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Relevant parameters for assessing the environmental impact of some pyridinium, ammonium and pyrrolidinium based ionic liquids

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HIGHLIGHTS

- Environmental impact of pyridinium, ammonium and pyrrolidinium based ionic liquids.
- Aqueous solubility, octanol/water partition coefficient and diffusion in water.
- Chromatographically derived lipophilicity.
- Effect of oxygenated moieties on the environmental impact of ionic liquids.

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ABSTRACT

Several physico-chemical properties relevant to determine the environmental impact of ionic liquids – aqueous solubility, octanol/water partition coefficient, chromatographically derived lipophilicity and infinite dilution diffusion coefficients in water – were measured in ionic liquids based on pyridinium, ammonium and pyrrolidinium cations with bis(trifluoromethylsulfonyl)imide anions. The influence of the presence of hydroxyl or ester groups in the physico-chemical properties of these liquids was checked. It appeared that the presence of functional oxygenated moieties reduces the lipophilicity of ionic liquids and so decreases the risk of bioaccumulation in environment.

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1. Introduction

Ionic liquids (ILs) have interesting properties that make them promising candidates as low environmental impact media for chemical processes. Some prospective work predicts their commercial application in nearly all of the chemical industry fields (Plechkova and Seddon, 2008) but recent researches have demonstrated that some ILs can be toxic (Pham et al., 2010) and resistible to biodegradation (Coleman and Gathergood, 2010). For the development of ILs in wide scale applications, data concerning their environmental impact is necessary. These data includes toxicity, biodegradation, bioaccumulation, degradation rates (chemical, photochemical or biological) but also physico-chemical parameters that provide information about their transport and fate in the compartments of the environment and often serve as a basis for the establishment of reliable prediction models of the environmental impact (Mackay, 1991).

The determination of the fate of a substance in the environment is complicated, as it has to take into account several phenomena not always easily quantifiable. The knowledge of the vapor pressure, of the aqueous solubility and of the partition coefficients between the environmental compartments of a substance contributes to determine its fate in natural ecosystems but several other processes, often very significant, have to be taken into account such as degradation and other transformation reactions (chemical, photochemical or biochemical). The transport of a chemical in water or in the soil is also a complex process. The knowledge of the aqueous diffusion coefficient is necessary as it can be used, together with the volumetric properties of the chemical, to model the mass transfer in

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the aqueous and soil compartments. Other data are necessary to take into account the very important contribution in real environmental conditions of sorption processes (physical or chemical), advection and convection to the transport of chemicals.

In the case of ILs, because they have negligible vapor pressures, the physico-chemical properties considered relevant for the determination of their environmental impact are their atmosphere–water partition coefficient, their aqueous solubility, their octanol–water partition coefficient and their aqueous diffusivity.

The aqueous solubilities of ILs are often determined by the anion, some anions rendering them fully miscible with water at ambient temperature, e.g. Cl^-, NO_3^-, OAc^-, and CF_3COO^- (Schrekker et al., 2007; Freire et al., 2009). When ILs are only partially miscible with water, the molecular structure of the cation is relevant to determine the IL/water miscibility ranges. For example, longer alkyl chains in the cation usually lead to ILs that are less soluble in water (Freire et al., 2008, 2009).

The diffusion coefficient of ILs in water is rarely reported, only imidazolium ILs with different anions have been studied so far (Su et al., 2007; Wong et al., 2008; Sarraute et al., 2009; Deng et al., 2011a).

The octanol/water partition coefficient (K_{OW}) is the ratio of the equilibrium concentrations of the substance in 1-octanol saturated with water (C_O) and in water saturated with 1-octanol (C_W). It is an important factor determining fate and distribution in the environment (Sangster, 1997). Since it directly reflects the lipophilicity of a specific substance, it correlates with its biological activity, soil sorption constant, and allows the prediction of its biological, biochemical and toxic effects (Danielsson and Zhang, 1996; Ropel et al., 2005). It is widely used as a parameter for quantitative structure–activity relationships (QSARs) and plays an important role in the early stages of the environmental risk assessment for a chemical (Danielsson and Zhang, 1996; Berthod and Carda-Broch, 2004). K_{OW} is often determined experimentally by the shake flask method (Sangster, 1997) especially for low lipophilic compounds of basic or ionic character. It is known, however, that retention time on a reversed phase type of column can be used as a measure of lipophilicity and is considered as a convenient tool for modeling biological and environmental barriers (Nasal et al., 2003). This simplified experimental technique minimizes uncertainty in hydrophobicity measurements and also eliminates the influence of the anionic part on the overall solubility of the organic cation. Reverse phase liquid chromatography operating on chemically bonded phases (Bard et al., 2009) was recently proposed and will be used herein to measure the lipophilicity of the ILs.

Only few published studies concern the determination of K_{OW} for ILs. Experimental determinations have been reported for imidazolium based ILs (Choua et al., 2003; Ropel et al., 2005; Lee and Lee, 2009; Deng et al., 2011b) and some successful predictions, based on the ILs molecular structures, have been reported (Stepnowski and Storoniak, 2005). Other groups (Domanska et al., 2003; Chapeaux et al., 2007) have used indirect experimental methods to obtain estimates of K_{OW} for imidazolium, pyridinium and quaternary ammonium based ILs, from the ratio of their solubility in pure water and in pure 1-octanol, a value that does not correspond to the exact definition of K_{OW}. Stepnowski and Storoniak, 2005 and later Ranke et al. (2007a) and Studzinska et al. (2007) applied chromatographic methodologies for estimating the lipophilicity for a series of IL cations. Recently Chul-Woong et al. (2011) determined experimentally and by DFT calculations (LFER parameters) the lipophilicities of selected ILs. At present, the authors found no published direct measurements of K_{OW} of ILs based on other than imidazolium cations.

The reported K_{OW} values of 3-methyl-1-alkyl-imidazolium ($[C_n mim]$) based ILs show huge discrepancies but some tendencies can nevertheless be identified. Except for $[C_6mim][Tf_2N]$ and $[C_8mim][Tf_2N]$, imidazolium based ILs have K_{OW} lower than 1. For ILs with same anion, the values of K_{OW} increase as the size of the alkyl side chain on the cation increases. ILs with the $[Tf_2N]^-$ anion have K_{OW} larger than those with other anions such as $[Br]^-$, $[BF_4]^-$, $[NO_3]^-$, $[Cl]^-$ and $[PF_6]^-$. ILs based on the $[Br]^-$, $[NO_3]^-$ or $[Cl]^-$ anions have values of K_{OW} that are extremely low.

It has been reported in the literature that the introduction of ester or ester plus ether groups, which are susceptible to enzymatic hydrolysis, in the alkyl side chains of imidazolium (Gathergood et al., 2004, 2006; Garcia et al., 2005) and pyridinium (Harjani et al., 2009) based ILs also can greatly improve their biodegradability. Other properties characterizing the environmental impact of the oxygen functionalized ILs have only been determined for imidazolium-based ILs (Deng et al., 2011a) and, to our knowledge, only rarely for non-imidazolium-based ILs.

In this work, we have measured experimentally the aqueous solubility, the octanol–water partition coefficient, the relative lipophilicity and the aqueous diffusivity of different ILs. All the ILs studied are based on the bis(trifluoromethylsulfonyl)imide ($[Tf_2N]^-$) anion associated with three different families of cations: pyridinium, containing an aromatic cycle, pyrrolidinium, a cyclic quaternary ammonium and a linear quaternary ammonium. We have also checked the influence of the presence of oxygenated functional groups (hydroxyl or ester) in the cations on these properties in order to estimate their effect on the environmental impact of the ILs.

2. Materials and methods

2.1. Materials

The structures of the ILs used in this study are listed in Fig. 1. $[C_3Py][Tf_2N]$, $[C_1COOC_2Py][Tf_2N]$, $[C_3OHPy][Tf_2N]$), and $[C_1mPyr][Tf_2N]$ were purchased from Iolitec (Germany) with a purity claimed to be superior to 98%. $[N_{11120OCCH3}][Tf_2N]$ was purchased from Solvionic (France) with purity claimed to be superior to 98%. $[C_6mPy][Tf_2N]$, $[C_4mPyr][Tf_2N]$, $[N_{4111}][Tf_2N]$ and $[N_{1132OH}][Tf_2N]$ were supplied by Queen's University Belfast, UK with a purity above 99% as estimated by ^{1}H NMR. The water used was distilled. HPLC-gradient grade methanol and acetonitrile were purchased from Scharlau Chemie (Spain).

2.2. Aqueous solubility measurements

The solubility of the ILs in water was measured at 22 ± 1 °C and ambient pressure, roughly following the *OECD Guideline 105* (OECD, 1995 105). A two-phase mixture of IL and water was slowly stirred for 48 h at 25 °C, and then was left at 22 °C for 24 h. The concentration of IL in the liquid phase was measured using an UV–vis spectrometer (*UVIKON 941*). The total uncertainty of the measurements was evaluated as 4%. The temperature stability of ±1 °C (instead of the ±0.5 °C recommended by the *OECD Guideline 105* (OECD, 1995 105)) does not influence the results obtained, to within the uncertainty stated.

The aqueous solubility of the pyrrolidinium and ammonium-based ILs was determined visually. A two-phase mixture (water–IL) was prepared and then water was added until the disappearance of the IL phase after stirring for 24 h.

2.3. Octanol/water partition coefficient measurement

The K_{OW} of pyridinium-based ILs were measured following the *OECD Guideline 123* (OECD, 2006 123) at 22 ± 1 °C. The vial containing the system of water pre-saturated with 1-octanol, 1-octanol pre-saturated with water, and IL was closed tightly and stirred

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