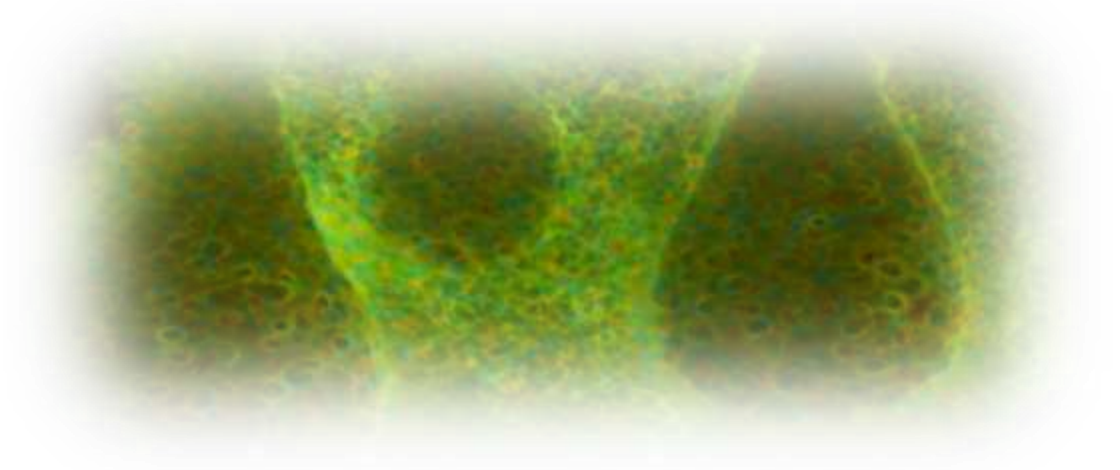
Supported ionic liquid membranes (SILMs) for CO_2 capture

Master Thesis
David Domingo Huguet



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June 2022

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Centre Tecnològic de Catalunya

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Acknowledgments

These last few months have been a new experience of which I am very proud to have been able to take part. At the beginning I was not sure if I would be able to go ahead with a project like this at the same time that I was dedicating the necessary hours to study and pass the subjects of the master's degree, but today, writing these words, I can assure that it is one of the best decisions I have ever made. The knowledge, not only academic, but also personal, that I gained during this period has helped me to define myself as a person and to make clear decisions regarding my academic and professional future. It is for these reasons that I would like to leave a record and, above all, I would like to thank all those people who have supported me from the very beginning, because without them I would not arrive until here.

First of all, I would like to thank my supervisor Dr. Adrianna Nogalska for all the effort and time she has dedicated to me and for everything I have learned from her. Without forgetting the fact that she was there to support me when the experimental world shows that things don't always work out the first time (or even the fiftieth time), but, nevertheless, always finding some use for the results or small discoveries that were made. Without her, this work would not have been nearly as profitable as it has turned out to be.

Secondly, I would like to thank Dr. Cyril Godard, academic supervisor, for his guidance and advice during this time. Together with his effort, since the topic dealt with in this work comes out his field of work.

On the other hand, I would like to thank all those people from the Chemical Technology Unit at Eurecat Tarragona who have been and are present during these months. Colleagues with whom we have shared lunches, dinners and much more. Thanks to whom I have acquired a great deal of new knowledge. To Dr. Miriam Diaz de los Bernardos, Dr. Iuliana Cota, Dr. Isabel Vicente, Dr. Alexey Shavel, Dr. Magdalena Olkiewicz, Dr. Bartosz Tylkowski, Dr. David Santiago, David Raya, Óscar Navarro, Meritxell Salvadó, Pere Verdugo and Alberto Martis for their advice, support and help both in and outside the laboratory. To Dr. Aitor Gual for his help with the ILs and his proposals for new compounds that could improve the results. To Enric Ros and Xavier Lara, the young fellows with whom I have spent so many hours synthetizing ILs. I would especially like to give special thanks to those who have spent more hours in the lab with me, such as Anna Mas and Roger Miró, thanks to whom the hours always pass more quickly even if things do not turn out as expected. To Laia Gil for always having a moment to have a quick coffee and talk about everything that we need, even though she is in total stressful moments writing her PhD thesis. And especially to Emma Fernàndez for all the help and all the times she has listened to me complaining and has given me the motivation to continue when you see that

the results do not come out as expected. Not forgetting Montse Carrasco, who is always on top of all the urgent orders and who watches me pass by at exorbitant speeds no matter what time it is.

The new PhDs Dr. Víctor Llamas for the help with his superlaser cutting necessary materials for my set-ups and Dr. Andreu Bonet for the designs of 3D printed materials for the project.

I would like to thank the staff of the Scientific and Technical Resources Service of the URV for their help in the characterisation of the membranes and the explanation of techniques such as ESEM, EDX or NMR, specifically Rita, Mariana and Ramon. Together with Ernest who was in charge of making the necessary module to test the membranes.

Agraeixo als meus amics que han estat allí per treure'm de casa sigui a fer una cervesa o un cafè (perquè són massa sanitos...) fent-me sentir que aquí a Tarragona també tinc una petita família que és allí per tot quan se'ls necessita.

No vull acabar sense la menció especial a la família, més concretament als meus pares qui han fet possible que pogués estar aquí durant aquests mesos ajudant en tots els sentits, escoltant-me, aconsellant-me i venint tots aquells mesos que jo no podia visitar-los, juntament amb la petita de la casa qui també m'ha donat tot el suport emocional i més.

Finally, I would like to thank the Eurecat Foundation for giving me the opportunity to do my Master's final thesis with them, also to SunCOChem project for letting me be a part of an European project with the high influence that it has and to the coordinators of the Master's degree for the guidance and the help given.

Abstract

One of the main gases responsible for the greenhouse effect is CO_2, coming from different anthropogenic sources, largely from the combustion in the industry sector. The European commission has a commitment to diminishing its emission in, at least, a 55% before 2030. To accomplish this objective, different approaches are being studied, such as redesign production processes to avoid CO_2 formation as by-product. The problem is dealing with the industrial processes that can not be replaced nowadays by greener ones e.g. combustions in power plants. In these cases, the only approach is the treatment of flue gases from the outlets before its final emission in the atmosphere. In this work, a new group of novel polysulfone membranes modified with ionic liquids based on imidazole rings (SILM's) have been synthesized, characterized, and tested for CO_2 capture abilities for further exploitation as one carbon source in industry.

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1) **Introduction**

The continued increase in world population and therefore its dependence on fossil fuels an energy source has been traduced in an increase in the atmospheric carbon dioxide (CO_2) concentration. This steadily rises in anthropogenic CO_2 emissions from the beginning of the industrial era has been traduced into an increase of atmospheric CO_2 from ~280 ppm in 1750[1] to ~415 ppm in 2020[1]. Carbon dioxide is considered a greenhouse gas (GHG), among others, because of its capacity to absorb the infrared range of electromagnetic radiation. This radiation comes from Earth's surface after the irradiation of sunlight, avoiding the dissipation of this energy through the atmosphere to the space leading to an increase in the global temperature. The rise in global temperature was limited by the Intergovernmental Panel on Climate Change (IPCC) up to 1.5 ºC by the end of the century. For achieving that purpose, a drastic reduction in CO_2 emissions is required, until the total decarbonization of the industry for 2050. Having a look at the principal industrial CO_2 emitters, refineries, power plants operated by fossil fuels, steel-producing plants, cement plants and the chemical industry, are the main ones responsible for the total emissions.[2] *Table* 1, shows more in detail the global emissions of CO_2 by sector in 2019, taking into account oil extraction, industry, energy and heat production and transport.[3]

Table 1: Global emissions of CO2 by sector in 2019

Sector	CO_2 emitted ($MtCO_2$)
Energy and Heat production	15761.94
Transport	8222.07
Industrial processes	1608.5
Oil + Fuel combustion	1891.51

Nowadays, different strategies are being implemented in order to reduce the CO_2 total emissions in different fields such as transport, in which the use of hybrid, electrical or less contaminant combustion vehicles is rising in number. In industry, new catalysts are being developed and reactions are being optimized to reduce the formation of waste-products is applied. Nevertheless, carbon dioxide is present in the industry and, in some cases, it cannot be avoided such as in the case of power plants or heating systems for industry. In them, the consumption of fossil fuels or other materials is the better way to produce efficiently this heat. Normally, this CO_2 produced in industry, with other gases such as nitrogen, oxygen and water vapour, is concentred in the flue gases coming through the industrial pipes. The concentration of it is quite variable in function of the type of industrial process in which is generated. As general values, the concentration of carbon dioxide in the flue gases of industry ranges between 3-4% in gas turbine power plants and 15-30% in steel and cement plants.[1] Lot of research has been carried out with the purpose of mitigating this CO_2 emission with different ideas, such as its capture or sequestration in solid absorbents using porous adsorbents.[4] The materials more studied for this purpose are namely porous organic polymers (POPs), metal-organic frameworks (MOFs), zeolites and modified zeolites, carbonaceous materials and graphene-based materials. The principal problem of CO_2 sequestration is the storage of materials containing high amounts of CO_2 to avoid its spread. The storage in underground reservoirs has been proposed as a principal solution, but it can only alleviate the problem, without being a final solution. Moreover, problems of underground leaking can be possible, traduced to soil contamination and acidification due to the acidic nature of the gas, becoming a bigger problem.[2]

In recent years, a new field of investigation has appeared proposing a solution, not the avoiding of CO_2 production but its capture and utilization as a reagent.[5] Because of the nature of CO_2 and composition, having two atoms of oxygen and one carbon atom can be seen as a cheap and global available one carbon feedstock. There are different industrial procedures in which CO_2 is already being used as feedstock such as urea production or polymers obtention.[6,7] Urea production is largely used worldwide because is a key intermediate for nitrogen-based fertilizers production but, the total consumption of CO_2 in this process is not enough to minimize the total emission of CO_2. Moreover, the CO_2 used in the synthesis, normally coming from captured CO_2 from flue gases, returns to the atmosphere within days of fertilizer application due to its decomposition in the presence of urease enzyme in soils (Figure 1).[8]

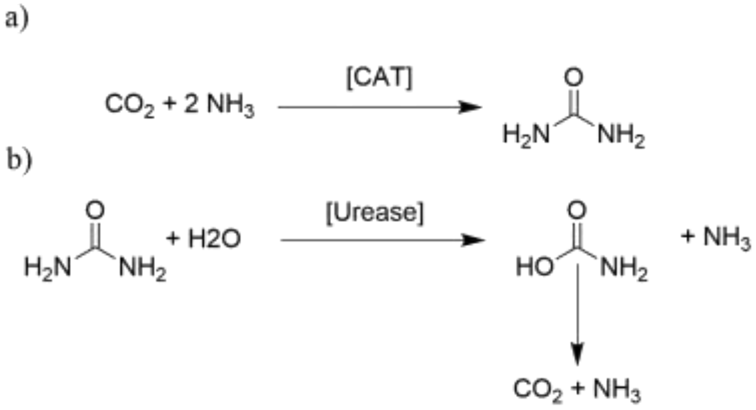


Figure 1: a) urea synthesis; b) urea decomposition in presence of urease enzyme

In the case of polymers obtained using CO_2 as feedstock, polyurethanes are one of the most widely spread using a reaction in which a polyol and a bis-isocyanate react to form the polymer.[9] The key lies in the use of propylene oxide in presence of CO_2 and a diol to synthetize the desired polyol monomer for the polymer (Figure 2).[7] Nevertheless, the consumption of CO_2, as in the case of urea production, is not enough to minimize the amount of CO_2 produced.

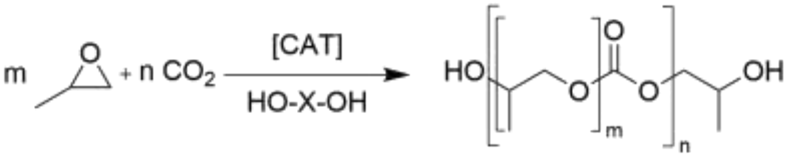


Figure 2: Polyol synthesis using CO_2 for polyurethanes production

The most recent advances are focused on the use of CO_2 as a reagent for the production of methanol, formic acid, cyclic compounds or carbon monoxide (CO), a key component for syngas production, among other valuable products.[10,2] This reagent is very important for the hydroformylation industry among others. Nowadays is being produced on large scale from steam reforming or coal gasification, both depending on fossil fuels as feedstock. The proposed methodologies for carbon monoxide, syngas and other valuable products obtention directly from CO_2 are based on electrochemical and photochemical reactions, a new field of chemistry that is growing up in publications every day due to its high versatility and lower energy consumption (Figure 3).[11,12]

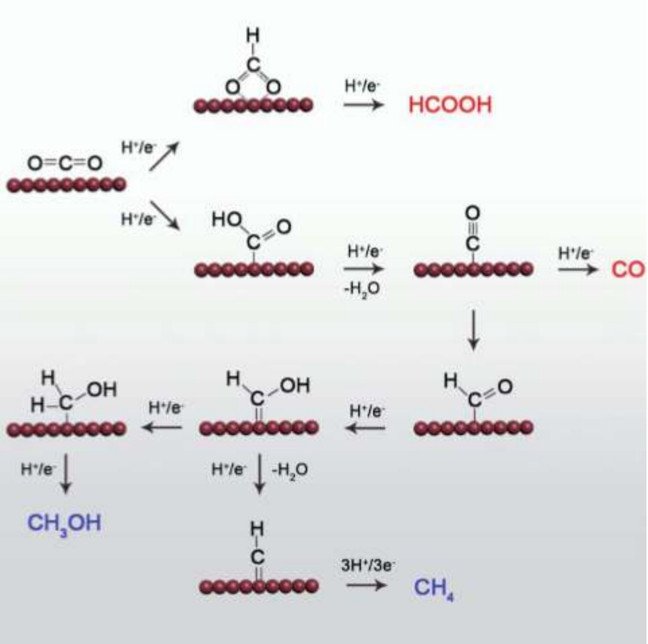


Figure 3: Electrochemical reaction of CO_2 to obtain valuable products. Figure reprinted from: ***J. Mater. Chem. A, 2020, 8, 15458–15478***

For this type of reactions, highly concentrated CO_2 is required and, in addition, it must be as pure as possible in order to avoid poisoning in the different catalysts used.[13] Normally, as mentioned before, flue gases contain other components such as nitrogen, water vapour and in most cases, if they comes from a combustion, sulfurated compounds that are the major responsible compounds of catalysts poisoning.[14] Because of that, a high number of methodologies are being proposed for a selective capture of CO_2 coming from flue gases. Among them, the use of selective permeable membranes is one of the most promising methodologies.

1.1) Membranes for CO_2 capture

Membrane technology for gas purification was first studied in the 1980s for natural gas as an alternative to amine solvents.[15] The idea of using membranes lies in the development of a very thin and highly porous material that allows the selective permeation of a target gas between all the compounds present in the gas mixture due to its properties. This technology is very efficient because the energy consumption in the process is nearly zero but the low partial pressures in which the flue gas comes out from the industrial pipes make it very difficult to efficiently capture the CO_2.[16] This procedure is based on the mass transfer between one side and the other side of the membrane and it is directly proportional to the amount of CO_2 present in the flue gas and the porosity of the membrane. In addition, high selectivity is difficult to achieve using only a membrane because normally the gases pass through the membrane porous without chemical interaction and are mostly distinguished by size.[17] Normally the selective separation between CO_2, N_2, O_2 and other possible gases such as CH_4 is very difficult. Because of that, a different approach has been highlighted in the literature, the use of combined systems considering one of the most characteristic properties of CO_2, its acidity. This system, named gas-liquid membrane contactor, has a porous membrane and a selective solvent with absorption capacity. Here, the membrane separates the gas phase and the solvent phase providing a high contact surface in the interface for the improved mass transfer.[18] Using this approach selectivity towards CO_2 is also increased because of the absorbing solvent nature. Having a specific type of solvent other gases diffusion into the absorbent solution can be neglected.

The liquid sorbent must have some characteristics: 1) a high reactivity towards the acidic molecule of CO_2 to increase its absorption, 2) high surface tension to avoid membrane wetting, 3) a moderate viscosity to facilitate CO_2 diffusion, 4) chemical compatibility with the membrane for long-time stability and, 5) low vapour pressure to avoid the loss of the solvent by evaporation.[19] Normally the solvents used at industrial levels are based on basic aqueous solutions, being alkanolamines, such as monoethanolamine, and potassium hydroxide solutions the most used. These aqueous solutions have high alkalinity reacting very fast with the acidic molecule of CO_2 and forming carbamates or carbonates depending on the nature of the solution.[20,21] However, these absorbent solutions present different problems due to their corrosive nature, the aqueous base of the solution, making them volatile and, the post-capture CO_2 desorption from the system to use the CO_2. This desorption is not chemically favoured as absorption, so a high amount of energy is required to desorb the CO_2 and regenerate the absorbent solution for its reuse.[20] To overcome these problems, new solvents are being studied with this purpose such as ionic liquids or deep eutectic solvents, having a high solubility of gases, high stability and practically non-vapour pressure. Moreover, they have excellent electrochemical properties, thus there is no need to desorb the CO2 as it can be used directly in the synthesis of added-value products. The membrane plays a key role in the system and its material study and development are crucial. Different characteristics must be accomplished by the membrane to fulfil its purpose. As mentioned before, the membrane must be a porous material with chemical stability against the solvent and the gases. On the other hand, it must be physically stable to be compatible with the operating conditions of pressure or temperature and have different properties such as hydrophobicity to avoid the wetting of the membrane and therefore, the filling of the pores with the solvent reducing the total surface area of the membrane.[22] Moreover, it must be processable and cheap to ensure that it can be manufactured at a big scale for its application at a reasonable price. Polymers are very interesting materials to be used as the matrix for the membrane due to the high number of different existing monomers, different polymerization technics and possible additives to ensure the desired chemical and mechanical properties. Regarding also its low price and easy preparation. One of the most used technics for porous polymeric membrane (PMs) preparation is phase inversion. For this procedure, a viscous solution of the desired polymer and a suitable solvent is prepared, then strudel or cast into a surface. Finally, it is immersed into a non-solvent bath where the polymer precipitates in form of a porous flat sheet or hollow fiber..[23] One of the characteristics of this procedure is that with the same polymer and different solvents, the internal morphology and the porosity of the obtained membrane can change, making possible to obtain the desired internal structure of the membrane depending on its application by control of the preparation conditions. Normally, the solvents used are organic solvents such as chloroform, dimethylformamide or n-methyl pyrrolidone and the non-solvent bath is mainly water. The solvent and non-solvent must be miscible liquids. Depending on the demixing of the solvent and the water, the pore shape can be controlled and therefore the internal morphology of the membrane. Normally the internal morphology of the membranes is a sponge-like porous structure. This porous structure can, moreover, be divided by the shape that the macrovoids present in the porous structure have. Being the more characteristics ones the drop-like macrovoids and the finger-like macrovoids (Figure 4), this last one formed due to fast diffusion of the non-solvent into the membrane.[23]

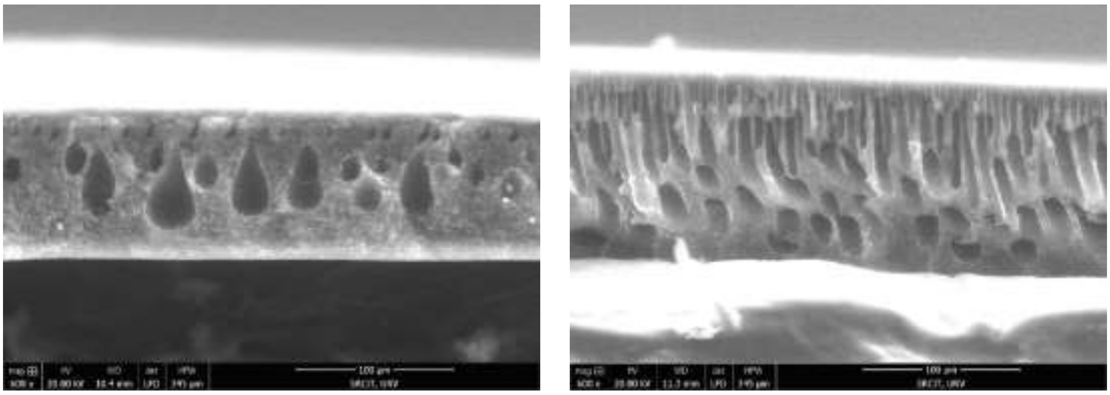


Figure 4:Left) drop-like structure membrane; Right) finger-like macrovoids structure

The polymeric materials commercially available mainly used form contactor membranes can be seen in Figure 5 but among them polysulfone (PSU) is the chosen for the membranes of this work due to its properties that can be listed as: 1) mechanical strength; 2) thermo-stability; 3) chemical stability; 4) relative hydrophobicity; 5) can be easily handled.[24,25,26] Furthermore, control of membrane morphology can be achieved easily by changing the preparation conditions.[27]

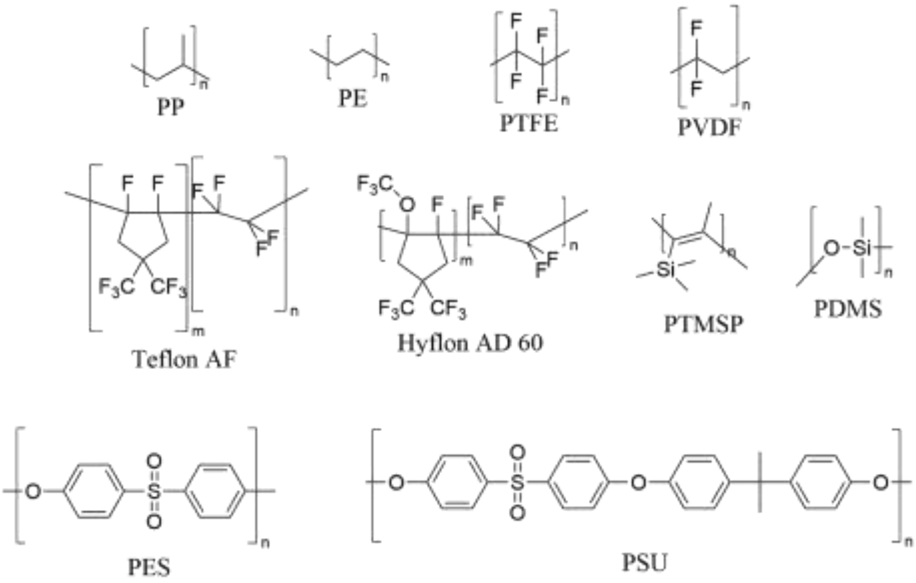


Figure 5: Polymer for contactor membrane preparation; PP: polypropylene; PE: polyethylene; PTFE: polytetrafluoroethylene; PVDF: Polyvinylidene fluoride; Teflon amorphous fluoropolymers; Hyflon amorphous perfluoro polymer; PTMSP: poly (1-trimethylsilyl-1-propyne); PDMS: polydimethylsiloxane; PES: polyethersulfone; PSU: polysulfone

1.2) Ionic liquids for CO2 capture

As mentioned in the chapter before, 1.1) Membranes for CO_2 capture, ionic liquids are one of the most promising absorbents for CO_2 capture using contactor membranes. Basically, ionic liquids are ionic compounds, also called salts or electrolytes, with a melting point under 100ºC. They are formed by a mixture of an organic cation and an organic or inorganic anion.[28,29] A list of the principal properties of ionic liquids can be seen below:[30]

- Negligible vapour pressure
- High thermal stability
- Non-flammable compounds
- High solubility of different polarity compounds
- High polarity solvents
- Stable against air and water
- High chemical stability in redox conditions
- Large electrochemical window
- High versatile compounds due to the number of possible cation-anion combinations

Figure 6 displays the most usual cations and anions used in ionic liquids.

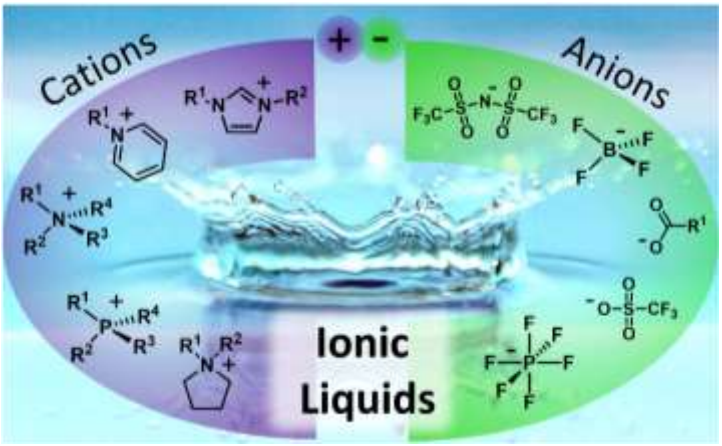


Figure 6: Main anion and cation used for ionic liquids. Online source: https://www.uni-saarland.de/en/chair/kay/ionische-fluessigkeiten.html (01/06/2022)

To facilitate the difference in properties among all the possible ionic liquids that can be synthetized they have been divided into different groups. Room-temperature ionic liquids (RTILs), task-specific ionic liquids (TSILs) and poly ionic liquids (PILs) are the mainly used. RTILs are widely used in different fields such as solvents in catalysis due to their tunable physicochemical properties providing a solvent that can easily dissolve organometallic catalysts and organic reagents in the same phase.[31] The problem with them is that their properties are not specific, and their application for CO_2 capture in flue gases with low concentration by physical or chemical interaction is difficult.[32] On the other hand, TSIL have been developed by applying concrete modifications to its cations or anions in order to ensure the desired properties. As example, one of the first TSIL developed was an amino group functionalized ionic liquid for CO_2 capture.[33] Ionic liquids can adsorb CO_2 by 2 different mechanisms.

The first mechanism belongs to one of the most singular properties of ionic liquids, its supramolecular structural organization. A physical absorption by non-covalent interactions is promoted by the accommodation of the CO_2 molecules in the cavities near the alkyl groups of imidazolium-based ionic liquids, known as the free volume effect.[34,35,36] Different computational studies have been performed in order to correlate the molar volume of ionic liquids and the CO_2 solubility in them.[37,38] As example, Figure 7 shows a molecular dynamics simulation of the accommodation of CO_2 molecules solvating the cation (1-butyl-3-methylimidazolium) in the cavities formed between the cation and the anion (PF_6^-). They have seen that CO_2 solubility increases as higher are the ILs molecular weight, molar volume and free volume.

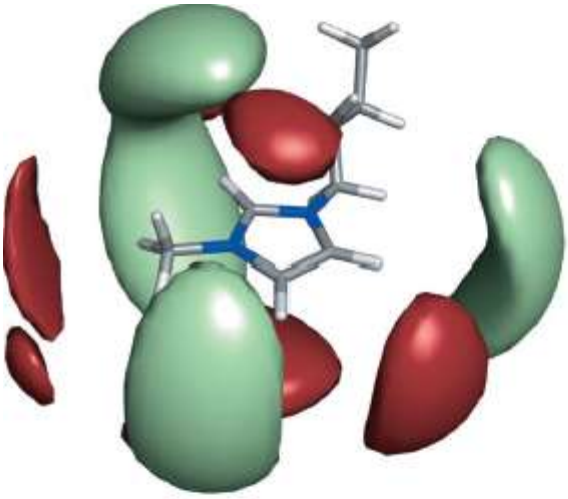


Figure 7: MD simulation for PF_6^- (green) and CO_2 (red) near 1-buthyl-3-methylimidazolium cation.
Reprinted from: ***Angew. Chem. 2013, 125, 13262 –13265***

The second mechanism is a chemisorption mechanism in which the acidic molecule of CO_2 reacts with the anion, known as Lewis acid-basic effect. Normally, this effect is produced when the anion contains a functionalized group such as amines, that can further react directly with the CO_2 molecule.[39,40] This can occur when CO_2 molecules are localized near the anions of the IL. Moreover, the CO_2 molecule can have a strong interaction with the cation, concretely in imidazolium-based ionic liquids. This is promoted by the reaction of the CO_2 molecule with the very basic centre formed by deprotonation of the most acidic hydrogen of the imidazolium ring.[41] Figure 8 shows the proposed mechanism in which the most acidic proton (in red) reacts with the carboxylic anion of the IL (in blue). Then the CO_2 molecule reacts with the transient carbene formed by the carbon deprotonation, giving an imidazolium-carboxylate compound that finally is stabilized by the same proton by hydrogen bonding, upper reaction.[41,42] As special case, the proline anion in this family of imidazolium-based ionic liquids has been reported to act as the responsible for the CO_2 chemisorption, due to the basic amino group present, stabilizing at the same time the cation of the IL, bottom reaction.[43]

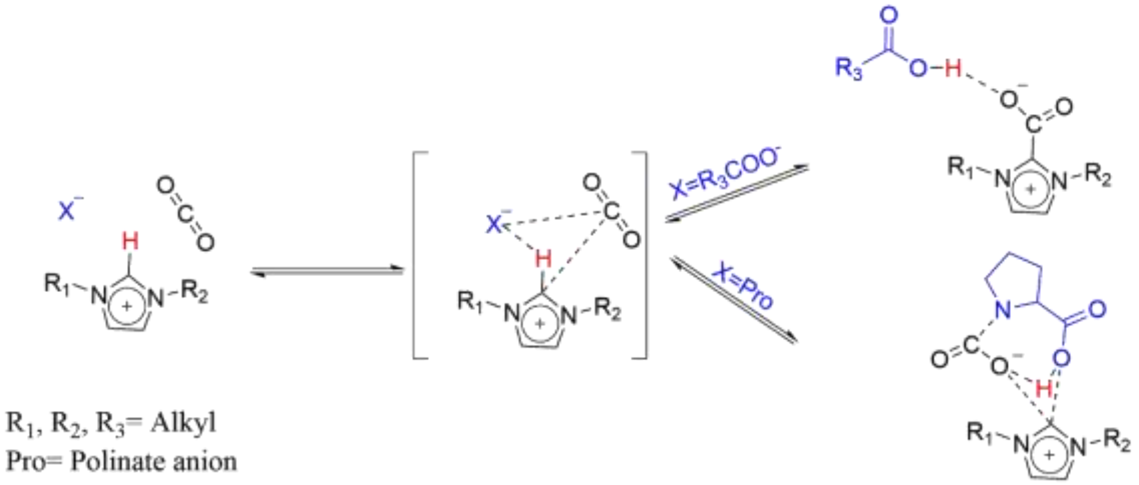


Figure 8: Proposed mechanism in literature for chemical interaction between CO_2 and imidazolium-based ionic liquids

This reactivity has been demonstrated using computational methods (DFT calculations) and experimental characterization such as NMR (^{1}H, ^{13}C, ^{15}N) spectroscopy, IR, Raman spectroscopy and ESI mass spectrometry.[34,41–44]

Normally, ionic liquids are proposed as absorbent solutions for CO_2 capture, but they can be used to increase the selectivity of absorption in membranes by immobilization of the ionic liquid inside the membrane structure. These novel materials are called supported ionic liquid membranes (SILMs).[45] In them, the ionic liquid in the structure is mainly supported by physical adsorption into the pores of the membrane using different technics such as direct soaking, impregnation, encapsulation or vacuum-assisted infiltration.[46] Recent publications in this field show the great number of possible applications based on this type of membrane and concretely its application for selective CO_2 capture from flue gases.[47,48]

1.3) SunCOChem project

This master thesis is part of the SunCoChem project, from the European Union’s Horizon 2020 research and innovation programme under grant agreement No. 862192. The project is addressed to the need of reduce the dependence on carbon feedstocks coming from non-renewable sources in the European Chemical Industry. The project aims to produce and distribute a tandem photoelectrocatalytical reactor coupled to a CO_2 capture device for the efficient production of valuable oxo-products from solar energy and CO_2. The key part of the project is to develop a system in which a direct CO-carbonylation of chemical precursors is carried out using sunlight as unique energy source and carbon dioxide captured from the flue gases of the chemical industry as feedstock for the carbonylation reactions. Is for this purpose that the development and study of new membrane materials are necessary to provide the pure feedstock and accomplish the principal objective of the project, to reduce the fossil fuel dependence on the chemical industry by using as an alternative a high and worldwide spread production green-house gas effect, the CO_2. Therefore, in order to be able to achieve this objective the novel membrane for the CO_2 capture stage must:

- Have a porous structure that provides an optimal morphology for mimicking leaf structure being capable of reaching high CO_2 assimilation ratios.
- Be modified using ionic liquids to obtain supported ionic liquid membranes (SILMs) to improve the membrane efficiency, mass transfer and selectivity. Furthermore, study the stability of these ionic liquids in the membrane along time with the modification method selected.
- Provide a high selectivity for the proper operation of the CO_2 conversion in the photoreactor, preventing the pass of other gases present in the flue gas such as oxygen, nitrogen or water vapour.

2) **Objectives**

This project was born looking at the current environmental problems originated from industrial human production and the atmospheric pollutants derived from it. Looking forward to the European commitment for the reduction of one of the mainly contributors to the greenhouse effect gases before its emission, this project aims to fulfil the specific requirements of the SunCOChem project (Figure 9).

- The principal objective of this master thesis is to prepare, characterize and test a porous membrane based on polysulfone for the CO_2 separation from flue gases from DOW plants. Moreover, to improve the CO_2 solubility, permeability and selectivity of the membrane by its modification with physical incorporation of ionic liquids in its porous structure.
- As secondary objectives, the synthesis and characterization of different ionic liquids. In addition, scaling up of the synthetic procedure for ionic liquids preparation will be also studied.

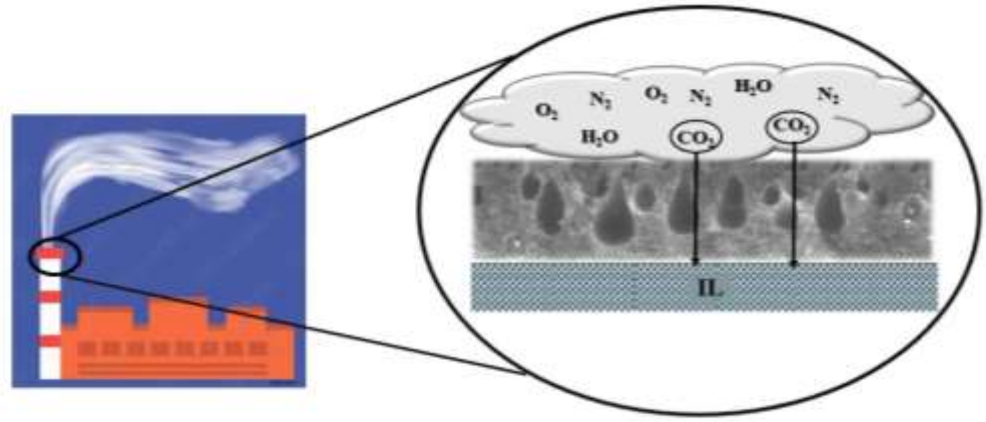


Figure 9: Representative scheme of the project

3) Experimental Section

3.1) General Methods

N,N Dimethylformamide (DMF, 99%); Acetonitrile (ACN, 99,8%); 1,2-Dichloroethane (DCE, 99%); Sodium hydroxide in pellet form (NaOH,97%); Acetic acid glacial (99%) and Succinic acid (99,5%) were purchased from Fisher; 1-Methyl-2-pyrrolidone (NMP, 99%); 1-Chlorobutane (99%); Benzoic acid (99%); and Oxalic acid dihydrate (99,5%) were purchased from Acros Organics; Polysulfone (PSU) (Mw 35,000 Da) in transparent pellet form; 1-Methylimidazole (99%); Pivalic acid (99%); DL-Proline (99%) and Imidazole (99%) were purchased by Sigma-Aldrich; Phthalic acid (99%) and Amberlite IRA-402(Cl) ion exchange resin were purchased by Alfa-Aesar; Formic acid (99%) was purchased by Merck, Ethyl Acetate (99,9%) was purchased by VWR Chemical and gases (CO_2 and N_2) were purchased from Linde.

Polysulfone (PSU); N,N Dimethylformamide (DMF) and 1-Methyl-2-pyrrolidone (NMP) were used for membrane preparation. 1-Chlorobutane;1-Methylimidazole; 1,2-Dichloroethane (DCE); Acetonitrile (ACN) and Ethyl Acetate were used for Ionic Liquids preparation. Sodium hydroxide (NaOH), Amberlite IRA-402(Cl) ion exchange resin, Acetic acid glacial, Succinic acid, Oxalic acid, Benzoic acid; Pivalic Acid, DL-Proline, Formic acid, Imidazole and Phthalic acid were used for the preparation of task-specific ionic liquids preparation.

Nuclear Magnetic Resonance (NMR) was used to determine the composition of synthesized ionic liquids. Monodimensional (^{1}H) experiments were performed in a Bruker Aveance Neo 400 MHz spectrometer using deuterium oxide (D_2O) as solvent. Chemical shifts (ppm) were given relative to trimethyl silane (TMS) in ^{1}H NMR (16 scans).

Fourier transform infrared spectroscopy (FT-IR) was used to verify the presence of the ILs in modified membranes. Spectra were obtained by using a Bruker Vertex-70 instrument with Attenuated Total Reflectance (ATR) sample holder by acquiring 32 cumulative scans with a resolution of 4 cm^{-1}.

Physical characterization was done by Environmental Scanning Electron Microscopy (ESEM) using a FEI Quanta model 600 electron microscope with a resolution of 3 nm. Morphological characterization was carried out under a low vacuum with a large feed detector (LFD). The ESEM micrographs were recorded with 600 magnifications. Membrane composition was obtained with PentaFETx3 Link Dispersive Energy X-ray Spectroscopy (EDXS) managed by Inca Oxford installed in the same equipment. Membranes were fractured in liquid nitrogen after cleaning by immersion in ethanol and fixed to the suitable support for the cross-section analysis. Micrographs obtained from ESEM were analysed with ImageJ software to determine membrane thickness.

Viscosity measurements were carried out using an IKA Rotavisc Lo-Vi Complete, with an extender connector Vols 1.11, a Spindle Vol SP-6.7 and a sample chamber Vol-C-RTD-1.

Surface tension was determined using a pendant drop system with a Dataphysics OCA 15EC. 75% w/w solutions of ionic liquid in miliQ water were placed in a Hamilton de 500/gt syringe and the maximum droop volume was achieved using a continuous flow dispenser controlled manually. All determinations were carried out per triplicate at room temperature from a digital image by SCA software included in the apparatus.

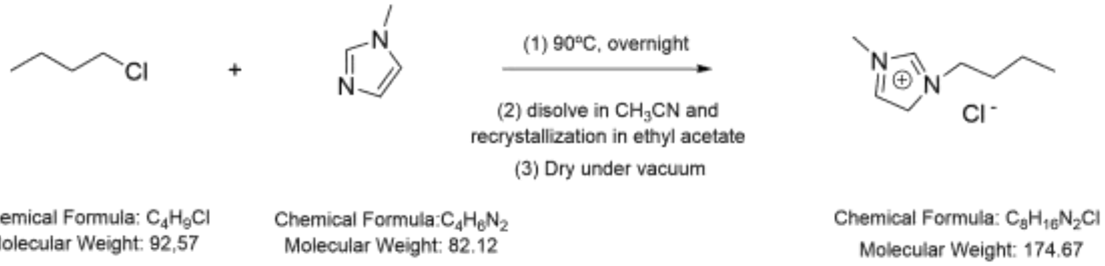
3.2) Membrane preparation

In a 250 mL bottle, a 20% w/w solution of polysulfone was prepared by mixing (20 g, 0.57 mmol) of polysulfone with (85 ml) of dimethylformamide (DMF). The solution was stirred over 48h to ensure the complete dissolution of the solid, having at the end a dense colourless solution. This procedure was repeated using n-methyl-2-pyrrolidone (NMP) as solvent in order to study the solvent effect on the membrane morphology. After that, the solution was kept for 24 h without stirring to avoid the presence of air bubbles in the solution.

Membranes were prepared by phase inversion method, namely by immersion precipitation, at room temperature. The procedure consists of the casting of the obtained homogeneous solution onto a glass support with a casting knife (gap 200 μm) and the direct immersion into a coagulation bath containing water. Membranes precipitate instantly by solvent exchange with water (acting as a non-solvent) having as product a white, thin and flat solid film, that was dried at air for 48 h and stored.

3.3) Synthesis of bench ionic liquids (ILs)

3.3.1) 1-methyl-3-butyl-imidazolium chloride synthesis (BMI.Cl)



Scheme 1: BMI.Cl synthesis

In a 250 mL round bottom flask with double neck, 79.52 g (0.85 mol) of 1-chlorobutane and 70.52 g (0.85 mol) of 1-methylimidazole were mixed. The solution was heated under reflux at 90 ºC for 72h with stirring. After 72h the unreacted reagents were evaporated under vacuum at 50 ºC and the obtained solid was purified by recrystallization using acetonitrile as a solvent and ethyl acetate as a crystallization phase. A white crystalline solid was obtained as a product, that was filtered and dried under vacuum leading to 132 g of 1-buthyl-3-methylimidazolium chloride with a 90% of yield. Product was characterized by ^{1}H NMR (see SP: figure S.I. 1)

3.3.2) 1-methyl-3-butyl-imidazolium chloride scale-up synthesis

In a 2 L round-bottomed glass reactor with a lid of 6 openings (Figure 10), 267 g (2.85 mol) of 1-chlorobutane and 237 g (2.85 mol) of 1-methylimidazole were mixed. The solution was heated under reflux at 80ºC for 96h without stirring. After reaction time, unreacted reagents were evaporated under vacuum at 50ºC and the solid obtained was purified by recrystallization using acetonitrile as solvent and ethyl acetate as crystallization phase. A white crystalline solid was obtained as a product, that was filtered and dried under vacuum leading to 480 g of 1-buthyl-3-methylimidazolium chloride with an 96% of yield.

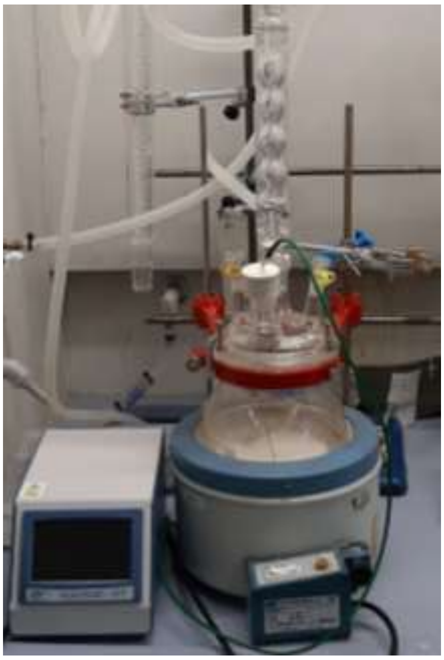
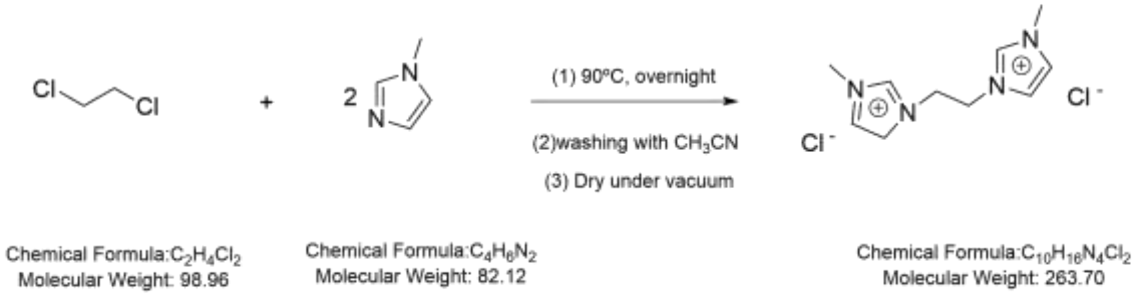


Figure 10: Scale-up set up for BMI.Cl and BISCAT.Cl synthesis

3.3.3) 2,2(ethanediyl)-bis-(1-methyl-imidazolium) chloride synthesis (BISCAT.Cl)



Scheme 2: BISCAT.Cl synthesis

In a 250 mL round bottom flask with double neck, 56,98 g (0.57 mol) of 1,2-dichloroethane and 94,54 g (1.15 mol) of 1-methylimidazole were mixed. The solution was heated under reflux at 90 ºC for 24 h with stirring. After reaction time, the unreacted reagents were evaporated under vacuum and the obtained solid was washed with acetonitrile. A white crystalline solid was obtained as a product, that was finally dried under vacuum leading to 130 g of 2,2-(ethanediyl)-bis-(1-methyl-imidazolium) chloride with an 86% of yield. Product was characterized by ^{1}H NMR (see SP: figure S.I. 23)

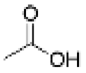
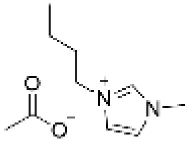
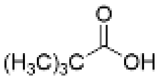
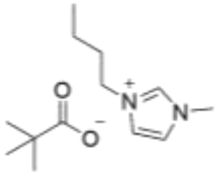
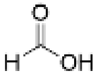
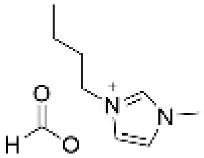
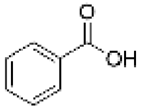
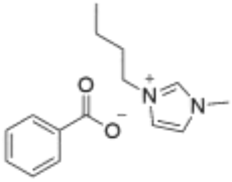
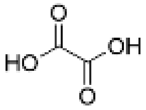
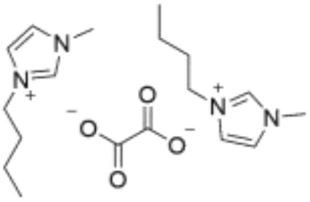
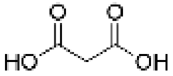
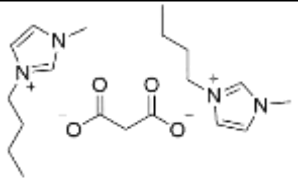
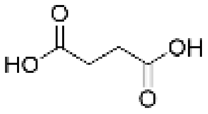
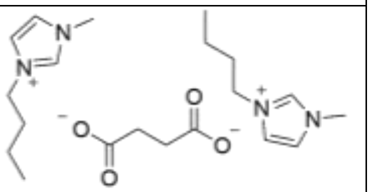
3.3.4) 2,2(ethanediyl)-bis-(1-methyl-imidazolium) chloride scale-up synthesis

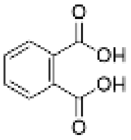
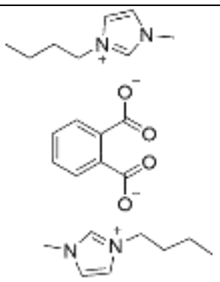
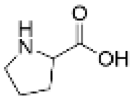
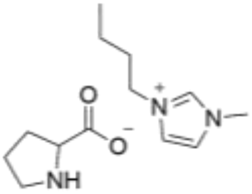
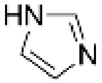
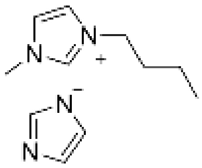
In a 2 L round-bottomed glass reactor with a lid of 6 openings (Figure 10), 241 g (2.41 mol) of 1,2-dichloroethane and 400 g (4.82 mol) of 1-methylimidazole were mixed. The solution was heated under reflux at 70ºC for 96 h without stirring. After reaction time, unreacted reagents were evaporated under vacuum at 40ºC and the solid obtained was washed with acetonitrile. A white crystalline solid was obtained as a product, that was finally dried under vacuum leading to 540 g of 1-buthyl-3-methylimidazolium chloride with an 85% of yield.

3.4) Task-specific ionic liquids synthesis by anion exchange

Using a glass column (3 cm x 50 cm) with 7 cm of a strong base ion exchange resin (21.5 g) the chlorine anion of the previously synthesized BMI.Cl was exchanged for the different conjugated bases of the acidic compounds which can be seen in Table 2.

Table 2: Compounds used for the ionic liquid anion exchange and ionic liquids obtained.

Carboxylic acid	Structure	Carboxylic acid pKa	Ionic liquid obtained
Acetic acid (OAC)		4.8	
Pivalic acid (PIV)		5.0	
Formic acid (FORM)		3.7	
Benzoic acid (BENZ)		4.2	
Oxalic acid (OXA)		1.2 / 4.2	
Malonic acid (MAL)		2.8 / 5.0	
Succinic acid (SUC)		4.2 / 5.4	

Phthalic acid (FTAL)		2.9 / 5.5	
Proline (PRO)		2.0 / 11.0	
Imidazole (IM)		6.9	

The procedure for the anion exchanges was the same for all the compounds in Table 2. First, to ensure that all the active sites of the resin were free of chlorine anions, 100 mL of a 2 M solution of NaOH in mili Q water were passed through the column. After that, 750 mL of mili Q water were passed to eliminate the excess of hydroxy anions and have a neutral pH in the resin. All the procedure was controlled by a pH indicator. Then, the resin was activated by reaction of the hydroxy anions of the solution with the triethylamine active sites of the resin. Previously the active sites were occupied with chorine anions that form sodium chloride (NaCl) with the sodium cations presents in the aqueous sodium hydroxide solution. Then, aqueous solutions of 0.1M of 1-buthyl-3-methylimidazolium chloride were passed through the column with an additional pass of 250 mL of mili Q water to wash out the remaining ionic liquid. Finally, the calculated weight of the desired acidic compound was added directly to the aqueous solution and stirred in a 1 L Erlenmeyer for 48 h to ensure the pH equilibrium and the total interchange between hydroxy anions and the carboxylate or basic anions. In the end, the water was evaporated under reduced pressure using a rota-vapour with an 80ºC water bath and the ionic liquid obtained was totally dried under vacuum for 12h at 50ºC. All obtained ILs are listed in Table 2 and were characterized by ^{1}H NMR and IR (see S.I. 1.1).

3.5) Density Ionic Liquids and Ionic Liquids 75% w/w solutions

All Ionic Liquids were first dried under high vacuum for 4 h at 60 ºC before density determination. Then, using an electronic pipette (Sartorius Picus NxT Electronic Pipette, 50-1000µL) 1 mL of Ionic Liquid was collected and its weight was measured using an analytical scale for triplicated to obtain the ionic liquid density (g/ml). The same procedure was followed for 75% w/w in milli Q solutions of ILs, where water was added to dry ILs.

3.6) Viscosity Ionic Liquids 75% w/w solutions

The viscosity of ILs solutions used for membrane modification (75 % w/w ionic liquid in mili Q water) was measured per triplicate using an IKA Rotavisc Lo-Vi. All measurements were carried out at room temperature the same day in order to ensure similar temperatures for all of the solutions (21.5-22 ºC).

3.7) Surface tension Ionic Liquids 75% w/w solutions

The surface tension of ILs solutions used for membrane soaking (75% w/w ionic liquid in mili Q water) was measured per triplicate by taking a photo of the bigger volume achieved in pendant drop before its fall. As reference, syringe diameter was taken and the density of the solution determined before. Measurement was obtained by automatically drop contour set using SCA software, see Figure 11.

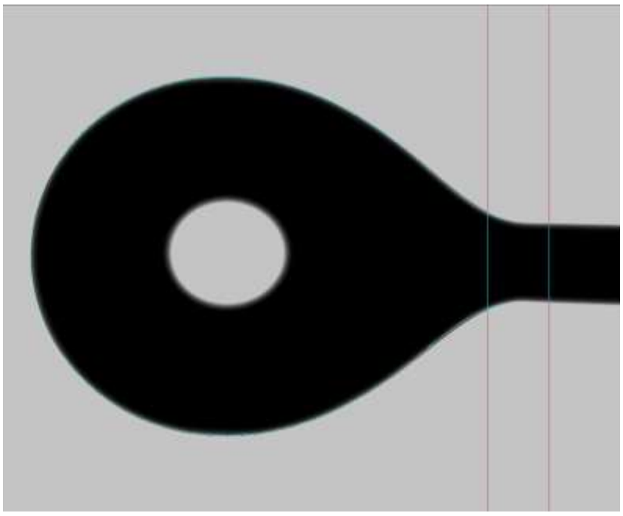


Figure 11: Automatic drop contour identification by SCA software for surface tension determination

3.8) Membrane modification by soaking with ionic liquid

Membranes were cut using a surgical knife in two different sizes 3 x 3.5 cm and 8 x 8 cm and placed in an oven at 60 ºC for 72h. Dry membranes were weighted using an analytical scale (Sartorius ED224S Extend Analytical Balance) and immersed into a 75% w/w solution of ionic liquid and mili Q water. Membranes were left in the solution for 72 h with a flip at 35 h to ensure the homogeneous interaction of all the membrane volume with the solution. After that, the membranes were blot dried and placed in the oven at 60 ºC for 72 h to ensure water removal and weight gain. The difference in weight before and after soaking gave the value of the amount of the ILs introduced to the membrane.

3.9) CO_2 solubility tests

The CO_2 solubility in obtained membranes was determined by its pressure decay in a closed chamber. All tests were carried out in a stainless-steel reactor of 50 mL volume with glass filler to reduce the total volume of the system to 28 mL. All experiments were performed at 30 ºC to ensure reproducibility. The pressure was acquired by an electronic manometer (STORK-Solutions, model UPS-HSR-B02P5G, range -1 to 2.5 bar).

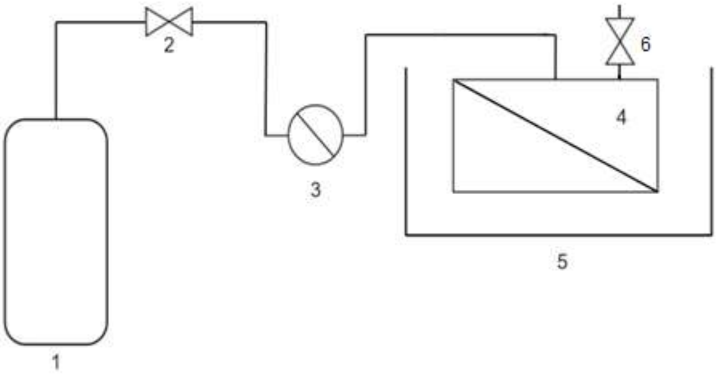


Figure 12: Solubility system: 1) CO2 bottle, 2) valve to close the system, 3) electronic manometer, 4) reactor containing membrane, 5) water bath at 30ºC, 6) exit valve.

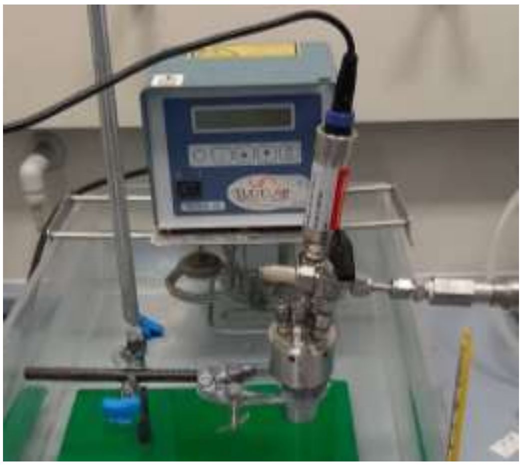


Figure 13: Real set-up for solubility experiments.

The procedure for conducting the experiments was as follows. The membrane (3 x 3 cm), previously dried at 60 ºC for 72 h and stored under non-humidity ambient until ambient temperature, was introduced into the reactor. Then, the reactor was immersed in the water bath

(Figure 12, Figure 13). After temperature stabilization, the system was purged with 2 bar of pure N_2 three times to ensure complete air removal from the reactor volume. The next step was pressurizing the system until 2 bar by closing the valves with pure N_2 for 30 minutes until pressure stabilization to confirm its hermeticity. Then, the system was depressurized, directly charged with pure CO_2 until 2 bar and the total pressure of the closed system was measured for 5 h. Finally, the system was opened and the membrane extracted for further characterization.

To determine the solubility coefficient, first of all, the adsorbed CO_2 moles must be determined following the next equation (see Equation 1).

$$n_{CO2} = \frac{(P_i - P_f) * (V_v - V_m)}{R * T}$$

Equation 1: Adsorbed moles calculation

In which:

n_{CO2} – adsorbed moles [mol]
P_i – initial pressure [Pa]
P_f – final pressure [Pa]
V_v – volume empty chamber [m^3]
V_m – volume membrane material [m^3]
R – gas constant (8,314 [$m^3 \cdot Pa \cdot K^{-1} \cdot mol^{-1}$])
T – temperature [k]

To calculate the volume of membrane material (PSU+ILs), polysulfone density ($d_{polysulfone}$=1.24 g/mL)[25] and ionic liquids density is required, value previously determined experimentally (see 0. The real volume of the membrane is measured based on the correlation between the mass of 1cm^2 and polysulfone density, and ionic liquid volume is determined by the mass increase of the membrane.

The solubility coefficient was determined following Equation 2.

$$S = \frac{V_{stp}}{V_m * P_f}$$

Equation 2: Solubility coefficient determination

In which:
S – solubility coefficient [m^3 (STP) $m^{-3}_{membrane}$ atm^{-1}]
V_{stp} – the volume of CO_2 adsorbed in standard conditions STP [m^3] (at 1 atm and 273.15 K)
V_m – membrane material volume [m^3]
P_f – final pressure after stabilization [atm]

3.10) CO_2 Permeability tests

All tests were carried out in a home-made stain-still module equipped with an electronic manometer (STORK-Solutions, model UPS-HSR-B02P5G, range -1 to 2.5 barg), a manometer (model P915, range 0 to 2.5 bar) and a manual bubble flow meter (Supelco Manual Bubble Flowmeter (standard Version) model 20432).

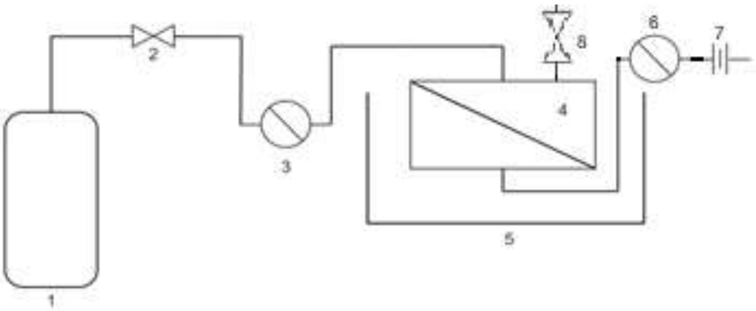


Figure 14: Permeability system: 1) CO2 bottle, 2) valve to close the system, 3) manometer, 4) still module containing membrane, 5) water bath at 30ºC, 6) electronic manometer, 7) manual bubble gas flow meter, 8) exit valve.

Figure 15: Real set-up for permeability experiments.

The procedure for conducting the experiments was as follows. The membrane (8 x 8 cm), previously dried at 60ºC for 72 h and stored under non-humidity ambient until ambient temperature, was introduced in the stain-steel dead-end module (Figure 14, Figure 15). Then, the system was immersed in the water bath at 30ºC. After temperature stabilization, the pure CO_2 or N_2 passed through the system, above the membrane, and was set at different inlet pressures (0.5, 1, 1.5 and 2 bars). Once stabilized, the outlet pressure, as well as the outlet gas flow, were measured on the other side of the membrane and the obtained values were used to calculate the CO_2 permeability.

While the gas used is pure CO_2 or pure N_2 its concentration in the inlet and outlet gas was supposed to be 100%. So, the permeability only depends on the gas inlet pressure, outlet pressure, the gas flow, the temperature and the membrane area. First of all, the volumetric flow rate in standard conditions must be determined by the following Equation 3

$$Q_{STP} = \frac{P * Q * T_{STP}}{T * P_{STP}}$$

Equation 3: Volumetric flow rate determination in standard conditions

In which:

Q_{STP} – volumetric flow rate in standard conditions [cm^3 (STP)/s]
P – exit pressure [cmHg]
Q – exit flow [cm^3 / s]
T_{STP} – standard temperature [k]
T – temperature [k]
P_{STP} – standard pressure [cmHg]

After that, the permeability can be obtained by the following Equation 4

$$Perm = \frac{Q_{STP} * l}{A * \Delta P}$$

Equation 4: Permeability determination

In which:

Perm – Permeability in barrer [cm^3 (STP) * cm/ (cm^2 * s* cmHg)]
l – membrane thickness [cm]
A – membrane area [cm^2]
ΔP – pressure difference across membrane [cmHg]

Finally, the diffusion coefficient of the gas across the membrane can be obtained by division of the permeability by the solubility previously determined, see Equation 5.

$$D = P/S$$

Equation 5: Diffusion coefficient determination

4) Results and discussion

4.1) Membrane modification supporting Ionic Liquids

Before determining the effect of the incorporation of Ionic Liquids in the membranes on their physico-chemical properties, first, the internal morphology of the membrane has been studied. In order to determine which conditions were the best to obtain membranes that have the best characteristics to immobilize the Ionic Liquids in its porous structure. Two different membranes were prepared with the same methodology only changing the solvent used for the polymeric solution preparation. Table 3 shows the conditions used for membrane preparation.

Table 3: Supporting membrane preparation conditions

	M_Blanc_1	**M_Blanc_2**
Process	Immersion precipitation	
Polymeric Solution	20% w/w of polysulfone	
Solvent	DMF	NMP
Casting Knife (µm)	200	
Support	Glass	
Membrane Thickness(µm)	100.7 ± 0.7	130 ± 2

The internal pore morphology was determined by a cross-section study using Environmental Scanning Electron Microscopy (ESEM), Figure 16 and Figure 17, show the micrographs obtained.

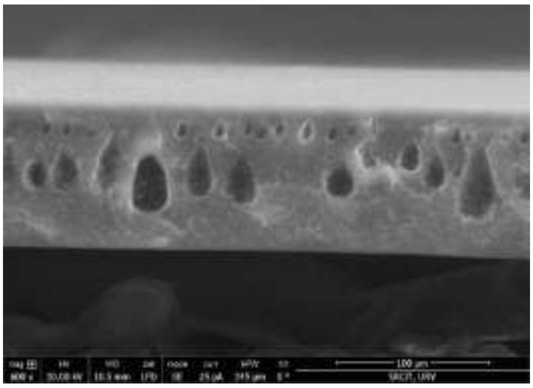


Figure 16: ESEM image of M_Blanc_1

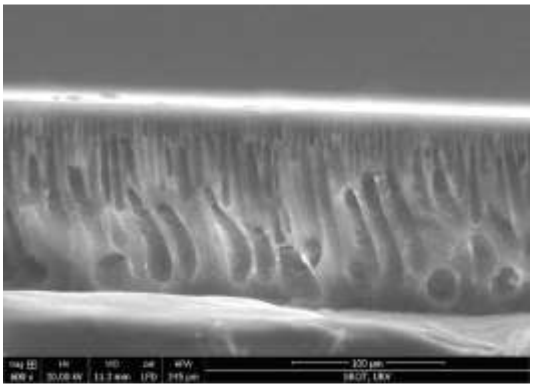


Figure 17: ESEM image of M_Blanc_2

As can be seen, the internal structure of **M_Blanc_1** membrane (Figure 16) was filled with micropores and macrovoids with a drop-like structure while **M_Blanc_2** membrane (Figure 17) was filled with macrovoids having a finger-like structure. A direct morphology dependency on the solvent used can be seen, and because of that, membranes obtained using DMF as solvent (drop-like pore structure) were chosen as the standard ones to perform the following experiments. This decision was made based on the pores structure, using as modification technic the soaking method the pore filling cannot be controlled and we supposed that finger-like pore type membranes can be completely obstructed by the presence of ionic liquids reducing the mass transfer and avoiding an increase in membrane efficiency.

To determine the effect of the incorporation of Ionic Liquids in the membranes to improve the CO_2 adsorption, a total of 12 different membranes have been prepared, having 1-butyl-3-methylimidazolium (BMI) as cation and different anions, chlorine (Cl) and the conjugated bases of different carboxylic acid (see Table 2). The conditions can be seen in Table 4. Three different types of ionic liquids were prepared and added to membrane in order to study influence of 1) carboxylic acid as anion (**M_2_BMI.Cl** to **M_6_BMI.BENZ**), 2) dicarboxylic acid as anion (**M_7_BMI.OXA** to **M_10_BMI.FTAL**) and 3) presence of nitrogen in both cation and anion (**M_11_BMI.PRO-M_12_BMI.IM**) on the membrane properties. The first group were ionic liquids having as anion a carboxylic acid and therefore one cation per mole of ionic liquid. The second group were ionic liquids having as anion dicarboxylic acids, having two cations per mole of ionic liquid. Finally, the third ones were ionic liquids that have nitrogen atoms in the cation and the anion, being one atom of nitrogen (**M_11_BMI.PRO**) or 2 atoms of nitrogen (**M_12_BMI.IM**).

Table 4: Different membranes prepared to determine the effect of ionic liquids

Membrane	Group division	Ionic liquid cation	Ionic liquid Anion	Soaking time (h)
M_Blanc_1	---	---	---	---
M_2_BMI.Cl	1	BMI	Chlorine	72
M_3_BMI.OAC		BMI	Acetate	72
M_4_BMI.PIV		BMI	Pivalate	72
M_5_BMI.FORM		BMI	Formate	72
M_6_BMI.BENZ		BMI	Benzoate	72
M_7_BMI.OXA	2	2 BMI	Oxalate	72
M_8_BMI.MAL		2 BMI	Malonate	72
M_9_BMI.SUC		2 BMI	Succinate	72
M_10_BMI.FTAL		2 BMI	Phthalate	72
M_11_BMI.PRO	3	BMI	Prolinate	72
M_12_BMI.IM		BMI	Imidazolate	72

4.1.1) Mass increase of membranes

One of the easiest ways to determine if the membranes have been modified by the incorporation of the ionic liquids in the pores was by measuring a mass change of the membrane before and after the soaking procedure. With that, a first approach on the ionic liquid adsorption has been obtained and can be correlated with the different ionic liquid structures and physical properties. The following graphics display the mass increase (%) obtained for the different groups of membranes (Figure 18, Figure 19 and Figure 20).

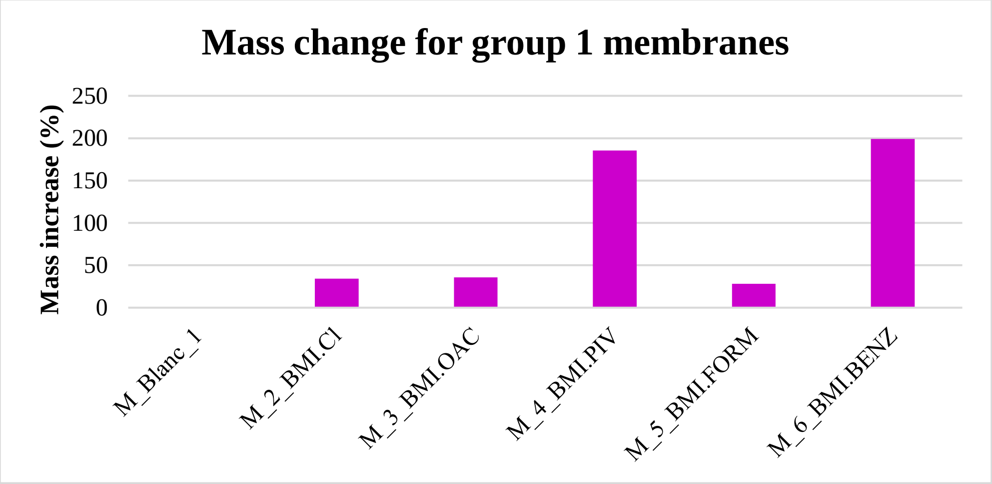


Figure 18: Mass increase of membrane after soaking in the desired group 1 ionic liquid

As can be seen in Figure 18, the best adsorption of ionic liquid in the membrane was achieved with **M_4_BMI.PIV** and **M_6_BMI.BENZ**, which were the ones soaked in ionic liquids having 1-methylimidazole as cation and pivalate and benzoate as anions respectively. The mass increase rises to values near 200%, while the others have a mass increase of less than 50%, indicating that these ionic liquids have much better adsorption.

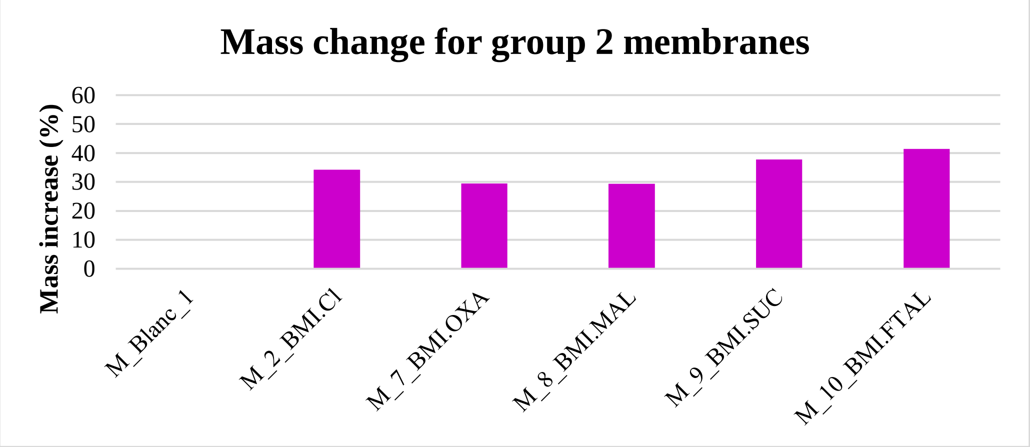


Figure 19: Mass increase of membrane after soaking in the desired group 2 ionic liquid

Figure 19, displays the mass increase values for the membranes soaked in dicarboxylic acid derived ionic liquids. In this case, the values were similar among the used ILs and were lower than 50%, comparable to those obtained with the first group of membranes (except **M_4_BMI.PIV** and **M_6_BMI.BENZ**).

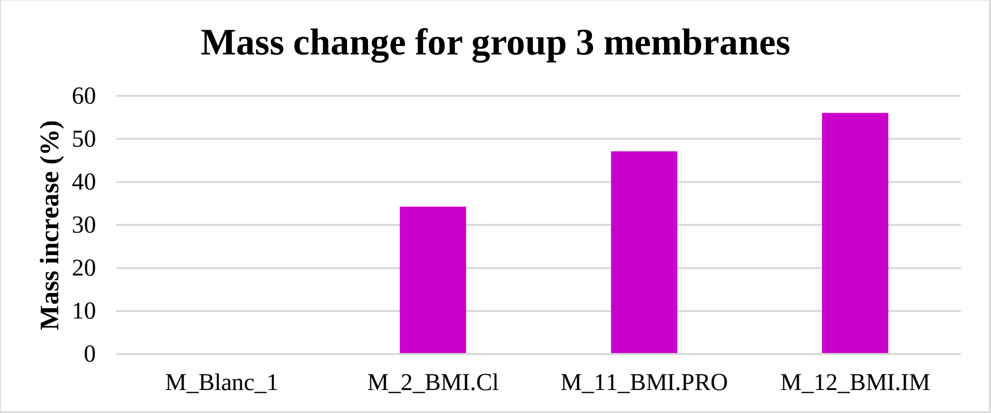


Figure 20: Mass increase of membrane after soaking in the desired group 3 ionic liquid

For the last group, the values obtained (Figure 20) were quite higher than with the dicarboxylic derived ionic liquids, but being lower than the values obtained from **M_4_BMI.PIV** and **M_6_BMI.BENZ**.

This difference in mass introduced to the membrane between ionic liquids has been tried to be correlated with the viscosity of the ionic liquids or rather the viscosity of the solutions used for soaking (75%wt) (see S.I. 1.3), but no direct correlation has been encountered. As the incorporation of ILs into the membrane was done by capillary forces it can be also related to the density of the solution and its surface tension, thus also these two parameters were determined (see S.I. 1.2 and 1.4). Neither here a direct correlation between these parameters and the mass increase of membranes have been demonstrated. It was expected that as higher was the solution surface tension (ϒ) or as lower was the density (ρ) a larger amount would be introduced to the membrane. This relation was given by Jurin's Law, (see Equation 6).[49] We omit the influence of the gravity and the pore size as they are constant, relating the height (h) with the mass increase, as higher it is a higher a faster mas increase would be expected. Moreover, the adsorption of a determined volume in a material depends on its sorptivity,[50] but in our case all the membranes are based on the same material and with the same pore size. Then, we can only correlate the mass increase with the absorption height. Based on that, the highest mass increase must be expected for **M_4_BMI.PIV**, **M_5_BMI.FORM**, or **M_8_BMI.MAL** in which the surface tensions were 61.7 mN/m, 51.9 mN/m and 61.5 mN/m respectively and the densities 1.0745 g/mL, 1.0407g/mLand 1.0588 g/mL. But Figure 18 shows that the highest mass increase was achieved for membranes **M_4_BMI.PIV**, that can be related with the expected theoretical approach and

M_6_BMI.BENZ, that has a surface tension of 47.5 mN/m and a density of 1.1010 g/mL. For this last case, a chemical interaction has been proposed as explanation, the supramolecular interactions between polysulfone aromatic rings and benzoate aromatic ring (π-π stacking) can be the responsible for the stabilization of the ionic liquid in the structure providing the higher mass increase. Nevertheless, more studies will be needed to confirm this theory. However that the mass increase of M_4_BMI.PIV can be explained, the values obtained in soaking solutions characterization did not follow a direct correlation with the modified membranes mass increase values. We can confirm that no direct correlation was observed between the mass increase of membranes and the viscosity, density or surface tension of the ILs solutions. To complete the studies contact angle measurements of the ILs solutions on the membrane surfaces is programmed.

$$h = \frac{2\gamma cos\theta}{\rho g r}$$

Equation 6: Capillary rise in a tube calculation

In which:

h = height of a liquid in a column
ϒ = surface tension (mN/m)
ρ = density of the liquid (g/mL)
g = local acceleration due to gravity
r = tube radius
θ = contact angle

Derived from the mass increase, the amount of adsorbed ionic liquid in mol was also calculated for comparison purposes as the difference between molecular weight in the ionic liquids used for the study was high. Figure 21, displays the moles of ionic liquid adsorbed by membrane, that can be directly correlated with the chemisorption of CO_2, see Section 1.2).

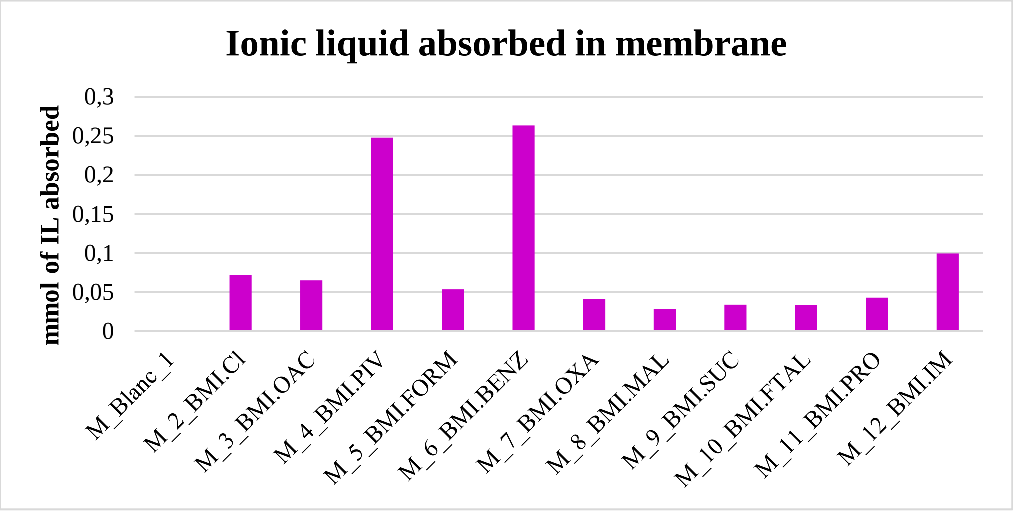


Figure 21: mmol of IL absorbed in each membrane

4.1.2) Characterization of modified membranes

Further characterization was needed to confirm the presence of ionic liquids in the membrane internal structure and also its effect on the morphology and pores structure.

First of all, membrane thickness has been checked to determine if the soaking process promotes an expansion of the membrane increasing the thickness. Figure 22, displays membrane thickness showing similar values between 90 µm and 110 µm.

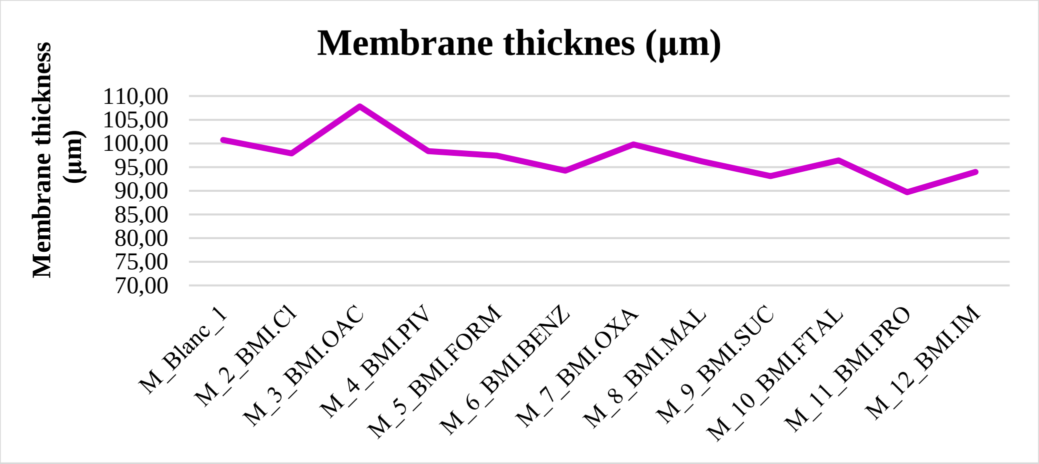


Figure 22: Membrane thickness representation.

The second step to confirm the presence of ionic liquids on the membranes was to perform some infrared studies of the membrane and compare them to the blanc membrane in order to see different bands between them. The most characteristic bands that can confirm the presence of ionic liquids in the membrane were the ones that correspond to the stretching of the bond between a carbon atom and a nitrogen atom (from the ionic liquid cation) that can be seen at around 1640 cm^{-1} and the presence of bands corresponding to the stretching carbonyl simple bond symmetrical and asymmetrical (from the carboxylic acid derived anions) that can be seen at around 1360cm^{-1} and 1570 cm^{-1} respectively. Also, no bands showing new chemical bonds between the ionic liquid and polysulfone have been detected, confirming that the ionic liquids where incorporated physically to the membrane by pores and macrovoids filling and not by chemical reaction. Figure 23, displays the IR spectra of the blanc membrane (**M_Blanc_1**) in which bands only correspond to polysulfone, a membrane modified with ionic liquid (**M_6_BMI.BENZ**) and the ionic liquid (BMI.BENZ) (For all IR spectra see S.I 1.1 and 2.3). Even though the IR cannot pass through the totality of the solid and it can only characterize the first 4 μm of the membrane, we were able to confirm the presence of ILs in the membrane structure always obtaining strong influence of the polysulfone in the spectrum.

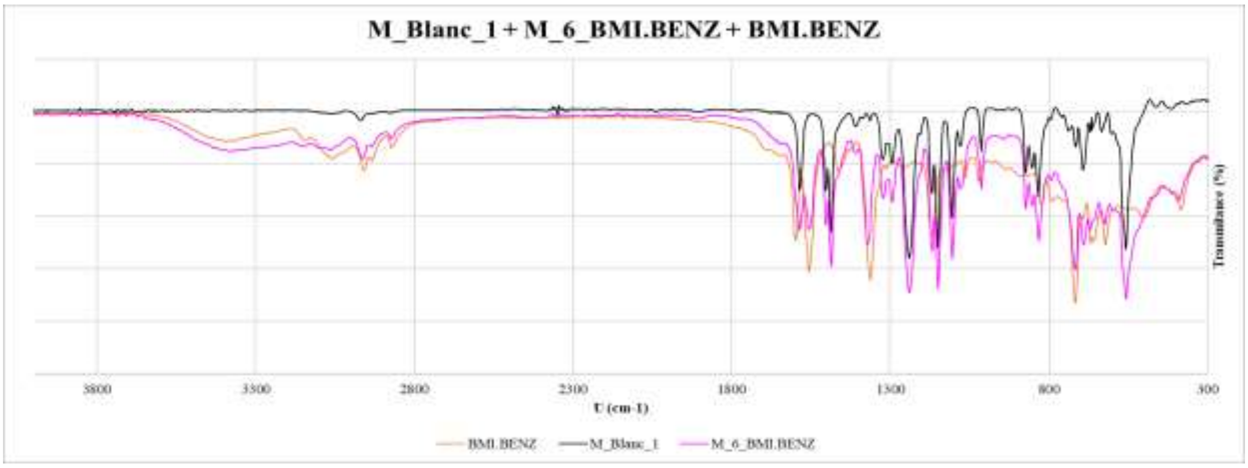


Figure 23: IR spectra of membranes M_Blanc_1, M_6_BMI.BENZ and BMI.BENZ ionic liquid

In order to have a total demonstration of the ionic liquid incorporation in the structure and its structure, an energy dispersive X-Ray elemental analysis of the cross-section of membranes has been also performed. The presence of nitrogen inside the membranes was assigned to the imidazolium cation and confirms the presence of ionic liquid. Figure 24, displays an elemental analysis characterization of **M_6_BMI.BENZ** membrane cross-section, showing a good dispersion of nitrogen (blue) along all the membrane and confirming ionic liquid presence inside the membrane. It is important to notice that ionic liquid was well dispersed and not concentrated in the macrovoids of the structure (for all micrographs see S.I 2.2). Nevertheless, we cannot discard a partial clogging of the more external pores, near the top or the bottom surface of the membrane, because the determination of nitrogen by EDX normally presents several problems because of the reference material used in the instrument. Moreover, the quantification values of nitrogen obtained with the analysis did not correlate with the mass increase values obtained. In addition, the cross-section samples were prepared by immersion in ethanol for cleaning the surface and facilitate the fracture. Although the immersion was very fast, a partial removal of the ionic liquid from the membrane cannot be discarded and, therefore a partial clogging of the pores cannot be excluded as possibility, especially the sponge-like structure near the surfaces.

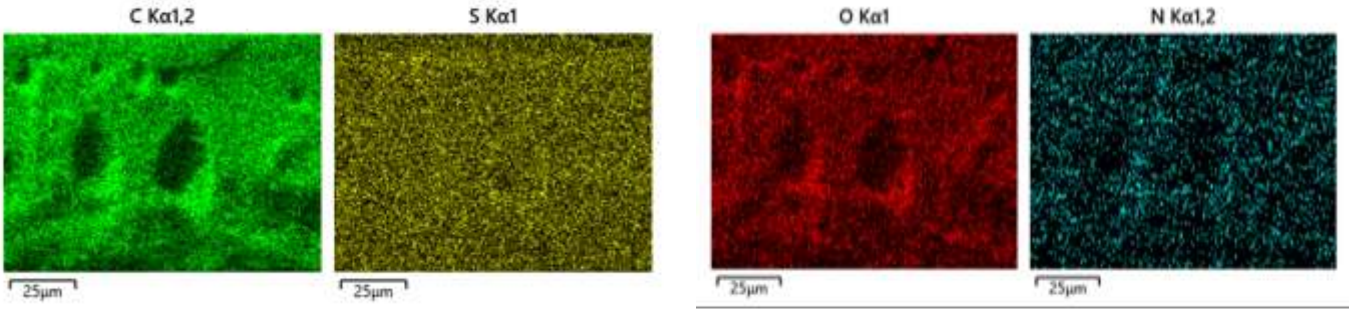


Figure 24: EDX analysis of M_6_BMI.BENZ

4.2) CO_2 Solubility tests results of modified membranes

Solubility tests of all membranes were performed first to determine which membranes were suitable to have a better performance for selective CO_2 absorption from flue gases. After this study, the best membranes were scaled up to perform permeability tests. This was very important because with only the solubility tests the absorption of CO_2 in the membrane was determined but if this absorption was very high the real purpose of the membrane will be not achieved. The gas will be fixed inside of the membrane and it will not pass through it to be used directly as starting material for further reactions.

The data was obtained following the procedure from Section 3.9). Different studies have been performed. First of all, the solubility coefficient has been determined to see the volume of CO_2 absorbed per volume of the membrane. Moreover, it has been normalized by mol of ionic liquid incorporated for each membrane to determine if any direct tendency appears. Finally, the ratio of CO_2 mol absorbed per mol of ionic liquid has been calculated in order to compare obtained values to the values reported in the literature. In addition, a selective absorption of CO_2 has been observed for modified membranes. While the system was filled with N_2, no pressure decreasing can be detected, in contrast a pressure increasing was observed due to the expansion of the gas when temperature increases. In the other hand when the system was filled with CO_2 a fast decrease in pressure was observed until stabilization of the pressure at different times for each membrane as can be seen in Figure 25 for the case of **M_ 6_BMI.BENZ** membrane.

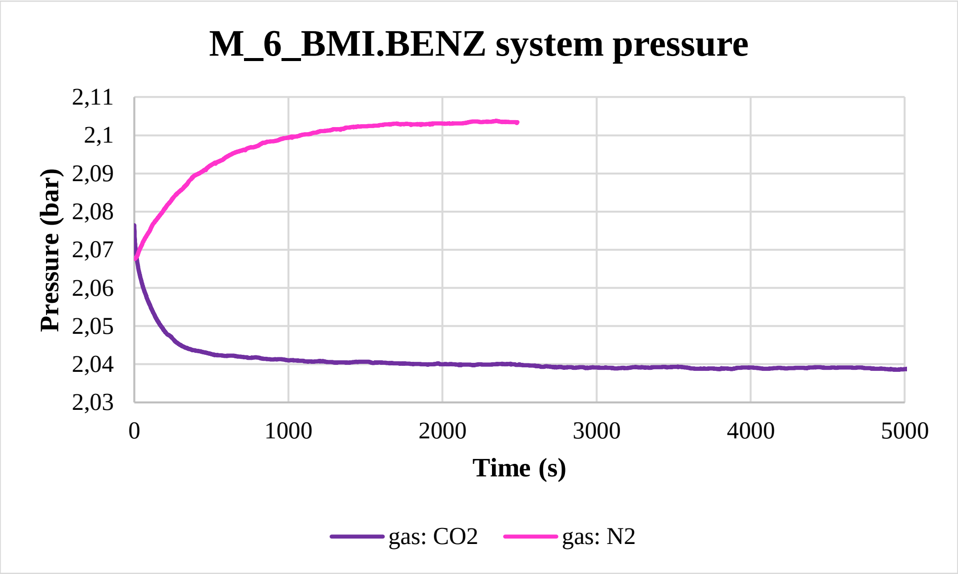


Figure 25: System pressure behaviour in presence of M_6_BMI.BENZ membrane for different gases

4.2.1) Solubility coefficients

- **Carboxylic acid-derived group 1:**

Table 5: Solubility Coefficients for carboxylic acid derived group 1

Membrane	Ionic liquid cation	Ionic liquid Anion	Solubility Coefficient (S) (m^3(STP) $m^{-3}_{membrane}$ atm^{-1})	Solubility (S) per membrane mass (g) (m^3(STP) $m^{-3}_{membrane}$ atm^{-1} g^{-1})
M_Blanc_1	---	---	1.0955	31.1223
M_2_BMI.Cl	BMI	Chlorine	2.3294	47.1545
M_3_BMI.OAC	BMI	Acetate	0.6741	13.7862
M_4_BMI.PIV	BMI	Pivalate	9.7879	106.8550
M_5_BMI.FORM	BMI	Formate	2.8880	63.8942
M_6_BMI.BENZ	BMI	Benzoate	5.6956	55.1904

Table 5 displays the solubility coefficients obtained for the first group of modified membranes in comparison with the pristine **M_Blanc_1** membrane. It can be seen a general increase in the solubility coefficient in the modified membranes in comparison with the blanc one, having the highest increase for **M_4_BMI.PIV** and **M_6_BMI.BENZ**, while **M_3_BMI.OAC** has a lower performance than the blanc membrane, probably the ionic liquid captured the CO_2 directly covering the physisorption of the polysulfone membrane. These values were obtained with a single experiment and further experiments will be needed to confirm the coefficients obtained. Also, these results cannot be comparable at all due to the different amounts of ionic liquid supported in each membrane and the different molecular weights for each compound. If we compare the solubility coefficients with the mass change of membranes a direct correlation can be observed (Figure 26) but the highest solubility coefficient expected would be for **M_6_BMI.BENZ**, the membrane with higher mass change. In that case, the highest value for **M_4_BMI.PIV** could be demonstrated due to the highest acidity of the proton in the imidazole ring between both nitrogen atoms. This proton is the one that has been proposed in the literature to be deprotonated and stabilized by a very reactive carbene that can further react with CO_2 molecule. This hypothesis can be partially confirmed by ^1H NMR (see figure S.I.: 5) in which the signal of this proton for the ionic liquid 1-butyl-3-methylimidazolium pivalate (BMI.PIV) has a lower integral due to its easy interchange with the deuterated solvent. ^1H NMR experiments with CO_2 pressure could not be performed to demonstrate this chemisorption.

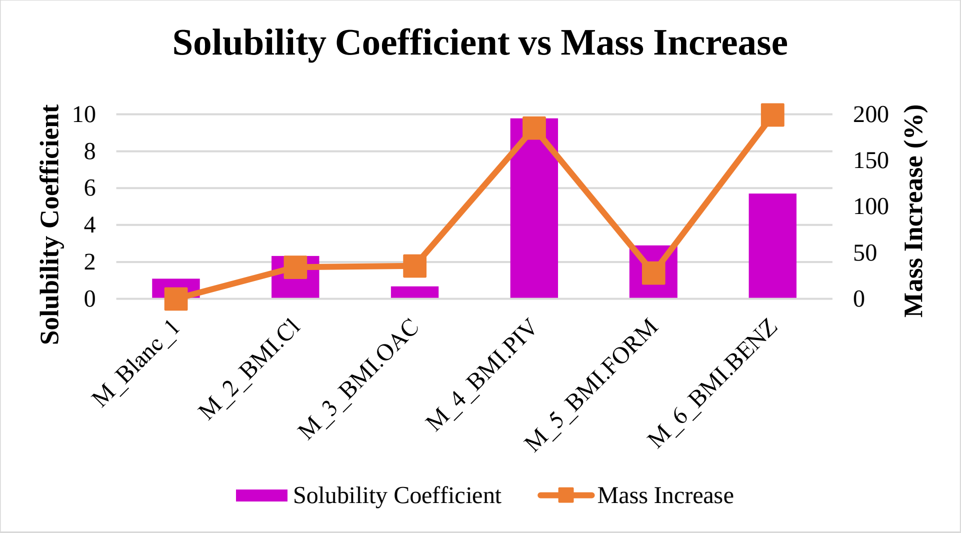


Figure 26: Comparison between solubility coefficient and mass increase for group 1

- **Dicarboxylic acid-derived group 2:**

Table 6: Solubility Coefficients for dicarboxylic acid derived group 2

Membrane	**Ionic liquid cation**	**Ionic liquid Anion**	**Solubility Coefficient (S) (m^3(STP) m$^{-3}_{\text{membrane}}$ atm^{-1})**	**Solubility (S) per membrane mass (g) (m^3(STP) m$^{-3}_{\text{membrane}}$ atm^{-1} g^{-1})**
M_Blanc_1	---	---	1.0955	31.1223
M_7_BMI.OXA	2 BMI	Oxalate	1.7928	38.8903
M_8_BMI.MAL	2 BMI	Malonate	4.5614	99.5947
M_9_BMI.SUC	2 BMI	Succinate	3.0264	64.2555
M_10_BMI.FTAL	2 BMI	Phthalate	3.7944	75.5474

Table 6 displays the solubility coefficients obtained for the dicarboxylic acid derived group of membranes in comparison with **M_Blanc_1** membrane. In this case, all the membranes have a better performance than the blanc one with the highest increase of solubility in **M_8_BMI.MAL**. If the mass increase was correlated with the solubility coefficient a notable dependency can be seen however **M_8_BMI.MAL** reveals better performance with a lower amount of ionic liquid in the membrane than **M_9_BMI.SUC** or **M_10_BMI.FTAL**, as can be seen in Figure 27. This behaviour could be explained by the nucleophilic nature of the carbon between the carboxylic groups of the phthalate anion. It can also be explained by the free volume of the ionic liquid, increasing as higher is the size of the anion, but in this case a better performance would be expected for **M_9_BMI.SUC** or **M_10_BMI.FTAL**. In comparation with group 1 membranes, the solubility coefficient was lower than the obtained with the better membranes (**M_4_BMI.PIV** and **M_6_BMI.BENZ**) but taking a look on the solubility coefficient per gram of membrane one of the better results was obtained being only lower than the obtained with **M_4_BMI.PIV**.

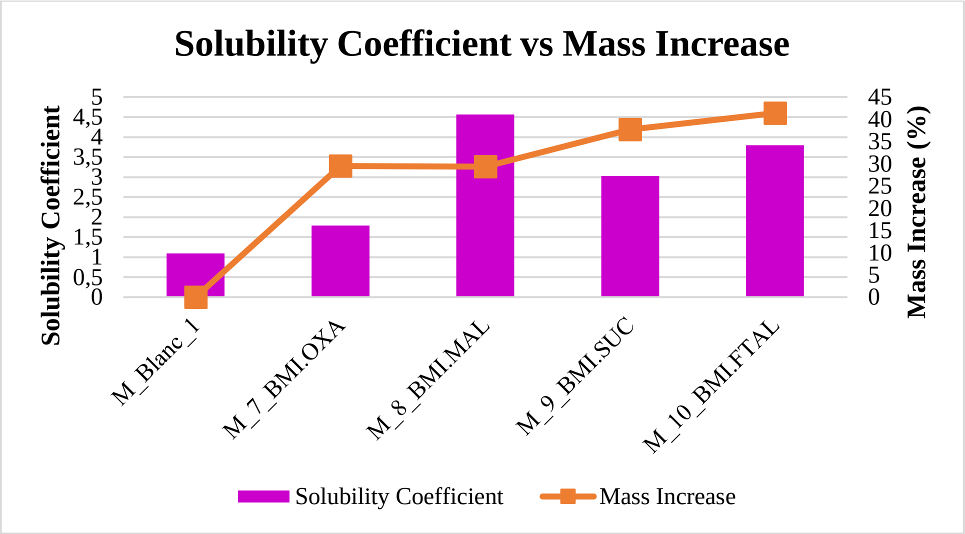


Figure 27: Comparison between solubility coefficient and mass increase for group 2

- **Nitrogen presence in the anion group 3**

Table 7: Solubility Coefficients for nitrogen presence in the anion group 3

Membrane	**Ionic liquid cation**	**Ionic liquid Anion**	**Solubility Coefficient (S) (m^3(STP) $m^{-3}_{membrane}$ atm^{-1})**	**Solubility (S) per membrane mass (g) (m^3(STP) $m^{-3}_{membrane}$ atm^{-1} g^{-1})**
M_Blanc_1	---	---	1.0955	31.1223
M_11_BMI.PRO	BMI	Prolinate	4.5404	85.9938
M_12_BMI.IM	BMI	Imidazolate	2.6765	46.8740

Finally, Table 7 displays the solubility coefficients obtained for the two membranes modified with ionic liquids that have nitrogen atoms in both, the cation and the anion. In this case, both membranes have a better performance than **M_Blanc_1** but no correlation can be seen with the number of nitrogen atoms in the anion. **M_11_BMI.PRO** has a higher solubility coefficient with only one nitrogen atom in the anion and also having a slightly lower ionic liquid content absorbed by the membrane, as can be seen in Figure 28. However, the nitrogen of the prolinate anion was much more basic (pKa 10.96 for amino group of proline, while pKa for the conjugated acid of the amino group of imidazole is 6.95, being 14.5 the direct pKa)

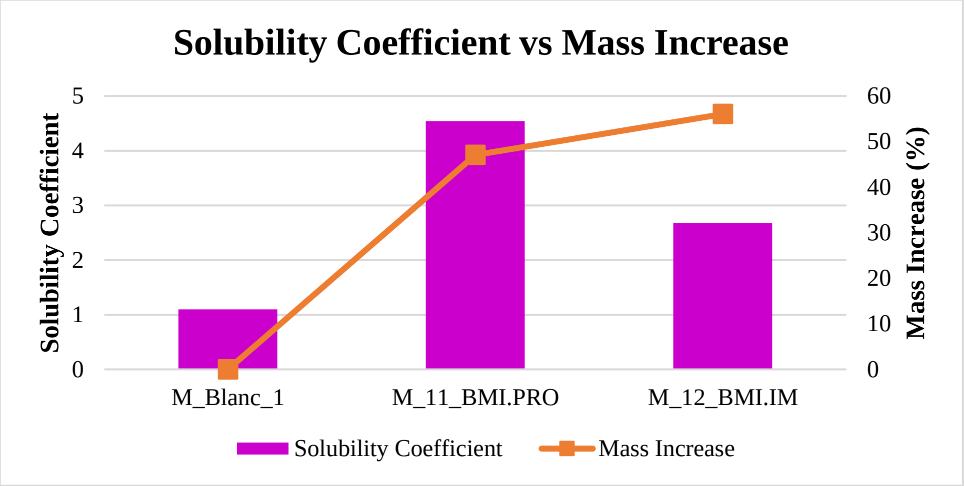


Figure 28: Comparison between solubility coefficient and mass increase for group 3

After performing the solubility tests, all membranes were studied under FT-IR in order to determine if CO_2 has been bonded chemically with the imidazolium cation as proposed in literature[51,52] . No significant new bands had appeared in comparison with the membrane before the solubility tests. As reported in previous literature 2 bands will be expected, a band around 2345 cm^{-1},[53] for the CO_2 dissolved in the ionic liquid with no chemical bond formation, and a band at 1663 cm^{-1} for the carboxylate formation upon reaction of the imidazolium cation and CO_2.[54] This could be because of the low ionic liquid amount in comparison with the polysulfone amount in membrane or the CO_2 was physiosorbed. Further studies are needed to confirm this hypothesis.

4.3) CO_2 absorption in Ionic Liquids

Large number of studies have been performed on use of ionic liquids as sorbents for CO_2 capture. Table 8 shows previously reported CO_2 solubilities in different 1-buthyl-3-methylimidazolium-based ionic liquids with a bench of different anions. As can be seen, values were compressed between 0.06 and 0.6 mol of CO_2 per mol of ionic liquid. Also, for the same ionic liquid, we can see that the solubility has a dependence on the CO_2 pressure applied, where the highest solubility was obtained with higher pressure. The temperature has a significant role too, as expected, higher temperatures provide lower solubility in the same ionic liquid. All reported data was obtained with temperatures ranging from 20 ºC up to 60 ºC and pressures of at least 6 bar of CO_2.

In this study solubility experiments with the modified membranes were carried out at 30 ºC and only 2 bars of CO_2 pressure. In order to calculate the CO_2 solubility in the ILs the value obtained for the blank membrane was subtracted from the modified one. Further the values were normalized for mol of ILs in each membrane. The results obtained, Table 9, cannot be directly compared with the values from Table 8 because the experimental conditions were not the same, but a general conclusion can be drawn. With low pressure (2 bar) and relatively high temperature (303.15 K), conditions that might not be the optimal ones for CO_2 solubility, values from 0.13 to 0.85 have been obtained for ILs supported on membranes showing better results than the ones reported for neat ionic liquids. Specifically, for membranes **M_5_BMI.FORM**, **M_8_BMI.MAL**, **M_9_BMI.SUC**, **M_10_BMI.FTAL** and **M_11_BMI.PRO** high solubility values were obtained. In the other hand, **M_3_BMI.OAC** membrane show a very low value (-0.04), being one of the ILs more studied for CO_2 capture. In this particular case, we suspect that the impregnation of the ionic liquid in the membrane was more concentred in the surface, blocking the pores and avoiding the dual absorption in the ionic liquid and the membrane. In this study, our purpose was to determine if the introduction of ionic liquids in membranes can increase the solubility of CO_2 in the membrane and its selectivity among other gases. The ILs not only improved the membranes absorption of CO_2, but it was evident that by supporting ionic liquids in porous media we improved its contact area with the gas phase and the same increased the CO_2 solubility in the ILs themselves. Most importantly pressure used was only 2 bar. The best performance was achieved with membrane **M_8_BMI.MAL**, where1-buthyl-3-methylimidazolium malonate was supported, with a ratio of CO_2/IL larger than 0.80. This value can seem to be unexpected, but it is important to notice that this ionic liquid is formed by 2 cations per mol of ionic liquid, that is responsible for the chemical sorption of CO_2. For membranes modified with ionic liquids with a monoanionic compound as the counter anion, the best performance was obtained with **M_11_BMI.PRO** in which the ionic liquid of choice was 1-buthyl-3-methylimidazolium prolinate. We suspect that the basic amine group present in its structure can be responsible for this behaviour, as reported previously in literature and explained in Introduction, see 1.2.

Table 8: Reported CO_2 solubilities in imidazolium-based IL's

Ionic liquid	Acronym	T (K)	P (bar)	Solubility (mol CO_2/ mol IL)	Ref.
1-Butyl-3-methylimidazolium acetate	BMI.OAC	333.3	12.75	0.2510	55
		323.09	755.26	0.5990	55
1-Butyl-3-methylimidazolium trifluoroacetate	BMI.TFA	293.43	9.79	0.2250	55
		293.59	436.25	0.6790	55
		298.1	19.99	0.3010	56
1-Butyl-3-methylimidazolium tetrafluoroborate	BMI.BF_4	303	10	0.1461	55
		333	10	0.0895	55
		293.65	73	0.6100	57
		293.25	10.5	0.1410	57
1-Butyl-3-methylimidazolium dicyanamide	BMI.DCA	303	10	0.1434	58
		333	10	0.0997	58
1-Butyl-3-methylimidazolium thiocyanate	BMI.SCN	303	10	0.0978	58
		333	10	0.0664	58
		313.65	99	0.4300	57
		292.35	10.5	0.1260	57
1-Butyl-3-methylimidazolium hexafluorophosphate	BMI.PF_6	303	10	0.1662	58
		333	10	0.1012	58
		298.15	6.66	0.122	59
1-Butyl-3-methylimidazolium methylsulfate	BMI.$MeSO_4$	303	10	0.1190	58
		333	10	0.0733	58
1-Butyl-3-methylimidazolium propionate	BMI.PROP	298.2	19.9	0.3900	56
1-Butyl-3-methylimidazolium isobutyrate	BMI.ISB	298.2	20	0.4030	56
1-Butyl-3-methylimidazolium pivalate	BMI.PIV	298.1	19.9	0.4310	56
1-Butyl-3-methylimidazolium levulinate	BMI.LEV	298.1	19.9	0.4600	56
1-Butyl-3-methylimidazolium succinamate	BMI.SUCN	298.1	19.9	0.2320	56
1-Butyl-3-methylimidazolium iminoacetic acid acetate	BMI.IAAc	298.1	19.9	0.1910	56
Bis(1-Butyl-3-methylimidazolium) iminodiacetate	BMI_2.IDA	298.1	19.9	0.3950	56

Table 9: Absorbed moles of CO2 and solubility in ILs at 303,15 K and 2 bar CO2 pressure

Membrane	CO_2 absorbed moles in membrane	CO2 Solubility of ILs (mol CO_2 / mol IL)
M_Blanc_1	8.68 x10^{-6}	---
M_2_BMI.Cl	1.80 x10^{-5}	0.13
M_3_BMI.OAC	5.67 x10^{-6}	-0.04
M_4_BMI.PIV	6.75 x10^{-5}	0.24
M_5_BMI.FORM	2.20 x10^{-5}	0.25
M_6_BMI.BENZ	4.10 x10^{-5}	0.13
M_7_BMI.OXA	1.36 x10^{-5}	0.12
M_8_BMI.MAL	3.28 x10^{-5}	0.85
M_9_BMI.SUC	2.11 x10^{-5}	0.37
M_10_BMI.FTAL	2.90 x10^{-5}	0.60
M_11_BMI.PRO	3.06 x10^{-5}	0.51
M_12_BMI.IM	2.04 x10^{-5}	0.12

4.4) Permeability tests of modified membranes

Permeability test were performed with the most promising membranes from results in 4.2. A scale-up production of **M_Blanc_1**, **M_4_BMI.PIV**, **M_6_BMI.BENZ**, **M_8_BMI.MAL** and **M_11_BMI.PRO** were performed until 8 cm x 8 cm, that is suitable membrane size for the experimental module. As expected using soaking method as modification method, the permeability of a gas across the membranes will be lower in comparation of **M_Blanc_1** membrane. This behaviour was due to the partial filling of the pores with the ILs reducing the facilitated transfer across the membrane due to the increase in the mass transfer resistance in the viscous ILs in the pores compering to the one in gas phase in case of open pores of the blank membrane. Moreover, this filling cannot be controlled and the pores can be filled in very different ways. As example, the filling can be partially or totally, producing a clogging of the channels. Also, macrovoids can incorporate the ionic liquids in the surface of the walls or inside having a partially filling of them. Permeability values have been only obtained with **M_Blanc_1** membrane, Table 10 shows the permeability and diffusion coefficient values obtained for each pressure and gas used.

Table 10: Permeability and diffusion coefficients obtained with M_Blanc_1 membrane

Membrane	**Gas**	**Pressure (bar)**	**Permeability STP (barrer)**	**Diffusion coefficient (cm^2/s)**
M_Blanc_1	N_2	0.5	12.28	11.2
		1	20.24	18.48
		1.5	24.26	22.15
		2	29.88	27.27
	CO_2	0.5	22.08	20.15
		1	25.83	23.58
		1.5	29.61	27.03
		2	34.33	31.35

It is important to notice that a partial selectivity between CO_2 and N_2 exists using a membrane without modification, because working in both cases with pure gases, permeability and solubility coefficient were higher when CO_2 was used as inlet gas in the system. For **M_Blanc_1** membrane a diffusion coefficient of 31.35 cm^2/s was obtained for CO_2, while 27.27 cm^2/s was obtained for N_2 working at 2 bar pressure.

For the modified membranes, the pressure and flow across membrane values obtained were very low. Concretely, for **M_4_BMI.PIV** and **M_6_BMI.BENZ** membranes, the flow was completely 0 after more than 4 hours for both gases. This behaviour can be explained by the absorption of ionic liquid in the membrane. More specific, these membranes where the ones that have a higher mass increase after the soaking in ionic liquid solutions, arriving to values near of 200% increase of mass. Probably because of that, the top part or the bottom part of the pores can be clogged by the ionic liquid. Other possible explanation for this behaviour was a strong chemical absorption of the CO_2 in the ionic liquids, providing a high solubility but avoiding the transport of the gas across the membrane. However, this theory is excluded as the same behaviour was found also for N2 which was found inert in the solubility studies. For **M_11_BMI.PRO** membrane a flow was observed when using CO_2 as inlet gas, but being lower than the instrumental limit of quantification. In this case, also an improved selectivity between gases was observed, while the use of CO_2 shows a low but existing flow, when N_2 was used as inlet gas no flow was observed after time, working at the highest pressure in both cases, 2 bar. By the other hand, the stability of the membrane was compromised working at these conditions. After performing the experiments at 2 bar of inlet pressure small drops of ionic liquid appeared in the outlet face of the membrane, confirming that using the soaking method the ionic liquid was only physically trapped in the porous structure and can be exudate at high pressures. For **M_8_BMI.MAL** a similar behaviour has been observed, but in this case a flow was observed using both gases, noticing that also being lowers than the limit of quantification, it was faster for CO_2 than for N_2. A new set of experiments with a different set-up attached to a gas chromatography system will be needed to determine and quantify the total gas flux trough the membrane and the real selectivity between gases. A possibility to determine better the permeability is to use a carrier gas in the outlet part of the membrane, such as pure N_2, to promote a higher concentration gradient across membrane and improve the diffusion of CO_2.We can confirm that a chemical absorption of CO_2 occurs, by solubility experiments, but the diffusion through the modified membranes was very low due to mass transfer resistance caused by clogged pores (see Table S.I. 29).

We have only performed experiments with pure CO_2 and pure N_2, but to be more realistic, a mix gas containing both gases in different proportions will be used to fulfil the requirements of the final application in the SunCoChem project. But we can conclude that a higher selectivity in CO_2 capture can be induced by modification of membranes with imidazolium-based ionic liquids. Moreover, the soaking method seems to be useful for some of the ionic liquids, but a control of time or the ILs solution concentration will be necessary to avoid a total absorption of ionic liquid in the structure clogging the pores.

5) Conclusions

A group of novel membranes based on polysulfone matrix have been prepared with the aim of capture CO_2 selectively from flue gases coming from industries. Moreover, a set of eleven ionic liquids have been synthetized at different scales, from 10g to 500g and tested for membrane modification by using the soaking method. All the ionic liquids and membranes have been characterized to determine physico-chemical properties and CO_2 affinity

In total 12 different membranes have been prepared and tested under specified conditions to determine the solubility, permeability and diffusion of CO_2 over N_2. Incorporation of the ionic liquids into the membrane structure by soaking method have been studied and no correlation between the introduced amount of ILs with its density, viscosity or surface tension was found. Only M_4_BMI.PIV membrane behaviour could be explained theoretically. The set-up and the procedure to carry out these tests have also been prepared and optimized. We found that the incorporation of ILs into membranes strongly improves its CO_2 solubility. Concretely, **M_4_BMI.PIV**, **M_8_BMI.MAL**, **M_11_BMI.PRO** have the highest solubility per gram of membrane. The ILs supported in membrane gave higher CO_2 solubility values compared to the bulk ILs studies from the literature. In addition, these values were obtained working under lower conditions than the reported ones.

Four of the best performing membranes were scaled up and used to perform permeability test in order to confirm the membrane improvement by modification. The permeability determination set-up was also prepared and optimized for carrying out the experiments. The quantitative values of CO_2 and N_2 permeability were obtained only for blank polysulfone membrane and not for modified ones. Thus, we can conclude that the membranes are capable to adsorb CO_2 however its transport across the membrane. It is important to highlight that soaking method can cause res clogging, preventing the permeation of the gas through the membrane if the introduced amount is too high. By the other hand, a qualitative selective flow of CO_2 was achieved when membranes were modified with ionic liquids. Concretely with **M_8_BMI.MAL** and **M_11_BMI.PRO** working at low pressures of inlet gas, only 2 bar. However, the stability of ionic liquids inside of the membrane was compromised at these working conditions.

More studies will be needed to optimize the modification methodology of the membranes and to determine in a quantitative mode the behaviour of the membranes under different gases to conclude if the selectivity and the absorption is improved with the incorporation of imidazolium-based ionic liquids.

The project outlooks are:

- Perform solubility replicate studies to conclude the absorption value of modified membranes
- Optimize the amount of introduced ILs to the membrane to improve the gas permeability
- Perform permeability test using as feeding gas mixtures of CO_2/N_2 or even other gases such as water vapour to determine the selectivity of modified membranes
- Scale-up the membrane preparation to achieve the required size for SunCOChem project
- Perform contacting experiments with the absorbent solution to incorporate the membrane in the project device.

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