

Stability of supported ionic liquid membranes as studied by X-ray photoelectron spectroscopy

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Abstract

This work evaluates the use of room temperature ionic liquids (RTILs) in supported liquid membranes (SLMs). The physicochemical properties of RTILs, namely their reduced solubility in water and high interfacial tension, make their use very attractive in order to obtain stable supported liquid membranes.

Preliminary results showed that, under relatively mild stirring conditions, there was no evidence of ionic liquid displacement from the membranes' pores. In this work, further studies were conducted in order to assess the SLMs' operational stability under dynamic conditions. Dynamic stability studies were performed to evaluate the stability of a SLM with [C₈MIM][PF₆] when submitted to more aggressive and well-defined hydrodynamic conditions.

Additionally, X-ray photoelectron spectroscopy (XPS) was used to characterise the SLMs obtained by immobilizing the ionic liquids [C_nMIM][PF₆] (*n* = 4, 8) and [C₁₀MIM][BF₄] in a polyvinylidene fluoride (PVDF) supporting membrane. This technique allows for the determination of the surface chemical composition of a sample and was used for the characterization of both the supported liquid membranes and the ionic liquids. The SLMs were analysed immediately after preparation and after being immersed for 1 week in de-ionised water. This way, it was possible not only to assess the presence of the RTILs in the membrane after preparation, but also to identify whether there were any chemical modifications on the SLMs' surface after contact with an aqueous solution, thus obtaining valuable information about their integrity and stability.

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1. Introduction

Room temperature ionic liquids (RTILs) are air and water stable electrolytes composed entirely of ions, normally an organic cation and either an organic or an inorganic anion, that are liquid at room temperature.

RTILs, especially those based upon the 1-*n*-alkyl-3-methylimidazolium cation, have been the object of ever

growing research interest [1,2]. Unlike traditional inorganic molten salts such as NaCl, NaAlF₆ or the eutectic mixture LiCl–KCl, room temperature ionic liquids present a high degree of asymmetry that inhibits crystallisation at room temperatures.

In particular, their ability to solvate a wide variety of organic and inorganic species has made their use as alternative green solvents, namely as reaction media for synthesis, catalysis and biocatalysis, extremely appealing [3–5]. Additionally, the non-measurable vapour pressure of RTILs combined with their reduced solubility with various solvents, including

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water, has made their use as organic phase in supported liquid membranes (SLMs) very attractive [6–8].

SLM applications have been widely studied during the past 20 years, namely for the recovery of metal ions, the removal of contaminants from industrial effluents, and the recovery of fermentation products [9–13]. Nevertheless, their industrial application is still limited, mainly due to concerns about SLM stability and long-term performance [14]. Reduction in solute flux and membrane selectivity has been reported to occur during operation. These effects have been attributed to a loss of solvent from the supporting membrane, either by evaporation or by dissolution/dispersion into the adjacent phases. A possible approach to minimising instability problems is the adequate design of both the supporting membrane and the contacting phases. In this context, the possibility of tailoring the physicochemical properties of ionic liquids by the adequate selection of the cation and the anion is extremely promising.

We recently evaluated the use of room temperature ionic liquids, based upon the 1-*n*-alkyl-3-methylimidazolium cation $[C_n\text{MIM}^+][X^-]$ in supported liquid membranes [15]. The physicochemical properties of the synthesised ionic liquids were determined; especially those with an impact on the transport flux – viscosity and on the SLM stability – water solubility in the RTILs and solubility of these RTILs in water. The effect of the supporting membrane material on the stability of the SLM was also evaluated. Four membranes of distinct materials were selected and the stability of the SLM obtained, when the ionic liquid $[C_4\text{MIM}][\text{PF}_6]$ was immobilized in each supporting membrane, was evaluated [15].

Two different, complementary approaches were followed in the studies mentioned above [15]. In one case, wetting tests were conducted to verify if, after contact with the aqueous phases, the supported liquid membranes still maintained their hydrophobic character. In the second case, experiments were performed to verify if, during operation, the ionic liquid was displaced from the membrane pores to the contacting aqueous solutions. The results obtained showed [15] that when a hydrophilic polyvinylidene fluoride (PVDF) membrane was used as the supporting membrane under relatively mild stirring conditions, the SLM maintained its hydrophobic character after operation. Additionally, the concentration of ionic liquid in the aqueous contacting phases remained essentially constant during the entire experiment, suggesting that the ionic liquid was not displaced from the membrane pores.

Although there was no evidence of ionic liquid displacement from the membrane's pores, the stirring conditions used were relatively mild and not comparable with usual operating conditions. For that reason, further studies were conducted, in the present work, in order to assess the SLMs' operational stability under dynamic conditions. Therefore, dynamic stability studies were performed to evaluate the operational stability of a SLM with $[C_8\text{MIM}][\text{PF}_6]$ when submitted to more aggressive and well-defined hydrodynamic conditions. Additionally, SLMs with $[C_n\text{MIM}][\text{PF}_6]$ ($n = 4$,

8) and $[C_{10}\text{MIM}][\text{BF}_4]$ were prepared and characterized using X-ray photoelectron spectroscopy (XPS). This technique allows for the determination of the surface chemical composition of a given sample [16] and was used both for the characterization of the supported liquid membranes and the ionic liquids. The SLMs were analysed immediately after preparation and after 1 week's immersion in de-ionised water. This way, it was possible not only to assess the presence of the RTILs in the membrane after preparation, but also to identify whether there were any chemical modifications on the SLMs' surface after contact with an aqueous solution, thus obtaining valuable information about their integrity and stability.

2. Experimental

2.1. Materials

The following are the room temperature ionic liquids used in this study, which were prepared following reported procedures [17–19]:

- 1-*n*-butyl-3-methylimidazolium hexafluorophosphate— $[C_4\text{MIM}][\text{PF}_6]$;
- 1-*n*-octyl-3-methylimidazolium hexafluorophosphate— $[C_8\text{MIM}][\text{PF}_6]$;
- 1-*n*-decyl-3-methylimidazolium tetrafluoroborate— $[C_{10}\text{MIM}][\text{BF}_4]$.

In case of the ionic liquids $[C_8\text{MIM}][\text{PF}_6]$ and $[C_{10}\text{MIM}][\text{BF}_4]$, the anion exchange, from the corresponding chloride, was made using HPF_6 and HBF_4 , respectively, while for $[C_4\text{MIM}][\text{PF}_6]$ NaPF_6 was used, followed by flash silica chromatography purification.

All the RTILs synthesised were dried under vacuum at 40 °C for 48 h prior to use and their initial water content was determined by Karl–Fisher analysis, as a control measure, in order to assure that the ionic liquids were always as dry as possible. The water content for the RTILs used was always lower than 2.5 $\text{g}_{\text{water}}/\text{l}_{C_4\text{MIMPF}_6}$, 1.8 $\text{g}_{\text{water}}/\text{l}_{C_8\text{MIMPF}_6}$, and 3.5 $\text{g}_{\text{water}}/\text{l}_{C_{10}\text{MIMBF}_4}$. The spectral data (^1H and ^{13}C NMR) obtained for the ionic liquids prepared were identical to those reported in the literature [17–19]. All ionic liquids were stored in closed vessels, and kept under vacuum in a desiccator prior to use. The solubility of water in the ionic liquids $[C_n\text{MIM}][\text{PF}_6]$ ($n = 4, 8$) and $[C_{10}\text{MIM}][\text{BF}_4]$ and the solubility of $[C_n\text{MIM}][\text{PF}_6]$ ($n = 4, 8$) in water were measured as described in Fortunato et al. [15]; the values measured were 27.84 $\text{g}_{\text{water}}/\text{l}_{C_4\text{MIMPF}_6}$, 15.73 $\text{g}_{\text{water}}/\text{l}_{C_8\text{MIMPF}_6}$, 84.61 $\text{g}_{\text{water}}/\text{l}_{C_{10}\text{MIMBF}_4}$, 19.2 $\text{g}_{C_4\text{MIMPF}_6}/\text{l}_{\text{water}}$ and 2.25 $\text{g}_{C_8\text{MIMPF}_6}/\text{l}_{\text{water}}$.

A hydrophilic polyvinylidene fluoride membrane (FP-Vericel, Pall Gelman Laboratory, USA) was used as supporting membrane. The membrane nominal pore size and thickness were $r_p = 0.2 \mu\text{m}$ and $l = 123 \mu\text{m}$, respectively.

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