Ecotoxicity and biodegradability of short aliphatic protic ionic liquids – are they really green solvents?

Brezana Peric, Jordi Sierra, Esther Martí, Robert Cruañas and M. Antonia Garau
Laboratori d’Edafologia, Facultat de Farmàcia, Universitat de Barcelona, Spain – brezana@hotmail.com

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Ionic liquids (ILs) are an exciting and fast growing family of compounds. They are considered to be environment friendly substitutes for the volatile organic solvents in industrial applications. ILs are liquids composed entirely of ions; they are salts with a melting point lower than 100°C. Their vapor pressure is practically zero, so there is no air pollution risk related to their use. But water solubility of many ILs is not negligible, and their release into aquatic and terrestrial environments may lead to water and soil pollution and related risks. In the recent years, a tremendous progress has been made, in both industry and academia, regarding their synthesis, properties and ecotoxicological profile. There are two main groups of ionic liquids: aprotic (AILs) and protic (PILs) ionic liquids. Up till now, the dominant group of ILs has been the group of aprotic ionic liquids. AILs are designed with bulky organic cations, such as imidazolium, pyridinium, pyrrolidinium, quaternary ammonium, etc., with alkyl chain substituents and different inorganic anions such as Cl\textsuperscript{−}, Br\textsuperscript{−}, BF\textsubscript{4}\textsuperscript{−}, BF\textsubscript{6}\textsuperscript{−}, N(CN)\textsubscript{2}\textsuperscript{−}, etc. It has been proven that many commonly used ionic liquids have a certain level of toxicity. A new group of PILs with short aliphatic anions and cations has been designed and should have a potentially smaller environmental impact. The new group molecule includes polysubstituted amines and organic anions. Considering the interest in these substances as more environmentally sustainable solvents, is is important to examine their potential toxicity, especially taking into account the need of this information to fulfil the REACH (Registration, Evaluation, Authorisation and Restriction of Chemical Substances) criteria.

Series of tests have been done in order to determine terrestrial and aquatic toxicities of PILs. In terms of terrestrial toxicity analysis performed includes plants’ germination and growth test, and carbon and nitrogen mineralization tests (all done according to OECD and ISO guidelines). In order to assess the toxic effects on the aquatic organisms the following tests were performed: algal growth inhibition test and inhibition of the luminescence of Vibrio fischeri (according to OECD and ISO guidelines). As far as biodegradability in water and soil is concerned the tests performed also followed OECD guidelines. EC\textsubscript{50} values for ecotoxicity tests are between 826-18663 mg/kg for the terrestrial toxicity tests, and between 104-2453 mg/kg for the tests of aquatic toxicity. According to the Globally Harmonized System of classification and labeling of chemicals\textsuperscript{14} there is no toxic effect of these PILs on soil microflora and higher plants, except in a case of one ionic liquid (TEA-PEN) with one of the three analyzed plants (Raphanus sativus) where the obtained EC\textsubscript{50} was 826 mg kg\textsuperscript{−1} (which is below the limit value of 1000 mg kg\textsuperscript{−1} set by the regulation). According to the EU regulation they have no toxic effects on aquatic organisms either (all of the EC\textsubscript{50} are above the limit value of 100 mg L\textsuperscript{−1}).

Figure 1 shows Raphanus sativus plants before and after uprooting in the plants’ germination and growth test.

![Figure 1](image_url)
Figure 2 shows the inhibition in specific growth rate of algae produced by different concentration (1, 10, 100, 1000 and 5000 mg L\(^{-1}\)) of three PILs compared to the control during the algal growth inhibition test. There is inhibition only at very high concentrations.

![Figure 2 - Percentage of algal specific growth rate](image)

The compounds show substantial degree of biodegradability (between 54 and 85%). Figure 3 shows the percentage of biodegradation in water for three representatives of the new family of PILs. The % of biodegradation is calculated according to the formula proposed in OECD guideline, dividing biochemical oxygen demand after 28 days of incubation with theoretical oxygen demand for the analyzed molecule. Both biodegradation in soil and water were also determined by HPLC quantification after 5 and 28 days.

![Figure 3 - Biodegradation in water presented in % of biodegradation after 28 days of incubation](image)

The obtained results from ecotoxicity tests are coincident and suggest that the analyzed PILs are not only non toxic in the terms of acute and chronic toxicity, but could also be biodegradable in water and soil matrix. So these compounds could be safer alternatives to other more toxic substances, and further analyses will be done on other test organisms and trophic levels in order to confirm this hypothesis completely.

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**References**