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ScienceDirect

Procedia Chemistry 9 (2014) 40 – 52

Procedia Chemistry

International Conference and Workshop on Chemical Engineering UNPAR 2013, ICCE UNPAR 2013

Toxicity Measurement of Imidazolium Ionic Liquids using Acute Toxicity Test

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Abstract

Ionic liquids (ILs) can be considered as environmentally friendly solvent, but they have the ability to dissolve in water and accumulate in the environment. Therefore, the toxicity of ILs should be assessed in order to prevent their harm to human and environment. This study was carried out to investigate the toxicity of ILs towards marine and freshwater fish. Three ILs have been tested, which are *1-Butyl-3-methylimidazolium hydrogen sulfate* and *1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide* toward marine fish and *1-Hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide* toward freshwater fish. Two different marine fish were employed, which are: *Cephalopholis cruentata* (grouper) and *Lates calcarifer* (barramundi). For freshwater fish, male *Poecilia reticulate* (guppy) was employed. The toxicity tests were conducted according to OECD (Organisation for Economic Cooperation and Development) guideline 203. For *1-Butyl-3-methylimidazolium hydrogen sulphate* [BMIM][HSO4], the median lethal concentration (LC_{50}) estimated toward *Cephalopholis cruentata*to be 199.98 $mg.L^{-1}$. For *1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide* [BMIM][TFSI], LC_{50} estimated toward *LatesCalcarifer*to be 374.11 $mg.L^{-1}$. While, for *1-Hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide*, [HMIM][NTf2], LC_{50} estimated toward *Poecilia Reticulate* to be 207.49 $mg.L^{-1}$. All the LC_{50} values obtained can be identified as practically nontoxic liquids based on Acute Toxicity Rating Scale by Fish and Wildlife Service (FWS). As to our knowledge, there is no previous reported toxicity studies of [BMIM][HSO4] and [BMIM][TFSI] on marine fish and [HMIM] [NTf2] on freshwater fish. Thus, this paper can be used as a benchmark for researchers who are dealing with these three ILs.

Peer-review under responsibility of the Organizing Committee of ICCE UNPAR 2013

Keywords: Ionic Liquds; Acute toxicity test, LC_{50}

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Peer-review under responsibility of the Organizing Committee of ICCE UNPAR 2013
doi:10.1016/j.proche.2014.05.006

Nomenclature

Y	Probit value
x	Log Concentration (mg/L)

1. Introduction

The world of Ionic Liquids (ILs) started in 1914 by Walden [1] who synthesized ethylammonium nitrate $[EtNH_3][NO_3]$. ILs are composed of ions only and they are fluid below 100^oC due to asymmetry of one of the ions. ILs thermally stable with liquid range up to 300^oC compared to 100^oC for water and show very low vapour pressure, being of great interest due to these properties. ILs'typically consist of bulky organic cations, such as imidazolium, pyridinium, ammonium, phosphonium, etc. paired with various anions, such as hexaflurophosphate (PF_4^-), bromide (Br^-), etc. Due to ILs unique properties, they are used as media for catalysts, material synthesis, liquid crystals and extraction in electrochemistry and separation processes [2-6].

There are several imidazolium, ammonium, pyridinium, and phosphonium based ILs which have been synthesized in the past and are commercially available. Although intensive information and data regarding ILs' physical and thermodynamic properties have been reported and continuously published, only limited data with regard to the toxicity and ecotoxicity of ILs' were reported [7-10]. Even though ILs are known to be environmental friendly as they do not contribute to the air pollution, somehow ILs are soluble in water [11], which make them to have the ability to dissolve in the water and accumulate in the environment.

In general, the toxicity of chemicals can be measured using: (a) mammalian acute toxicity test (b) bacteria acute toxicity test (c) fish acute toxicity test and (d) biological dissociation test [12]. Aquatic toxicity acts as an indicator to show the level of toxicity of chemical that exists in the water. OECDGuideline 203 [13] has recommended some test species, which are zebrafish (*Danio rerio*), fathead minnow (*Pimephales promelas*), common carp (*Cyprinus carpio),* ricefish (medaka) *(Oryzias latipes),* guppy (*Poecilia reticulata*), bluegill (*Lepomis macrochirus*), and rainbow trout (*Oncorhynchus mykiss*).

Acute toxicity test of several ILs have also been conducted using several types of aquatic organism and fish such as ILs toxicity on the freshwater crustacean *Daphnia magna*[14-16], zebrafish *Danio rerio*[17], and guppy fish *Poecilia reticulata*[18-19].

In this study, the acute fish toxicity study was conducted according to the prescribed guideline OECD 203 using marine fish [*Cephalopholis cruentata* (grouper) and *Latescalcarifer* (barramundi)] and freshwater fish [male *Poecilia reticulate* (guppy)] to estimate the toxicity of threeImidazoliumILs. To our knowledge there is no published literature regarding the toxicity (LC_{50}) of these ILs.

2. Materials and Methods

2.1 Materials

The ILs used in this study were obtained from the Ionic Liquid Research Centre located at Universiti Teknologi Petronas, Perak Malaysia. The ILs which were tested on marine fish are *1-Butyl-3-Methylimidazolium hydrogen sulphate* [BMIM][HSO4] and *1-Butyl-3-Methylimidazolium bis (trifluoromethylsulfonyl) imide* [BMIM][TFSI]. The IL tested on freshwater fish, *Hexyl Methylimidazoliumbis (trifluoromethylsulfonyl) imide* [HMIM][NTf2] and it's also obtained from the same research centre. The three ILs were prepared and synthesized using the Metathesis Process.

2.2 Test organism

The two species of marine fish employed in this study are *Cephalopholis cruentata* (grouper) and *Lates calcarifer* (barramundi/siakap). The fish were obtained from the area close to Kumpung Setiawan in Lumut, Perak, Malaysia. The length of the fish is about 1 cm (the weight ranged from 0.1 to 0.2 g) (Fig. 1).