

Comparative ecotoxicology study of two neoteric solvents: Imidazolium ionic liquid vs. glycerol derivative

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ARTICLE INFO

Article history:

Received 9 December 2015

Received in revised form

24 March 2016

Accepted 25 May 2016

Available online 2 June 2016

Keywords:

Solvents

Ecotoxicology

Ionic liquid

Glycerol-derivative

ABSTRACT

In this study we have compared the acute ecotoxicity of two solvents, with very different structure and origin, but sharing many physical-chemical properties, so they can be used for similar purposes; a well-known ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) and a solvent partially derived from biomass, 3-bis(2,2,2-trifluoroethoxy)propan-2-ol (BTFIP). We have used three biomodels (*Vibrio fischeri*, *Daphnia magna* and *Danio rerio*) and performed the comparison applying the Environmental, Health and Safety (EHS) hazard assessment. According to the results, ecotoxicity of [BMIM][PF₆] and BTFIP is quite similar in the simplest model *Vibrio fischeri*, while in *Daphnia magna* [BMIM][PF₆] is clearly more toxic. However, in *Danio rerio*, toxicity of these chemicals is again quite similar and both can be classified as “nontoxic”. The higher index value of [BMIM][PF₆] in water mediate effect in the EHS assessment indicates that this ionic liquid is more dangerous than BTFIP, although accumulation and degradation properties have not been taken into account. Further studies will be necessary to ascertain these conclusions.

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1. Introduction

The search for new solvents, coming from new sources and/or able to provide special features (often known as neoteric solvents), is a field of growing interest, especially in connection with the possibility of using renewable raw materials to produce harmless solvents, more respectful with the environment than those derived from petroleum (the so-called green solvents). For many years, ionic liquids (IL) have been considered as the “solvents of the future” (Earle and Seddon, 2000), due to their very particular combination of physical-chemical features: high polarity, almost null volatility, immiscibility with low-polar organic solvents, and, in some cases, with water as well. As a consequence, there is a huge amount of studies describing the use of IL for numerous different applications, and many IL are nowadays available from commercial sources. 1-Butyl-3-methylimidazolium hexafluorophosphate (henceforth [BMIM][PF₆]) is one of the most prominent examples of successful IL. However, as more knowledge has been gained on the toxicological profiles of this family of compounds, it has become clearer that the label of “green solvents” is not deserved in many cases (Bubalo et al., 2014; Deetlefs and Seddon, 2010; Petkovic et al.,

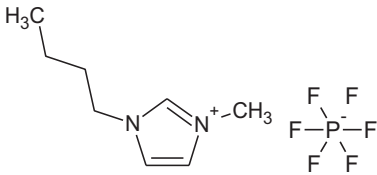
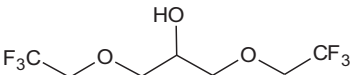
2011; Romero et al., 2008). For instance, in the case of [BMIM][PF₆] it has been reported that the hexafluorophosphate anion can decompose in aqueous acidic medium to lead to 1-butyl-3-methylimidazolium fluoride hydrate, and hence to the toxic product HF (Holbrey et al., 2003; Swatoski et al., 2003).

On the other hand, biomass-derived chemicals are attracting a great interest in the last years, in connection with the development of the biorefinery concept. Agricultural and some industrial activities are able to generate huge amounts of raw materials, capable of being used to produce commodity and fine chemicals. In this sense, glycerol is one of the platform molecules that has received much attention in the last years (Katryniok et al., 2011; Pagliaro et al., 2007; Zhou et al., 2008). Glycerol appears as a concomitant product in the production of biodiesel, amounting ca. 10% weight of the total output. At present, the world production of glycerol coming from vegetable oil transformations surpasses 2 million metric tons, so it constitutes a valuable starting point to obtain bio-based chemicals, useful as, for instance, solvents (Díaz-Álvarez et al., 2011; Díaz-Álvarez and Cadierno, 2013; García et al., 2014; Gu and Jerome, 2010). In this context, our research group has described the synthesis and application as solvents of a family of glycerol ethers (García et al., 2010). Some of these glycerol derivatives, namely those bearing fluoroalkyl chains, exhibited especial physical-chemical features, in some way similar to those displayed by some IL: high polarity, low vapour pressure at room

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Table 1.
Studied solvents and some of their relevant physical-chemical properties.

Property	Solvent	
Name	1-butyl-3-methylimidazolium hexafluorophosphate	1,3-bis(2,2,2-trifluoro-ethoxy)propan-2-ol
Code	[BMIM][PF ₆]	BTFIP
Structure		
Molecular mass (g mol ⁻¹)	284.18	256.14
Density (g cm ⁻³)	1.365 ^a	1.384 ^b
Refraction index	1.411 ^a	1.352 ^b
m.p. (°C)	-8 °C ^a	-6 °C
b.p. (°C)	> 350 °C	197 °C ^b
Vap. P at r.t. (mm Hg)	~0	0.4 ^b
Viscosity at r.t. (cP)	312 ^a	8.14 ^b
Water solubility (wt./wt.)	0.0230 ^c	0.0284 ^b
Solvatochromic polarity parameters:		
E _T ^N	0.64–0.69 ^d	0.70 ^b
π*	0.89–1.04 ^d	0.38 ^b
α	0.63–0.68 ^d	0.82 ^b

^a Carda-Broch et al. (2003).

^b García et al. (2010).

^c Chapeaux et al. (2007).

^d Jessop et al. (2012).

temperature, an immiscibility both with hydrocarbons and with water. The most prominent example of these compounds is 1,3-bis(2,2,2-trifluoroethoxy)propan-2-ol, henceforth BTFIP, which can be efficiently prepared from trifluoroethanol and epichlorohydrin (a commodity produced from glycerol using the Solvay procedure). Table 1 gathers the comparison of some physical-chemical properties of [BMIM][PF₆] and BTFIP.

Both [BMIM][PF₆] and BTFIP have been used as solvents for biphasic enantioselective catalysis in two comparative studies carried out by our group. In the first one, the use of BTFIP in an enantioselective conjugate reduction catalysed by chiral azabis(oxazoline)-cobalt complexes showed to superior to that of [BMIM][PF₆], allowing better recovery of the catalytic phase and better enantioselectivities (90–96% ee vs. 40–85% ee with the IL (Aldea et al., 2010). The same situation arose in the second study, where the biphasic enantioselective Kharasch-Sosnovsky allylic oxidation, based on neoteric solvents and copper complexes of ditopic ligands, was studied (Aldea et al., 2012).

The question arises as to whether BTFIP can be considered an environmentally benign solvent or not, given the total lack of experimental evidences on its toxicity and ecotoxicity. We hypothesize that the ecotoxicity of this solvent, partially originating from biomass, is lower than the abovementioned ionic liquid. With the aim of verifying our hypothesis, the ecotoxicity of BTFIP and [BMIM][PF₆] has been obtained through the evaluation of the toxic effect in three bioindicators (bacteria, crustacean and fish) corresponding to several trophic levels.

In order to perform a comparative study, the studied solvents have been evaluated making use of Environmental, Health and Safety (EHS) hazard assessment. This method was firstly proposed by Koller et al. (2000) as an intermediate attempted to account for the problems of early design phases. Environmental, Health and Safety (EHS) aspects are assessed in several categories corresponding to environmental, health or safety related properties.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) was provided by Sigma-Aldrich (purity ≥ 97%). In order to minimizing the water content, [BMIM][PF₆] was periodically dried for 24 h under a vacuum of ca. 0.05 kPa with stirring and stored before use in a desiccator.

1,3-Bis(2,2,2-trifluoroethoxy)propan-2-ol (BTFIP) was synthesised by the following procedure:

In a round bottom flask were placed 1 mol of trifluoroethanol (100 g, aprox. 75 mL) and then 1 mol (140 g) of potassium carbonate. The flask was heated up at 70 °C, and 0.5 mol of epichlorohydrin (47 g) were then dropped into the flask. After 2 h the reaction was complete. Cooling down the flask, the mixture was filtered to remove the carbonate salt. The unreacted fluorinated alcohol was removed by heating under vacuum in a rotary evaporator. The remaining product was purified by vacuum distillation to yield 108 g of BTFIP (84%, GC purity > 99.5%).

Trend analysis and quantitative structure–activity relationship (QSAR) models were evaluated previously using the QSAR Toolbox, 2.3 (2009) which helped to select the concentrations to be tested. QSAR is based on the correlation between structural molecular characteristics of series of molecules and their chemical reactivity or biological activity. Additionally, a previous study was carried out to refine the range of concentrations and make sure the tested concentrations within EC₅₀/LC₅₀.

2.2. Ecotoxicological tests

2.2.1. *Vibrio fischeri* (*V. fischeri*) Inhibition of bioluminescence test

The lyophilized *V. fischeri* (strain NRRL-B-11177) used for Inhibition of bioluminescence test were purchased from Macherey-Nagel (ref. 945 006). This experiment was carried out according

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