



Ecotoxicological evaluation of magnetic ionic liquids



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ABSTRACT

Although magnetic ionic liquids (MILs) are not yet industrially applied, their continued development and eventual commercial use may lead to their appearance into the aquatic ecosystem through accidental spills or effluents, consequently promoting aquatic contaminations. Furthermore, the deficient information and uncertainty surrounding the environmental impact of MILs could be a major barrier to their widespread industrial application and international registration. Thus, in the present work, a range of cholinium salt derivatives with magnetic properties was synthesized and their ecotoxicity was evaluated towards the luminescent bacteria *Vibrio fischeri*. The results suggest that all MILs structures tested are moderately toxic, or even toxic, to the bacteria. Furthermore, their toxicity is highly dependent on the structural modifications of the cation, namely the alkyl side chain length and the number of hydroxyethyl groups, as well as the atomic number of the metal anion. Finally, from the magnetic anions evaluated, the $[\text{MnCl}_4]^{2-}$ is the less toxic. In order to improve the knowledge for the prospective design of environmentally safer MILs, it is important to expand this study to other aquatic organisms at different trophic levels.

1. Introduction

The increasing attention that ionic liquids (ILs) are attracting is justified by their unique properties, such as their negligible vapor pressure, high chemical and thermal stability, their non-flammability, high ionic conductivity, wide electrochemical potential window and high solvation ability (Rogers and Seddon, 2003). Furthermore, these ionic compounds are considered as “designer solvents” due to their tunable properties, which means that they can be designed for a specific application by the proper combination of the adequate cation and anion (Rogers and Seddon, 2003). Some reviews have highlighted the industrial applications of ILs as an innovative approach to “Green Chemistry” and sustainability (Rogers et al., 2002). However, the fact that they have a negligible vapor pressure is not enough to assure that these compounds can be considered as environmentally harmless solvents. Actually, even the most hydrophobic ILs present some solubility in water and thus, they may constitute an environmental risk to aquatic ecosystems (Nacham et al., 2015). A broad range of testing models (bacteria, fungi, algae, aquatic plants, crustaceans, mammalian cell lines and vertebrates) has been used to evaluate the toxicity of distinct ILs (Amde et al., 2015; Cvjetko Bubalo et al., 2014; Petkovic et al., 2011; Santos et al., 2015). In what concerns their aquatic toxicity,

the most tested trophic levels are decomposers represented by marine bacteria (e Silva et al., 2014; Ventura et al., 2012), producers represented by microalgae (Samorì et al., 2015; Ventura et al., 2012) and primary consumers represented by cladocerans (Samorì et al., 2015; Ventura et al., 2012). Magnetic ionic liquids (MILs) appear as an emerging class of ILs that are inherently paramagnetic, being able to respond to an external magnetic field. These magnetic compounds favorably combine the advantageous properties of ILs with magnetic characteristics, which can be interesting for applications in process and product engineering as an expanding field full of opportunities to create devices, processes and products (Clark et al., 2016; Santos et al., 2014a). In fact, MILs have been studied in fluid-fluid separations (Zhao et al., 2016), in the extraction of nucleic acids like DNA (Clark et al., 2015), in chemical reactions, namely as catalysts (Bica and Gaertner, 2008), reaction medium (Mohammad Fauzi et al., 2014) and solvents (Zakrzewska et al., 2013), in polymer chemistry (Dobbelin et al., 2011), in electrochemical devices (Branco et al., 2011) and as magnetic fluids (Guerrero-Sanchez et al., 2007). The paramagnetic properties of MILs may be located on the anion, cation or both. Their synthesis is normally based on the use of transition metals or lanthanide complexes in the anion structure (Santos et al., 2014a). The first MIL, namely the 1-butyl-3-methylimidazolium tetrachloroferrate, $[\text{C}_4\text{mim}]$

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[FeCl₄]⁻ was reported in 2004 (Hayashi and Hamaguchi, 2004). Since then, other MILs based on transition-metal coordination complexes such as Fe(III) (Del Sesto et al., 2008; Santos et al., 2014b; Yoshida and Saito, 2006), Co(II) (Del Sesto et al., 2008; Pitula and Mudring, 2010; Santos et al., 2014b) and Mn(II) (Del Sesto et al., 2008; Pitula and Mudring, 2010) have been reported. Furthermore, lanthanide complexes, like gadolinium (Gd), neodymium (Nd) and dysprosium (Dy), have also emerged due to their strong response to an external magnetic field and, in some cases, luminescent properties (Mallick et al., 2008; Santos et al., 2014b). In general, these magnetic anions have been combined with imidazolium- (Yoshida and Saito, 2006), phosphonium- (Del Sesto et al., 2008; Pitula and Mudring, 2010; Santos et al., 2014b), cholinium- (Frade et al., 2013; Zakrzewska et al., 2013) and ammonium-based cations (Zhang et al., 2012). Recently, the first magnetic chiral ILs, which simultaneously contain chiral and magnetic properties, have been synthesized by the simple combination of a chiral cation with the tetrachloroferrate magnetic anion (Li et al., 2009). Considering not only the variability of structures and properties (including the magnetic ones) and the importance of MILs in different applications using water as the principal media, it seems to be crucial to analyze and evaluate their (eco)toxicity. In this context, Luis et al. (2011) have evaluated the ecotoxicity of some MILs towards the *Vibrio fischeri* (*V. fischeri*) bioluminescent marine bacteria. In addition, a Quantitative Structure-Activity Relationship (QSAR) based on group contribution methods was applied to describe the influence of the molecular structure of common ILs and MILs on the (eco)toxicity (Luis et al., 2011). The authors have shown that the presence of iron in the molecular structure of imidazolium-based ILs leads to an increase in ecotoxicity (Luis et al., 2011). Alvarez-Guerra and Irabien (2011) reported a new approach for estimating the (eco)toxicity of ILs, including MILs, using a Partial Least Squares-Discriminant Analysis (PLS-DA). In this study, the [FeCl₄]⁻ anion had the most severe influence on the PLS-DA model as positive discriminator, being more toxic than toluene, taken as reference for common volatile solvents. Despite the initial efforts carried to offer a preliminary insight into the environmental behavior of MILs, data on their ecotoxicity is still scarce, and needs to be expanded to improve the knowledge for the adequate design of safer MILs. Moreover, the (eco)toxicological hazard profile of ILs with industrial potential must address a set of different rules, including those related with the regulatory demands defined by the European Union regulation for the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) (EC, 2007). In this context, the present study proposes the ecotoxicological assessment of a series of MILs based on the cholinium derivative cation in combination with [FeCl₄]⁻, [MnCl₄]²⁻, [CoCl₄]²⁻ and [GdCl₆]³⁻ anions, towards the *V. fischeri* marine bacteria. This work is part of an integrated study being performed by our group in which different cholinium IL structures have been analyzed. The purpose is not only to evaluate the effect of different anions conjugated with the cholinium cation but also to infer about the benign toxicological character normally claimed for cholinium-based ILs and derivatives when this structure is conjugated with magnetic anions.

2. Experimental

2.1. Materials

All solvents were distilled prior to use. All chemicals were purchased from Sigma-Aldrich.

2.2. General method for the synthesis of MILs

2.2.1. General method for cholinium chloride derivative based ILs

Synthesis of [N_{x,x,x,x}]Cl (x = alkyl or ethanol) was adapted from (e Silva et al., 2014; Rosatella et al., 2016). In a closed vessel at room temperature, it was added *N*-methyl-diethanolamine (143 mmol), or *N*-

dimethylethanolamine (143 mmol) to the correspondent alkyl chloride (1–4 mol eq.), and sodium iodide (10–30 mol eq.). In some procedures acetonitrile was used as a solvent. The solution was heated at 60–80 °C for 1–7 days. The solvent was removed on a rotary evaporator. The resulted salt was dissolved in dichloromethane and the sodium halide removed by filtration. The obtained salt was dried under vacuum and used in the next step without further purification. For more details see the Supporting Information.

2.2.2. General method for magnetic ILs [N_{1,1,n,2(OH)}][MCl_y] and [N_{1,n,2(OH),2(OH)}][MCl_y]

The MILs were prepared using the reported procedures with some modifications (Del Sesto et al., 2008; Frade et al., 2013; Rosatella et al., 2016). The metal chloride hydrated salt MCl_y·H₂O (1 equiv. for FeCl₃·6H₂O; 0.5 equiv. for CoCl₂·6H₂O and MnCl₂·4H₂O, and 0.3 equiv. for GdCl₃·6H₂O) was added to a solution of cholinium derivative chloride salt (10 mmol) in methanol (20 mL). The reaction mixture was stirred overnight at room temperature. The solvent was evaporated on a rotary evaporator at 50 °C, and then kept under vacuum for 48 h at 1–4 × 10⁻² mbar (rotatory pump) and for 48 h at 6 × 10⁻⁵ mbar with stirring at 50 °C. More detailed information about the synthesis of MILs is reported in the Supporting Information, namely in Table S1.

2.3. Standard Microtox[®] liquid-phase assays

In order to evaluate the ecotoxicity of the MILs prepared, the Standard Microtox[®] liquid-phase assay was applied in this work. The Microtox[®] test is based on the evaluation of the bioluminescence inhibition considering the bacteria *V. fischeri* (strain NRRLB-11177) tested at 15 °C. The bacteria was exposed to a range of diluted aqueous solutions (from 0 to 81.9 wt%) of each tested compound, where 100% corresponds to the stock solution concentration. The light output of *V. fischeri* was measured after 5, 15 and 30 min of exposure to each MIL, and compared with the light output obtained for the blank control sample, an aqueous solution without the presence of any MIL (Figs. 1–4). Then, the corresponding 15 min- and 30 min-EC₅₀ values considered as the most reliable parameters to take into account (concentration of MIL which promotes 50% of bacteria luminescence inhibition), plus the corresponding 95% confidence intervals, were estimated for each compound tested by a non-linear regression, and using the least-squares method to fit the data to the logistic equation. Considering that the luminescence changes as a direct function of the bacteria's overall viability, the lower the EC₅₀ value, the higher the MIL toxicity. In order to obtain the correct EC₅₀ values, prior to Microtox[®] testing, the water content of each MIL was determined by Karl Fischer (KF) titration using a Metrohm 831 KF coulometric titrator.

3. Results and discussion

Distinct cholinium and cholinium derivatives, with different number of hydroxyethyl groups and lengths of the alky side chain, were combined with the magnetic anions [FeCl₄]⁻, [MnCl₄]²⁻, [CoCl₄]²⁻, [GdCl₆]³⁻ in order to obtain 24 MILs, whose toxicities were tested against the marine bacteria (Fig. S1). All MILs were soluble in water for the range of concentrations used. The ecotoxicological impact of these MILs was evaluated using the standard Microtox[®] acute assay. Although this is not a standard toxicity test defined in the European Union legislation and by REACH, it is nevertheless a quick and cost-efficient first-approach to evaluate the toxicity of various compounds. Moreover, this is a methodology well accept in the development of QSAR models for the prediction of ILs toxicity (Das et al., 2016, 2015; Luis et al., 2007), and the QSAR approach for toxicity predictions is encouraged by REACH legislation of the European Union. This assay has been widely used to evaluate the toxicity of ILs, including cholinium derivatives (e Silva et al., 2014; Ventura et al., 2012). This test is based on the bioluminescent bacteria *V. fischeri*, with the luminescence being a

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