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Study of the behavior of magnetic ionic liquids supported membranes for selective transport

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Introduction and aims:

A new generation of magnetic sensitive ionic liquids - magnetic ionic liquids (MILs), exhibiting a strong response to the magnetic field has been developed [1,2]. MILs are comprised by anions containing transition metal complexes, having physical properties (solubility, viscosity, surface tension and molecular orientation), that may be influenced by the presence of an applied magnetic field [1-3]. Actually, magnetically induced changes of IL solubility were confirmed by the dependence found between the concentration of binary MIL/water mixtures and the applied magnetic field strength [1].

The main goal of this work is to provide a better knowledge about the behaviour of MILs, in order to determine the influence of magnetic fields with different intensities and orientation vectors on their structural organization. It is expected that the presence of local structures play a key role in the magnetic behaviour of MILs physico-chemical properties [1]. Therefore, studies were performed in order to evaluate the impact of the magnetic field on the intrinsic physico-chemical properties of MILs, such as, solute solubility, rheological behaviour, solvation capacity and on the diffusion mechanism of solvents/solutes through MILs.

The magnetic behaviour of MILs suggests their potential to control the transport of different molecular species through supported liquid membranes, leading to improved selectivity and permeability, through a fine tuning of the magnetic field conditions.

Moreover, the magnetic behaviour of MILs was also study using a molecular scale approach aiming at understanding the presence of magnetically induced molecular mechanisms underlying the variation of the MILs macroscopic properties. ^{1}H-NMR – Proton nuclear magnetic resonance relaxometry technique provides direct information about the molecular dynamics in a system. Therefore, proton spin relaxation studies were conducted in order to infer about the influence of the motions and orientations of the anionic molecules of MILs on the local structure, and on the molecular dynamics of the cationic counter-part. Ultimately, this study will provide information about the impact of different magnetic field conditions on the MILs molecular organization.

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Experimental and Results:

The magnetic dependence of the viscosity and solubility in water of different MILs, such as: $AliquatFeCl_4$, $C_4mimFeCl_4$, $C_8mimFeCl_4$, $P_{66614}FeCl_4$, $(C_8mim)_2CoCl_4$ and $(Aliquat)_2MnCl_4$, were determined by exposing the MILs to magnetic fields of different intensities from 0 to 2 T. Studies of MILs viscosity in the presence of magnetic field was allowed by using a capillary viscosimetry technique. Additionally, the solubility of MILs in water was inferred by Inductively Coupled Plasma (ICP) analysis.

It was found that the increase of the magnetic field intensity from 0.5 to 2.0 T led to the decrease of the MIL viscosity, for $AliquatFeCl_4$ and $P_{66614}FeCl_4$, as shown in Fig. 1. In contrast, and accordance to that observed by. *S. Lee et all* [1], the solubility of MILs in water increased in the presence of the magnetic field with intensities ranging 0.5-2.0 T.

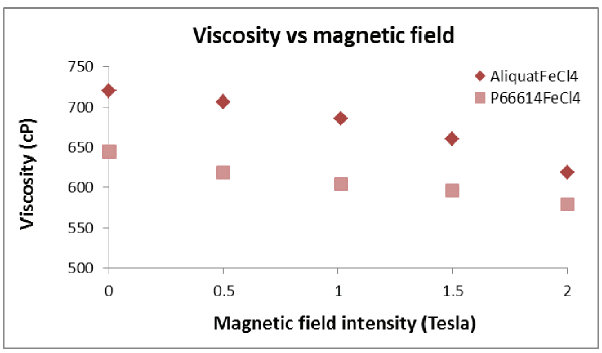

Fig.1. Viscosity dependence with magnetic field for $AliquatFeCl_4$ and $P_{66614}FeCl_4$

The [1]H-NMR results depicted in Fig.2 show the existence of a specific relaxation mechanism associated with the presence of the magnetic anions. The additional para-magnetic relaxation [8] is clearly observed on the high Larmor frequency part of the spin-lattice relaxation time (T_1) dispersion. The effect of the local order changes due to the magnetic anions is also detected in the rotations/reorientations and self-diffusion of cation motions, in comparison with molecular dynamics in non-magnetic counter-part ionic liquids.

In this way, it is possible to estimate the self - diffusion coefficients of MILs as well as the influence of the presence of magnetic anions on this parameter. This approach allows for establishing a comprehensive correlation between the magnetic induced molecular rearrangements within the MILs network and their physico-chemical macroscopic properties (e.g. solubility, viscosity) and transport/diffusion mechanisms of different solvents/solutes through MILs.

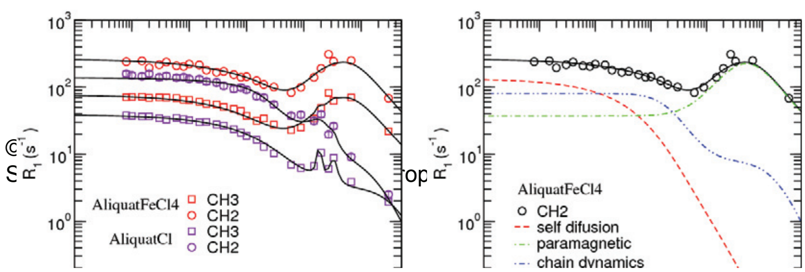

Fig.2. ^{1}H-NMR results for the non-magnetic ionic liquid AliquatCl and magnetic ionic liquid AliquatFeCl$_4$

Conclusions:

The research work aims to provide useful information of the magnetic behaviour of MILs that may drive the development of MILs with optimal designs and properties allowing the development of SLMs, with improved chemical and structural stability. These supported liquid membranes are capable of changing reversibly their intrinsic properties when exposed to magnetic fields under different conditions, leading to their enhanced selectivity and efficient separations processes.

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Keywords: magnetic ionic liquids, supported liquid membranes, magnetic responsive membranes, modulation of ionic liquids properties