presented in Barrer (1 Barrer = 10⁻¹⁰ cm³(STP)·cm·cm⁻²·s⁻¹·cmHg⁻¹ (Eq. (1)).

$$\text{Permeability, } P_{\text{gas}} = \frac{\text{Flux}_{\text{gas}} (\text{cm}^3 (\text{STP}) \cdot \text{cm}^{-2} \cdot \text{s}^{-1}) \times \text{Thickness} (\text{cm})}{\Delta p_{\text{gas}} (\text{cm} \cdot \text{Hg})} \quad (1)$$

The separation factor (α) of two competing gases was calculated using Eq. (2), considering the mole fraction (x) of gas i and j in both feed and permeate streams. The mixed gas separation performance was previously discussed [34], and the best performing MMMs are with 14–16 wt% Zr-MOF particle loadings.

$$\alpha_{i/j} = \frac{x_i^{\text{perm}} / x_j^{\text{perm}}}{x_i^{\text{feed}} / x_j^{\text{feed}}} \quad (6-2)$$

2.3. High-pressure performance evaluation

The membranes were placed in a proprietary high-pressure permeation module obtained from the European Membrane Institute (EMI, The Netherlands). The membrane was supported with an S&S 589/1 black ribbon ash-less filter paper on a perforated plate to avoid membrane deformation during the high-pressure testing. The sample was sealed with an o-ring system providing for an effective membrane area of 0.78 cm². Both feed and retentate sides were connected by high-pressure Swagelok quick-connects whereas the permeate gas was collected using a 1/8 in. Swagelok connector.

The permeation module was placed inside a Memmert UF450 forced air circulation oven, connected to a proprietary high-pressure permeation set-up at SINTEF Materials and Chemistry, Oslo for gas separation measurement (Fig. 1). The permeation set-up is designed to withstand pressures up to 92 bar with a forced air temperature control up to 300 °C. The feed (150 cm³(STP)·min⁻¹) and permeate (10 cm³(STP)·min⁻¹) flow rates were controlled by automated Bronkhorst High-Tech mass controllers (MFC), equipped with a back pressure controller (Bronkhorst High-Tech, P-512C equipped with an F-033C control valve, max of 92 bars) on the feed side for pressure

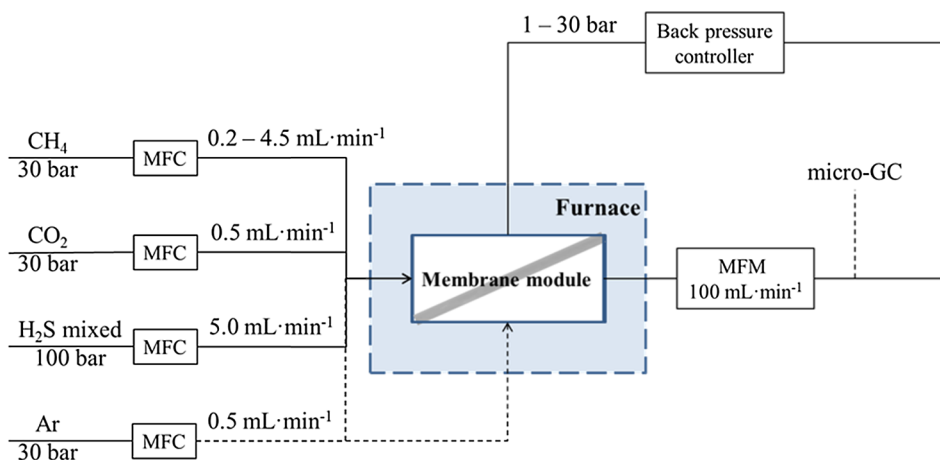


Fig. 1. Schematic representation of the high-pressure experimental set-up. The mass flows are calibrated at standard temperature and pressure condition.

Table 1

CO₂, CH₄ permeability and CO₂/CH₄ selectivity of neat 6FDA-DAM and its Zr-MOF MMMs, measured 35 °C, at a pressure difference of 2 bar with an equimolar binary mixture of CO₂ and CH₄.

Membrane	Gas permeability (Barrer)		CO ₂ /CH ₄ Selectivity
	CO ₂	CH ₄	
Neat	335	17.7	19.3
MMM UiO-66 14 wt%	888	35.9	25.1
MMM UiO-66-NH ₂ 16 wt%	521	21.9	23.8
MMM UiO-66-NH-COCH ₃ 16 wt%	459	18.1	25.4

regulation. The atmospheric-pressure permeate gas analyzed by a two-channel column (MolSieve 5A, MS5 and PoraPLOT U, PPU) Agilent 490 micro-GC, coupled with thermal conductivity detectors (TCD). The micro-GC was calibrated for low CO₂ (0–12 vol%), CH₄ (0–5 vol%) and H₂S (0–0.5 vol%) concentrations in argon. Good correlation coefficients of $R^2 = \geq 0.999$ were obtained for the μ -GC response as a function of CO₂, CH₄, and H₂S concentration. The fluxes were calculated from the measured permeate concentrations and the calibrated flow of Ar sweep gas.

High-pressure gas permeation measurements were conducted accordingly to the following experimental sequence, and the separation performances were calculated correspondingly to Eqs. (1) and (2).

1. Pressure variation with 50:50 vol% CO₂: CH₄ feed mixture: Preliminary measurement at 2 bar and 35 °C was conducted to validate the initial membrane performances, and the pressure was subsequently increased to 5 and 10 bar. Before proceeding to 20 bar, the CO₂ feed content was decreased to 10 vol% for the second step measurements.
2. CO₂ feed content variation at the feed pressure of 20 bar: At 20 bar, the 10 vol% CO₂ feed content was subsequently increased to 20 vol%, 30 vol%, and 50 vol% with CH₄.
3. The effect of temperature variation on the separation performance, with 30:70 vol% CO₂:CH₄ feed mixture at 20 bar: The temperature increase was conducted by stepwise increments from 35 °C to 45 °C and 55 °C, and followed by a reduction back to 35 °C prior to the H₂S introduction (step no. 4).
4. Investigation of separation performance in the presence of H₂S with 30:5:65 vol% CO₂:H₂S:CH₄ feed mixture was conducted at 20 bar and 35 °C.
5. Finally, the H₂S in feed was removed and the system was allowed to purge before the separation efficiency was re-evaluated with 30:70 vol% CO₂:CH₄ feed mixture, at 20 bar and 35 °C.

It is important to note that the samples were allowed to reach permeation steady-state overnight, after each pressure or feed composition change. Specific attention was given to Health, Safety and Environmental (HSE) matters, and the lab was equipped with preventive safety measures which include H₂, CO, and H₂S detection systems, personal portable gas detectors, and separate floor level ventilation suction.

3. Results and discussions

In the previous publication [34], we found very promising performance indicators for several 6FDA-DAM MMMs with Zr-MOFs when tested at low pressure (2 bar), with the best performance observed for membranes that contain 14–16 wt% Zr-MOF. An increase in the Zr-MOF loading shows a clear permeability-selectivity trade-off, and selectivity reductions have been observed [34,44]. Table 1 shows the re-measured gas separation performance of the duplicate membranes, at 35 °C, with a pressure difference of 2 bar with an equimolar binary mixture of CO₂ and CH₄ in SINTEF facility. The permeability values are lower than the published data [34], possibly due to the aging phenomenon which may have occurred during shelf-storage at room temperature for over 250 days. However, the similar improvement trends upon Zr-MOF incorporation were observed. The presence of 14 wt% UiO-66, 16 wt% UiO-66-NH₂ and 16 wt% UiO-66-NH-COCH₃ improves the CO₂ permeability of 6FDA-DAM ($P_{CO_2} = 335$ Barrer) by 165%, 56% and 37%, respectively. These enhancements are well-related to the CO₂-philic nature of the Zr-MOFs where a stronger energetic interaction between CO₂ (higher quadrupole moment than CH₄) and the nanoparticle surfaces at zero coverage, and to the increments in fractional free volume (FFV) in the MMMs (Neat 6FDA-DAM, FFV = 0.238). 14 wt% UiO-66 MMM presents the highest increment value of 39%, followed by 16 wt% UiO-66-NH₂ and 16 wt% UiO-66-NH-COCH₃ with 16% and 22%, respectively. The CO₂/CH₄ selectivity of the samples also increased by 23–32%.

At these observed optimum loadings, the Zr-MOFs addition enhances both CO₂ permeability and CO₂/CH₄ selectivity tremendously. Besides a higher gas diffusion in the Zr-MOFs, the NPs addition improved the MMM gas diffusivity by inducing an ancillary selective interface phase [45] with additional free volume [46,47]. Agglomeration of the NPs was more prominent at the highest loadings, and the concurrent reduction of the selectivity reduction is likely due to the formation of non-selective by-pass channels in the filler agglomerates [46] and possibly micro-voids in the filler-polymer interface region [41], although such morphological features are not observed by SEM analyses. All the MMMs also presented excellent distribution and inorganic filler-polymer interface interaction (please refer to SEM images, Fig. S5 in the previous publication [34]).

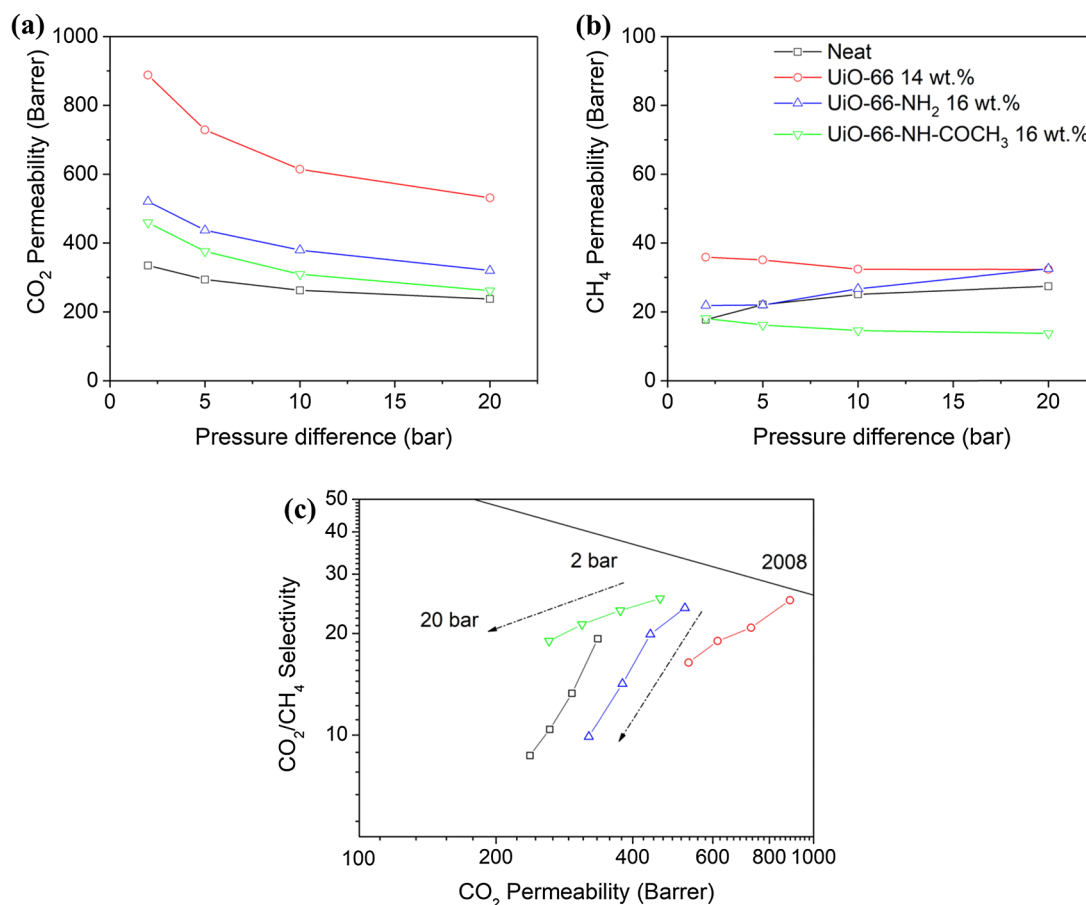


Fig. 2. (a) CO₂ and (b) CH₄ permeabilities of 6FDA-DAM and its Zr-MOFs as a function of feed pressure, measured with 50:50 vol% CO₂: CH₄ feed mixture at 35 °C. Their corresponding CO₂/CH₄ selectivity values are presented in (c), against the 2008 Robeson upper bound [58].

3.1. Effect of feed pressure variation to mixed gas separation

Most of the fundamental studies on Zr-MOF polyimide MMMs related to Matrimid® and 6FDA-copolyimides have been conducted at low pressures where CO₂-induced plasticization is expected to be of minor importance [31,48,49]. Here, we have investigated the gas separation performance of 6FDA-DAM and its Zr-MOF MMMs at a pressure ranging from 2 to 20 bar in a 50:50 vol% CO₂:CH₄ feed mixture at 35 °C. The obtained mixed gas permeability and CO₂/CH₄ selectivity behavior as a function of pressure are shown in Fig. 2.

The CO₂-induced plasticization pressure is defined to occur at the minimum observed in the CO₂-permeability as a function of CO₂-partial feed pressure. In the case of mixed gases, the permeation rate of all gases is affected due to swelling of the polymer matrix and the increased chain mobility caused by the high CO₂ concentration. The permeation enhancement is more pronounced for the least permeable gases, resulting in a decrease of the selectivity as a function of pressure. In contrast, for all samples in the present study, a monotone decrease in CO₂ permeability with increasing pressure is observed (Fig. 2), which does not indicate substantial plasticization [21]. The decrease in CO₂ permeability reduction is a result of competitive sorption and the concave shape of the sorption isotherm [25,50]. This constitutes a reduction in driving force for transport with increasing pressure and also gradual saturation of the material may result in lower mobility. Overall, this results is further supported by the clear decrease in permeation coefficient in the polymer matrices (see Fig. S1). The CO₂ permeability continuously decreases with increasing pressure indicating there is no apparent CO₂-induced plasticization in the thick membrane [21], opposite to the reported single-gas CO₂-plasticization pressure of neat

6FDA-DAM membrane between ~10–20 bar, at 35 °C [51,52]. The plasticization pressure differences may be attributed to different physical properties, i.e., molecular weight, density, and polymer free volume, as previously discussed [31,34].

The pressure dependence of the CH₄ permeability (Fig. 2(b)) over the measured pressure range, however, suggests that the neat 6FDA-DAM starts to swell immediately after the first pressure increment. It can be explained by dynamic swelling of the polymer matrices upon exposure to the CO₂ at high pressure [53], where the penetrating CO₂ causes the material dilation and subsequently increases its macromolecular mobility. Several researchers have reported the thermodynamics of swollen glassy polymers by a penetrant [54,55], and a thorough discussion was recently presented by Ogieglo et al. [53] when studying the glassy polymer relaxation in this films. The phenomenon, to the function of pressure, causes extensive dilation of the matrices, influencing the penetrants' permeation. Here, the effect is more apparent in CH₄ permeability increase compared to the readily high-permeability CO₂. In the case of UiO-66-NH₂ MMM, the high CO₂-affinity amino functional group increases the CO₂ adsorption in the polymer matrices and directly further influences the molecular dynamic dilation. Even though it is not the membranes' plasticization pressure, their CO₂/CH₄ selectivity reduced by 55% and 58% respectively. This behavior also defined as swelling-induced perm-selectivity losses [34], which was observed in several other co-polyimides, such as 6FDA-APAF and TPDA-APAF, when measured with CO₂/CH₄ binary mixture up to 25 bar feed pressure, at 35 °C [56]. Heck et al. [57] also observed similar behavior in (6FDA-mPDA)-(6FDA-durene) block co-polyimide, for which they reported an increase in CH₄ permeability with pressure (up to 20 bar feed pressure), causing CO₂/CH₄ and He/CH₄ selectivity

reductions.

The continuous decrease of CH₄ permeability in both UiO-66 and UiO-66-NH-COCH₃ MMMs demonstrated the competitive sorption effect [59], where CO₂ penetrated the membranes' sorption sites which associated to the non-equilibrium free volume in glassy polymer and hindered CH₄ to permeate. Polymer plasticization was not observed in these membrane samples.

3.2. Effect of CO₂ feed composition in high-pressure separation

Fig. S2(a-b) show the CO₂ and CH₄ permeability of the neat 6FDA-DAM and Zr-MOF MMMs, measured at 20 bar feed pressure and 35 °C, with a different CO₂ feed content between 10 and 50 vol%. The significant differences in the initial CO₂ permeabilities between the membranes were discussed in the previous publication [34]; higher CO₂ permeability in the UiO-66 MMM is attributed to the easiness of CO₂ to diffuse into its frameworks, compared to the higher steric hindrance functionalized-MOFs, and also its higher FFV.

The CO₂ permeability in the neat 6FDA-DAM and its Zr-MOFs MMMs decreases between 9 and 22%, with the increase of CO₂ partial pressure when tested at 20 bar. The lowest reduction of 8.7% was observed for the UiO-66 MMM. The observation, however, is opposite to the previously reported CO₂ permeability relationship with CO₂ partial pressure at low-pressure measurements, i.e., 6FDA-DAM Zr-MOF MMMs (at 2 bar) [34] and PES/SAPO-34/2-hydroxyl 5-methyl aniline MMMs (at 3 bar) [60]. At the low pressure, a higher CO₂ partial pressure produced a more prominent competitive sorption effect, where an increase in CO₂ solubility and transport through the membrane medium was observed and inversely decreased the second component's ability to permeate, in this case, CH₄.

Evidently, the continuous CO₂ permeability reduction with increasing pressure suggests that the competitive sorption effect at high pressure is less influenced by the CO₂ partial pressure (see Fig. 3). Instead, it is related to the gradual saturation of permeating gases inside the polymer micro-voids [18]. Nevertheless, a slight increase in the CH₄

permeability for the neat membrane (9%) and UiO-66-NH₂ MMM (21%) is observed, indicating the possibility of CO₂-induced plasticization that started to take effect [61,62]. These samples exhibited the highest CO₂/CH₄ selectivity reductions of between 28 and 33% in all the samples (shown in Fig. S2(c), relative to 2008 Robeson's upper bound [58]). Despite this CH₄ permeability increment, the behavior can be explained as swelling-induced perm-selectivity losses, an early stage in polymer plasticization [56].

With regard to the initial separation performance (with 10 vol% CO₂), similarly to the previous discussion, neat 6FDA-DAM showed a lower CO₂/CH₄ selectivity than that of MMMs (UiO-66-NH₂ < UiO-66 < UiO-66-COCH₃). The proportional selectivity increase in MMMs to the increasing CO₂ partial pressure [63–65], which only observed in UiO-66 MMM at the tested feed pressure of 20 bar (3% selectivity increment) represents the membrane's extended CO₂ sorption capability due to the CO₂-induced plasticization or swelling at constant pressure [63]. Its reduction conversely was explained based on CO₂ self-inhibition as a consequence of saturation of the filler active sites at a high CO₂ concentration in a feed mixture [60,66]. Referring to that hypothesis, a lower reduction exhibited by UiO-66-NH-COCH₃ MMM (13%) compared to UiO-66-NH₂ MMM (28%), represented by its lesser concave shape in the permeability isotherm, may be due to a higher CO₂ affinity towards acetamide functional groups, with a higher number of adsorption sites compared to UiO-66-NH₂ NPs. Moreover, constant selectivity values demonstrate no dependency of an MMM system towards the increasing CO₂ partial pressure, as also revealed in the PES/SAPO-34/HMA MMM system, measured at 3 bar [60]. This hypothesis implies that only a minor amount of the active sites is occupied at low pressure.

3.3. Effect of operating temperature in the high-pressure separation

Fig. S3(a-c) shows the CO₂ and CH₄ permeability and the CO₂/CH₄ selectivity as a function of the operating temperature applying a 30:70 vol% CO₂:CH₄ feed mixture at 20 bar. A minor increase in CO₂ permeability of < 6% was recorded for all samples, whereas for CH₄

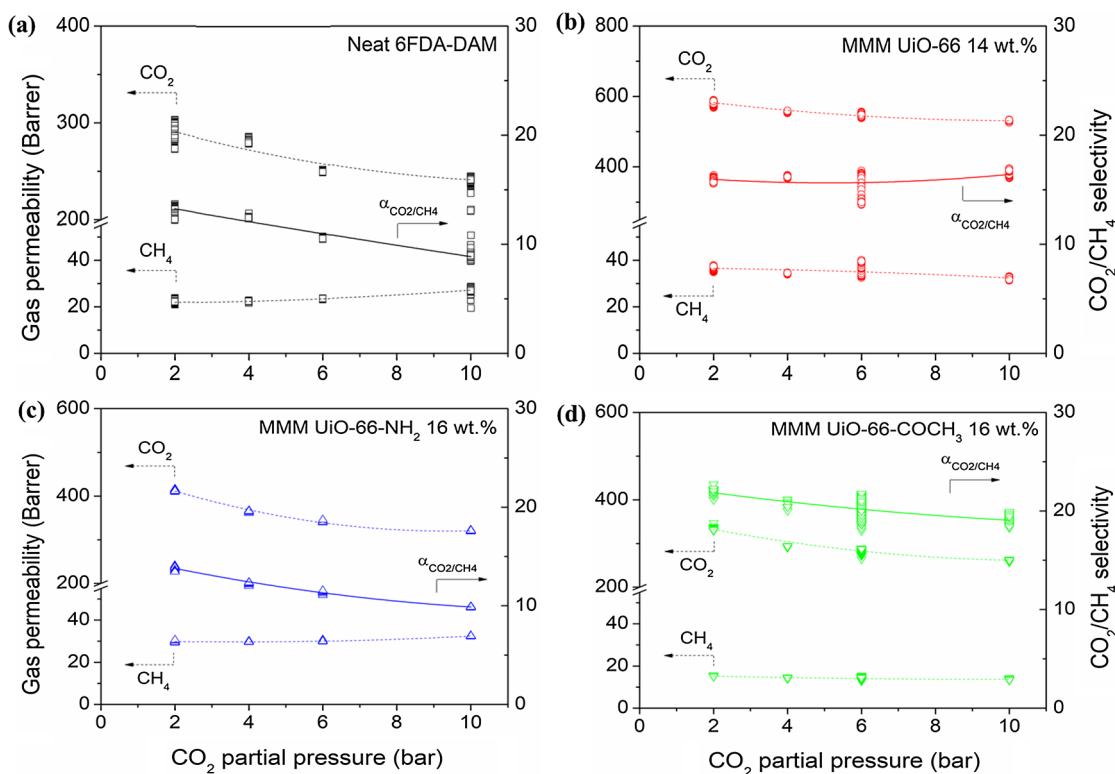


Fig. 3. CO₂ and CH₄ permeabilities, and CO₂/CH₄ selectivity of 6FDA-DAM and its Zr-MOF MMMs against CO₂ partial pressure, at 20 bar and 35 °C.

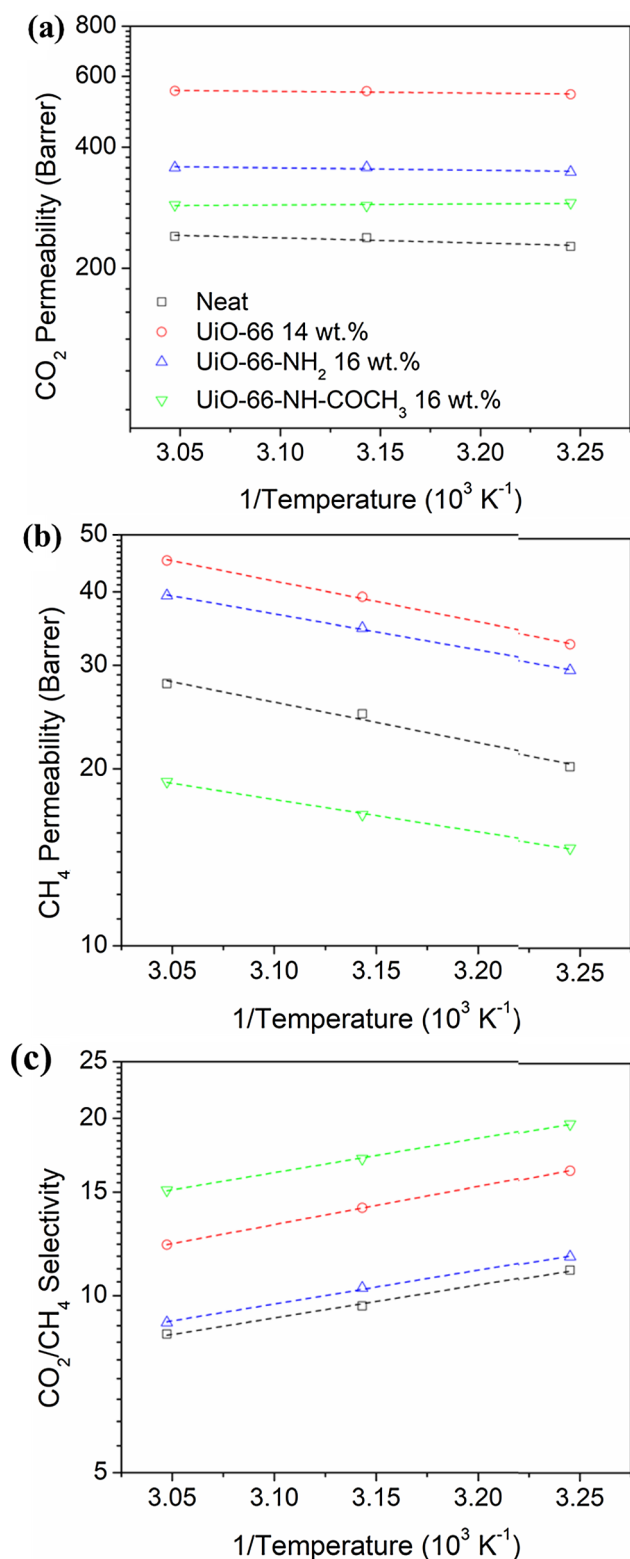


Fig. 4. (a) CO_2 and (b) CH_4 permeability and its (c) perm-selectivity to temperature dependence, for neat 6FDA-DAM and its Zr-MOFs membranes at the measurement temperature of 35–55 °C.

permeability, the increments were higher in between 28 and 37%, as the operating temperature increased from 35 to 55 °C. The effect of temperature on the gas permeability can be quantitatively observed in their activation energy for permeability, following Arrhenius rule using Eq. (3) [67]:

Table 2

Activation energy of permeation for CO_2 and CH_4 in neat 6FDA-DAM and its Zr-MOF MMMs, calculated for the temperature operating range of 35–55 °C, with 30:70 vol% CO_2/CH_4 at 20 bar.

Gas	Membrane	Permeability activation energy,
		E_a , (35–55 °C)
CO_2	Neat	0.16
	MMM UiO-66 14 wt%	0.05
	MMM UiO-66-NH ₂ 16 wt%	0.07
	MMM UiO-66-NH-COCH ₃ 16 wt %	-0.03
CH_4	Neat	0.85
	MMM UiO-66 14 wt%	0.86
	MMM UiO-66-NH ₂ 16 wt%	0.76
	MMM UiO-66-NH-COCH ₃ 16 wt %	0.68

$$P = P_0 e^{-\frac{E_a}{RT}} \quad (3)$$

where P_0 is a pre-exponential factor of permeation, E_a is activation energy for permeability ($\text{kJ}\cdot\text{mol}^{-1}$), R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}$), and T is the temperature in K. Using CO_2/CH_4 selectivity expression of the permeability coefficient ratio of CO_2 over CH_4 , the gas selectivity is defined as the following:

$$\alpha(\text{CO}_2/\text{CH}_4) = \frac{P_{\text{CO}_2}}{P_{\text{CH}_4}} = \frac{P_0(\text{CO}_2)}{P_0(\text{CH}_4)} \exp\left(-\frac{E_p(\text{CO}_2) - E_p(\text{CH}_4)}{RT}\right) \quad (4)$$

Fig. 4 indicates that CH_4 permeability in the 6FDA-DAM neat membrane and its Zr-MOF MMMs followed Arrhenius rule in the temperature range of 35–55 °C, while the CO_2 permeability was less influenced by the temperature. Their permeability coefficients are summarized in Table 2. The permeability dependency is a combination of the diffusion and solubility coefficients temperature dependencies, and the lower CO_2 and CH_4 activation energies in MMMs as compared to the neat polymer indicate the gas transport through filler porosity [49], and in the interfacial voids on polymer-MOF and MOF-MOF regions which may also reduce the overall permeability E_a of MMMs. Regarding 6FDA-DAM, in addition to polymer matrix compression at the high pressure, the overall CO_2 activation energy trend does not show a clear correlation to the membrane FFVs (MMM (UiO-66; 0.331 > UiO-66-COCH₃, 0.292 > UiO-66-NH₂; 0.277) > neat 6FDA-DAM, 0.238). Instead, the activation energy seems profoundly influenced by the presence of Zr-MOF nanoparticles in MMMs, in the order of their group functionalities (UiO-66-NH-COCH₃ > UiO-66-NH₂ > UiO-66 > neat 6FDA-DAM). It also concludes that the CO_2 permeation is predominately influenced by its solubility (sorption) in the membrane systems, and less dependent on temperature. The higher activation energies presented by the non-polar CH_4 also indicated that its diffusion or transport was more influenced compared to CO_2 molecules, giving higher CH_4 permeability increments and consequently reduced the CO_2/CH_4 selectivity by 22–26%. This observation is also consistent with activated diffusion of non-polar molecules in glassy polymers (related to chain mobility and polymer free volumes) [68], where the least permeable gas often possesses higher activation energy and realizes a more substantial permeability increase with increasing temperature. In any event, the activation energies (temperature-dependent) are low for both the neat polymer membrane and the MMMs, compared to the other 6FDA-based polyimides in the literature (see Table S2). This suggests a low penetrant-membrane interaction perhaps because there is a relatively large difference between the CO_2 and CH_4 kinetic diameter and the membrane controlling pore size.

Lower CO_2 temperature-dependency at this high-pressure separation also indicated by its fugacity coefficient values, closing to 1.0 (ideal

Table 3

The compressibility Z factors for CO₂ and CH₄, calculated using Dranchuk and Abou-Kassem equation of state (DAK – EOS) [69], presented at 35 °C, 45 °C and 55 °C, at 20 bar.

Temperature, °C	Compressibility Z factor		Fugacity coefficients, ϕ		Fugacity (bar)	
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
35	0.9049	0.9699	0.9953	1.0293	19.9051	20.5858
45	0.9953	0.9735	0.9998	1.0258	19.9953	20.5153
55	0.9998	0.9767	1.0000	1.0227	19.9998	20.4539

Calculated from the following constant values and critical state variables:

CO₂: gas constant, $R = 188.92 \text{ J kg}^{-1} \text{ K}^{-1}$; isentropic exponent = 1.301; $p_{\text{crit}} = 73.77 \text{ bar}$; $T_{\text{crit}} = 30.98 \text{ °C}$.

CH₄: gas constant, $R = 518.27 \text{ J kg}^{-1} \text{ K}^{-1}$; isentropic exponent = 1.304; $p_{\text{crit}} = 45.92 \text{ bar}$; $T_{\text{crit}} = -82.59 \text{ °C}$.

gas) when temperature is increased (see Fig. S4(a) and S4(b)), proves that the molecule's non-ideal behavior is less influenced by the increasing temperature but predominantly by pressure. It is supported by the fact that CO₂ possesses lower fugacity coefficients at the tested separation conditions Table 3 (overall compressibility factor and fugacity coefficient calculated values are presented in Fig. S4). The compressibility factors were determined by an eleven-constant Dranchuk and Abou-Kassem equation of state (DAK-EOS) [69]. The detail is presented in the supporting information document.

Besides that, the CH₄ permeability increase was also influenced by the increase of polymer free volume (as a function of polymer chain packing and intersegmental motion) by the effect of elevated temperature. The activated diffusion often proves to be a significant advantage in the separation of non-polar H₂ from CO₂, giving enhanced H₂/CO₂ selectivity at higher temperatures as demonstrated in 6FDA-mPBI [68] and PBI-ZIF8 MMMs [70].

$$\log P_0 = \frac{E_p}{R} \times 10^{-3} + Z \quad (5)$$

Regardless of common polymer chemical structures, Van Krevelen [71] presented a positive slope of 1×10^{-3} for $\log P_0$ and E_p/R plot (Eq. (5)), with Z values of -7.0 and -8.2 for rubbery and glassy polymers respectively, for permeability measurement below their glass transition temperatures. Fig. S5 indicates that the addition of Zr-MOFs into 6FDA-DAM altered CO₂ permeability-temperature dependency significantly, giving a negative E_p/R slope of -0.15×10^{-3} , while only reduced CH₄ permeability-temperature dependency by roughly 70% (CH₄ permeability E_p/R slope = 0.32×10^{-3}).

3.4. Effect of the presence of H₂S on membrane separation

The concentration of H₂S in the natural gas mixture varies depending on the geo-origin and can be more than 5 vol% [4,72]. As aforementioned, besides investigating the 6FDA-DAM and its Zr-MOF MMMs performances for H₂S separation, it is important to understand the H₂S effect on membrane performance. We studied the gas separation performance of 6FDA-DAM and its Zr-MOF MMMs with 30:70 vol% CO₂:CH₄ feed mixture at 20 bar and 35 °C, before adding 5 vol% of H₂S, making the feed composition to 30:5:65 vol% CO₂:H₂S:CH₄. The separation performance after H₂S exposure was also investigated and summarized in Table 4.

Upon the addition of 5 vol% H₂S in the mixed gas, P_{CO_2} in all samples decreased by an average of 28–34%, accordingly to their functionality order: MMMs (UiO-66-NH-COCH₃ > UiO-66-NH₂ > neat 6FDA-DAM). 6FDA-DAM MMMs showed a higher CO₂ permeability reduction in the presence of H₂S, compared to the neat membrane. The observation exhibited the influence of Zr-MOFs in the MMMs, of which their active metal sites also preferentially adsorb H₂S and thus reduce their CO₂ adsorption capacity. $P_{\text{H}_2\text{S}}$ values are in the range of 137–352 Barrer, slightly lower than those of P_{CO_2} , contributing to the total acid gas permeability of between 304 and 737 Barrer. The increments directly presented the acid gas selectivity over

Table 4

Gas separation performances of 6FDA-DAM and its 14–16 wt% Zr-MOFs MMMs, tested with binary (30:70 vol%; CO₂:CH₄) and tertiary (30:5:65 vol%; CO₂:H₂S:CH₄) feed mixture at 20 bar, 35 °C.

Feed mixture	Separation performances	6FDA-DAM membranes			
		Neat	MMM UiO-66	MMM UiO-66-NH ₂	MMM UiO-66-NH-COCH ₃
CO ₂ :CH ₄ (30:70 vol%)	P_{CO_2}	231	541	359	291
	P_{CH_4}	21.7	33.0	33.1	14.8
	$\alpha_{\text{CO}_2/\text{CH}_4}$	10.6	16.4	10.8	19.7
CO ₂ :H ₂ S:CH ₄ (30:5:65 vol%)	P_{CO_2}	167	385	243	193
	$P_{\text{H}_2\text{S}}$	137	352	224	172
	$P_{(\text{CO}_2 + \text{H}_2\text{S})^*}$	304	737	466	365
	P_{CH_4}	18.5	25.4	25.7	10.6
	$\alpha_{\text{CO}_2/\text{CH}_4}$	9.1	15.2	9.5	18.2
	$\alpha_{\text{H}_2\text{S}/\text{CH}_4}$	7.4	13.6	8.7	16.2
CO ₂ :CH ₄ (30:70 vol%)	$\alpha_{(\text{CO}_2 + \text{H}_2\text{S})/\text{CH}_4}^*$	16.4	29.0	18.1	34.4
	P_{CO_2}	227	543	347	284
	P_{CH_4}	20.4	33.7	29.8	14.3
	$\alpha_{\text{CO}_2/\text{CH}_4}$	11.1	16.1	11.7	19.8

Permeability is in Barrer.

* Acid gas, CO₂ + H₂S.

CH₄ of 16.4 for the neat 6FDA-DAM and in the range of 18.1–34.4 for its MMMs. Besides the competitive sorption of a two-component gas mixture, the presence of a third component intensifies the gas mixtures non-ideal behavior and influences each penetrant permeation rate, especially at elevated pressures [21]. Based on gas permeability values, the observed adsorption preference trend is in the order of CO₂ > H₂S > CH₄, well-agreed to the gasses' isosteric adsorption heat in UiO-66 (CO₂; 25.7 kJ·mol⁻¹ > H₂S; 23.8 kJ·mol⁻¹ > CH₄; 18.8 kJ·mol⁻¹, reported at 30 °C [36]). Functionalized UiO-66 derivatives presented higher values, in the same order. The gas physical properties; dipole moment (Debye), quadrupole moment (au) and polarizability (a_0^3), also greatly contributed to the competitive sorption outcomes and H₂S high polarizability explained its higher permeability despite its relatively low content in the feed mixture compared to CO₂; CH₄: 5.4×10^{-6} Debye, 0 au, $17.3 a_0^3$; CO₂: 0 Debye, 3.2 au, $18 a_0^3$; H₂S: 0.978 Debye, 0 au, $25 a_0^3$ [73]. Hence, the observed $\alpha_{\text{CO}_2/\text{CH}_4}$ reduction can be explained by a larger competitive sorption effect induced by H₂S (its solubility is larger than that of CH₄) in the membrane systems. In addition to H₂S competitive sorption effect, the reduced CO₂/CH₄ selectivity may also be contributed by the fact that CH₄ partial pressure in binary mixed gas (70 vol% in feed) is higher than that in ternary system (65 vol% in feed). As a higher CH₄ partial pressure will result in its higher permeability, subsequently lowers the CO₂/CH₄ selectivity and its competitive sorption effect towards H₂S and CO₂ permeability may also not be the same.

In the presence of H₂S, all MMMs presented higher CO₂, H₂S and acid gas selectivities compared to the neat 6FDA-DAM ($\alpha_{\text{CO}_2/\text{CH}_4} = 9.1$;

Table 5

Separation comparison of 6FDA-DAM and its Zr-MOF MMMs with several other dense membranes, when tested with ternary mixed gas feeds containing ≤ 15 mol.% of H_2S at $35^\circ C$.

Polymer	Pressure (bar)	Feed compositions mol.% ($CO_2:H_2S:CH_4$)	Permeability (Barrer)		Selectivity		Refs.
			CO_2	$CO_2 + H_2S$	CO_2/CH_4	$(CO_2 + H_2S)/CH_4$	
6FDA-DAM	20	30:5:65	167	304	9.1	16.4	This study
MMM UiO-66	20	30:5:65	385	737	15.2	29.0	
MMM UiO-66-NH ₂	20	30:5:65	243	466	9.5	18.1	
MMM UiO-66-NH-COCH ₃	20	30:5:65	193	365	18.2	34.4	
Cellulose acetate	10	29:6:65	2.4	4.6	22.0	41.5	[77]
Pebax 1074	10	18.1:12.5:69.4	155	850	11.0	61.6	[77]
PU2	10	18.1:12.5:69.4	195	813	5.6	23.4	[77]
PIM-6FDA-OH	34.5	15:15:70	54.7	90.7	27.8	46.1	[81]
6FDA-DAM:DABA (3:2)							
Annealed at $180^\circ C$	48	20:10:70	55.6	81.0	32.1	46.7	[82]
Annealed at $230^\circ C$	48	20:10:70	50.8	74.4	31.1	45.5	[82]
6FDA-DAM	6.9	20:20:60	414	672	24.4	39.7	[79]

Abbreviation: 6FDA: 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane diandrydride; DAM: 2,4,6-trimethyl-1,3-diaminobenzene; PEBAX: polyether block amide; PU: polyurethane; PIM: polymers of intrinsic microporosity; DABA: 3,5-diaminobenzoic acid.

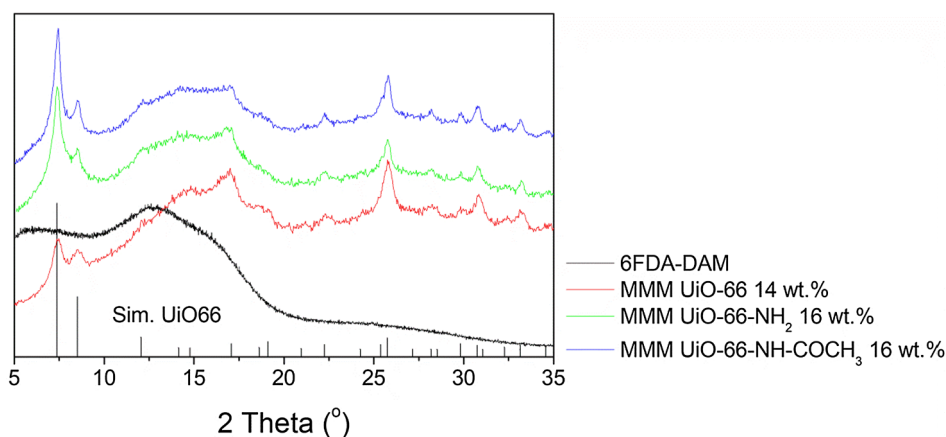


Fig. 5. XRD patterns of UiO-66 (simulated [80]), 6FDA-DAM and its Zr-MOF derived MMMs after H_2S -exposure in the tertiary mixture (30:5:65 vol%; $CO_2:H_2S:CH_4$) separation, at 20 bar, $35^\circ C$.

$\alpha_{H_2S/CH_4} = 7.4$; $\alpha_{(CO_2+H_2S)/CH_4} = 16.4$) with the highest values presented in UiO-66-NH-COCH₃ MMM ($\alpha_{CO_2/CH_4} = 18.2$; $\alpha_{H_2S/CH_4} = 16.2$; $\alpha_{(CO_2+H_2S)/CH_4} = 34.4$). The UiO-66-NH-COCH₃ MMM presented similar or higher α_{H_2S/CH_4} selectivity than several reported membranes, such as in 6FDA-PAI-3/TmpDA (ideal $\alpha_{H_2S/CH_4} = 10.9$), Torlon® 4000 T (ideal $\alpha_{H_2S/CH_4} = 14.8$), both tested at 4.5 bar, $35^\circ C$ [74], and in a rigid (6FDA-mPDA)-(6FDA-durene) block co-polyimide, ($\alpha_{H_2S/CH_4} = ca. 15$), tested with 1 vol% H_2S in a $CO_2:H_2S:N_2:CH_4$ quaternary mixture at 3.8 bar, $22^\circ C$ [75]. The performance is also comparable to the commercial poly(ester urethane) urea, PEUU, $\alpha_{H_2S/CH_4} = 16$ [76] ($CO_2:H_2S:CH_4$ feed ratio of 5.4:3:remaining, at $55^\circ C$, 20 bar) and cellulose acetate, CA, $\alpha_{(CO_2+H_2S)/CH_4} = 41.5$ [77] ($CO_2:H_2S:CH_4$ feed ratio of 29:6:65, at $35^\circ C$, 10 bar). In the separation of an actual natural gas sample containing 5008 ppm H_2S , water vapor, C_1-nC_5 , and mercaptan, commercial polyphenylene oxide hollow fibers presented $\alpha_{H_2S/CH_4} = 2.9$, while a commercial poly(ester urethane) urea (PEUU) flat sheet membrane gave $\alpha_{H_2S/CH_4} = 3.4$, measured at $40^\circ C$ and $23^\circ C$, respectively [78]. The separation performances of several other dense membranes to the ternary gas mixture with H_2S at $35^\circ C$ are presented in Table 5 for comparison. Most interestingly, Liu *et al.* [79] also demonstrated acid gas permeability and selectivity over CH_4 improvement of 6FDA-DAM ($P_{CO_2+H_2S} = 671.8$ Barrer, $\alpha_{(CO_2+H_2S)/CH_4} = 39.7$) by incorporating 30 wt% Y-fum-fcu-MOF ($P_{CO_2+H_2S} = 1057.7$ Barrer, $\alpha_{(CO_2+H_2S)/CH_4} = 52.8$) and 19 wt% Eu-naph-fcu-MOF ($P_{CO_2+H_2S} = 747.8$ Barrer, $\alpha_{(CO_2+H_2S)/CH_4} = 49.2$).

Interestingly, after the H_2S exposure for a period of 20–40 h, both

P_{CO_2} and α_{CO_2/CH_4} of all membranes were regained to pre- H_2S exposure values, indicating H_2S presence only causes reversible competitive sorption between the permeating molecules, no H_2S -induced plasticization and no other permanent effect. Referring to the XRD patterns (Fig. 5), based on their characteristic diffraction peaks of Zr-MOF [80], we found that the MOF maintained their crystallinity phase in the polymer matrix, after H_2S -exposure (average H_2S -exposure time of 20–30 h). These remarkable results confirmed 6FDA-DAM and its Zr-MOF MMMs capability, effectiveness and stability for simultaneous acid gases separation from CH_4 .

4. Conclusion

6FDA-DAM polyimide offers an attractive opportunity in gas separation application, and the incorporation of the highly stable zirconium-based UiO-66 and its functionalized derivatives as MMM further enhanced the separation properties. The membranes possessed excellent CO_2/CH_4 separation performance and presented high-performance stability at conditions relevant to actual gas processing (pressure, CO_2 content, temperature). The Zr-MOFs improved not only 6FDA-DAM gas separation properties but also deterred CO_2 -induced plasticization and swelling. Additionally, in the presence of high H_2S content (50,000 ppm in feed mixture) at high total pressure, both CO_2 - and H_2S -induced plasticization were suppressed, and only reversible competitive sorption effect was observed. This successful high-pressure testing of 6FDA-DAM MMMs with Zr-MOFs is encouraging and

industrially relevant for natural gas sweetening at high pressure. Nevertheless, the separation understanding in the presence of water vapor and condensable hydrocarbons needs to be addressed beforehand. These impurities are not only suspected to reduce the separation performance but could also deteriorate the physical integrity of a membrane system.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2019.115858>.

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