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Review

A brief overview of the potential environmental hazards of ionic liquids

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ABSTRACT

Over past decades ionic liquids, a promising alternative to traditional organic solvents, have been dramatically expanding in popularity as a new generation of chemicals with potential uses in various areas in industry. In the literature these compounds have often been referred to as environmentally friendly; however, in recent years the perception of their *greenness* dramatically changed as the scientific community began to proactively assess the risk of their application based on the entire life-cycle. This review gives a brief overview of the current knowledge regarding the potential risks linked to the application of ionic liquids – from preparation to their disposal, with special emphasis on their potential environmental impacts and future directions in designing inherently safer ionic liquids.

Contents

1. Introduction

A growing area of research in the development of *green* technologies is devoted to designing new, more environmentally friendly solvents (Alfonsi et al., 2008; Brennecke and Maginn, 2001). From the point of *green* chemistry, solvents should be non-toxic, readily biodegradable and synthesized by an environmentally friendly synthetic procedure, while also meeting technological and economical demands (Matzke et al., 2010). Over past decades ionic liquids (ILs), organic salts consisting entirely of ions and with melting points lower than 100 °C, have been in the spotlight of the scientific and industrial community as a promising alternative to traditional organic solvents, from both the environmental and technological perspectives. Regarding the structure of ILs, cations are usually variously substituted bulky organic molecules of low symmetry containing a positively charged nitrogen, sulfur or phosphorus atom (e.g. *N*, *N*′-dialkylimidazolium, *N*-alkylpyridinium, alkylammonium, alkylphosphonium, alkylsulphonium and tiazolium

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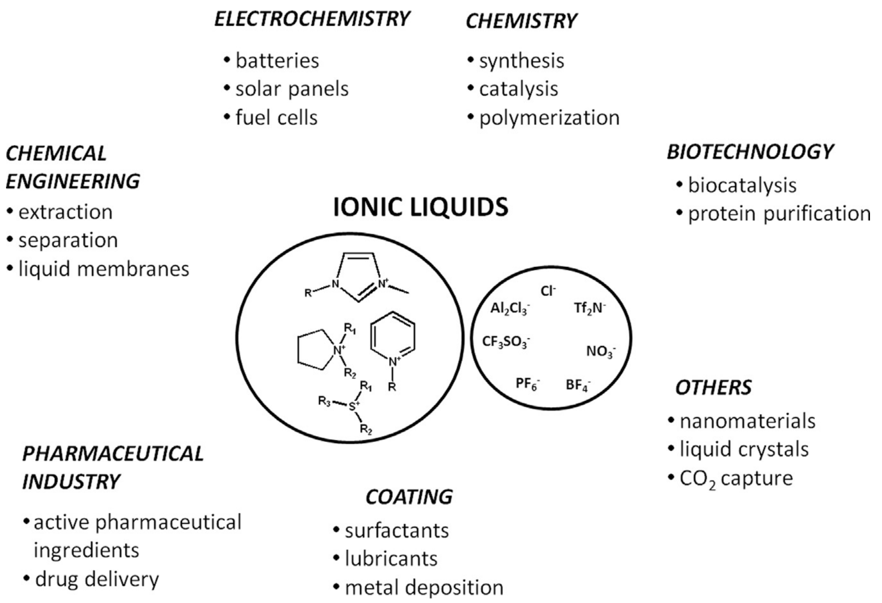

Fig. 1. Possible applications of ILs (Adapted from Pham et al., 2010).

cation), while typical anions are usually inorganic or organic species such as halides (e.g. Br^-, Cl^-), tetrafluorborate (BF_4^-), hexafluorphosphate (PF_6^-), bis(trifluoromethylsulfonyl)imide ($(CF_3SO_3)_2N^-$), acetate ($CH_3CO_2^-$) and dicyanamide ($N(CN)_2^-$) (Fig. 1) (Earle and Seddon, 2000; Petkovic et al., 2011). These solvents are referred as non-flammable compounds with negligibly low vapor–pressure (often 10^{-11}–10^{-10} mbar) and excellent thermal stability (the thermal decomposition temperature of ILs is generally in range from 250 °C to 450 °C). However, since ILs are heterogeneous group of compounds with diverse physicochemical properties, mentioned features of ILs should not be generalized since no general ILs properties exist, a part of that included into the definition of this compounds (salt with melting point below 100 °C). Additionally, some attributes used to describe ILs are even partially wrong. For example, Smiglak et al. (2006) observed that imidazolium, pyridinium and phosphonium ILs should not be necessarily considered safe when working with or near a heat or ignition source, while Meine et al. (2010) showed that 10 percent of 1-butyl-3-methylimidazolium bromide degraded upon heating at 200 °C for 24 h.

ILs are intensively studied for application in a variety of different areas, such as organic synthesis and (bio)catalysis, electrochemistry, analytical chemistry, separation technology, nanotechnology, renewable resource utilization, and in use as functional fluids (e.g. lubricants, heat transfer fluids, corrosion inhibitors) (Plechkova and Seddon, 2008: Pham et al., 2010). It is important to emphasize that the possible combinations of different cations and anions are enormous and it is estimated that roughly 10^{18} ILs are accessible. This fact ensures the possibility of tuning the chemical and physical properties (e.g. melting point, solubility, acidity, hydrophobicity, density and viscosity) in order to design an optimal IL for a specific purpose (Earle and Seddon, 2000). Additionally, the possibility of using IL mixtures to increases synthetic flexibility and tunability for specific purpose has recently mobilized researches to explore their properties (Niedermeyer et al., 2012). Namely, Taige et al. (2010) have demonstrated that imidazolium and pyridinium ILs could be combined to give binary mixtures with reduced viscosity and enhanced conductivity, while Annat et al. (2012) showed that in a number of the pyridinium and phosphonium IL mixtures the crystallization of both components was completely suppressed. Recently, a new class of ILs with an entirely new cationic substructure and a completely different charge distribution, so-called Tunable Aryl Alkyl Ionic Liquids (TAAILs), have been developed (Ahrens et al., 2009; Stolte et al., 2013). These ILs distinguished from classical imidazolium ILs by the substitution pattern of the imidazolium core, whereby electronic interaction between the aromatic substituent and the core allows fine and more precisely tuning of properties than is possible for currently available ILs (Stolte et al., 2013).

Even though ILs are not currently widely used for commercial purposes, some companies have started their industrial use. In 1998, the French Petroleum Institute approved the commercial use of ILs in the preparation of polybutene (Difasol process), important in the production of plastics, rubber or similar materials (Olivier, 1999). However, the first large-scale industrial application of ILs was in 2003 through BASF's BASIL process (Biphasic Acid Scavenging Utilizing Ionic Liquids), in which *N*-alkylimidazole was used to remove acid from a particular process in situ, forming ILs that could be easily removed from the reaction mixture (Masse and Massonne, 2005). In 2004, this process was awarded the prestigious Innovation Award and is now conducted in multi-tone scale (Plechkova and Seddon, 2008).

To date, introducing ILs into various processes has resulted in process improvements in terms of yield and productivity, and also in improvements from the economical perspective if ILs reuse and recycle is included. To our knowledge, there are no data confirming the presence of ILs in natural environment, although rising interest for these compounds and great number of possible applications would result in their uncontrolled transfer in the environment someday in the near future. Thus, in the case of larger production (over one metric tonne per year) safety information on the ILs should be provided, as current legislations such as European Union Regulation REACH demand (REACH, 2006). So far the properties of ILs which gained them attribute of being “environmentally friendly” are non-volatility (reduced air pollution), non-flammability (process safety) and excellent stability (recycling and reusing potential). Regardless ILs' declarative *green* properties, in recent years the perception of their *greenness* dramatically changed as the scientific community began to carefully assess the risk of their application based on the entire lifecycle, including preparation methods, methods of their degradation after use and their impacts on the ecosystem (Fig. 2) (Coleman and Gathergood, 2010; Siedlecka et al., 2011; Pham et al., 2010).