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Development of membrane contactors using volatile amine-based absorbents for CO_2 capture: amine permeation through the membrane

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Abstract

Non-porous membrane contactor offers the possibility to reduce the amine emissions if the membrane layer is specifically designed to act as a barrier for the amine transport. In the present paper, the amine permeation through an AF2400 self-standing membrane, previously identified as the best dense layer material, have been investigated to evaluate the amine-emission preventing capacity of the membrane for the first time. The transport properties of different amine-based aqueous solutions (monoethanolamine, 3-methylaminopropylamine and diethylethanolamine) through a 10μm-thick self-standing AF2400 membrane have been characterized through pervaporation experiments in a temperature range of a typical amine absorption step (25 – 60 ºC). Humid CO_2 permeation tests were also carried out to simulate the real gas membrane absorption separation conditions. A limited decrease (up to 25%) of the CO_2 permeability was observed from dry state to fully humidified conditions, suggesting that the membrane contactor can be operated with humid flue gas to prevent solvent dehydration. The amine fluxes were found at least two orders of magnitude lower compared with CO_2, demonstrating the ability of the membrane to favor the transport of CO_2 over the amines.

Keywords: **Membrane contactor; CO_2 capture; Pervaporation; Amine permeation; Amine evaporation prevention.**

1. Introduction

The latest bulletin from the World Meteorological Organization (WMO) [1] highlighted that in 2015 the CO_2 concentration in the atmosphere reached a level of 400 ppm for the first time in human history, and the overall outlook suggests that this level will be maintained for years to come. The implementation of more efficient CO_2 capture technologies has never been so urgent. Amine absorption is now the most applied technology in post-combustion CO_2 capture, but the high-energy requirements and serious environmental issues due to the solvent emissions result in a pressing need to develop CO_2 absorbents with superior energy efficiency and a system that can prevent the amine emissions. Among the criteria used for the amine selection (cyclic capacity, regeneration energy requirement, corrosion, degradation, etc..), one important property is volatility, as large amounts of organic amines in clean flue gas lead to the formation of dangerous secondary components (e.g., nitrosamine) [2] and require additional water washing steps that can increase the cost of the overall capture process [3]. Aerosol formation related to amine emissions can also be a significant problem related to the absorption process [4], in particular when the size of the aerosol particles is too small (< 2.5μm) to be captured by simple water washing [5]. It has been reported that mist formation accounts for a large part of amine emissions, which can be increased by two orders of magnitude (from 2 to 200 ppm) compared with the condition where only amine evaporation takes place [6].

Recently, amine blends based on primary (or secondary) and tertiary amines have been proposed as a suitable solution to decrease the energy penalty associated with the capture process. For example, mixtures of N,N-Diethylethanolamine (DEEA) and 3-(Methyl-amino)propylamine (MAPA) have up to 50% higher cyclic capacity than 30 wt% monoethanolamine (MEA), the typical reference for amine-based absorbents [7]. The overall mass transfer coefficient of unloaded DEEA-MAPA blends are twice as high as that of MEA solutions [8]. Experimental data also show that at least some of the blends absorb CO_2 faster than 30wt% MEA at the process relevant loadings and temperatures [9]. A short-cut evaluation based on vapor-liquid equilibrium and heat of absorption data indicates that DEEA-MAPA mixtures require reboiler duties around 2.6 MJ/kg$_{CO2}$, much lower compared to the base case (30wt% MEA, requiring 3.5 MJ/kg$_{CO2}$) [10]. Similar energy numbers has also been reached experimentally in a lab scale pilot [11], making the blends very interesting as energy efficient absorbents. The screening investigation also showed that mixtures of Triethylenetetramine (TETA) and DEEA represent a promising option to make post-combustion capture more economically feasible [12], but in both cases the high volatility of the organic components limits their up-scaling to an industrial level. Table 1 shows that amine volatility can be very different depending on the nature of the amines. Typically it increases with the operating temperatures and the amine concentration in the liquid phase, but tends to decrease slightly with CO_2 loading [13].

Membrane contactors have been reported in the literature as an alternative to conventional absorption processes for CO_2 capture. Recent publications have shown the feasibility of using membrane contactor technology for the absorption step in pre-combustion [14, 15] and post-combustion [16-18] processes. Furthermore, attempts to use membrane contactors for the regeneration of liquid absorbents have been reported in recent years [19-21]. Compared to conventional absorption columns, membrane contactors offer several advantages, such as high operational flexibility in view of the possibility of managing fluid flows independently, more predictable performances due to the constant interfacial area, high modularity and a small footprint [22]. In addition, they are also able to prevent issues typically existing in absorption columns, such as foaming, flooding and channelling. However, the presence of a membrane represents an additional mass transfer resistance for CO_2. To minimize the impact of a membrane on CO_2 transport, porous membranes [17, 23, 24] were initially preferred as they were able to ensure high transmembrane flux, but their long-term operation were often compromised due to wetting phenomena, which are reported to have frequently taken place [25-27]. Recently, the use of a thin composite membrane has been proposed as a solution to the wetting issue, and high free volume polymers have been chosen in order to minimize their effect on mass transfer resistance [16, 28, 29].

Table 1 – Volatility of various amines in aqueous-based solvents for operating conditions considered suitable for the absorption step.

SOLVENT SYSTEM [a]	***AMINE TYPE*** [b]	C_{AMINE}	p_{AMINE} (40°C)	p_{AMINE} (60°C)	***Ref***
-	-	mol%	Pa	Pa	
3.5m MEA	MEA	6.3	4.2	13.2	[13]
7m MEA	MEA	12.6	10	27.1	[13]
11m MEA	MEA	19.8	12	40.2	[13]
28.3m MEA	MEA	50.9	34.8	138	[30]
2m PZ	PZ	3.6	2.2	6.78	[13]
5m PZ	PZ	9.0	5.1	17.2	[13]
8m PZ	PZ	14.4	-	37	[13]
0.3m AMP	AMP	0.5	1.6	7.1	[31]
0.9m AMP	AMP	1.6	4.2	18.1	[31]
4.6m AMP	AMP	8.3	13.9	63.4	[31]
11.5m AMP	AMP	20.7	28.4	124.2	[31]
8m EDA	EDA	14.4	24.1	166	[13]
12m EDA	EDA	21.6	57	430	[13]
1M MAPA 5M DEEA	DEEA	26	240.2	822.6	[32]
1M MAPA 5M DEEA	MAPA	5	9.7	41.2	[32]
3M MAPA 3M DEEA	DEEA	14	205.5	706.7	[32]
3M MAPA 3M DEEA	MAPA	14	29.6	135.7	[32]
5M MAPA 1M DEEA	DEEA	4	246.5	466.7	[32]
5M MAPA 1M DEEA	MAPA	20	56.1	147.5	[32]
			p_{AMINE} (30°C)	p_{AMINE} (40°C)	
2.5% NH_3	NH_3	2.5	3307	4961	[33]
5% NH_3	NH_3	5	7087	10866	[33]
10% NH_3	NH_3	10	16299	24094	[33]
15% NH_3	NH_3	15	29764	45354	[33]
2.5% NH_3 0.41m Pz	NH_3	2.5	3602	5297	[33]
5% NH_3 0.43m Pz	NH_3	5	8686	11017	[33]
10% NH_3 0.45m Pz	NH_3	10	18008	27119	[33]

[a] m = molality; M = molarity.

[b] MEA = monoethanolamine; PZ = piperazine; AMP = 2-Amino-2-methyl-1-propanol; EDA = ethylenediamine; MAPA = 3-(methylamino)propylamine; DEEA = diethyletahnolamine; NH_3 = ammonia.

In addition to the above-mentioned advantages, the use of a non-porous thin composite membrane can also be an optimal solution to reduce the amine evaporation towards the gas phase, thus allowing the use of absorbents with better energy performance but cannot be used in absorption columns due to their high volatility. In particular, the thin dense layer in a composite membrane must be designed in order to have minimal impact on the CO_2 mass transfer resistance, while functioning as a barrier to the amine transport (Figure 1). To understand the feasibility of this concept, the amine transport through the membrane must be quantitatively studied.

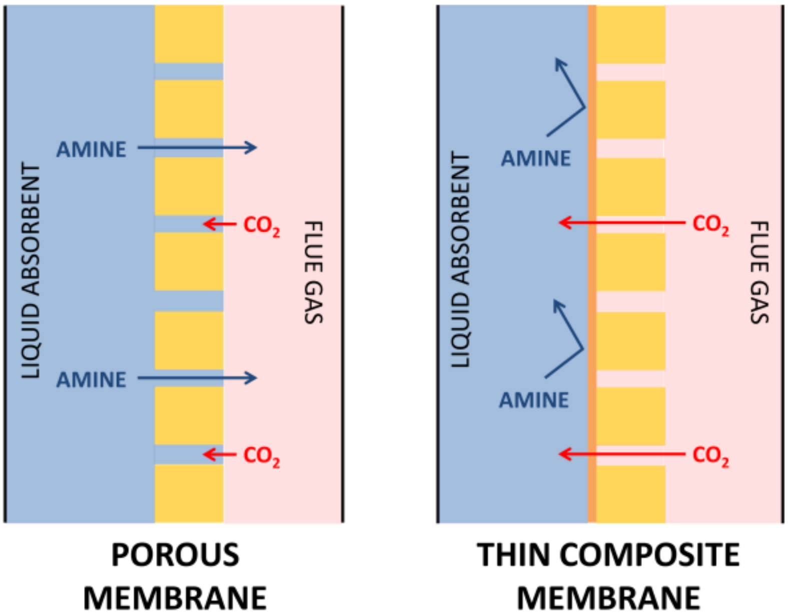

Fig 1 – Membrane contactor schematic representation using porous membranes or thin composite membranes as the interface between the liquid absorbent and flue gas.

A few literatures on non-porous membrane contactors have been published in recent years, but most of them only reported the CO_2 mass transfer coefficient or the CO_2 removal efficiency of the membrane contactors, and mainly focused on the MEA-based absorbents. To the best of the authors' knowledge, amine evaporation from the liquid phase to the vapor phase through a dense membrane layer has never been documented. In this work, amine evaporation through a thin, dense membrane layer has been investigated for the first time. In a membrane contactor the dense layer is in direct contact with the liquid phase, thus amine pervaporation tests were used to investigate the amine permeation, as they are closer to the real membrane contactor configuration compared with the permeation of amines in vapor phase. In addition, vapor and liquid permeation through the AF polymer family has been reported to differ [34]. The large kinetic size of amine molecules and their low concentration in the aqueous solution results in a low amine flux through the membrane. Therefore, pervaporation tests have been run for up to 5 days under the same experimental conditions in order to ensure the correctness of the results.

In the present paper, in addition to the MEA solutions, some promising but highly volatile absorbents based on DEEA-MAPA blends were tested in the membrane contactors to represent a group of very volatile and aggressive absorbents. The compatibility tests in our early work [35] indicated that compared with MEA-based absorbents, the DEEA-MAPA blends required superior stability for the membrane interface, and the Teflon AF series appeared to be the most suitable choice for these absorbents. This family of polymers (e.g., AF1600 and AF2400) owns a high free volume, but compared with other known high free volume polymers (such as PTMSP), it has been reported to suffer less from physical aging [29, 36, 37], making it particularly attractive for long-term operations. Both AF1600 and AF2400 have been reported as a dense layer for membrane contactor applications using MEA-based solutions with good separation performance [16, 28, 29]. In particular, their rigidity associated with their glassy nature makes them attractive for separating light gases from long chain molecules [38].

In this work amine pervaporation tests through Teflon AF2400 were carried out, and the amine flux and permeability through the membrane were quantified for different absorbents. Humid CO_2 permeation tests were also performed to give a comparison of the expected CO_2

flux with that of the amines under the same conditions, which reflects the ability of the membrane to favor CO_2 transport over that of the amines. The characterization was carried out at a wide range of operative temperatures (25 – 60 °C) considered suitable for the CO_2 absorption step.

2. Experimental

2.1. Materials

The Teflon AF2400 (amorphous copolymer, T_g = 240 °C) was purchased from Chemours Company (Wilmington, US); the FC-72 fluorosolvent was purchased from 3M (Kemi-Intressen, Sweden). The diethylethanolamine (DEEA, > 99% purity), 3-methylaminopropylamine (MAPA, > 97% purity) and monoethanolamine (MEA, > 98% purity) were purchased from Sigma Aldrich. All the solvents were used with no further purification. Deionized water was used for the liquid mixture preparation. The certified N_2/CO_2 gas cylinder (90 vol% N_2, 10 vol% CO_2) and pure CH_4 (grade 3.5) were supplied by AGA Gas (AGA Gas Norge, Oslo, Norway).

2.2. Sample preparation

The free-standing polymeric films of Teflon AF2400 were prepared using the solvent evaporation method. In particular, the polymer was dissolved in an FC-72 fluorosolvent (boiling point = 56 °C) in order to achieve a 1 wt% solution, and stirred overnight until a clear polymer solution was obtained. The solution was subsequently poured into a levelled glass petri dish and stored inside a fume hood overnight. The samples were then removed from the petri dish using a few water droplets and subsequently treated at 200 °C under vacuum conditions for 24h in order to completely remove the solvent. The membrane thickness was measured after the heat treatment procedure using a micrometer (Mituyoto Digimatic Indicator ID-H), and was found to be within the range of 10 – 20 µm.

The absorbent solutions were prepared by mixing different ratios of DEEA and MAPA with H_2O to achieve different molar concentrations of amines. In particular, 1 M DEEA 5 M MAPA (subsequently referred to as 1D5M), 3 M DEEA 3 M MAPA (3D3M) and 5M DEEA 1 M MAPA (5D1M) were prepared according to a previously reported procedure [39]. The 5 M MEA aqueous solutions were prepared and used as a reference for the CO_2 absorbents. The molar compositions of the absorbents are reported in Table 2. The contact angle between the AF2400 film and all the liquid solutions used in the present work has been reported in our prior publication [35].

Table 2 – Molar fraction (*x*) of the different absorbents considered in the study.

	x_{H_2O}	x_{MEA}	x_{MAPA}	x_{DEEA}
5M MEA	0.889	0.111	-	-
1D5M	0.762	-	0.199	0.040
3D3M	0.728	-	0.136	0.136
5D1M	0.684	-	0.053	0.264

2.3. Pervaporation tests

The permeation of the liquid absorbents through the Teflon AF2400 membrane was tested using a homemade pervaporation setup. A diagram of the design is shown in Figure 2. The sample holder was placed inside a heating cabinet and the feed solution was continuously recirculated on top of the membrane using a magnetic gear pump with a suction-shoe design (GA Series, Micropump). The liquid flow was set to 100 ml/min, which is much higher than the transmembrane flux measured in the experiments, and thus able to ensure a constant concentration of the liquid at the liquid-membrane interface. Two heating coils were placed inside the heated cabinet before the sample holder in order to ensure that the liquid was able to reach the temperature of the cabinet. The liquid temperature was measured with a thermocouple and the port was placed next to the sample holder. The pressure on the liquid side was monitored with a pressure indicator (Wika, S-10) and kept at a constant atmospheric pressure. On the downstream side of the membrane, a vacuum was continuously pulled using a diaphragm pump (MD-4C-NT, Vacuubrand) to maintain a stable vacuum pressure of 3 – 4 mbar. The pressure on the downstream branch was monitored with an absolute pressure gauge (Type 626, 100 mbar, Baratron MKS). The permeate was collected inside a homemade glass trap (sampling LN_2 trap) cooled with liquid nitrogen (LN_2), whereas another cold trap (safety LN_2 trap, KF54V, KGW Isotherm) was used to protect the pump and prevent the release of amines during the test.

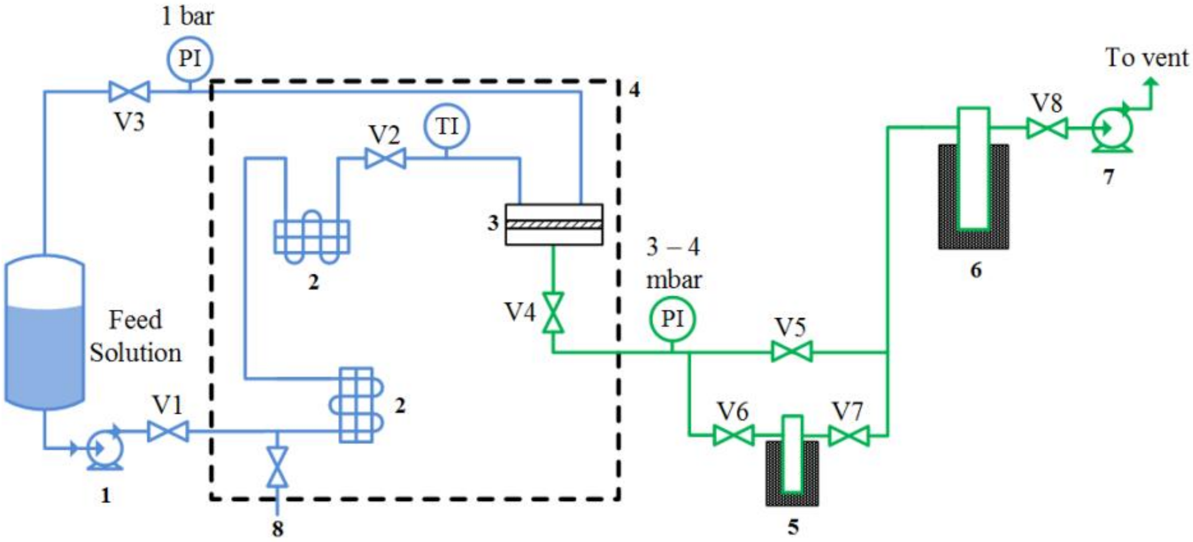

Fig 2 – Pervaporation setup (1: Liquid pump; 2: Heating coil; 3: Membrane module; 4: Heated cabinet; 5: Sampling LN_2 trap; 6: Safety LN_2 trap; 7: Vacuum pump; 8: Liquid purge).

In a typical test the liquid is recirculated on top of the membrane overnight in order to achieve steady state conditions, bypassing the sampling LN_2 trap (V5 open, V6 and V7 closed). Subsequently, the permeate stream is forced through the sampling glass (V6 and V7 open, V5 closed) and collected for a certain period of time. Depending on the operating conditions, a single test duration varied between 4 and 10 h. The sampling glass is measured before and after the experiment using an analytical balance (AB204-S/Fact, Mettler Toledo, readability 10^{-4} g) in order to quantify the amount of permeate. For a given liquid composition and temperature conditions, 5 repetitions were carried out in order to ensure the achievement of steady state conditions. Initially, a test was carried out using water as a liquid phase in order to verify the ability of the sampling trap to avoid sample losses during the experiment. The test was performed by placing two consecutive sampling traps on the vacuum line during 3 different pervaporation experiments. The losses were quantified in an amount lower than 2 % of the sample collected in the main trap.

Once all the data have been collected, the molar transmembrane flux per unit area (J_i, mol/(h cm^2)) of the *i*-th penetrant are calculated as:

$$J_i = \frac{m_{perm} \cdot w_{perm,i}}{A \cdot MW_i} \tag{1}$$

where $\dot{m}_{perm}$ is the total permeate mass flow (g/h), $w_{perm,i}$ is the mass ratio of the *i*-th penetrant, A is the membrane area (cm^2) and MW_i is the molecular weight (g/mol). Subsequently, the permeability (P_i, *Barrer*) can also be calculated according to:

$$P_i = \frac{J_i \cdot \ell}{(p_{i,up} - p_{i,down})} \tag{2}$$

$$p_{i,up} - p_{i,down} = (\gamma_i(T, x_i) \cdot p_i(T) \cdot x_i) - (p_{down} \cdot y_i) \tag{3}$$

where ℓ is the membrane thickness (cm), while $p_{i,up}$ and $p_{i,down}$ are the partial pressure of the *i*-th component on the upstream (or liquid feed) side of the membrane and on the downstream side (Pa), respectively. The upstream partial pressure is calculated as the pressure of the *i*-th component in equilibrium with the liquid mixture, considering the activity coefficient $\gamma_i (T,x_i)$, the saturation pressure at the given temperature $p_i^*(T)$ and the concentration in the liquid x_i. The downstream partial pressure is calculated as the overall downstream pressure p_{down} and the molar concentration of the *i*-th component in the permeate, as measured from the amine concentration analysis. The saturation pressures for the organic components are calculated according to the Antoine equation using the parameters reported in Table 3.

Table 3 – Antoine equation coefficients for MEA, DEEA and MAPA.

	A	***B***	***C***	***Ref***
MEA[a]	7.8709	1819.8	194.62	[40]
DEEA[b]	13.92	3198	-89.9	[32]
MAPA[b]	14.86	3530.43	-67.82	[32]

[a] $ln(p^*) = A - B/(C + T)$ p in Torr, T in K
[b] $log(p^*) = A - B/(C + T)$ p in kPa, T in °C

In the case of MEA, the permeate samples obtained from every single pervaporation test were analyzed through titration analysis (Metrohm 702 SM Titrino) to determine the amine concentration. In the case of the DEEA-MAPA blends, the permeate samples were analyzed by Ion Chromatography (Thermo Scientific Dionex ICS-5000) in order to measure the concentration of every single amine in the permeate stream (DEEA and MAPA). In addition, titration was performed on some samples to confirm the results obtained from IC and to minimize errors. As at room temperature the permeate samples collected after a reasonable experimental interval was too small to be analyzed with IC, the temperature range was fixed within 40 and 60 °C. More information on the instruments and methods used to determine the amine concentration can be found in [41, 42].

2.4. Gas permeation tests

According to theory, in a membrane contactor where chemical absorbents are used as the liquid phase, the main mass transfer resistance is placed in the membrane [22]. In particular, if a thin composite membrane is used as the interface between the liquid and gas, the dense coating is believed to offer a major contribution to the resistance to the mass transfer. In this way the CO_2 permeability of the polymer chosen as the dense layer is a crucial parameter for the design of the membrane contactor [28]. For this reason the effect related to the presence of water vapor in the AF2400 matrix on the CO_2 permeability was investigated using the system reported in Figure 3 [43]. The membrane was placed inside a sample holder and continuously flushed with a gaseous stream. A calibrated CO_2/N_2 (10/90) cylinder was used to supply the feed gas, whereas pure CH_4 was used as the sweep gas. The pressures were kept constant at 1.6 bar for the feed side and at 1.05 bar for the sweep side for all the experiments. The feed and sweep flows were set at 400 ml/min and 100 ml/min. The value of the feed flow was chosen in order to have negligible differences between the gas composition of the feed and the retentate stream.

The permeability (P_i) of the i-th component was measured using the following formula:

$$P_i = \frac{N_{perm} \cdot (1 - y_{H_2O}) \cdot y_i \cdot l}{A \cdot (\langle p_{i,feed} \, , \; p_{i,ret} \rangle - p_{i,perm})} \tag{4}$$

where N_{perm} is the total permeate flow measured with the bubble flow meter (mol/s), y_{H_2O} is the molar fraction of the water in the permeate flow calculated according to the RH value and the vapor pressure at the given temperature, y_i is the molar fraction of the i-th penetrant in the permeate as measured through the GC, ℓ is the membrane thickness (cm), A is the permeation area (cm^2), and $p_{i,feed}$, $p_{i,ret}$ and $p_{i,perm}$ are the partial pressure of the i-th component in the feed, retentate and permeate (Pa), respectively.

All the permeability coefficients are reported in Barrer (1 Barrer = 3.348×10^{-16} mol/(m s Pa)).

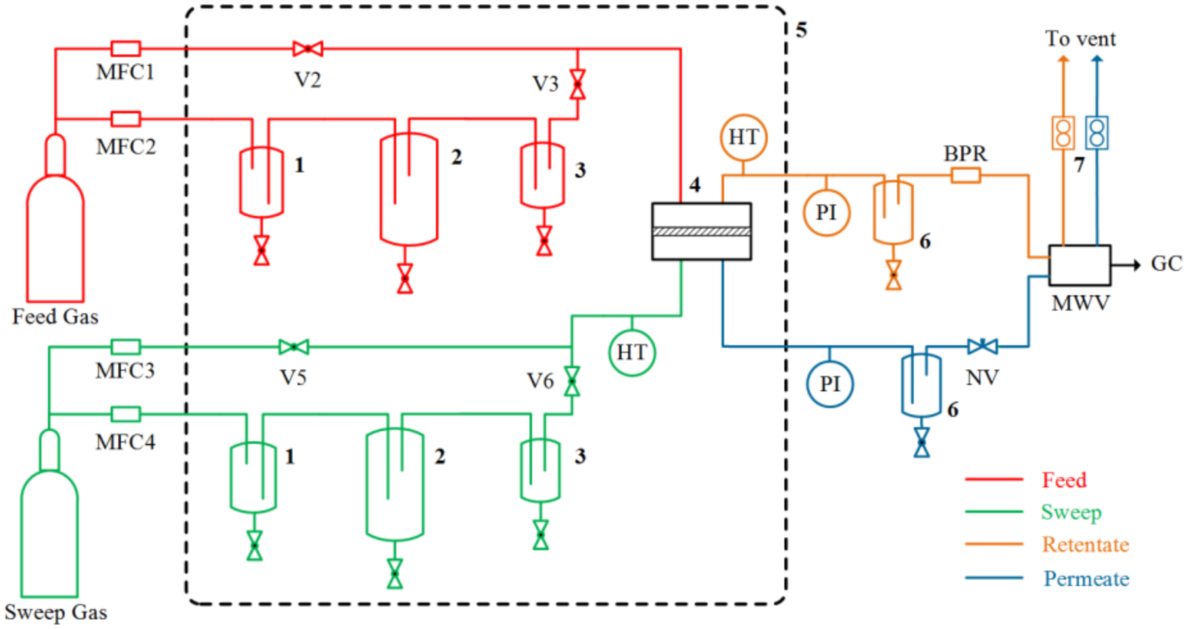

Fig 3 – Mixed gas permeation rig (1: MFC-safety trap; 2: Humidifier; 3: Droplet trap; 4: Membrane module; 5: Heated cabinet; 6: Water knockout; 7: Bubble flowmeters; MFC: mass flow controller; NV: Needle valve; BPR: Back pressure regulator; PI: Pressure indicator; HT: Humidity and temperature sensor; MWV: Multi-way valve; GC: Gas chromatograph).

Furthermore, the literature data show that the effect of water vapor on the gas permeability of polymeric membranes is strictly related to the vapor sorption [44]. Therefore, to better understand the effect of vapor on CO_2 permeation across the membrane layer, sorption experiments were carried out using a pressure decay setup that is frequently reported in the literature [45, 46]. With this technique the mass uptake is evaluated by measuring the pressure decrease associated with the uptake in a calibrated volume. The pressure is monitored using an absolute pressure gauge (Type A122, 100 mbar, Baratron MKS). The system is placed inside a cabinet equipped with a temperature control system. Initially, the sample is evacuated in order to ensure the removal of the dissolved penetrants. Subsequently, a certain amount of vapor is expanded into the sample chamber, and the pressure decrease is monitored until the equilibrium conditions are reached, thus allowing the calculation of the uptake.

2.5. CO_2/amine transport selectivity

According to the results obtained from the humid permeation experiments and the pervaporation tests for the liquid absorbents, it is possible to evaluate the ability of the membrane to favor the CO_2 permeation over that of the organic penetrants. It must be considered that the amine flux and the CO_2 permeation take place counter-currently across the membrane, and different driving forces apply. For this reason, the typical selectivity characterizing gas separation membranes cannot be used, and a new term 'CO_2/Amine Transport Selectivity' (α) has thus been defined. This quantity describes the extent to which the membrane selectively allows the transport of CO_2 compared to amines, and is defined as the ratio between fluxes of CO_2 and amine (which take place counter-currently) in the given process conditions. Therefore, it is calculated as the ratio of the fluxes of CO_2 and amines, according to the following equation:

$$\alpha(T) = \frac{J_{CO_2}(T)}{\sum_j J_j(T)} = \frac{P_{CO_2}(RH,T)\cdot\Delta p_{CO_2}}{\sum_j P_j(T,x_j)\cdot\Delta p_j} \tag{5}$$

$$\Delta p_{CO_2} = 0.13\ bar, \quad \Delta p_j = \left(\gamma_j(T,x_j)\cdot p_j(T)\cdot x_j\right) \tag{6}$$

where the index *j* refers to the amine components present in the liquid absorbent (MEA for the 5M MEA, DEEA and MAPA for the phase change solvent blends). The CO_2 driving force (Δp_{CO_2}) is calculated assuming a flue gas with a CO_2 concentration of 13 vol% released at atmospheric pressure, which represents the driving force in real process conditions. If different process conditions are used, the transport selectivity value will be consequently changed. In the case of amines, the permeability value is the one measured in the pervaporation tests of the amine-based mixtures and the driving force corresponds to the partial pressure of the amine in the equilibrium with the liquid solution at the given temperature condition. Therefore, the proposed quantity describes a property of the material that is valid for a process with a low stage cut.

3. Results and discussion

3.1. Pervaporation of liquid absorbents

In order to investigate the amine transport through the Teflon AF2400, pervaporation tests were carried out on a 10 µm-thick self-standing membrane sample using pure H_2O, 5M MEA and different DEEA-MAPA blends. All the liquids were used unloaded (i.e., no CO_2 was absorbed). The pervaporation tests of all the samples were performed over 5 days of continuous operation, thus ensuring the achievement of a real steady state.

3.1.1 Water permeation

Figure 4 shows the water vapor flux and permeability for the 5 different liquids considered in this study, within a temperature range from room temperature to 60 °C. At room temperature, the H_2O permeability was measured as being equal to 3985 Barrer, similar to the value reported in the AF2400 datasheet from the producer. On increasing the temperature to 40 and 60 °C the fluxes increase exponentially. This is related to the enhancement of the driving force of the penetrant with the increase in temperature, due to the exponentially increased saturation pressure of the penetrant. Nevertheless, the permeability coefficient showed an opposite trend compared with the flux, with values of 2771 and 2292 Barrer obtained at 40 and 60 °C, respectively. This clearly suggests that that the flux increases to a less extent if compared with the enhancement of the driving force, likely due to the fact that the solubility coefficient plays a major role in the H_2O permeation in the Teflon AF2400. In view of the high free volume of the membrane matrix, the diffusion of the penetrants with a small kinetic size (such as H_2O) is not hindered by the glassy nature of the AF2400, therefore it is reasonable to assume that an increase in temperature has a limited effect on the diffusion coefficient.

For the sake of completeness, the pure H_2O value measured in this work at room temperature is slightly different from the one reported in our prior work [35], but this difference is believed to be related to the different experimental conditions. In particular, the use of dynamic rather than static conditions for the liquid feed can affect the performance: the dynamic conditions in the current work ensure better contact between the liquid and membrane, and reduce possible temperature drops at the liquid membrane interface due to water evaporation.

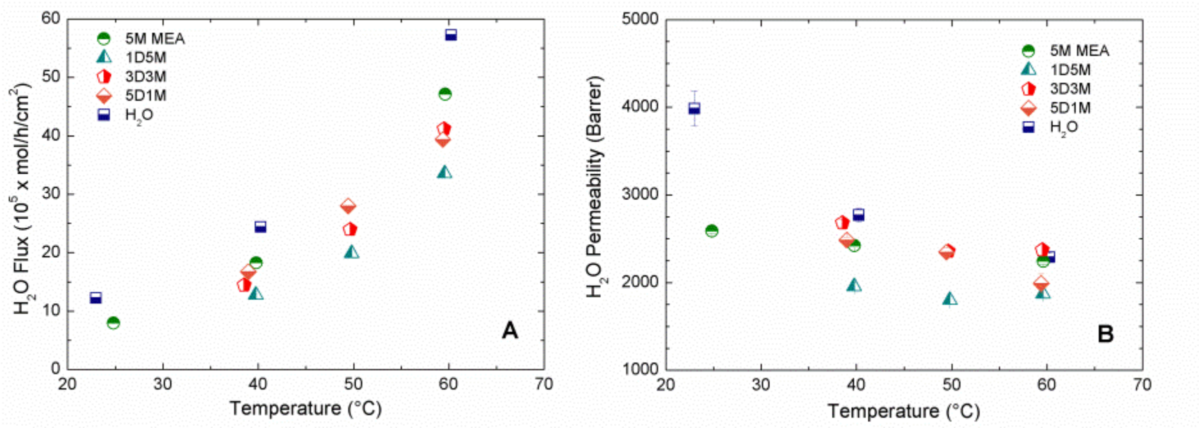

Fig 4 – H_2O flux (A) and permeability (B) obtained from pervaporation experiments for pure H_2O and various absorbents (5M MEA, 1D5M, 3D3M and 5D1M) at different temperatures.

When the 5M MEA solution was tested as a liquid absorbent, a lower water flux was observed as compared with the one obtained for pure H_2O, throughout the entire temperature range. This effect may be attributed to the lower water concentration in the liquid and to the reduced activity coefficient (Table 4). However, the lower H_2O permeability compared with that of the pure H_2O clearly suggests that other phenomena took place. One possible explanation could be related to the competitive sorption between the MEA molecules and H_2O molecules inside the membrane matrix. Furthermore, amine aqueous solutions are non-ideal solvents, where the molecules interactions can have a significant effect on the sorption and diffusion across the membrane layer. Similar to this observation, it has been reported that the diffusion coefficients of some low molecular weight alcohols in AF2400 decrease with the penetrant concentration in the polymer matrix, the main reason being related to their tendency to form clusters that hinder the molecule diffusion through the highly hydrophobic matrix [47]. However, this effect becomes less important at higher temperatures, and at 60°C the H_2O permeability for the pure component and that in the MEA-based mixture are found to be similar.

Table 4 – Liquid molar composition (x), H_2O and MEA activity coefficient (γ) of the 5M MEA solution. The activity coefficient was calculated through the NRLT model using the literature parameters [48].

	25 °C	40 °C	60 °C
γ_{H2O}	0.991	0.990	0.990
γ_{MEA}	0.319	0.365	0.421

A further decrease in the H_2O flux can be observed in the case of the DEEA-MAPA blend aqueous solutions, which can be related to the lower water molar fraction in the liquids (Table 2) and to the H_2O activity coefficient (Table 5). For the highest concentration of MAPA in the solvent mixtures the lowest water transmembrane flux has been detected, whereas minor changes can be observed for the other two solvent compositions. Despite the fact that in the case of 1D5M the water molar fraction is higher compared with the other compositions, the activity coefficients appeared to be always below 0.89, thus affecting the driving force of the water transport. In the case of the permeability, the values appeared to be lower compared with that of the pure H_2O, but in the case of 3D3M and 5D1M the values appeared similar to the one obtained for MEA. Only in the case of 1D5M does the H_2O permeability remain constantly below 2000 Barrer. DEEA-MAPA blends are non-ideal solutions where clustering may take place [49, 50], which consequently affects the permeation of water molecules across the membrane layer.

Table 5 – H_2O, DEEA and MAPA activity coefficient (γ) and total pressure (p_{tot}) of the DEEA-MAPA blends considered (1D5M, 3D3M, 5D1M) within the temperature range 40 – 60 °C. The activity coefficient was calculated through the UNIQUAC model according to the literature parameters [32].

	1D5M			3D3M			5D1M		
	40 °C	50 °C	60 °C	40 °C	50 °C	60 °C	40 °C	50 °C	60 °C
γ_{H_2O}	0.8331	0.8592	0.8834	0.9558	0.9885	1.0181	1.143	1.1802	1.2126
γ_{DEEA}	5.6613	5.6298	5.5696	2.5034	2.4928	2.4737	1.4598	1.4766	1.4891
γ_{MAPA}	0.1795	0.221	0.2679	0.1489	0.1808	0.217	0.1215	0.1444	0.1704
p_{tot} (mbar)	49.4	85.6	142.8	54.4	94.5	157.7	60.5	104.9	174.6

3.1.2 Amine permeation

Figure 5, 6 and 7 report the results obtained in terms of flux (A) and permeability (B) of the different amines and amine solutions considered in the liquid phase. For all the amines the flux was detected to be three orders of magnitude lower compared with that of water (Figure 4), which is probably related to two aspects: the lower amine concentration (Table 2) and the larger kinetic size of amines compared with H_2O. The first factor directly affects the driving force of the permeation, whereas the second one influences the ability of the amine molecules to diffuse across the dense layer. In particular, within the rigid molecular chains of glassy polymers, the larger the kinetic size of the penetrant, the larger the energy requirement to overcome the transport barrier. Similar to the H_2O case, the fluxes of all amines increase at increasing operating temperature due to the increase of the driving forces with temperature. For example, the MEA flux (Figure 5A) shows an 8-fold variation within the tested temperature range.

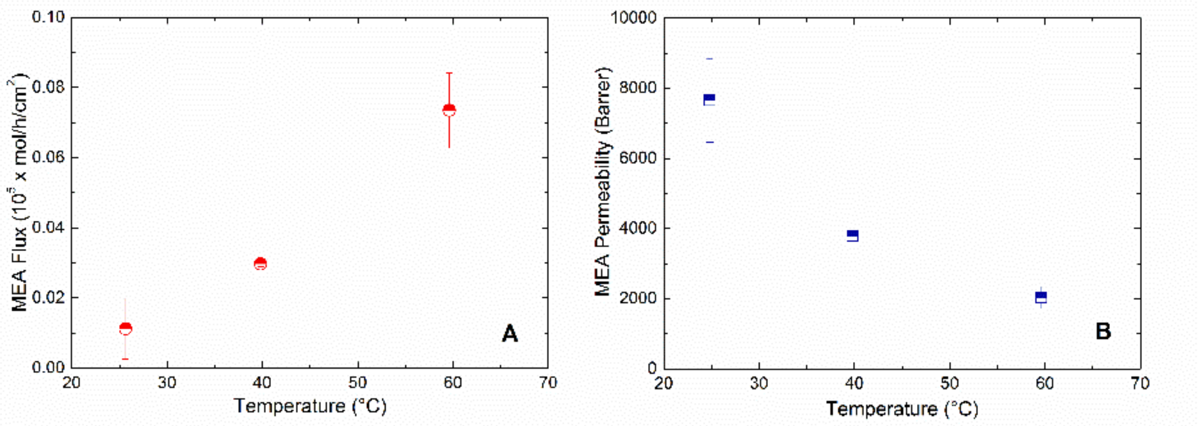

Fig 5 – MEA flux (A) and permeability (B) obtained from pervaporation experiments using 5M MEA as a liquid feed at various temperatures.

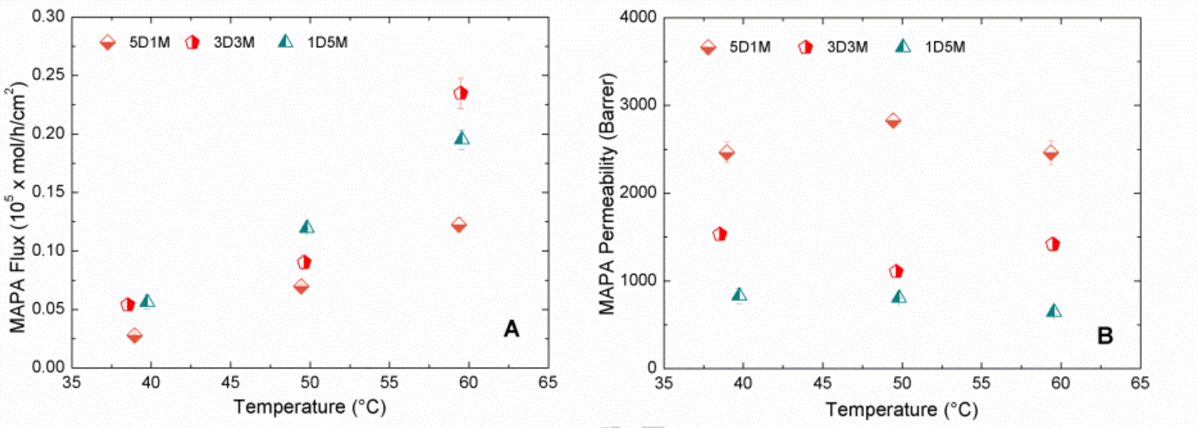

Fig 6 – MAPA flux (A) and permeability (B) obtained from the pervaporation experiments using various DEEA-MAPA blends as a liquid feed at various temperatures.

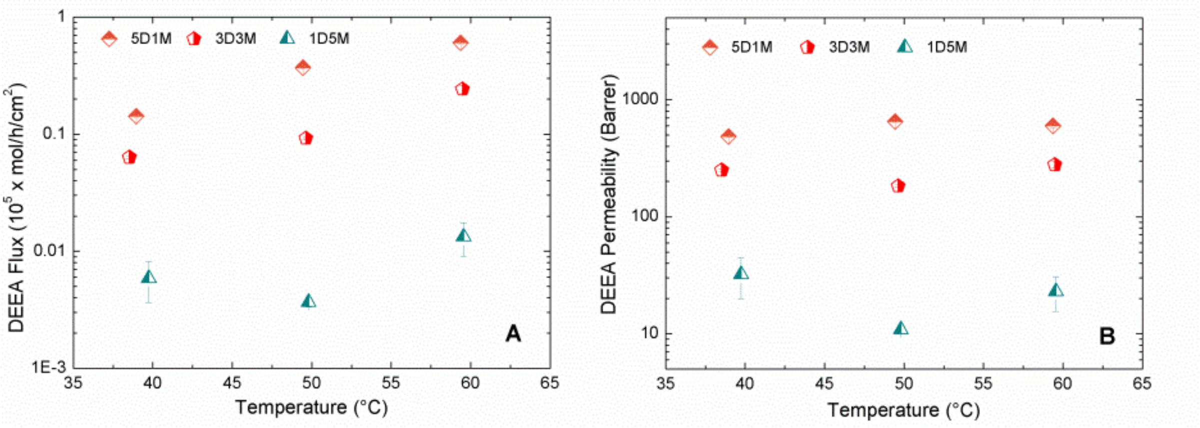

Fig 7 – DEEA flux (A) and permeability (B) obtained from the pervaporation experiments using various DEEA-MAPA blends as a liquid feed at various temperatures.

As shown in Figure 6A, the MAPA flux increases along with both the temperature and the concentration of the amine in the liquid feed, and both factors are believed to be resulted from the increase in the driving force, with the effect of temperature appearing to be more significant.

DEEA is the most volatile compound among the amines investigated in the present work, and is characterized to have a large activity coefficient (see Table 5) when mixed with water [32]. As can be observed in Figure 7, the DEEA transport properties are strongly affected by the amine concentration in the liquid feed, with more notable variations compared with those observed in the above-mentioned penetrants. The DEEA flux (Figure 7A) is shown to be one order of magnitude lower than MAPA and MEA for the low DEEA concentration (x_{DEEA} = 0.04 mol/mol$_{tot}$), but the values become similar for DEEA of higher concentrations. As shown in the figure, the increase in the operating temperature still has a positive effect on the DEEA transport across the membrane layer, but it is less significant compared with the effects associated with the change of amine concentrations.

The MEA permeability coefficient value of 7656 Barrer was obtained at room temperature, but a drop to 3795 and 2032 Barrer was observed at 40 and 60 °C, respectively. This is believed to be related to the solubility coefficient, which plays a dominant role in the MEA permeation across the dense layer. Interestingly, a different effect is observed for the permeability of MAPA (Figure 6B) and DEEA (Figure 7B), as the temperature showed a negligible impact on the permeation coefficient for all the DEEA-MAPA blends tested. The solubility decrease was probably compensated by the increase in the diffusion coefficient, considering the much larger kinetic size of these amines. In the case of 1D5M, the MAPA permeability was within the range 646 – 830 Barrer, increasing to 1108 – 1531 for 3D3M, and to 2464 – 2826 for 5D1M. The results obtained in terms of permeability were also within the same range of the value obtained for pure MAPA (1320 Barrer [35]) at room temperature.

In the case of DEEA, the amine concentration played a much stronger role in the determination of its permeation coefficient. For 1D5M, the DEEA permeability is within the range 11 – 32 Barrer, which is increased to 183 – 278 Barrer for 3D3M and to 484 – 650 Barrer for 5D1M. The permeability trend with the DEEA concentration in the liquid feed identified in the present work is also consistent with the value obtained for pure DEEA (1440 Barrer [35]) in room temperature conditions in our previous work.

3.2. CO_2 permeation under humid conditions

The CO_2 permeability of the polymer used as a coating layer material is an important parameter for the non-porous membrane contactor, as it is expected to be the main mass transfer resistance for the CO_2 transport. Competitive sorption phenomena will likely take place between CO_2 and compounds from the liquid absorbents, which may lead to a decrease in the gas permeability coefficient [44, 51]. For this reason, the CO_2 permeability under different operating conditions (25 to 60 °C) within the entire relative humidity range has been investigated, as shown in Table 6. According to the literature [52], the CO_2 permeability of the Teflon AF2400 is greater than the majority of glassy polymers in view of its high free volume. At room temperature and in dry conditions, a value of 4115 Barrer was obtained in our test, similar to the values reported in the literature [52]. However, the N_2 permeability was also high (1290 Barrer), resulting in a selectivity value not attractive for direct CO_2/N_2 separation. As can be seen in Table 6, by increasing the operating temperature the CO_2 permeability decreases markedly (3313 and 2495 Barrer at 40 and 60 °C, respectively), suggesting that the solubility of the penetrant is dominating in the CO_2 permeation, as in the case of H_2O and MEA. Similar trends were also observed for the N_2 permeation. According to these results, the activation energy of the permeation is negative, and the value for CO_2 (-11.1 kJ/mol) is determined. Despite the high hydrophobicity of the polymer, the water vapor had an effect on the gas transport. At room temperature, the permeability coefficient decreased with the increasing relative humidity of both the feed and sweep gas, with an overall reduction of 7% in the dry value at the maximum RH (Figure 8). A similar effect has also been reported for the other polymer in the AF series, the AF1600 [53].

On increasing the operating temperature to 40 and 60 °C, the effect of water became more evident, determining a drop of 15% and 25% with respect to the dry value, respectively. The explanation for this may be related to the competitive sorption of water in the free volume of the polymer, which acts to the detriment of the ability of CO_2 to solubilize in the matrix. However, the variation is rather limited, especially if compared with other hydrophobic polymers, such as polyimides [44, 51], fluorinated polymers [54] and polymers of intrinsic microporosity (PIM) [55], where the reduction can be higher than 50% of the dry value in a high humidity region.

Table 6 – Gas permeability coefficient and activation energy of the permeation process (E_a) obtained for a Teflon AF2400 self-standing membrane (upstream total pressure 1.6 bar, gas composition: 10 vol% CO_2 in N_2)

	P CO_2 (Barrer)				***P N_2 (Barrer)***			
RH (%)	***23 °C***	***40 °C***	***60 °C***	***E_a (kJ/mol)***	***23 °C***	***40 °C***	***60 °C***	***E_a (kJ/mol)***
0	4115	3313	2495	-11.1	1290	1040	797	-10.7
30	4065	3106	2339	-12.3	1264	969	768	-11.0
60	4009	3032	2121	-14.1	1206	937	705	-11.9
95	3827	2816	1871	-15.9	1095	809	579	-14.1

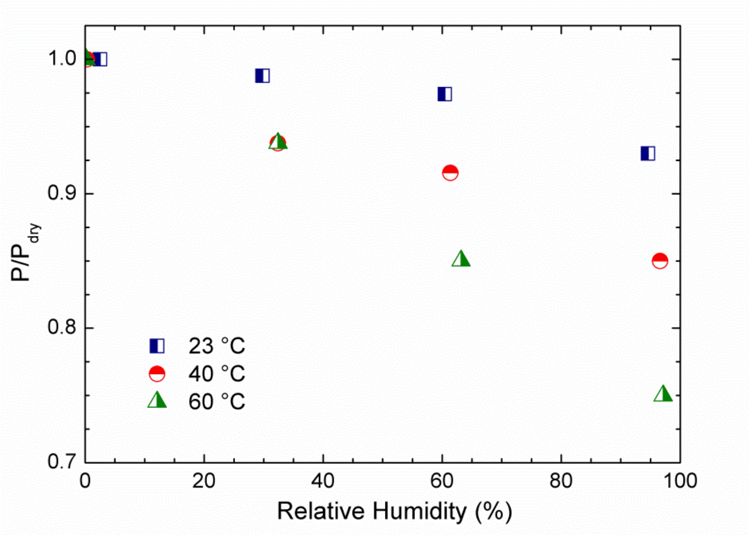

Fig 8 – Relative variation of CO_2 permeability at different RH compared to the dry value (P_{dry}). For the numerical values refer to Table 2.

The limited reduction in CO_2 permeability in the presence of water vapor suggests that it would be possible to operate with a humid flue gas stream with no significant effect on the overall mass transfer resistance in the membrane phase. In this way, problems related to the dehydration of the solvents can be avoided, as the presence of water vapor in the flue gas would consistently reduce the driving force of the H_2O permeation and suppress the H_2O evaporation from the liquid phase.

3.3. Sorption test

In order to have a better idea of the possibility effect of H_2O or amine sorption in the AF2400 matrix, sorption tests of pure vapors (H_2O, DEEA and MAPA) were performed using a pressure decay technique. The results are reported in Figure 9. The water uptake is extremely low throughout the entire activity range, which is in agreement with the high hydrophobicity of the polymer. If compared with other hydrophobic polymers (e.g., polyimides [44, 54, 56], polymerized ionic liquids [57], poly(methyl methacrylate) [58]), the concentration of water in the polymer matrix is one order of magnitude lower. The MAPA appeared to be more soluble than the DEEA, but they both showed a similar uptake compared to water, suggesting that they tend to occupy a similar part of the fractional free volume of the polymer if a similar activity is considered. The concentration measured for both the DEEA and MAPA is found to be rather low if compared with non-polar organic compounds (e.g., toluene, acetone, chloroform [29]), but within the same range of the one measured for lower alcohols (methanol, ethanol [29]), suggesting that the hydrophobic nature of AF2400 limits the uptake of hydrophilic penetrants. Finally, the limited uptake obtained for the considered penetrants also confirms the negligible weight variation observed after the immersion of the AF2400 samples in pure liquids [35].

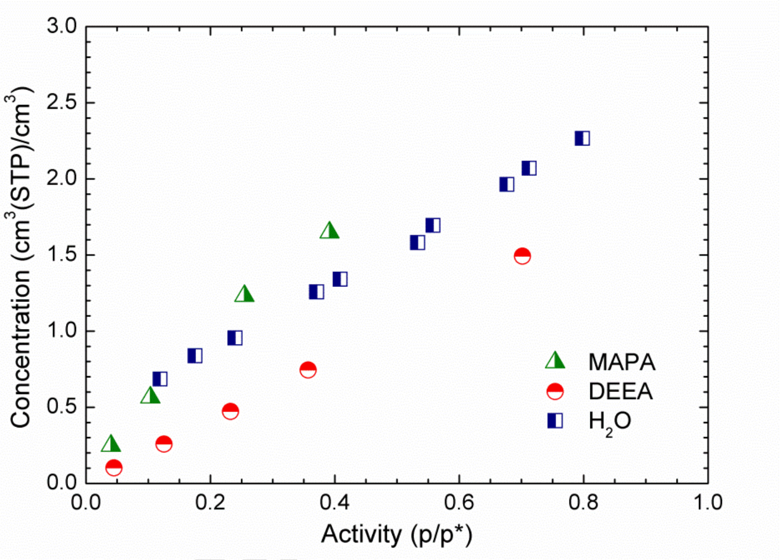

Fig 9 – Uptake of pure H_2O, DEEA and MAPA in the Teflon AF2400 at 35 °C.

3.4. CO_2/amine transport selectivity

In order to prevent amine evaporation in a membrane contactor, the major requirement for the membrane interface is to minimize amine transport towards the gas phase without enhancing the additional CO_2 mass transfer resistance. For this reason the term 'CO_2/amine transport selectivity' is defined and given as Equation 5. To have a realistic estimation of the CO_2 transmembrane flux in real process conditions, the influence of relative humidity on CO_2 permeability was taken into account. In particular, in order to prevent the solvent dehydrating, we opted to work with a wet flue gas stream, where the partial pressure of the water corresponds to the value at the equilibrium with the liquid absorbent, thus preventing any water flux through the membrane. Therefore, the CO_2 permeability value was chosen according to the variations reported in Figure 8 in the various operating conditions. This concept is summarized in Equation 7:

$$J_{CO_2} = f\left[P_{CO_2}(RH,T)\right], \qquad RH = \frac{p_{H_2O}(x_L,T)}{p^*_{H_2O}(T)} \tag{7}$$

where x_L refers to the liquid composition (5M MEA or DEEA-MAPA blends), and $p_{H_2O}(x_L ,T)$ is the partial pressure of the water in equilibrium with the liquid absorbent for the given liquid composition and temperature. The presence of amines should play a minor role in the CO_2 permeation, in view of the low uptake shown in Figure 9.

Figure 10 shows the results obtained when 5M MEA is used as the liquid feed. At room temperature the CO_2/amine transport selectivity is close to 6000, suggesting that the membrane strongly favors CO_2 transport over that of amines. However, the increase in the operating temperature corresponds to an exponential decrease in this parameter, which reaches a value of 1650 and 428 at 40 and 60 °C, respectively. This is related to the fact that the temperature increase has a negative impact on CO_2 permeability and does not correspond to any enhancement of the driving force, thus decreasing the transmembrane flux. On the other hand, the MEA flux increases along with the operating temperature, despite the decrease in the permeability coefficient (Figure 5). The combination of these two effects generates a sharp decrease in the CO_2/amine transport selectivity, suggesting that the ability of the membrane to prevent amine evaporation will be reduced at higher temperatures.

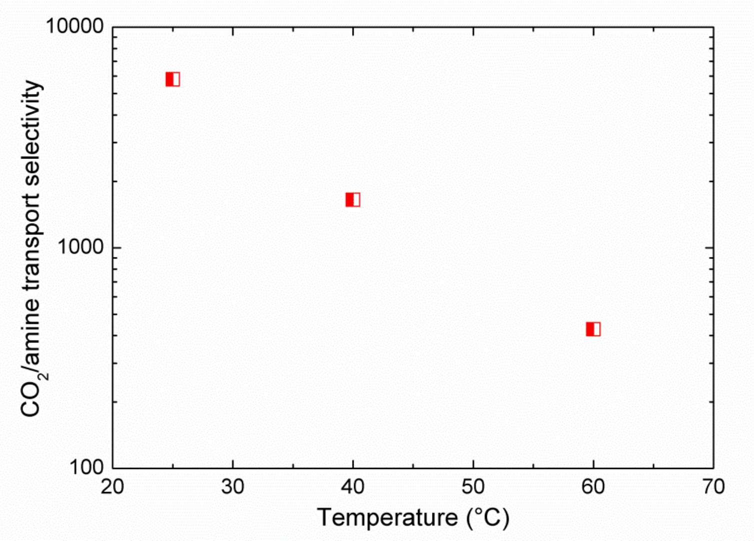

Fig 10 – CO_2/amine transport selectivity offered by the Teflon AF2400 at various temperatures when 5M MEA is considered as a liquid absorbent.

Figure 11 shows the CO_2/amine transport selectivity with various DEEA-MAPA blends as liquid absorbents. In view of the greater volatility of the solvents based on DEEA and MAPA and the higher amine concentration, the CO_2/amine transport selectivity appears to be lower than that of the 5M MEA for all of the three different liquid compositions considered in this work. In addition, the larger the amount of the most volatile amine (i.e., DEEA), the less the ability of the membrane to favor CO_2 transport over amines. At 40 °C a CO_2/amine transport selectivity of 776 is obtained for 1D5M, which decreases to 406 and 276 in the cases of 3D3M and 5D1M, respectively. Furthermore, similar to the MEA case, the parameter is negatively affected by the increase in the operating temperature. In this case, the permeability coefficient of both amines appears to be negligibly affected by temperature, meaning that a greater enhancement of the flux takes place at higher operating temperatures. At 60 °C, the CO_2/amine transport selectivity showed a value higher than 100 (161) only for 1D5M, whereas values of 69 and 44 were obtained in the cases of 3D3M and 5D1M, respectively. Furthermore, better selectivity was obtained with respect to the values calculated from the permeation of pure components at room temperature [35]. This is mainly related to the fact that amine-based aqueous solutions are systems that are far from ideal, and for this reason their behavior is difficult to predict, even for the properties of pure compounds.

From the present results it is clear that for the membrane contactor, operating at lower temperatures is preferable to limit amine evaporation, suggesting a trade-off between the optimum operating conditions for the CO_2 absorbent and to prevent amine evaporation by using the membrane contactor. However, we expect that differences can arise in terms of CO_2 permeation through the thin composite membrane between a gas separation operation or a membrane contactor operation, perhaps due to pore condensation in the porous support [29]. Therefore, membrane contactor tests using phase change solvents will be performed to validate the present results in a future work.

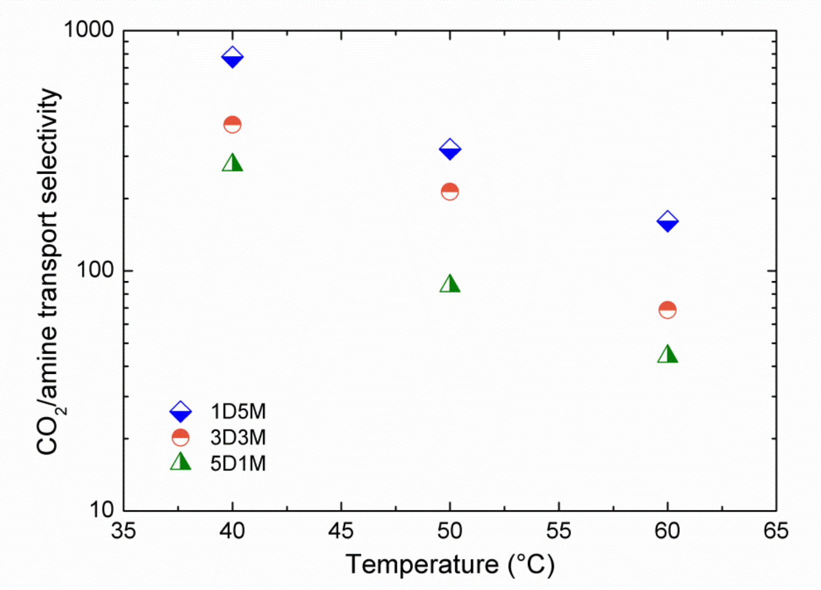

Fig 11 – CO_2/amine transport selectivity offered by the Teflon AF2400 at various temperatures when DEEA-MAPA blends (1D5M, 3D3M and 5D1M) are considered as liquid absorbents.

3.5. Amine evaporation prevention

The amine evaporation prevention capacity of a non-porous membrane contactor using AF2400 polymeric membrane was estimated using the CO_2 and amine flux results obtained from this study and compared with the amine evaporation rate of a typical absorption column. A simplified model was developed for the estimation. More information about the simplified model and the assumptions made for the estimation can be found in the supplementary material.

The results obtained in term of evaporation prevention (EP) index are reported in Figure 12. EP is calculated as the amount of the amine emissions avoided by means of using a membrane contactor instead of an absorption column:

$$EP = 1 - \frac{n_{amine,MC}}{n_{amine,C}} \tag{8}$$

where $n_{amine,MC}$ and $n_{amine,C}$ represent the amine released from the membrane contactor and at the top of the absorption column, respectively.

It is clear that for all the absorbents the EP index decreases at higher operating temperatures, due to the decrease of both the CO_2/amine transport selectivity and CO_2 permance through the AF2400 membrane. The reduced permeability leads to an increase of the surface area necessary to achieve the 90% capture goal, and thus larger amine emissions. According to the simulation, in the considered temperature range the membrane contactor is able to prevent the evaporation up to 80% compared to the absorption column when using highly volatile absorbents (DEEA-MAPA blends). It can be also seen that the EP index of a membrane contactor is significantly lower for low volatile absorbents (5M MEA), and the membrane contactor appeared to be only able to prevent amine evaporation in the low temperature range (up to 32%).

It is worth mentioning that in the present analysis the performances of the membrane contactor and the absorption column are compared at the same operating temperature. According to experiments, the optimum operating temperature for a membrane contactor can be lower compared with the absorption column. In this case a further increment of the evaporation prevention index could be expected.

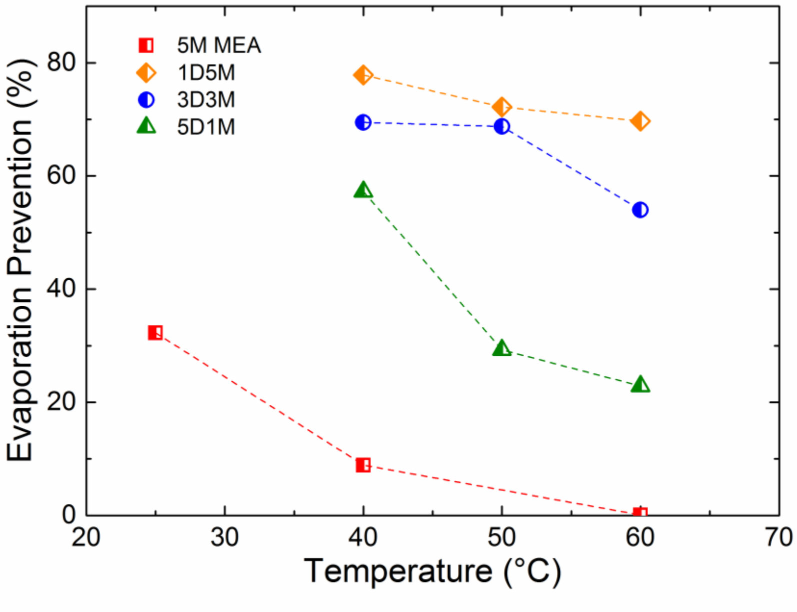

Fig 12 – Evaporation prevention estimated for a non-porous membrane contactor compared to an absorption column for the different absorbents (the dotted lines are intended only to guide the eye).

4. Conclusions

In the present work the pervaporation of several liquid absorbents through a dense membrane layer was investigated to evaluate the amine evaporation through a non-porous membrane contactor. The amine transport through a thin Teflon AF2400 dense layer was measured and, compared to traditional columns, the membrane showed great potential to reduce amine evaporation from highly volatile solvents.

High CO_2/amine transport selectivity with the CO_2 flux up to 3 orders of magnitude higher than those of the amines were achieved by using the selected membrane. Among the highly volatile solvents tested, the highest CO_2/amine transport selectivity (776) was obtained for 1D5M at 40 °C. However this parameter was negatively affected to a great extent by an increase in the operating temperature, as all the amine fluxes increase with the operating temperature. Furthermore, the prevention of the absorbent dehydration through the membrane layer can be achieved by operating the membrane contactor with humid flue gas, since a limited effect of water vapor on the CO_2 permeation (up to 25% decrease), has been observed in the humid permeability tests on AF2400. A preliminary estimation of the evaporation prevention was performed to compare the membrane contactor and an absorption column. In the case of high volatile absorbents (DEEA-MAPA blends), the membrane contactor is able to limit the amine emissions to a significant extent (up to 80%), but the effectiveness is significantly reduced if low volatile absorbents (e.g., 5M MEA) are considered. A more rigorous model is under development in order to take into account a more detailed module performance (e.g., variation of driving forces along the contactor length) and the effect of the CO_2 absorption on the VLE equilibrium for the amine absorbent, allowing a more accurate estimation of the emissions from the membrane contactor. This will be reported in a future work.

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References

[1] WMO, The State of Greenhouse Gases in the Atmosphere Based on Global Observations through 2015, in: Greenhouse Gas Bulletin, World Meteorological Organization, 12 October 2016.

[2] A.J. Reynolds, T.V. Verheyen, E. Meuleman, 16 - Degradation of amine-based solvents A2 - Feron, Paul H.M, in: Absorption-Based Post-combustion Capture of Carbon Dioxide, Woodhead Publishing, 2016, pp. 399-423.

[3] G. Puxty, W. Conway, P.H.M. Feron, 4 - Liquid absorbent selection criteria and screening procedures, in: Absorption-Based Post-combustion Capture of Carbon Dioxide, Woodhead Publishing, 2016, pp. 69-100.

[4] P. Khakharia, J. Mertens, M.R.M. Abu-Zahra, T.J.H. Vlugt, E.L.V. Goetheer, 19 - Overview of aerosols in post-combustion CO2 capture A2 - Feron, Paul H.M, in: Absorption-Based Post-combustion Capture of Carbon Dioxide, Woodhead Publishing, 2016, pp. 465-485.

[5] G.T. Rochelle, 3 - Conventional amine scrubbing for CO2 capture A2 - Feron, Paul H.M, in: Absorption-Based Post-combustion Capture of Carbon Dioxide, Woodhead Publishing, 2016, pp. 35-67.

[6] O.M. Bade, J.N. Knudsen, O. Gorset, I. Askestad, Controlling Amine Mist Formation in CO2 Capture from Residual Catalytic Cracker (RCC) Flue Gas, Energy Procedia, 63 (2014) 884-892.

[7] H.K. Knuutila, Å. Nannestad, Effect of the concentration of MAPA on the heat of absorption of CO2 and on the cyclic capacity in DEEA-MAPA blends, International Journal of Greenhouse Gas Control, 61 (2017) 94-103.

[8] J.G.M.S. Monteiro, H. Majeed, H. Knuutila, H.F. Svendsen, Kinetics of CO2 absorption in aqueous blends of N,N-diethylethanolamine (DEEA) and N-methyl-1,3-propane-diamine (MAPA), Chemical Engineering Science, 129 (2015) 145-155.

[9] M. Garcia, H. Knuutila, S. Gu, Determination of kinetics of CO2 absorption in unloaded and loaded DEEA+MAPA blend, Energy Procedia, In Print (2017).

[10] H.K. Knuutila, R. Rennemo, A.F. Ciftja, Novel solvent blends for CO2 capture:Screening and VLE performance, Under preparation, (2017).

[11] M.W. Arshad, P.L. Fosbøl, N. von Solms, H.F. Svendsen, K. Thomsen, Heat of Absorption of CO2 in Phase Change Solvents: 2-(Diethylamino)ethanol and 3-(Methylamino)propylamine, J. Chem. Eng. Data, 58 (2013) 1974-1988.

[12] Q. Ye, X. Wang, Y. Lu, Screening and evaluation of novel biphasic solvents for energy-efficient post-combustion CO2 capture, International Journal of Greenhouse Gas Control, 39 (2015) 205-214.

[13] T. Nguyen, M. Hilliard, G.T. Rochelle, Amine volatility in CO2 capture, Int. J. Greenhouse Gas Control, 4 (2010) 707-715.

[14] Z. Dai, L. Ansaloni, L. Deng, Precombustion CO2 Capture in Polymeric Hollow Fiber Membrane Contactors Using Ionic Liquids: Porous Membrane versus Nonporous Composite Membrane, Ind. Eng. Chem. Res., 55 (2016) 5983-5992.

[15] Z. Dai, L. Deng, Membrane absorption using ionic liquid for pre-combustion CO2 capture at elevated pressure and temperature, International Journal of Greenhouse Gas Control, 54, Part 1 (2016) 59-69.

[16] E. Chabanon, E. Kimball, E. Favre, O. Lorain, E. Goetheer, D. Ferre, A. Gomez, P. Broutin, Hollow Fiber Membrane Contactors for Post-Combustion CO2 Capture: A Scale-Up Study from Laboratory to Pilot Plant, Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles, 69 (2014) 1035-1045.

[17] V.Y. Dindore, D.W.F. Brilman, F.H. Geuzebroek, G.F. Versteeg, Membrane–solvent selection for CO2 removal using membrane gas–liquid contactors, Sep. Purif. Technol., 40 (2004) 133-145.

[18] E. Favre, H.F. Svendsen, Membrane contactors for intensified post-combustion carbon dioxide capture by gas–liquid absorption processes, J. Membr. Sci., 407–408 (2012) 1-7.

[19] C.A. Scholes, S.E. Kentish, G.W. Stevens, J. Jin, D. deMontigny, Thin-film composite membrane contactors for desorption of CO2 from Monoethanolamine at elevated temperatures, Sep. Purif. Technol., 156, Part 2 (2015) 841-847.

[20] A.A. Shutova, A.N. Trusov, M.V. Bermeshev, S.A. Legkov, M.L. Gringolts, E.S. Finkelstein, G.N. Bondarenko, A.V. Volkov, Regeneration of Alkanolamine Solutions in Membrane Contactor Based on Novel Polynorbornene, Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles, 69 (2014) 1059-1068.

[21] A.V. Volkov, S.E. Tsarkov, E.L.V. Goetheer, V.V. Volkov, Amine-based solvents regeneration in gas-liquid membrane contactor based on asymmetric PVTMS, Petroleum Chemistry, 55 (2015) 716-723.

[22] S. Zhao, P.H.M. Feron, L. Deng, E. Favre, E. Chabanon, S. Yan, J. Hou, V. Chen, H. Qi, Status and progress of membrane contactors in post-combustion carbon capture: A state-of-the-art review of new developments, J. Membr. Sci., 511 (2016) 180-206.

[23] F. Bougie, I. Iliuta, M.C. Iliuta, Absorption of CO2 by AHPD–Pz aqueous blend in PTFE hollow fiber membrane contactors, Sep. Purif. Technol., 138 (2014) 84-91.

[24] D. deMontigny, P. Tontiwachwuthikul, A. Chakma, Using polypropylene and polytetrafluoroethylene membranes in a membrane contactor for CO2 absorption, J. Membr. Sci., 277 (2006) 99-107.

[25] A. Bottino, A. Comite, C. Costa, R. Di Felice, E. Varosio, Wetting of Polypropylene Membranes by Aqueous Solutions in CO2 Absorbing Devices, Sep. Sci. Technol., 50 (2015) 1860-1869.

[26] S. Mosadegh-Sedghi, D. Rodrigue, J. Brisson, M.C. Iliuta, Wetting phenomenon in membrane contactors – Causes and prevention, J. Membr. Sci., 452 (2014) 332-353.

[27] R. Wang, H.Y. Zhang, P.H.M. Feron, D.T. Liang, Influence of membrane wetting on CO2 capture in microporous hollow fiber membrane contactors, Sep. Purif. Technol., 46 (2005) 33-40.

[28] P.T. Nguyen, E. Lasseuguette, Y. Medina-Gonzalez, J.C. Remigy, D. Roizard, E. Favre, A dense membrane contactor for intensified CO2 gas/liquid absorption in post-combustion capture, J. Membr. Sci., 377 (2011) 261-272.

[29] C.A. Scholes, S.E. Kentish, G.W. Stevens, D. deMontigny, Comparison of thin film composite and microporous membrane contactors for CO2 absorption into monoethanolamine, Int. J. Greenhouse Gas Control, 42 (2015) 66-74.

[30] J.A. McLees, Vapor-liquid equilibrium of monoethanolamine/piperazine/water at 35-70°C, M.S.E. Thesis (2006), The University of Texas at Austin

[31] H. Li, P.T. Frailie, G.T. Rochelle, J. Chen, Thermodynamic modeling of piperazine/2-aminomethylpropanol/CO2/water, Chem. Eng. Sci., 117 (2014) 331-341.

[32] A. Hartono, F. Saleem, M.W. Arshad, M. Usman, H.F. Svendsen, Binary and ternary VLE of the 2-(diethylamino)-ethanol (DEEA)/3-(methylamino)-propylamine (MAPA)/water system, Chem. Eng. Sci., 101 (2013) 401-411.

[33] J. Liu, S. Wang, A. Hartono, H.F. Svendsen, I. Kim, C. Chen, Vapor–liquid equilibria of NH3 in (NH3 + H2O) and (NH3 + PZ + H2O) system, Fluid Phase Equilib., 311 (2011) 30-35.

[34] A.M. Polyakov, L.E. Starannikova, Y.P. Yampolskii, Amorphous Teflons AF as organophilic pervaporation materials: Transport of individual components, J. Membr. Sci., 216 (2003) 241-256.

[35] L. Ansaloni, A. Arif, A.F. Ciftja, H.K. Knuutila, L. Deng, Development of Membrane Contactors Using Phase Change Solvents for CO2 Capture: Material Compatibility Study, Ind. Eng. Chem. Res., 55 (2016) 13102-13113.

[36] R.R. Tiwari, Z.P. Smith, H. Lin, B.D. Freeman, D.R. Paul, Gas permeation in thin films of “high free-volume” glassy perfluoropolymers: Part II. CO2 plasticization and sorption, Polymer, 61 (2015) 1-14.

[37] M. Yavari, S. Maruf, Y. Ding, H. Lin, Physical aging of glassy perfluoropolymers in thin film composite membranes. Part II. Glass transition temperature and the free volume model, Journal of Membrane Science.

[38] A.Y. Alentiev, V.P. Shantarovich, T.C. Merkel, V.I. Bondar, B.D. Freeman, Y.P. Yampolskii, Gas and Vapor Sorption, Permeation, and Diffusion in Glassy Amorphous Teflon AF1600, Macromolecules, 35 (2002) 9513-9522.

[39] M.W. Arshad, H.F. Svendsen, P.L. Fosbøl, N. von Solms, K. Thomsen, Equilibrium Total Pressure and CO2 Solubility in Binary and Ternary Aqueous Solutions of 2-(Diethylamino)ethanol (DEEA) and 3-(Methylamino)propylamine (MAPA), J. Chem. Eng. Data, 59 (2014) 764-774.

[40] S.-B. Park, H. Lee, Vapor-liquid equilibria for the binary monoethanolamine+ water and monoethanolamine+ethanol systems, Korean J. Chem. Eng., 14 (1997) 146-148.

[41] G. Fytianos, R. Callot, H.F. Svendsen, H.K. Knuutila, Quantitative determination of amines used in post-combustion CO2 capture process by ion chromatography, Int. J. Greenhouse Gas Control, 42 (2015) 372-378.

[42] S. Ma'mun, J.P. Jakobsen, H.F. Svendsen, O. Juliussen, Experimental and Modeling Study of the Solubility of Carbon Dioxide in Aqueous 30 Mass % 2-((2-Aminoethyl)amino)ethanol Solution, Ind. Eng. Chem. Res., 45 (2006) 2505-2512.

[43] Z. Dai, L. Ansaloni, D.L. Gin, R.D. Noble, L. Deng, Facile fabrication of CO2 separation membranes by cross-linking of poly(ethylene glycol) diglycidyl ether with a diamine and a polyamine-based ionic liquid, J. Membr. Sci., 523 (2017) 551-560.

[44] L. Ansaloni, M. Minelli, M. Giacinti Baschetti, G.C. Sarti, Effect of relative humidity and temperature on gas transport in Matrimid®: Experimental study and modeling, J. Membr. Sci., 471 (2014) 392-401.

[45] M. Minelli, G. Cocchi, L. Ansaloni, M.G. Baschetti, M.G. De Angelis, F. Doghieri, Vapor and Liquid Sorption in Matrimid Polyimide: Experimental Characterization and Modeling, Ind. Eng. Chem. Res., 52 (2013) 8936-8945.

[46] M. Chiara Ferrari, M. Galizia, M.G. De Angelis, G. Cesare Sarti, Vapor Sorption and Diffusion in Mixed Matrices Based on Teflon® AF 2400, in: Membrane Gas Separation, John Wiley & Sons, Ltd, 2010, pp. 125-142.

[47] A. Tokarev, K. Friess, J. Machkova, M. Šipek, Y. Yampolskii, Sorption and diffusion of organic vapors in amorphous Teflon AF2400, J. Polym. Sci., Part B: Polym. Phys., 44 (2006) 832-844.

[48] I. Kim, PhD Thesis: Heat of reaction and VLE of post combustion CO2 absorbents, PhD (2009), Norwegian University of Science and Technology.

[49] A.F. Ciftja, A. Hartono, H.F. Svendsen, Experimental study on phase change solvents in CO2 capture by NMR spectroscopy, Chem. Eng. Sci., 102 (2013) 378-386.

[50] J.G.M.S. Monteiro, H. Knuutila, N.J.M.C. Penders-van Elk, G. Versteeg, H.F. Svendsen, Kinetics of CO2 absorption by aqueous N,N-diethylethanolamine solutions: Literature review, experimental results and modelling, Chem. Eng. Sci., 127 (2015) 1-12.

[51] G.Q. Chen, C.A. Scholes, G.G. Qiao, S.E. Kentish, Water vapor permeation in polyimide membranes, J. Membr. Sci., 379 (2011) 479-487.

[52] I. Pinnau, L.G. Toy, Gas and vapor transport properties of amorphous perfluorinated copolymer membranes based on 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole/tetrafluoroethylene, J. Membr. Sci., 109 (1996) 125-133.

[53] C.A. Scholes, S. Kanehashi, G.W. Stevens, S.E. Kentish, Water permeability and competitive permeation with CO2 and CH4 in perfluorinated polymeric membranes, Sep. Purif. Technol., 147 (2015) 203-209.

[54] C. Tsvigu, E. Pavesi, M.G. De Angelis, M. Giacinti Baschetti, Effect of relative humidity and temperature on the gas transport properties of 6FDA–6FpDA polyimide: Experimental study and modelling, J. Membr. Sci., 485 (2015) 60-68.

[55] E. Lasseuguette, M. Carta, S. Brandani, M.-C. Ferrari, Effect of humidity and flue gas impurities on CO2 permeation of a polymer of intrinsic microporosity for post-combustion capture, International Journal of Greenhouse Gas Control, 50 (2016) 93-99.

[56] G.Q. Chen, C.A. Scholes, C.M. Doherty, A.J. Hill, G.G. Qiao, S.E. Kentish, Modeling of the sorption and transport properties of water vapor in polyimide membranes, J. Membr. Sci., 409–410 (2012) 96-104.

[57] L. Ansaloni, J.R. Nykaza, Y. Ye, Y.A. Elabd, M. Giacinti Baschetti, Influence of water vapor on the gas permeability of polymerized ionic liquids membranes, J. Membr. Sci., 487 (2015) 199-208.

[58] E.M. Davis, Y.A. Elabd, Prediction of Water Solubility in Glassy Polymers Using Nonequilibrium Thermodynamics, Ind. Eng. Chem. Res., 52 (2013) 12865-12875.

Highlights

- Amine transport through a AF2400 membrane was studied through pervaporation experiments
- Different amine-based solvents were investigated with a focus on high volatile solvents
- The CO_2 permeability of AF2400 membrane was measured at various temperature and humidity
- High CO_2/amine transport selectivity in membrane contactor using AF2400 membrane was documented
- The effect of increasing temperature on the CO_2/amine transport selectivity is negative