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Development of membrane contactors using phase change solvents for CO₂ capture: Material compatibility study

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Keywords

Membrane Contactor; CO₂ Capture; DEEA-MAPA absorbent; Membrane material; Amine permeation.

Abstract

Phase change solvents represent a new class of CO₂ absorbents with a promising potential to reduce the energy penalty associated with CO₂ capture. However, their high volatility is a major concern for their use at the industrial scale. It is believed that membrane absorption offers a solution to overcome this issue, particularly if the membrane can prevent amine evaporation. In the present work a compatibility study is carried out in order to identify suitable membranes in a membrane contactor using phase change solvents as liquid absorbent. Several porous and dense polymeric samples have been studied, and their chemical stability and ability to prevent amine evaporation have been investigated through immersion tests and amine permeation experiments. The experimental results indicate that to use the blend solvents based on DEEA/MAPA (diethyl-ethanolamine/3-methylamino-propylamine) in a membrane contactor requires a membrane with excellent stability. Porous membranes typically used for membrane contactors with MEA aqueous solution, such as polytetrafluoroethylene (PTFE) and polypropylene (PP) membranes, are not suitable to be used as a membrane interface with this new class of absorbents. A selection of membrane materials for the fabrication of thin composite membranes suitable for this application has been identified and their CO₂ and amine transport properties have been determined. Finally, the wettability of the most suitable polymer for the dense layer has been measured for different absorbent concentrations in order to ensure a good interfacial contact in the membrane contactor.

1. Introduction

One of the most important challenges of our age is related to the increase in the carbon dioxide concentration in the atmosphere and the consequent climate change. During the last century, the concentration of CO₂ in the atmosphere increased from 280 ppm in the pre-industrial era to 394 ppm in 2012¹. Emission scenarios suggest that, to prevent irreversible changes related to global warming, a 40 to 70% decrease in greenhouse gas (GHG) emissions from anthropogenic sources must be achieved by 2050^{2,3}. Carbon Capture and Storage (CCS) offers a prompt approach to reducing CO₂ emissions into the atmosphere without the need to reduce the use of fossil fuels, and it can be easily implemented for different existing CO₂ sources.

Amine-based absorption is the most commonly technology used for post-combustion CO₂ capture, but the development of a more cost-effective technology is required in order to make the process more economically feasible and environmentally friendly. Recently, a new category of absorbents forming two liquid phases upon CO₂ loading, referred to as “phase change solvents”^{4, 5}, has been developed and investigated. They show a promising perspective to achieve an economical post-combustion CO₂ capture from flue gas, as they are able to cut the energy requirements of the regeneration step down to 2.5 MJ/kgCO₂⁶. One promising example is represented by the aqueous solution of 3-methylamino-propylamine (MAPA) and diethyl-ethanolamine (DEEA)^{4,7,8}. Due to the peculiar feature of forming two phases (a CO₂ rich and a CO₂ lean one) after the CO₂ absorption, only the CO₂ rich phase must be regenerated, whereas the CO₂ lean phase can be directly recirculated inside the absorber. If compared to 5M MEA, the benchmark typically used for CO₂ absorbents, DEEA-MAPA mixtures are able to show a greater CO₂ sorption capacity at low temperature (40°C, typical for the absorption step), and a lower heat of absorption at high temperature (120°C,

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3 typical for the desorption step), making them particularly attractive in terms of the energy
4 efficiency of the capture process. However, vapour–liquid equilibrium (VLE) data showed
5 that a significant increase of the DEEA activity coefficient takes place for the ternary mixture
6 DEEA-MAPA-H₂O⁹. The larger DEEA activity coefficient and the higher vapour pressure of
7 pure MAPA and DEEA compared to MEA increase the volatility of this new class of
8 absorbents, threatening their use at the industrial scale. Indeed, large amine evaporation
9 towards the CO₂-purified flue gas stream affects the operating costs of the capture plant, and
10 can lead to environmental problems (e.g., the formation of aerosol)¹⁰. For this reason,
11 intensive water washing is required for the outlet gases from both the absorbers and the
12 desorbers, thus increasing the capital and operational costs of the process.
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25 Membrane contactor technology (also known as “membrane absorption”) can be a suitable
26 solution to achieve the optimal exploitation of this new class of absorbents. In a membrane
27 contactor a membrane is used as an interface between the gas and the liquid phase. In
28 particular, the membrane layer can be purposely designed to act as a barrier for the amine
29 compounds, allowing a reduction of the amine evaporation rate toward the gas phase.
30 Furthermore, membrane contactors own several advantages compared to traditional
31 absorption columns, such as lower footprint and capital costs, and larger interfacial area per
32 unit volume¹¹. The interface between the two phases is independent from the operating
33 conditions, and the modularity of the membrane contactor allows an easier scalability and
34 flexibility of the process, making this technology extremely attractive for CO₂ capture in
35 post-combustion application^{12, 13}. The absence of a direct dispersion¹¹ between the gas and
36 the liquid phases can also be beneficial to avoid problems related to mist and aerosol
37 formation, since the membrane prevents the dragging of liquid droplets from the liquid.
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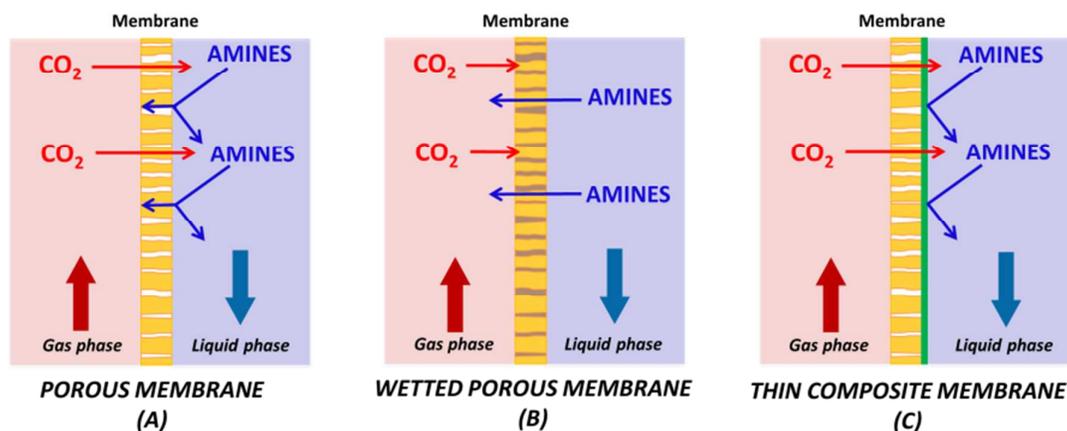


Figure 1 – Membrane contactor schematic representation in case of a porous membrane (A), a porous membrane affected by wetting phenomena (B) and a thin composite membrane (C) are considered as the interface between the gas and the liquid phase.

In the past two decades, membrane contactor performances have been investigated using different amine-based liquid absorbents. Several studies focused on MEA¹⁴⁻¹⁷, but Ammonia¹⁸, DEA^{19, 20}, MDEA²¹, AMP²², and other amine blends^{23, 24} have also been used, showing promising results in terms of CO₂ capture performance. Typically, porous membranes are used as an interface layer, as the membrane morphology was able to ensure a limited effect on the CO₂ overall mass transfer resistance, according to the resistance in the series model¹¹. If the gaseous penetrants occupy the membrane pores (Fig. 1A), the mass transfer coefficient for CO₂ is optimized, but the non-selective nature of the porous membranes can only prevent the amine evaporation to a very limited extent. However, if wetting phenomena (Fig. 1B, pores filled with the liquid phase) occur, the membrane contactor performance will be drastically deteriorated²⁵, and the decrease in the CO₂ mass transfer coefficient can be larger than 50%²⁶. From this point of view, the use of a thin composite membrane offers a proper solution to limit the solvent evaporation and to prevent wetting phenomena. Indeed, if the thin coating is designed with specific CO₂/amine selectivity and is able to ensure high CO₂ transmembrane flux, the actual evaporation can be

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3 consistently reduced. Literature studies have reported the use of a thin composite membrane
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5 in membrane contactors using MEA aqueous solutions^{15,27,28}, showing long-term stability of
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7 the separation performance under high pressure²⁹ or high temperature (desorption process)
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9 conditions³⁰. However, no data about the amine permeation through this layer have been
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11 reported.

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14 The present study focuses on the chemical compatibility of different membrane materials and
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16 morphologies with phase change solvents to identify the most suitable membrane materials
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18 and morphology in the membrane contactor. For this purpose both porous and dense
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20 materials have been considered. Porous materials have been selected according to their
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22 commercial availability, cost and surface properties. The dense materials were selected
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24 according to their CO₂ permeability (in case of Aquivion the permeability under humid
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26 conditions was referred³¹), chemical stability, and cost. Furthermore, the ability of the liquid
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28 phase to wet the identified porous materials has also been studied. Once that a proper
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30 membrane material has been identified, permeation tests for CO₂ and amines have been
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32 carried out to assess the ability of the membrane material to avoid evaporation of the amine
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34 compared to traditional absorption systems.
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42 **2. Experimental**

43 *2.1. Materials*

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46 Four porous polymeric membrane materials, commercially available for microfiltration and
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48 ultrafiltration purposes, were considered in the present study. The porous polysulfone
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50 membrane (PSF, GR61PP, MWCO 20 kDa) and composite fluoro polymer membrane (CFP,
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52 ETNA10PP, MWCO 10 kDa) were provided by Alfa Laval. The porous polypropylene
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54 membrane (PP, Celgard[®] 2400, average pore size 43nm) was supplied by Celgard LLC. The
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3 porous polytetrafluoroethylene membrane (expanded PTFE) was provided by GoreTex. Four
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5 different polymers were also considered as possible dense coating layer. Teflon AF2400 and
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7 AF1600 were purchased by Sigma Aldrich in pellet form; PDMS samples were prepared
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9 using Sylgard 184, purchased from Dow Corning Europe (France); Aquivion[®] E98-05 flat
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11 sheet samples were provided by Solvay Specialty Polymers (Italy). The FC-72 fluorosolvent
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13 was purchased by 3M (Kemi-Intressen, Sweden), whereas the diethylethanolamine (DEEA, >
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15 99% purity), 3-methylaminopropylamine (MAPA, > 97% purity), monoethanolamine (MEA,
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17 > 98% purity), and n-Hexane (anhydrous, > 95% purity) were purchased from Sigma Aldrich.
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19 All the solvents were used without further purification. Deionized water was used for the
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21 preparation of the liquid absorbents. Pure CO₂ (grade 5.0) was supplied by AGA Gas (AGA
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23 Gas GmbH, Hamburg, Germany).
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28 *2.2. Samples preparation*

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30 Free standing polymeric films of Teflon AF2400, AF1600, and PDMS were prepared through
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32 the solvent evaporation method. In particular, the Teflon AF2400 and AF1600 samples were
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34 prepared by dissolving a calculated amount of polymer in FC-72 fluorosolvent in order to
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36 achieve a 1 wt% solution and stirring overnight. The solution was subsequently poured into a
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38 levelled glass petri dish and stored inside a fume hood overnight. The samples were then
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40 detached from the petri dish and heated up to 200 °C for 24h in order to completely remove
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42 the solvent.
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46 The PDMS membranes were prepared by mixing the oligomer precursor with the curing
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48 agent at a 10:1 ratio, stirred for a few minutes, and left at room temperature for 3h.
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50 Subsequently, n-Hexane was added in order to achieve a solid concentration of 2 wt%, and
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52 the solution was stirred overnight. The PDMS solution was then poured into a PTFE petri
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54 dish until the solvent was completely evaporated, so that finally the PDMS film could be
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3 detached from the petri dish using tweezers. In order to achieve a high degree of crosslinking,
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5 the sample was cured at 150 °C for 6h and rapidly cooled down to room temperature ³².
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8 The absorbent solutions were prepared by mixing DEEA and MAPA with H₂O to achieve a
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10 molar concentration of 3 M DEEA 3 M MAPA (further referred as 3D3M), according to a
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12 procedure previously reported ⁷. A 5 M MEA (30 wt% MEA) aqueous solution was prepared
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14 and used as a reference for the CO₂ absorbents. Furthermore, 1 L of CO₂-loaded 3D3M
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16 solution was prepared by bubbling CO₂ into the solution until the total weight was found to
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18 be constant ³³. This operation is carried out at room temperature and atmospheric pressure. As
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20 previously reported ⁸, MAPA-DEEA-based absorbents tend to form two liquid phases upon
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22 CO₂ sorption: a CO₂-lean upper phase (hereinafter referred as 3D3M-UP) and a CO₂-rich
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24 lower phase (hereafter referred to as 3D3M-LP). The CO₂ concentration in the 3D3M-UP
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26 was measured through titration analysis and found to be equal to 0.06 mol/kg, whereas in the
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28 3D3M-LP it was 3.5 mol/kg. NMR characterization of the loaded DEEA-MAPA solution
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30 showed that several components (e.g., carbonate, bicarbonate, carbamate, and dicarbamate)
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32 were formed after the CO₂ reaction with the amines ³⁴. Furthermore, it was reported that in
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34 the loaded phase change solvent the upper phase is richer in DEEA, whereas the lower phase
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36 has an amine concentration similar to the unloaded solution (see Table S1).
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40 41 42 *2.3. Immersion tests*

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44 In order to investigate the chemical stability of the selected polymeric materials with the
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46 phase change solvents, the samples (dry weight: 10 – 20 mg) were immersed in liquid
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48 solutions and monitored over a period of 5 weeks. During the whole period the flasks
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50 containing the solution were placed in a heated cabinet (T = 60°C). In addition, the weight
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52 variation of the polymeric samples was measured over time, allowing the calculation of the
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3 mass gain (Ω_{sol}) within the sample scaled on the dry mass according to the following
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5 equation:

$$\Omega_{sol} = \frac{w(t) - w_{dry}}{w_{dry}} \quad (1)$$

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11 where $w(t)$ is the sample weight at a given time and w_{dry} is the sample weight under dry
12 conditions. To measure $w(t)$ the samples were removed from the flask, quickly dried with a
13 clean tissue in order to remove the liquid from the surfaces, weighed with an analytical
14 balance (Mettler Toledo ME204, with a precision of 0.1 mg) and finally re-immersed in the
15 liquid solution, according to the literature³⁵. To improve the significance of the measurement,
16 the values reported were obtained as the average of two different samples immersed in the
17 same solution. At the end of the immersion tests, the samples showing good compatibility
18 were dried in a vacuum oven overnight and weighed in order to evaluate possible weight
19 losses during the immersion.
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32 *2.4. Morphology characterization*

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34 In order to investigate the effect of prolonged immersion on porous materials, a Scanning
35 Electron Microscopy (SEM) investigation was carried out on selected samples. Specifically, a
36 TM3030 Tabletop Microscope (Hitachi High Technologies America, Inc) was used to
37 investigate the samples' morphology. In the analyses, an electron beam intensity of 15kV was
38 employed, and the back-scattered electron (BSE) signal was used to obtain the images. The
39 polymeric samples were gold sputtered (the coating time was 1.5 min in an Ar atmosphere) in
40 order to ensure good electrical conductivity.
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51 *2.5. Permeation tests*

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53 CO₂ permeability tests were performed using a constant volume variable pressure setup³⁶. For
54 the tests an upstream pressure of 1.5 bar was used, operating at room temperature conditions.
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Pure liquid permeation tests were performed on selected materials in order to estimate the amine permeability through the membrane layer. In particular, the constant volume variable pressure apparatus was slightly modified as shown in Figure 2. Similarly to the pure gas case, the membrane was placed inside a sample holder and evacuated overnight to ensure the complete removal of all the penetrants (V3, V4 and V5 are open; V1 and V2 are closed). The liquid was degassed before connecting the reservoir to the membrane holder. A leak test was also performed to ensure a suitable vacuum grade. Subsequently, the upstream side of the membrane was placed in contact with the liquid phase under static conditions, while the downstream pressure was monitored over time (V3, V4 and V5 are closed; V1 and V2 are opened).

The penetrant transmembrane flux, J , and the permeability, P , are calculated according to literature³⁷ as:

$$J_i = \left(\frac{dp_{i,d}}{dt} \right)_{t \rightarrow \infty} \cdot \frac{V_d}{R \cdot T \cdot A} \quad (2)$$

$$P_i = \frac{J_i \cdot l}{\Delta p_i} \rightarrow \Delta p_i = (p_{u,i} - p_{d,i}) \Big|_{Gas}, \quad \Delta p_i = (p_i^*(T) - p_{d,i}) \Big|_{Liquid} \quad (3)$$

where p_u and p_d are the upstream and downstream pressure, t refers to the time, V_d is the downstream volume, R is the gas constant, T is the temperature, A is the permeation area, l is the membrane thickness and $p^*(T)$ is the vapour pressure in equilibrium with the pure liquid at the given operating temperature.

Although vapour permeation is frequently measured by using vapour phases on both sides of the membrane as reported in literature³⁸, for Teflon AF polymers the vapour and liquid permeation can be significantly different³⁹. Therefore, the use of liquid feed was preferred in order to have a more realistic measurement of the amine transport. To measure the correct

vapour flux, consecutive steps were performed (typically 4 – 5). A single step consisted in monitoring the downstream pressure until it reached 10% of the saturation pressure value at the operating temperature, and then a vacuum was pulled on the downstream side. Typically, a steady state of the flux was observed after the second or third step. A similar procedure was reported in the literature to measure the permeability of vapours through dense polymeric membranes⁴⁰.

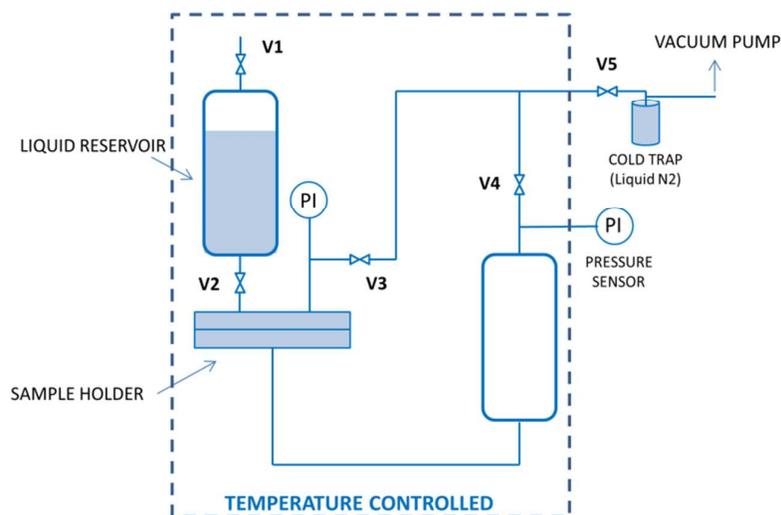


Figure 2 – Permeation setup layout

The results obtained from the transport measurements can also be used to determine the degree of the solvent evaporation prevented by comparing the CO₂ flux and the amine flux through the dense layer. Different from a typical gas separation membrane, in this case the amine flux and the CO₂ permeation take place counter-currently across the membrane, and different driving forces must also be considered to describe the real operating conditions. For this reason, the term “CO₂/Amine Transport Selectivity” (α) is used, which cannot be calculated simply as the permeability ratio, but as the ratio of the fluxes of CO₂ and the amine

(assuming the real operating condition for both the gas and the liquid phase), according to the following equation:

$$\alpha = \frac{J_{CO_2}}{J_{MAPA} + J_{DEEA}} = \frac{P_{CO_2} \cdot \Delta p_{CO_2}}{P_{MAPA} \cdot \Delta p_{MAPA} + P_{DEEA} \cdot \Delta p_{DEEA}} \quad (4)$$

$$\Delta p_{CO_2} = 0.13 \text{ bar}, \quad \Delta p_i = \gamma_i(T, x) \cdot p_i^*(T) \cdot x_i \quad i = DEEA, MAPA$$

where $\gamma(T, x)$ is the activity coefficient obtained from the VLE data for the mixture at the operating temperature and x is the molar concentration in the liquid absorbent. The data used to calculate the selectivity by Equation 4 were obtained from experiments at a low stage cut. This parameter illustrates the membrane ability of favouring the transport of CO₂ above amines, which is directly related to the capability of preventing the amine evaporation towards the gas phase.

2.6. Contact Angle and Surface Tension

In order to ensure a good contact between the liquid absorbent and the surface of the dense membrane layer, surface tension (γ_L) of the liquid mixtures have been measured and contact angle (θ) experiments have been carried out on the dense layer that showed the most suitable properties. In general, the wettability is favoured for lower values of the liquid surface tension and for contact angle that are lower than 90°. Pure H₂O, 5M MEA and 3 different DEEA/MAPA blends (1D5M, 3D3M, 5D1M) have been used as liquid phase. An optical tensiometer (Attension Theta, Biolin scientific) was used, adopting a sessile drop method with a liquid droplet volume of 6 ~ 8 μ l. The sampling time for each experiment was set to 1 min, with a sampling frequency of 3 fps.

3. Results and discussion

3.1. Porous membrane compatibility

In order to verify the chemical compatibility between the membrane materials and the liquid phase, different immersion tests were carried out for several polymeric membrane samples, both porous and dense. A systematic approach was adopted and the samples were immersed in the pure chemicals (H₂O, DEEA, MAPA), and in amine aqueous mixture (3D3M). Table 1 shows the results obtained. MAPA was found to cause major incompatibilities with the polymeric materials. In the case of the composite fluoropolymer (CFP), evident swelling phenomena appeared after 24h immersion in pure MAPA, causing a detachment of the fluoropolymer layer from the substrate after a few days of immersion (Fig. S1 in the Supporting Information). Similar effects were also observed when the samples were immersed in the 3D3M mixture. In the case of polysulfone (PSF), the polymer matrix showed a very high uptake of H₂O, DEEA, and 3D3M (always larger than 0.36 g/g_{pol}), but MAPA was found to be able to almost dissolve the PSF layer within a few hours of immersion (Fig. S2 in the Supporting Information). In view of the incompatibility with MAPA, CFP and PSF were not considered for further characterizations.

	Uptake (g/g _{pol})			
	H ₂ O	MAPA	DEEA	3D3M
CFP	0.51 ± 0.04	✘	0.63 ± 0.01	✘
PSF	0.36 ± 0.01	✘	0.56 ± 0.02	0.54 ± 0.01
PTFE	✓	0.35 ± 0.03	0.73 ± 0.09	0.63 ± 0.03
PP	✓	0.43 ± 0.03	0.59 ± 0.03	0.56 ± 0.03

Table 1 – Compatibility and solvent uptake measured at 60 °C for different porous polymers and liquid phases (“✘” = non-compatible polymer/solvent pair; “✓” = negligible liquid uptake). The uptake value is the average of at least 4 consecutive measurements over the 5-week monitoring campaign.

However, good chemical stability was observed in the case of PTFE and PP over the entire monitoring campaign: no evident changes in morphology were observed in the membranes. For this reason, immersion tests were also performed in a 5M MEA solution, used as a reference for the absorbent phase, and in CO₂ loaded 3D3M solutions. Figure 3 shows the time evolution of the liquid uptake for different liquid phases in the PTFE samples. According to the hydrophobic nature of the material, a negligible uptake for water was observed, but a different result was obtained for the amines. In the case of DEEA the absorption kinetics was very fast, showing high uptake values after the initial measurement, followed by a slow decrease.

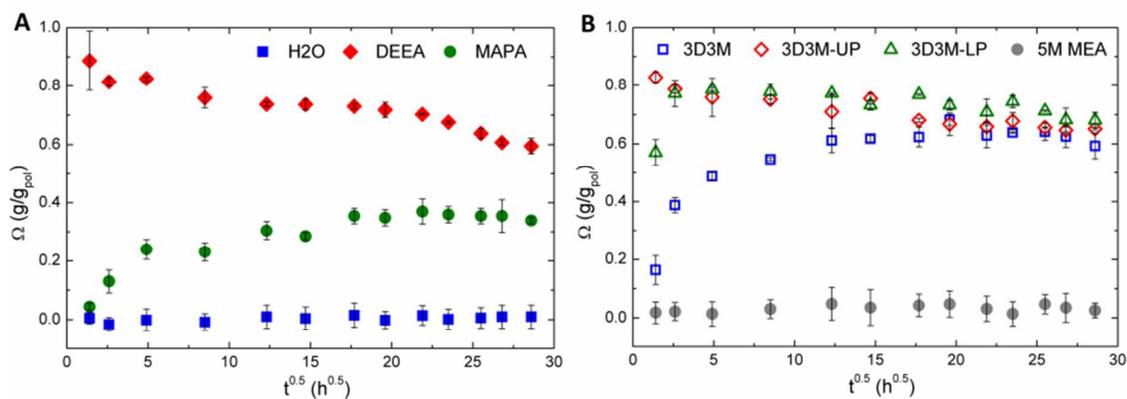


Figure 3 – Kinetics of the uptake in porous PTFE samples of different liquids: pure components (A) and amine mixtures (B).

A gradual change in colour of DEEA during the investigation was observed, while no colour change happened in the case of the 3D3M (Fig. S3 in the Supporting Information) or any other liquid used for the characterization. Ion chromatography analysis was carried out in order to determine possible degradation components, but no evidence was found. As it was beyond the scope of the present investigation, no further characterization of the phenomenon was carried out. In the case of MAPA, the absorption kinetics was much slower than the one

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3 observed in DEEA (thermodynamic equilibrium reached after 14 days), but the final
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5 equilibrium value was found to be 0.35 g/g_{pol}. When amine mixtures were tested, a negligible
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7 uptake was observed in the 5M MEA, pointing out that no wetting phenomena took place.
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9 This finding is consistent with the fact that PTFE is frequently used as a membrane material
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11 for membrane contactor applications using this type of amine solvent^{14, 17, 22, 41}. However,
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13 when the DEEA-MAPA blend was considered, the solvent uptake was found to be very high
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15 (0.63 g/g_{pol}) in accordance with the high uptake measured for both pure amines. When
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17 3D3M-LP and 3D3M-UP were tested, faster sorption kinetics was observed, suggesting that
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19 the presence of CO₂ accelerates the process, and the final equilibrium value was similar to the
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21 one observed for the unloaded solution. Despite the large solvent uptake, the initial weight of
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23 all the polymeric samples used for the immersion tests was retrieved with an error below 3%,
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25 confirming the good chemical stability of PTFE. Moreover, the slow kinetics observed for the
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27 amine mixture suggests that simple contact angle tests can be not enough to properly
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29 understand the arising of wetting phenomena, which can take place only after long term
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36 The PTFE samples immersed were also characterized in terms of morphology through SEM
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38 images (Fig. 4). Before the immersion, the PTFE morphology looked similar to those
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40 previously reported in the literature, but after 5 weeks immersion in an unloaded 3D3M
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42 solution the PTFE membrane showed an evident morphology change. In particular, the
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44 junctions of the PTFE fibers appear to have undergone a plasticization when being immersed
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46 in the DEEA-MAPA aqueous mixture.
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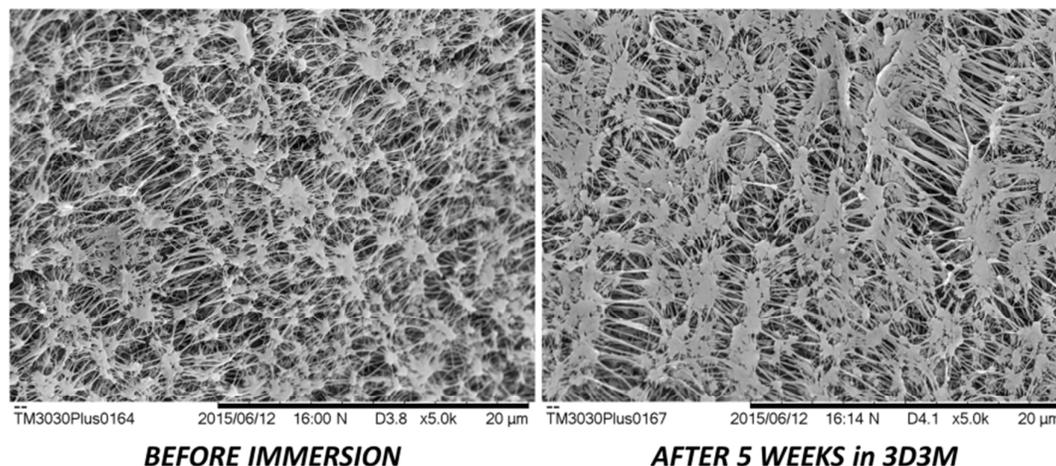


Figure 4 – SEM images of the PTFE membrane before and after immersion in 3D3M at 60 °C.

Figure 5 presents the time evolution of the uptake of different liquid solutions in the porous PP membrane. Similar to that of the porous PTFE membrane, the water uptake of PP membrane was found to be negligible, but the uptake of both DEEA and MAPA in the PP membrane was high, with equilibrium values of 0.43 and 0.59 g/g_{pol}, respectively. In this case, the kinetics of the uptake was fast for both amines, and the equilibrium was reached within the first 24h. In the case of mixtures, the 5M MEA solution showed a negligible solvent uptake, consistent with the fact that PP is frequently used in membrane contactor applications, where the liquid phase is 30 wt% MEA aqueous solution^{21, 22, 42}. However, the uptake of DEEA-MAPA aqueous blend increased significantly, reaching a value of 0.56 g/g_{pol}. Slightly higher values were obtained in the CO₂-loaded phases for both blend solvents (i.e., 3D3M-LP and 3D3M-UP), showing that the presence of CO₂ in the liquid phase may favour the uptake to some extent.

The SEM characterization was carried out in order to investigate possible morphology changes after immersion in the amine-based solvent, as shown in Figure 6. The sample

surface did not show any significant variation after the 5-week immersion in unloaded 3D3M, confirming the good chemical stability of PP with respect to the absorbent.

In view of the good chemical stability observed, PTFE and PP are considered suitable materials for the development of thin composite membranes for membrane contactors exploiting phase change solvents as liquid absorbent.

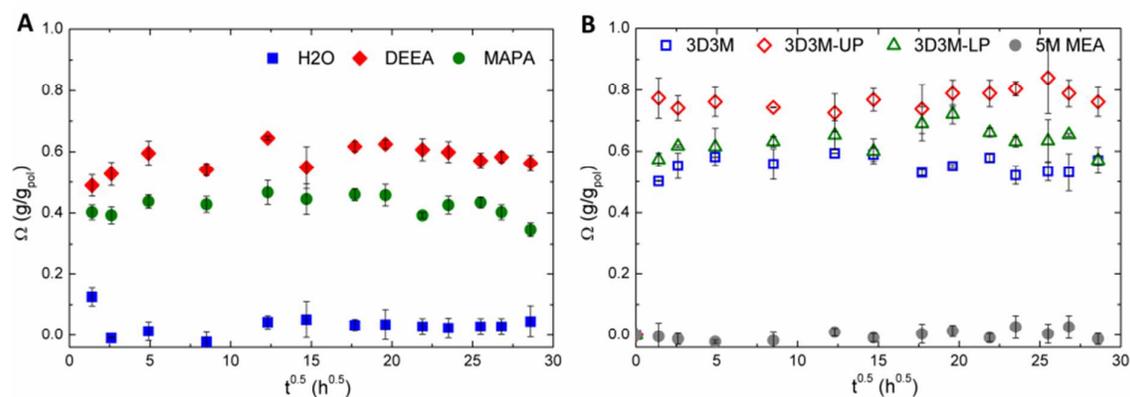


Figure 5 – Kinetics of the uptake in porous PP samples of different liquids: pure components (A) and amine mixtures (B).

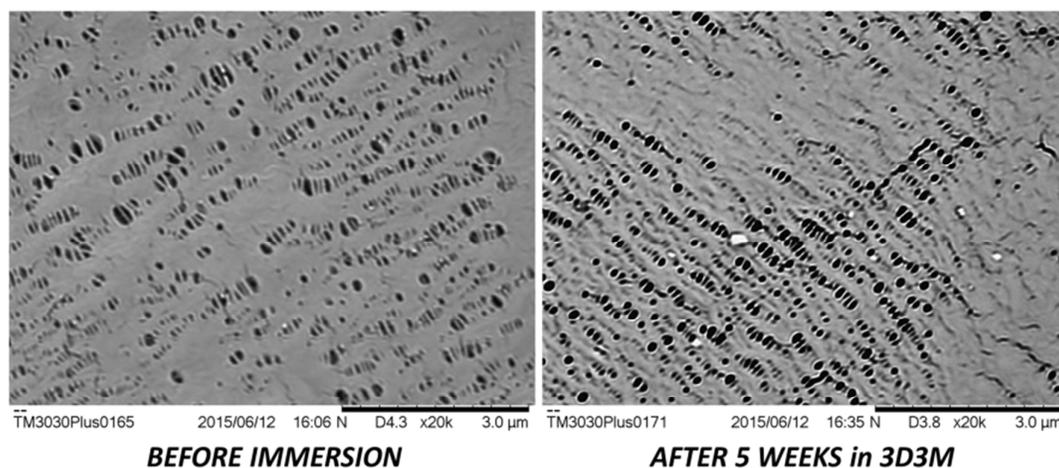


Figure 6 – SEM images of the PP membrane before and after immersion in 3D3M at 60 °C.

3.2. Dense membrane compatibility

The experimental results show that porous membranes are not suitable for application with phase change solvents, and non-porous composite membranes must be used to avoid wetting and the amine evaporation.

The chemical compatibility of different membrane materials for the non-porous membrane with the chosen solvents was investigated. In particular, 4 different commercial polymers were considered for this purpose: PDMS, a synthetic rubber with an organosilicate-based structure, Aquivion, a perfluorosulfonated ionomer, and Teflon AF 2400 and AF1600, a family of PTFE copolymers with different amounts of PTFE and dioxole monomers. Following the same procedure adopted in the immersion tests of porous materials, the polymeric samples were immersed in different liquids, and their chemical stability was checked over a period of 5 weeks through weight measurements.

	Uptake (g/g _{pol})			
	H ₂ O	MAPA	DEEA	3D3M
AQUIVION	0.14 ± 0.02	0.26 ± 0.02	0.23 ± 0.03	0.63 ± 0.04
AF2400	✓	✓	✓	✓
AF1600	✓	✓	✓	✓
PDMS	✓	✗	0.24 ± 0.1	✗

Table 2 – Compatibility and solvent uptake measured at 60 °C for different dense polymers and liquid phases (“✗” = non-compatible polymer/solvent pair; “✓” = negligible liquid uptake). The uptake value is the average of at least 4 consecutive measurements over the 5-week monitoring campaign.

In the case of PDMS, poor chemical stability was observed for the pure MAPA and 3D3M solution: a significant weight loss (about 30% of the initial value, Fig. S4) was measured within the first week of immersion, followed by the complete dissolution of the polymer in

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3 the liquid phase after the first week. Although PDMS is used in a broad spectrum of
4 applications in presence of amines (secondary and tertiary), the polymer is reported to
5 undergo significant swelling phenomena (as obtained in case of DEEA, Fig. S4)⁴³. In case of
6 MAPA, the presence of a primary and secondary amine makes the organic solvent even more
7 aggressive and is likely the cause of the observed results. Therefore, PDMS was not
8 considered for further characterization.
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11 On the other hand, Aquivion showed good compatibility with both pure chemicals and the
12 amine mixtures, but a large uptake was observed in both DEEA and MAPA, and also in the
13 case of 3D3M (Table 2). The H₂O uptake of 0.14 g/g_{pol} is consistent with the literature data⁴⁴,
14 but lower than the value reported in the material datasheet (about 40 wt%). For the sake of
15 clarity it must be pointed out that this difference can be related to the different temperature of
16 the experiments. Indeed, the liquid H₂O uptake of ionomers can be significantly affected by
17 temperature, as the polymer matrix can undergo through severe swelling phenomena⁴⁵.
18 Higher uptake values of 0.23 and 0.26 g/g_{pol} were obtained in the cases of DEEA and MAPA,
19 respectively, with slower kinetics in the case of DEEA (Fig. S5). Interestingly, a sort of
20 synergetic effect was observed in the case of the 3D3M solution, as the uptake appeared to be
21 significantly larger than the one observed in the case of pure liquids, reaching a value of 0.63
22 g/g_{pol}. Furthermore, in the case of DEEA and 3D3M the sample colour turned from
23 transparent to bright orange, suggesting that the amine was likely able to substitute the H⁺ ion
24 in the polymer structure⁴⁶. Finally, in order to better understand the ability of Aquivion to
25 represent a barrier for the amine evaporation towards the gas phase, a contact angle test of the
26 3D3M solution was carried out on immersed samples, as shown in Figure 7. Interestingly, it
27 was found that, immediately after the deposition of the droplet on the Aquivion surface,
28 significant swelling phenomena took place (Fig. 7B), and within a few seconds the droplet
29 was completely absorbed into the polymeric layer (Fig. 7C). Clearly, the polymer could not
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act as a barrier towards the amine permeation, and for this reason it was not considered for further characterization.



Figure 7 – Time evolution of a contact angle experiment performed depositing a 3D3M droplet on an Aquivion sample immersed for 24h in the 3D3M mixture at 60 °C.

Good chemical stability was observed for the Teflon AF series: both the AF2400 and AF1600 displayed a negligible uptake for all the investigated liquids, including the pure amines. Figure 8 shows the uptake variation in AF2400 and AF1600 over the 5-week investigation. The weight recovery check at the end of the immersion test confirmed the good compatibility of the membrane with the liquid phase, as the initial weight of the samples was retrieved with less than a 3% variation for the samples immersed in all the liquid phases.

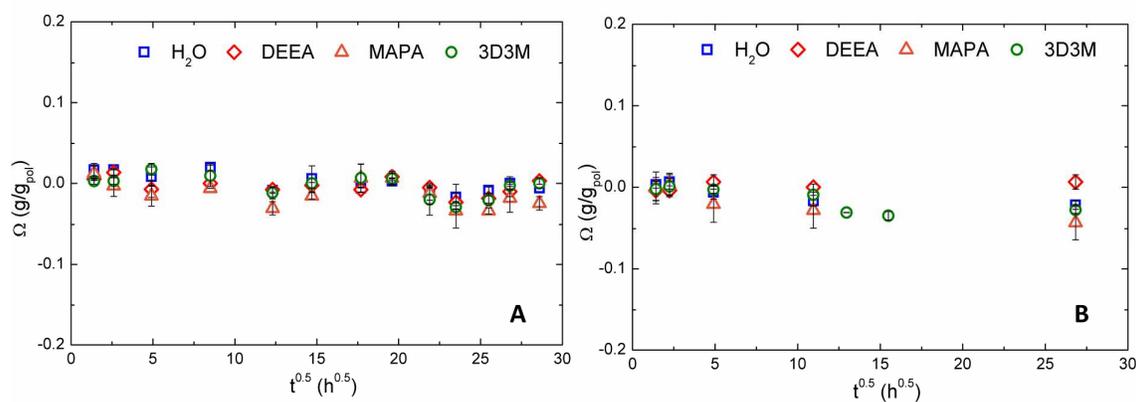


Figure 8 – Immersion test of Teflon AF2400 (A) and AF1600 (B) in pure H₂O, DEEA, and MAPA, and in the 3D3M absorbent.

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3 According to the results obtained, the Teflon AF 2400 and 1600 appears to be the most
4 suitable membrane material for the contact with the DEEA-MAPA aqueous solution in a
5 composite membrane. Furthermore, porous polypropylene can be considered the most
6 suitable porous support for the composite membrane preparation, in view of the good
7 chemical stability and the cheaper cost compared to PTFE. Literature studies have shown the
8 feasibility of using PP coated with Teflon AF 2400^{15, 47} and AF 1600²⁷ for a membrane
9 contactor configuration, using MEA as a liquid absorbent.
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19 *3.3. Amine permeation through the Teflon AF membrane*

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21 The Teflon AF series seems the most promising polymer family to be used as a membrane
22 interface between the gas phase and the DEEA-MAPA-based liquid absorbent. In addition,
23 literature studies also show that among the known high free volume polymers, the Teflon AF
24 series is the one that suffers aging phenomena to the lowest extent^{27, 48, 49}. However, in order
25 to be able to reduce the amine evaporation, the selected membrane must be able to ensure
26 certain CO₂/amine selectivity. The transport properties of AF2400 and AF1600 have already
27 been reported in the literature for several gases and vapors^{39, 50-52}, but no data could be found
28 in case of organic amines. For this reason, permeability tests for pure component (i.e., CO₂,
29 H₂O, DEEA, and MAPA) were performed on self-standing AF2400 and AF1600 membranes.
30 The thickness of the polymeric layers was within the range of 30 – 55 μm. Figure 9 shows the
31 results obtained in terms of transmembrane permeability and flux for pure liquids and CO₂ at
32 room temperature. The trend is similar for AF2400 and AF1600, even though lower fluxes
33 were obtained for the AF1600 consistently with its lower fraction free volume⁵³.
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50 The CO₂ permeability tests (Fig. 9A) were performed at a total pressure of 1.5 bar, showing
51 CO₂ permeability of 3000 Barrer and 530 Barrer for AF2400 and AF1600, respectively,
52 which are in good agreement with the literature data^{48, 51, 52, 54, 55}. The relative CO₂ flux
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3 showed in Fig. 9B was calculated according to the real operating conditions for flue gas CO₂
4 capture (i.e., CO₂ partial pressure = 0.13 bar) to offer a realistic comparison. In the case of
5 H₂O, permeability of 2400 Barrer and 530 Barrer (Fig. 9A) have been obtained for AF2400
6 and AF1600 respectively. In the case of the latter, the value is in good agreement with
7 literature data⁵⁴ obtained for the vapour permeation, whereas they are slightly different from
8 the one reported in the material data sheet. However, these differences can also be related to
9 the different procedure used for the membrane preparation (e.g., different boiling point of the
10 solvents), as reported in the material patent⁵⁶. The fluxes reported in Fig. 9B refer to the one
11 obtained for the pure liquid water and appeared to be one order of magnitude lower than that
12 of CO₂, consistently with the hydrophobic nature of the material family. In the case of the
13 amines, similar permeability values have been obtained (1450 and 1320 Barrer through
14 AF2400 and 500 and 390 Barrer through AF1600 for DEEA and MAPA respectively) that
15 were also in the same order of magnitude of the data obtained for water and CO₂. The amine
16 vapour pressures ($p^*(T)$) have been calculated using Antoine equation using the parameters
17 reported in literature for DEEA and MAPA⁹. However, looking at the fluxes measured for the
18 membrane samples, it is possible to see that a two order of magnitude difference exists
19 between the CO₂ and the organic penetrants, suggesting that the membrane is able to offer
20 certain selectivity between the CO₂ and the amines. This variation is likely related to the
21 much larger kinetic size of the organic compounds compared to the CO₂ molecule, which can
22 significantly limit their diffusion across the membrane layer. DEEA appeared to be slightly
23 less permeable than MAPA, likely due to the more branched molecular structure. However, a
24 larger experimental error is observed in case of the tertiary amine due to its lower flux. In the
25 case of DEEA, the error is in the range 25 – 35%, whereas in case of MAPA it reduced to 10
26 – 15%. Despite the experimental error, a clear difference exists between the CO₂ and the
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amines fluxes, pointing out that the membrane is able to favour the CO₂ permeation over amines.

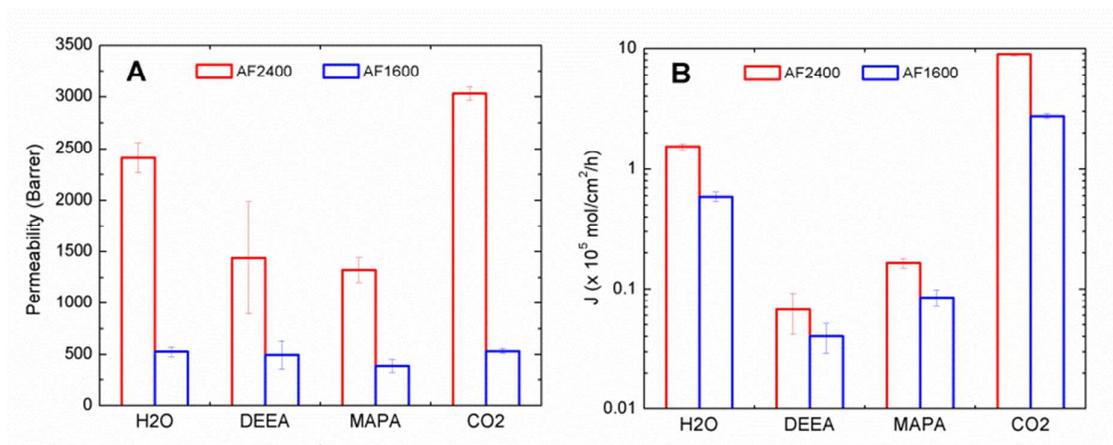


Figure 9 – CO₂, H₂O, DEEA, and MAPA permeability (A) and flux (B) through Teflon AF2400 and AF1600 dense membranes at room temperature (Error bars are calculated as standard deviation of consecutive measurements). The CO₂ flux is related to a CO₂ partial pressure of 0.13 bar (typical value for flue gas conditions), whereas in the case of H₂O, DEEA, and MAPA the fluxes are obtained from pure liquid experiments.

According to the fluxes obtained, the CO₂/Amine Transport Selectivity (α) was calculated according to Equation 4, and the results are shown in Figure 10. In order to have an idea of the effect of different DEEA-MAPA ratio, 3 different blends simulating possible volatile solvent compositions have been considered, namely 1D5M (1M DEEA, 5M MAPA, corresponding to a total amine content of ~ 62 wt%), 3D3M (3M DEEA, 3M MAPA, corresponding to a total amine content of ~ 68 wt%) and 5D1M (5M DEEA, 1M MAPA, corresponding to a total amine content of ~ 74 wt%). For the calculation of the amines flux for the specific DEEA-MAPA blend, the parameters reported in Table 3 are used to estimate the real amines driving force expected for the absorbent.

	ω_{AMINE}	x_{H_2O}	x_{DEEA}	x_{MAPA}	γ_{H_2O}	γ_{DEEA}	γ_{MAPA}
1D5M	0.62	0.774	0.038	0.189	0.801	5.736	0.110
3D3M	0.68	0.738	0.131	0.131	0.903	2.584	0.094
5D1M	0.74	0.688	0.260	0.052	1.081	1.395	0.083

Table 3 – Amine mass fraction (ω), liquid molar fraction (x) and activity coefficient (γ) of H₂O, DEEA and MAPA for the 3 different DEEA-MAPA blends taken as examples for the phase change solvents calculated from VLE data⁹.

Despite the larger free volume, which typically corresponds to a lower selectivity, larger CO₂/Amine transport selectivity was observed for Teflon AF2400, within the range 350 – 500 for the three different absorbent compositions considered. In the case of AF1600, the range decreased to 180 – 260, suggesting that the ability of preventing the amine permeation through the membrane is related to the amount of dioxole monomer rather than the PTFE block in the copolymer structure. A low concentration of DEEA in the absorbent (1D5M case) allows to reach a larger selectivity, compared to the other cases (3D3M and 5D1M), where the blend composition appears to have a rather limited effect on the CO₂/Amine transport selectivity. This effect is likely related to the larger activity coefficient of DEEA compared to that of MAPA, which makes the selective parameter more dependent on the concentration of the tertiary amine in the liquid phase. For the sake of clarity it must be specified that these results refer to an ideal case, where no interactions between H₂O, DEEA, MAPA, or CO₂ take place during the permeation, the feed liquid mixture is assumed to have ideal behaviour, and the permeability coefficient of the liquid is assumed to be constant over the entire concentration range. In order to verify the present outcomes, pervaporation experiments using the real mixture and membrane contactor tests must be carried out. This will be reported in a future work.

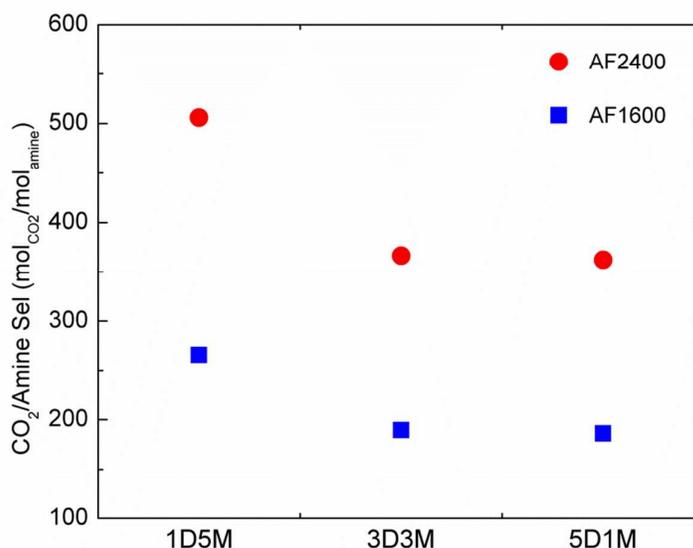


Figure 10 – CO₂/amine transport selectivity at room temperature for Teflon AF2400 and AF1600 calculated for different DEEA-MAPA ratios of the liquid mixtures, representing possible phase change solvents.

3.4. Wettability of AF2400

According to the results on the compatibility and gas/amine permeation properties, Teflon AF2400 has been identified as the most suitable material as the dense layer. In this view, contact angle experiments and surface tension measurements have been carried out with different liquid absorbents in this study in order to evaluate the wettability of the dense layer. The results for pure H₂O, 5M MEA and three DEEA/MAPA blends with different amine concentrations are reported in Figure 11. Water is used as reference, and the values of the contact angle and surface tension with regard to water are consistent with literature and the material data sheet^{57,58}. In case of 5M MEA, the surface tension decreased slightly compared to water, reaching values similar to the one reported in literature⁵⁸. Similarly, the contact angle of 5M MEA is also decreased, but remaining above 90°. When the DEEA/MAPA

blends are considered, lower surface tension values ($\gamma_L < 30$ mN/m) were obtained, likely related to the presence of the tertiary amine⁵⁹. Likewise, their contact angles with the polymer are decreased significantly, reaching values between 80 and 67°. According to these results, when phase change solvents are used as liquid absorbents and Teflon AF2400 is used as the membrane-liquid interface, the polymer wettability should not represent an issue for the mass transfer in a membrane contactor.

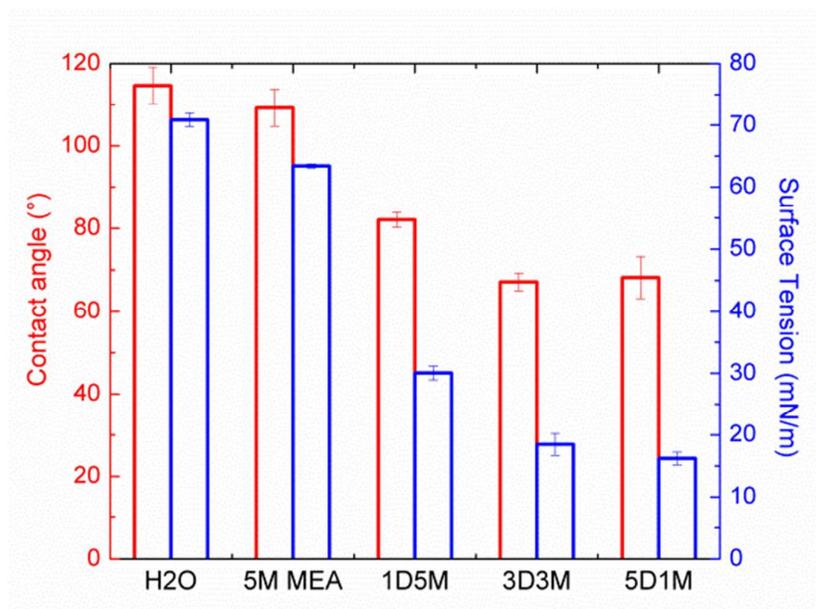


Figure 11 – Surface tension values for different liquids and their contact angles on Teflon AF2400 at room temperature.

4. Conclusions

In the present work, a thorough compatibility study of different polymeric membrane materials with the phase change volatile solvents was carried out to identify the best membrane material and morphology for the development of membrane contactors using energy efficient solvents. Chemical stability tests performed on porous materials indicate that porous PTFE and PP membranes have good stability towards the studied solvent systems

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3 based on DEEA-MAPA blends. However, immersion tests suggest that wetting phenomena
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5 are likely to happen for these two porous membranes in long-term operations.
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8 On the other hand, thin composite membranes can be used as a suitable gas/liquid interface
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10 for a membrane contactor using DEEA-MAPA blends. Dense Teflon AF series materials
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12 with high CO₂ permeability were found to be the most suitable solution. The transport
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14 properties of amines through the dense layers showed a difference as large as two orders of
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16 magnitude between pure amines and the CO₂ flux, which resulted in a CO₂/Amine transport
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18 selectivity larger than 300 in case of AF2400 and 150 in case of AF1600 for the various
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20 liquid compositions considered. In view of the larger CO₂ permeation rate and the higher CO₂
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22 and amine flux difference, the Teflon AF2400 can be considered the most suitable membrane
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24 material for the dense layer, as larger prevention of the amine evaporation can be expected.
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26 Contact angle tests, together with the low surface tension measured for the DEEA/MAPA
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28 blends, suggest that the ability of the phase change solvents to wet the membrane surface
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30 should not represent an issue in the membrane contactor application.
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34 Future study will be focused on the evaluation of the CO₂ separation performance in a
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36 membrane contactor using the phase change solvents and also on the improvement of
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38 efficiency of the dense layer in preventing the amine evaporation towards the gas phase.
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43 **Supporting information**

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45 Table S1, Composition of unloaded and CO₂-loaded 3D3M solution; Figure S1 and S2,
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47 Effect of pure MAPA on CFP and on PSF; Figure S3, colour variation observed for pure
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49 DEEA and for the 3D3M mixture; Figure S4 and S5, kinetics of liquids uptake in PDMS and
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51 Aquivion.
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Nomenclature

1D5M = 1M DEEA 5M MAPA aqueous solution;

3D3M = 3M DEEA 3M MAPA aqueous solution;

3D3M-LP = CO₂-loaded 3D3M solution, lower phase (CO₂-rich);

3D3M-UP = CO₂-loaded 3D3M solution, upper phase (CO₂-lean);

5D1M = 5M DEEA 1M MAPA aqueous solution;

A = permeation area;

AF2400 = Amorphous Teflon ($T_g = 240^\circ\text{C}$);

AF1600 = Amorphous Teflon ($T_g = 160^\circ\text{C}$);

AMP = 2-amino-2-methyl-1-propanol;

CFP = composite fluoropolymer;

DEA = diethanolamine;

DEEA = diethyl-ethanolamine;

FC-72 = fluorinated solvent;

J = transmembrane flux;

MAPA = 3-methylamino-propylamine;

MDEA = methyldiethanolamine;

MEA = mono-ethanolamine;

p_d = downstream pressure;

p_u = upstream pressure;

$p^*(T)$ = vapour pressure at saturation;

PDMS = polydimethylsiloxane;

PP = polypropylene;

PSF = polysulfone;

PTFE = polytetrafluoroethylene;

R = gas constant;

T = temperature;

V_d = downstream volume;

w = mass of a polymeric sample;

x = liquid molar concentration;

y = vapour molar concentration.

Greek Letters

Ω = liquid uptake;

θ = contact angle;

γ = activity coefficient;

γ_L = liquid surface tension.

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Table of Contents (TOC) Graphic

