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Polymer–ionic liquid composite membranes for propane/propylene separation by facilitated transport

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ABSTRACT

In this work we propose the use of novel PVDF-HFP/BMImBF₄-Ag⁺ facilitated transport membranes to carry out the separation of olefin/paraffin gas mixtures. These membranes exhibit good thermal, chemical and mechanical stability, good separation properties and easy manufacturing. The effect of membrane composition was evaluated concluding that the membrane with 80% polymer-20% IL w/w shows the best compromise between separation properties and mechanical resistance. The separation performance of membranes containing different concentrations of Ag⁺ in the range 0–80% w/w at temperatures between 293 and 323 K and different operational conditions has been evaluated. The facilitated transport membranes herein prepared provided very promising results when tested with 50/50%v/v C₃H₈/C₃H₆ mixtures obtaining C₃H₆ permeabilities up to 6630 barrer and C₃H₈/C₃H₆ selectivities over 700, placing these membranes well above the Robeson upper bound for polymeric and inorganic membranes. Moreover, these membranes showed excellent stability during long-term experiments carried out for 10 days.

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1. Introduction

For nearly seven decades, separation of olefins such as ethylene and propylene from refinery catalytic cracking and steam cracking off-gases have been performed by distillation and adsorption processes. The large capital expense as well as the energy cost associated to these conventional technologies provides the incentive for ongoing olefin/paraffin separation technology research [1].

In this sense, membrane technology presents a great potential for energy and capital saving and therefore the use of membranes has been the focal point of research of many authors. Criteria for selecting the most suitable membrane for a given application are complex; nonetheless, durability, mechanical and thermal stability at the operating conditions, productivity and separation efficiency and costs are important stipulations that must be considered [2]. Among these requirements selectivity and permeation rate are clearly the most basic, while the relative importance of the rest of them varies with the application. Therefore a wide variety of different membrane alternatives can be considered. The use of polymeric membranes for olefin/paraffin separation has been studied rather extensively [3], however polymeric membranes may suffer severe plasticization effect and therefore their performance has not met the requirements for commercial

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applications [4,5]. Inorganic membranes have been also explored because besides their higher tolerance to harsh environments, the gas separation performance of inorganic membranes can surpass the Robeson upper bound for the conventional polymeric membranes [6]. However, the typical poor mechanical resistance of the inorganic membranes, combined with their expensive and complex preparation methods have limited their use in large-scale application. More recently the use of polymer composite membranes with enhanced separation properties is becoming increasingly important [7]. Thus, the use of polymer/ionic liquid composite membranes has been successfully applied to CO₂/H₂ [8] and CO₂/CH₄ [9–13] mixtures enhancing the separation performance of the polymeric membrane by itself. On the other hand many researchers have turned their attention to use facilitated transport membranes, both in liquid and solid state, in order to improve the olefin permeability without compromising the separation selectivity [14]. The separation performance is mostly associated to the ability of the olefins to react selective and reversibly with silver cations Ag⁺, by π -complexation mechanism. Consequently silver ions act as carriers for the transport of olefins, thus facilitating their selective permeation across the membrane. Kang et al. [15–18] have investigated extensively the separation performance of different types of facilitated transport membranes in the solid state for olefin/paraffin separation and reported high selectivities. However low olefin permeabilities and chemical instability of the carrier should be overcome before this technology can be implemented. Some authors [19,20] have studied the performance of supported liquid membranes (SLMs) using

aqueous silver salt solutions for propylene/propane separation. Although good separation performances were reported, SLMs suffer from critical drawbacks such as the evaporative loss of solvent and that the solvent can be expelled from the support due to the high trans-membrane pressure. Other authors proposed the use of non-volatile solvents [21–23] in order to avoid solvent losses by evaporation; nevertheless the mechanical instability issues remain still unsolved, since the SLM configuration can fail if the pressure differential across the membrane is high enough to overcome the liquid–support interactions and push the liquid through the pores of the support.

In this work we propose the use of novel polymer/ionic liquid–Ag⁺ composite as facilitated transport membranes to carry out the separation of propane/propylene mixtures. Ionic liquids (IL) were selected as membrane additives because in addition to their negligible vapour pressure that avoids solvent losses by evaporation, they offer more affinity for the olefinic compounds compared to saturated hydrocarbons and at the same time they provide stability to the metallic cation dissolved inside [24–26] acting as a medium for facilitated transport with mobile carrier. Based on previous results the ionic liquid used in this work has been 1-butyl-3-methylimidazolium tetrafluoroborate (BMImBF₄) since it provided the best results in terms of separation selectivity and propylene solubility [27]. On the other hand, the polymer used in this work is poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) due to its well known thermal, chemical and mechanical properties. Furthermore it is partially miscible with BMImBF₄ and compatible with hydrocarbons which avoid plasticization effects. Once the membrane is fabricated the ionic liquid remains integrated within the polymer matrix, thereby increasing the stability of the membrane even at high transmembrane pressures. As the composite membrane is composed by a polymeric matrix and a liquid phase entrapped inside the polymeric matrix, the silver salt added to the membrane is distributed between these two phases. Therefore both facilitated transport mechanisms (fixed carrier and mobile carrier) take place, leading to high permeabilities combined with high separation selectivities.

2. Experimental section

2.1. Materials

Propylene and propane gas were purchased from Praxair with a minimum purity of 99.5%. The polymer PVDF-HFP (CAS number 9011-17-0) was supplied by Sigma Aldrich. The ionic liquid BMImBF₄ (CAS number 174501-65-6) was provided by Iolitec, with a minimum purity of 99% and residual halide content less than 500 ppm. The silver salt used was silver tetrafluoroborate (CAS number 14104-20-2) of 99% purity purchased from Apollo Scientific Ltd. Tetrahydrofuran (THF) (CAS number 109-99-9) supplied by Panreac was used as a solvent to prepare the membranes.

2.2. Membrane preparation

The PVDF-HFP/BMImBF₄-Ag⁺ composite membranes were prepared by the solvent casting technique. First of all the polymer is dissolved in 10 mL of THF at 40 °C for 8 h in a closed vial to avoid the evaporation of the solvent. Once the polymer has been dissolved, it is mixed with the ionic liquid and the silver salt and stirred for 5 min. Finally the membrane precursor mixture is placed in a Petri dish and the solvent is evaporated at 25 °C and 300 mbar under dark conditions for 24 h. For better understanding of the results presented in this work, it would be appropriate to clarify that the silver content of the membranes is expressed as a

percentage of the silver salt weight compared with the weight of the membrane without silver AgBF₄/(PVDF-HFP+BMImBF₄). The thickness of the membranes prepared in this work depends on the membrane composition, but in all cases the prepared membranes presented an average thickness around 120 ± 20 μm. Permeabilities have been calculated taking into account the real thickness of each membrane which was measured using a digital micrometer Mitutoyo Digmatic Series 369 (accuracy ± 0.001 mm).

2.3. Membrane characterization

Membranes thermal and mechanical stability was determined together with structural properties by thermogravimetric analysis (TGA), tensile tests, polarized light microscopy (PLM) and FTIR techniques.

2.4. Gas permeation experiments

Once the polymer-IL membrane has been prepared (A=39.6 cm²) it is placed into a permeation cell inside a water bath in order to control the temperature. The flow rate of each gas is adjusted by a mass flow controller and before starting the experiment the composition of the feed stream is analyzed by gas chromatography. The feed stream flows through the upper chamber, while the nitrogen used as sweep gas flows through the permeate side. The pressure of both streams is controlled using two micrometric valves. The flow rate of the permeate stream is measured using a mass flowmeter (as the sum of permeate and sweep gas) and at the cell outlet the composition of both, the feed stream and the permeate stream are analyzed by gas chromatography. The analysis was performed in a gas chromatograph HP 6890 equipped with a thermal conductivity detector (TCD) and a column HP Al/S (30 m length, nominal diameter of 0.53 mm). First of all the effect of the membrane composition (polymer/IL/Ag⁺) on the gas permeation fluxes and separation selectivity was studied. Afterward several experiments were carried out at different operational conditions in order to analyze the influence of trans-membrane pressure (0.5–3 bar), sweep gas flow rate (0–20 mL/min) and operation temperature (293–323 K). A schematic diagram of the experimental set-up is shown in Fig. 1:

The experimental permeabilities of each gas are calculated according to Eq. (1):

$$J_i = P_{m,i} \frac{\Delta P_i}{\delta} \quad (1)$$

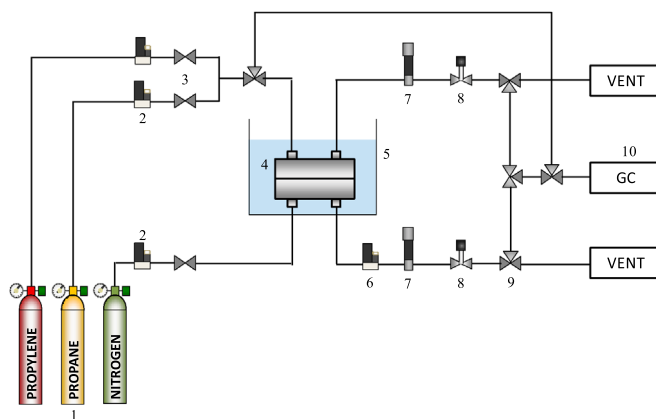


Fig. 1. Diagram of the experimental setup. 1—Gas bottles, 2—mass flow controllers, 3—two way valves, 4—permeation cell, 5—water bath 6—mass flowmeter, 7—pressure transducer, 8—micrometric valve, 9—three way valves, 10—gas chromatograph.

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