



## Removal of thiols from model jet-fuel streams assisted by ionic liquid membrane extraction



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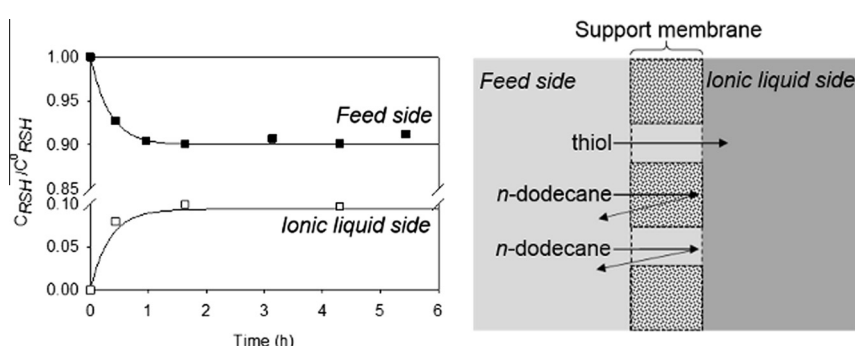
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### HIGHLIGHTS

- Ionic liquids are proved as alternative solvents for jet-fuel desulfurization.
- Target thiol is selectively extracted from *n*-dodecane (jet-fuel model compound).
- Ionic liquid and *n*-dodecane exhibit low mutual solubility preventing losses of fuel.
- Successful membrane-assisted extraction of target thiol from jet-fuel model system.

### GRAPHICAL ABSTRACT



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### ABSTRACT

This work focuses on the use of ionic liquids as alternative solvents for the removal of thiols, at room-temperature, from *n*-dodecane used as jet fuel model stream. The model extraction system composed by a selected ionic liquid, the thiol to be removed and an alkane representative of the jet-fuel, show high selectivities and low distribution ratios, which makes unfeasible the use of conventional liquid–liquid extraction processes due to the high volume of ionic liquid required. This work evaluates the use of supported ionic liquid membranes (SILMs) for the selective removal of thiols applying vacuum in the downstream side. This approach consists in the incorporation of the ionic liquid inside the membrane pores, while due to the vacuum applied, the thiol compound is scrubbed. To study the target solute transport from the feed to the ionic liquid, extraction experiments were carried out using different 1-ethyl-3-methylimidazolium cation-based ionic liquids. The mass transfer resistance was found to be higher in the ionic liquid phase, which results mainly from the high ionic liquid viscosities, hindering the thiol transport.

The SILMs stability was investigated by evaluating different membrane supports, with the various ionic liquids selected for study. The results obtained show that the ionic liquids were properly incorporated inside the pores of the membrane support. However, and despite the negligible mutual solubility between *n*-dodecane and the studied ionic liquids, *n*-dodecane permeation through the membrane support was found to be undesirably high. This problem was solved by using a membrane contactor with polypropylene hollow fibre membranes, not wetted by the ionic liquid, which receives the thiol compound transported. Under these conditions, *n*-dodecane was not detected in the receiving ionic liquid phase.

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## 1. Introduction

Petroleum industries are committed on reducing their sulfur emissions and improve or develop new desulfurization technologies, both to comply with regulatory requirements, and to optimize the fuel economy and conquer a superior treatment capacity.

Sulfur species, produced from fuel burning, are major pollutants responsible for severe environmental and health problems, which directed legislation towards more stringent limits on the fuel sulfur content, envisaging the use of ultra-low sulfur fuels. Further, the presence of these sulfurous compounds on fuel acts as a catalyst poison either on the fuel engine's exhaust emissions control systems, as in catalyst-aided refinery processes [1]. However, the availability of crude reserves with superior quality, i.e., with low sulfur content, diminished making refining industries prospect crudes with heavier and sourer compositions. The sulfur levels on these crudes can reach values almost up to 3.5% wt., that are much higher than those found on the light and sweet crudes, commonly treated due to their relative easy and cheap desulfurization [2]. Obviously, this quality deterioration on the supply side, and the more strict fuel specifications on the demand side, hinder the capacity and efficiency of conventional desulfurization processes (hydrocracking or hydrotreating processes), demanding an upgrade of the current processes [3].

The challenges presented are being pursued by several research groups, and comprise the development of more active catalysts for the traditional catalytic hydrodesulfurization, and new alternatives such as oxidative, adsorptive, extractive and biological desulfurization processes, and their combinations [2,4–13]. Among these, liquid–liquid extraction appears to be an attractive alternative related with the moderate operating conditions (low temperature and pressure) and low energy cost. Regarding the extracting solvents, ionic liquids have shown a great potential on substituting the conventional volatile organic solvents used [4,14–23] due to their negligible volatility, liquid state at a wide temperature, including room temperature, high thermal and chemical stabilities, among others [24]. Moreover, being composed by bulky and asymmetric organic cations and organic or inorganic anions, their endless possible combinations rise as another key characteristic, the ability of tailoring their physical, chemical and solvation properties, towards a specific application.

Taking the latest into account, our previous work [25] presented an intensive ionic liquid screening aiming to understand and select the most suitable ionic liquid as extracting solvent for the removal of thiols from kerosene, by experimental and COSMO-RS predictions of liquid–liquid equilibrium, selectivity and distribution ratio. Based in the ternary system model considered of ionic liquid, 1-hexanethiol and *n*-dodecane, it was found that these systems present a very high selectivity towards the target thiol compound, due to the almost negligible mutual solubility of the ionic liquid and the *n*-alkane studied. This is a remarkable feature since mutual contamination and losses of fuel and ionic liquid can be avoided in the separation process. Nevertheless, the thiol distribution ratios observed towards the ionic liquids tested were lower than unit, imposing extremely large volumes of ionic liquid in the liquid–liquid extraction process in order to attain the desired separation.

Yet, it is important to reiterate that, in spite of the unfavorable aspect referred, the difference between the thiol and alkane solubilities in the ionic liquid still qualifies the use of ionic liquids as a solvent in separation processes regulated by mass transfer kinetics, or by combining it with an efficient regeneration process.

For this purpose, membrane assisted extraction using supported ionic liquid membranes (SILMs) is considered a potential separation process, as suggested by several works that used an immobilized ionic liquid phase either for gas separation, [26–28] or liquid–liquid

extraction [29–32]. SILMs result from the immobilization of a selected ionic liquid, which acts as the selective medium, on a polymeric or ceramic porous support, responsible for the mechanical resistance of the membrane. By using an ionic liquid supported in a porous membrane, it is possible to provide a short diffusion path for the transport of the target thiol solute from the jet-fuel feed phase to a receiving compartment. Other advantages are the solvent volume required, much lower than in a conventional liquid–liquid extraction and, additionally, the low mass transfer resistance when compared with solid membranes [26,31,33–37].

In this work, making use of the non-volatility of ionic liquids, the thiol transport is driven by a chemical potential gradient across the SILM, by reducing the target solute concentration in the receiving compartment, where a reduced vacuum pressure is applied. The thiol permeates selectively across the liquid membrane from the liquid feed phase to the vapor phase in the permeate side. This approach assures a simultaneous extraction and stripping in one single stage, avoiding the equilibrium restrictions previously identified in these systems.

The stability and lifetime performance of the SILMs have an important impact on their industrial potential use [36]. Due to their negligible volatility and very low affinity for the feed phase mixture, the use of ionic liquids reduces drastically the deterioration of SILMs in comparison with conventional supported liquid membranes where the evaporation or dissolution of solvent into the contiguous phases may occur. Still, the integrity of the SILMs prepared should be tested under pressure differences identical to the ones employed during the extraction/stripping process, in order to assure that the ionic liquid is not displaced from the porous support.

Taking into account all previous considerations, the work here developed started with the study of the diffusion and mass transfer of the target thiol compound from the *n*-dodecane jet-fuel model feed to the ionic liquid phase, by performing liquid–liquid extraction experiments. As referred before, thiol species show low solubility in the ionic liquids, limiting the extraction capacity of the ionic liquid, which turns more relevant the selection of the most promising ionic liquids based on their transport characteristics. Nonetheless, the concern with a possible co-extraction of valuable fuel constituents requires the use of ionic liquids based on imidazolium cations, with small alkyl side chains, to guarantee the lowest mutual solubility with the aliphatic hydrocarbon [25].

Since the application of SILMs depends from the membrane stability and selectivity behaviors, the previous ionic liquids were also tested with different support materials in order to find the SILM that fulfills the necessary requisites.

## 2. Mass transfer model

The liquid–liquid extraction experiments were performed using an adapted Lewis cell which allows the two phases contacting with a well-defined interface. These experiments consist in registering the solute concentration along time, which provides information about the 1-hexanethiol transport from the feed phase (rich in *n*-dodecane) to the ionic liquid phase.

During these experiments, it was assumed that at the interface, an equilibrium state is established. Therefore, a mass balance over the feed phase leads to the mass transfer of the 1-hexanethiol compound between the *n*-dodecane feed phase and the ionic liquid phase, described by the Eq. (1):

$$-V_f \frac{d(C_f)}{dt} = K_f A_i (C_f - C_f^*) \quad (1)$$

In this equation,  $V_f$  ( $\text{m}^3$ ) is the feed phase volume,  $C_f$  and the  $C_f^*$  ( $\text{mol m}^{-3}$ ) are the 1-hexanethiol concentration in the phase under consideration and in equilibrium with the 1-hexanethiol concen-

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