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Separation performance of CO_2 through Supported Magnetic Ionic Liquid Membranes (SMILMs)

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ABSTRACT

Ionic liquids (ILs) have reached an enormous interest as CO_2 solvents due to their unique properties such as negligible vapour pressure and selectivity, making them very attractive in order to obtain stable supported liquid membranes. ILs containing magnetic metals in their anion are known as Magnetic Ionic Liquids (MILs) and they may show different behaviour in the presence of an external magnetic field.

This work evaluates the preparation and use of a new class of supported liquid membranes based on Magnetic Ionic Liquids: Supported Magnetic Ionic Liquid Membranes (SMILMs) for CO_2 separation/concentration. Four paramagnetic ionic liquids have been studied: $[P_{6,6,6,14}]_2^+[CoCl_4]^{2-}$, $[P_{6,6,6,14}]^+[FeCl_4]^-$, $[P_{6,6,6,14}]_2^+[MnCl_4]^{2-}$ and $[P_{6,6,6,14}]_3^+[GdCl_6]^3$; in combination with a hydrophobic or a hydrophilic PVDF porous support. An evaluation of the membrane stability was carried out and CO_2, N_2 and air permeabilites for stable SMILMs were experimentally determined. CO_2/N_2 and CO_2/air selectivities were estimated and introduced in the Robeson diagram for a comparison with previous reported materials. Pure gas permeation results demonstrate that these SMILMs show much higher CO_2 permeabilities when comparing with N_2 and air. This selectivity may indicate a potential application of using SMILMs for the selective removal/recovery of CO_2 from a gas stream and further work will perform the evaluation of an external magnetic field in the separation behaviour.

1. Introduction

Carbon dioxide (CO_2) absorption is an important separation process where efforts have to be applied in order to develop sustainable processes for greenhouse gases mitigation. The existing process for CO_2 capture uses a reversible absorption in amines. Typically, this process requires the application of high temperatures to a stripper re-boiler for solvent regeneration and CO_2 desorption, which poses as main drawbacks the energy consumption and the solvent losses.

As an alternative, gas separation using membrane technology offers numerous advantages over the absorption process, including their modular design, high surface area per unit volume and energy efficiency among others [1], but it remains with few technical applications due to the permeability and selectivity requirements of the process.

Some studies have applied the non-dispersive membrane-based technology for CO_2 absorption, such as hollow fibre membrane contactors, where gas and liquid flow on opposites sides of the membrane equipment and a fluid/fluid interface forms inside each membrane pore. Previous studies report different conditions for the carbon dioxide separation processes using membranes [2–4]. Specifically, recent works combine hollow membrane contactors with ionic liquids (ILs) for CO_2 absorption [5,6] since they can have an extraordinary affinity to this gas [7,8].

Microporous and/or dense membranes are very attractive but it is still possible to improve the selectivity and permeability of the gas separation process by using supported ionic liquid membranes (SILMs) [9–19]. In a supported ionic liquid membrane, an ionic liquid is immobilized inside the pores of a polymeric or a ceramic support. In this configuration, the solute molecule dissolves into the membrane at the feed/membrane interface, it diffuses through the membrane and desorbs at the opposite membrane surface. Although the combination of ionic liquids (ILs) with SLMs present advantages due to the high stability and non-volatile character of these liquids, these membranes still present limited mechanical stability, which restrict membrane flux needed for industrial application. As an alternative, polymerized ILs have been developed as dense membranes. These polymerized membranes present higher

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mechanical stability and can be easily fabricated into thin-layer films [20–23]. However, a decrease in permeability has been reported due to lower gas diffusivity [24]. Even though, supported ionic liquid membranes (SILMs) and (poly-ILMs) showed promising permeability/selectivity results that are among the best results presented in literature using other materials represented by the Robeson plot upper bound [14,15,20,22,24] for the CO_2/N_2 separation.

One of the most interesting properties of ionic liquids is the fact that their physical and chemical properties are tuneable, depending on the cation and anion present in their structure, making them to be considered as 'designer solvents'. This property has made possible the substitution of common anions for others with a metal ion, such us $FeCl_4^-$, conferring them a magnetic response. These Magnetic Ionic Liquids (MILs) are an interesting approach in selective separation processes, since the molecule to be separated, may have higher or lower permeability depending on the magnetic field strength applied to a SMILM [25]. An example described in literature using Magnetic Ionic Liquids has shown that the extraction of some organics increases using MILs in the presence of a magnetic field [26].

In this work, Supported Magnetic Ionic Liquid Membranes (SMILMs) including a number of new different phosphonium based MILs: $[P_{6,6,6,14}]_2^+[CoCl_4]^{2-}$, $[P_{6,6,6,14}]^+[FeCl_4]^-$, $[P_{6,6,6,14}]_2^+[MnCl_4]^{2-}$ and $[P_{6,6,6,14}]_3^+[GdCl_6]^3$ were studied. Two different microporous membranes (hydrophilic and hydrophobic) made of PVDF were used as support to evaluate the following properties: (1) immobilisation of MIL in polymeric membranes; (2) stability of these systems and characterisation of the ionic liquid support interaction; (3) gas permeability and selectivity towards CO_2 and (4) behaviour of the prepared membranes in the separation of CO_2/N_2 mixtures in comparison with the Robeson upper bound. Based in these results, future work will be focused on the influence of an external magnetic field in the SMILMs behaviour.

2. Materials and methods

2.1. Polymeric microporous membranes

The supported ionic liquid membranes were prepared using commercial microporous membranes made of polyvinylidene fluoride (PVDF) as supporting material. The membranes present similar pore size but different chemical nature: one is hydrophobic (from Millipore Corporation) and the other one hydrophilic (provided by Pall Corporation). They are characterized by their high chemical resistance and usefulness for a wide range of applications. The nominal pore size and thickness are included in Table 1.

2.2. Magnetic Ionic Liquids (MILs)

The following MILs based in the phosphonium cation were first synthesized in *Faculdade de Farmácia*, *Universidade de Lisboa* (*Portugal*) and studied in the present work:

- Phosphonium tretrachlorocobalt ($[P_{6,6,6,14}][CoCl_4]$).
- Phosphonium tretrachloroferrate ($[P_{6,6,6,14}][FeCl_4]$).
- Phosphonium tretrachloromanganese ($[P_{6,6,6,14}][MnCl_4]$).
- Phosphonium hexachlorogadolinium ($[P_{6,6,6,14}][GdCl_6]$).

Table 1
Commercial membranes used as the support of MILs.

	Material	Pore size (μm)	Thickness (μm)
Pall corporation	Hydrophilic PVDF	0.20	129
Millipore	Hydrophobic PVDF	0.22	125

All are based in the phosphonium cation, due to the relatively high CO_2 solubility reported in phosphonium-based MILs [27]. In addition, different metals presenting different magnetic response [28] are included in the anion, in order to study the stability and gas transport properties when MILs are immobilized in a polymeric porous support.

The ionic liquids were prepared according to the following procedures [28]. To a solution of $[P_{6,6,6,14}][Cl]$ (50 g, 0.096 mol) in dichloromethane was added cobalt chloride (11.45 g, 0.5 equiv.), iron (III) chloride hexahydrate (26.02 g, 1 equiv.), manganese chloride (26.02 g, 0.5 equiv.) or gadolinium (III) chloride hexahydrate (11.92 g, 0.3 equiv.). The solution was stirred at room temperature for 24 h. After that, two layers were formed, and the aqueous phase was decanted. The organic phase was dried over $MgSO_4$ and filtered. The solvent was removed under vacuum, and the IL stirred under vacuum (<1 mmHg) at 60 °C overnight. $[P_{6,6,6,14}]^+_2[CoCl_4]^{2-}$ was obtained as a blue viscous oil, yield 52.87 g (94%); $[P_{6,6,6,14}]^+[FeCl_4]^-$ brown viscous oil, yield 64.30 g (98%); $[P_{6,6,6,14}]^+_2[MnCl_4]^{2-}$ as a green viscous oil, yield 53.8 g (96%) and $[P_{6,6,6,14}]_3^+[GdCl_6]^{3-}$ colourless viscous oil, yield 56.12 g (96%).

The water content was determined by Karl–Fisher titration method, while in the case of $[P_{6,6,6,14}]^+[FeCl_4]^-$ was determined gravimetrically weighting 1 mL before and after 48 h of vacuum and heating. The CO_2 solubility was experimentally obtained by a thermogravimetric system at room temperature and atmospheric pressure in the absence of magnetic field [27]. Values are listed in Table 2.

The magnetic moment measurement procedure was described previously [29]. Results were provided by *Magnetism in Matter* group at CITIMAC, University of Cantabria, and they are shown in Table 3.

The results are in good agreement with the literature reported magnetic moments ($\chi_m T$) for $[CoCl_4]^{2-}$ (2.01–2.48 emu K/mol), $[FeCl_4]^-$ (3.74–4.46 emu K/mol), and $[MnCl_4]^{2-}$ (4.14–4.76 emu K/mol) but it does not agree well with the expected value for the gadolinium anion (7.72 emu K/ mol) reported in the literature [28–30].

2.3. Preparation of Supported Magnetic Ionic Liquid Membranes (SMILMs)

To immobilize the MILs, the microporous PVDF membrane was introduced into a vacuum chamber for 1 h in order to remove the air from the pores and, therefore allowing an easier introduction of MIL into their porous structure. Once the membrane was under vacuum for 1 h, drops of MILs are spread out at the membrane surface using a syringe, while keeping the vacuum inside the chamber. Then the liquid excess on the membrane surface was wiped up softly with a tissue. The amount of liquid immobilized in the membrane was determined gravimetrically, and the increase of thickness was measured using a micrometer before and after the immobilization procedure.

After soaking the membrane, their weight and thickness increased, depending on the hydrophilic or hydrophobic character of the liquid and the membrane. Table 4 shows that the increase is higher when using the more hydrophilic PVDF membrane. This difference may be due only to differences in the membrane porosity and thickness.

These results show an increase of 52.3–63.4% and 6.9–20% for weight and thickness respectively, depending on the MIL-microporous membrane combination.

2.4. Stability of SMILMs

The experimental set-up used for evaluation of membrane stability has been described elsewhere [9]. Basically, the SMILMs were placed in a dead-end filtration cell, with an effective membrane