



Phase behavior and permeability of Alkyl-Methyl-Imidazolium Tricyanomethanide ionic liquids supported in nanoporous membranes



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ABSTRACT

This work presents an investigation of the CO₂ and N₂ single and mixed gas phase permeability through supported ionic liquid membranes (SILMs) developed on ceramic nanoporous substrates with different pore size (1, 5 and 10 nm). ILs from the 1-alkyl-3-methylimidazolium tricyanomethanide family ([RMIM][TCM], with alkyl group, R: ethyl, butyl or octyl) were used as nanopore modifiers. These ILs exhibit high chemical and thermal stability, low viscosity and enhanced CO₂ absorption capacity compared to other imidazolium based ILs. Thermal analysis of the developed SILMs unveiled a drastic liquid-to-solid transition upon confinement of the ILs into the pore channels with a size of 1 nm. The IL crystals formed inside these extremely small cavities possessed considerable thermal stability and underwent thermally induced phase transitions that differed significantly from those occurring in the unconfined bulk IL phase or in the IL phase when entrapped into the larger pore channels. The different physical state of the IL under confinement into the pores of different size resulted to significant variation of the flux properties between the developed SILM membranes. The effect of temperature on the CO₂ permeability depended strongly on the crystal thermal stability and microstructure dictated by the confinement into the nanopores.

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1. Introduction

Interest in ionic liquids continues to grow, primarily because of their unique and tunable properties. The possibility of tuning their properties by selecting a specific combination of cations and anions among a great variety of possible ion pairs has led to an exponentially growing list of potential applications, such as gas separation and capture via selective absorption. The solubility and diffusion of several gases, has already been studied in a high number of Room Temperature Ionic Liquids (RTILs) [1–19] and the results showed very promising CO₂ absorption capacity and CO₂/N₂ selectivity performance, which might be suitable for energy and environmental applications such as carbon capture and separation (CCS). However one of the major drawbacks of RTILs, when used as net liquid solvents, is their relatively high viscosity (compared to common liquid absorbers and solvents) which leads to very slow CO₂ diffusion and makes their industrial scale application unfeasible. As a more convenient solution, immobilisation of

very thin layers of ILs on the top surface or into the pores of sufficiently permeable membranes has already evidenced the possibility to overcome the problem of slow diffusivity and improve the efficiency of CO₂ removal from flue gas. Up to date RTILs have been immobilized in macroporous, polymeric supports [20–31] and scarcely on inorganic nanoporous ones [32,33]. Previous testing of polymer based, Supported Ionic Liquid Membranes (SILMs) showed promising results with permeabilities/selectivities that were consistently above the upper bound of a Robeson plot for CO₂/N₂ separation [20,34,35].

With respect to polymeric membranes, the use of ceramic substrates allows for operation at higher temperature and transmembrane pressure. As a result, higher flux can be achieved without compromising the good separation performance. Moreover, issues related to the long-term stability of the support and the effects of acidic gases or the IL itself are not of concern. On the other hand, immobilisation into nanopores, instead of macropores can significantly contribute to the stability of the SILM membrane and the avoidance of phenomena such as the dissolution into the feed phase and the displacement of the IL from the pore structure.

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SILM membranes on nanoporous ceramic substrates can be prepared either by physical sorption (e.g. infiltration) or via chemical grafting. Ceramic substrates offer a high population of surface silanol or aluminol groups where a silylated ionic liquid can be chemically attached through the formation of covalent bond. The later method was recently applied by the authors [33] and has produced SILMs with prolonged performance stability and high CO₂ flux. Whatever the support, the ILs and the stabilization method are, the appropriate strategy to develop a feasible CO₂ separation process based on SILMs must be based on the ability to predict the performance of the SILMs under development and compare it with the target values.

The developed methodologies for predicting and projecting the upper limits for the permeability of a given gas through a SILM membrane start with the assumption that gas transport through the immobilised IL phase follows a dissolution/diffusion model:

$$P_e = DS \quad (1)$$

where P_e is permeability, S is solubility (in moles per volume per partial pressure), and D is diffusivity. In a further step, models that describe the components, S and D , in RTILs are taken into account and compared against SILMs data [9,15,26,36–40]. A general conclusion of previous studies, encompassing all RTIL families that interact physically with CO₂, is that the critical properties affecting SILMs performance are the molar volume and viscosity of the RTILs. Specifically, for CO₂/N₂ separation, decreasing the RTIL molar volume increases permeability–selectivity and increasing viscosity decreases CO₂ permeability. However, these conclusions are valid for SILMs casted on macroporous supports. As is known, the molecules of a confined liquid have different dynamics with respect to the bulk fluid [41,42]. In the bulk phase, the ILs form a 3-D hydrogen bond network as in the case of water molecules.

Confinement of ILs within pores comparable to their ion pair dimensions results in drastic alterations in what concerns their structure and physicochemical/thermophysical properties. Previous experimental and simulation studies have demonstrated that confined ILs undergo changes in phase behavior such as in glass transition temperature, T_g , and melting point, T_m [43–51]. These changes are induced by the microstructural conformation and the possibility of long-range molecular ordering or formation of new phases with different ionic self-diffusivity. The resulting ordering of the ionic moieties into specific arrangements depends on the extent of confinement, which is defined by the characteristics of the supporting material porous network (e.g. pore shape and pore size distribution) with respect to the dimensions of the ionic components. It is also dependent on the pore surface chemistry of the supporting material. In essence, the microstructure and phase transitions of the confined ILs are determined by the relative energy of the interactions among the ionic species (e.g. hydrogen bonds, electrostatic interactions, etc.) and those at interfaces between ion pairs and solid material, which favor crystallization and structural ordering. Regarding the stabilizing mechanism it was speculated that strong cationic/anionic interactions with functional groups present at the nanopores walls within a radial dimension of 1–10 Å may form structured matrix arrangement of the cations/anions within the nanopore networks. Such a formation could give rise to unique gas transport and separation properties different to ILs in bulk liquid condition.

In this work, SILM membranes have been developed via casting and imbibition of alkyl methylimidazolium tricyanomethanide ILs [RMIM][TCM] into the nanopores of ceramic monoliths. Our target was to exploit the promising CO₂ absorption/separation performance of the [RMIM][TCM] ILs and the stability offered by the embedment of the IL into the nanopore structure. A thorough investigation was also conducted on the effect of confinement on the gas permeation and selectivity performance of the developed

SILMs. To this end, single phase gas permeation properties were studied in relation to the pore size of the supporting materials. Moreover, we have evaluated the separation efficiency of the SILM membranes for CO₂/N₂ binary mixtures with respect to the mixture composition, the operation temperature, the pore size and the cation's alkyl chain length of the employed IL.

Proper evaluation of the effect of ILs confinement on the gas flux properties of the developed SILMs, demands for the outermost accuracy in the calculations producing the theoretical permeability of the bulk IL and the experimental permeability of the respective SILM. For that reason the CO₂ diffusivity and solubility in the selected ILs had been defined experimentally rather than from empirical models. Moreover, Raman cross section analysis of the SILM membranes provided accurate depth profiles of the IL phase, thus assisting to the outermost reliable definition of the permeability factor. Thermal analysis of the SILMs revealed changes in the phase behavior of the ILs under confinement and explained the variance observed between the permeability properties of the SILMs that had been developed on the substrates with different pore size. The temperature dependence of the CO₂ single gas permeability on the crystal thermal stability and microstructure of the embedded into the pores IL phase was also investigated and the existence of a correlation between the nanocrystalline structure of the ILs with the CO₂ permeabilities was concluded.

2. Materials and methods

2.1. Chemicals and materials

The RTILs used in this study were 1-ethyl-3-methylimidazolium tricyanomethanide ([EMIM][TCM]), 1-butyl-3-methylimidazolium tricyanomethanide ([BMIM][TCM]), 1-hexyl-3-methylimidazolium tricyanomethanide ([HMIM][TCM]) and 1-octyl-3-methylimidazolium tricyanomethanide ([OMIM][TCM]), provided by IoLiTech GmbH. The mass fraction purity of each IL was larger than 98% and the hydroscopic character was depended on the side chain length of the cationic species. The water content decreased in the order: [OMIM] (120 ppm) < [HMIM] (390 ppm) < [BMIM] (720 ppm) < [EMIM] (930 ppm).

Two types of commercial ceramic multilayered nanofiltration (NF) and ultrafiltration (UF) membranes have been used as porous supports with the purpose to develop the SILM systems. The NF membranes encompassed a thin microporous silica separation layer with nominal pore size of 1 nm whereas for the UF membranes the separation layer was a thin mesoporous γ -alumina layer having nominal pore size of 10 nm. The membranes (monochannel monoliths of 15 cm length, 0.67 cm ID, 1 cm OD) with glazed ends (1.5 cm) were obtained from Inopor[®] GmbH. The active surface of the NF and UF separation layer was 26.3 cm². In both membrane types, the separation layer, located in the bore side of the monochannel tubes was supported by a thick macroporous α -alumina support (outer side) and two successive macroporous α -alumina layers of intermediate pore size. Permeability and absorption measurements were conducted using the following gases: He (99.999%), N₂ (99.999%) and CO₂ (99.998%).

2.2. Membrane fabrication

The development of the supported ionic liquid membranes was attained by applying a liquid infiltration step. The membranes were accommodated into a specially designed tightly capped stainless steel module and initially degassed at 150 °C under vacuum. After lowering the temperature down to 30 °C, a certain volume of the bulk ionic liquid was suctioned through a throttle valve into the top layer side so as to completely fill the bore space of the tube

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