Journal of Molecular Liquids 212 (2015) 352–359

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

# Thermophysical properties and acute toxicity towards green algae and *Vibrio fischeri* of amino acid-based ionic liquids

Ouahid Ben Ghanem [a,*], Nicolas Papaiconomou [b,c,d], M.I. Abdul Mutalib [a], Sylvie Viboud [e], Mohanad El-Harbawi [f], Yoshimitsu Uemura [a], Girma Gonfa [a], M. Azmi Bustam [a], Jean-Marc Lévêque [g,*]

[a] Faculty of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak Malaysia
[b] Univ. Savoie, LEPMI, 73000, Chambéry, France
[c] Univ. Grenoble-Alpes, LEPMI, 38000, Grenoble, France
[d] CNRS, LEPMI, 38000, Grenoble, France
[e] Laboratoire CARRTEL, UMR INRA 42, CISM, Université de Savoie, 73376 Le Bourget-du-Lac Cedex, France
[f] Chemical Engineering Department, King Saud University, Riyadh 11421, Saudi Arabia
[g] Fundamental and Applied Sciences Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Tronoh, Perak 31750, Malaysia

ARTICLE INFO

*Article history:*
Received 6 July 2015
Received in revised form 1 September 2015
Accepted 9 September 2015
Available online xxxx

*Keywords:*
Amino acids
Ionic liquids
Thermo-physical properties
Toxicity
*Scenedesmus quadricauda* (green algae)
*Vibrio fischeri*

ABSTRACT

Four new ionic liquids (ILs) based on 1-(2-hydroxyethyl-3-methylimidazolium) cation with glycinate, serinate, alaninate, and prolinate amino acid anions have been synthesized, and their thermo-physical properties (density, viscosity, surface tension, and heat capacity) were measured. Data were described using empirical expressions to determine other physical–chemical properties, such as molecular volume, standard molar entropy, and lattice energy. Moreover, acute toxicity tests toward *Scenedesmus quadricauda* (green algae) and *Vibrio fischeri* have been conducted. The high values obtained for the 50% effective concentration ($EC_{50}$) indicated that these new ionic liquids can be considered eco-friendly.



## 1. Introduction

Ionic liquids (ILs) are organic salts with melting points typically below 100 °C. ILs are composed solely of bulky asymmetric organic cations and organic or inorganic anions. For more than a decade, ILs have been the subject of increasing interest in the scientific community because of their remarkable physical and chemical properties, notably, negligible vapor pressure, high thermal and chemical stability, wide liquid range, and electrochemical windows [1,2]. Moreover, the high number of possible combinations between cations and anions allows the properties of ILs to be developed for a specific task. Hence, ILs can be strategically designed for different applications that range from solvents in organic chemistry to lubricating agents or electrochemical media [2,3]. However, recent investigations indicate that most ILs are toxic to aquatic organisms and human cells [4–6]. Nowadays, the toxicity of ILs remains one of the main obstacles that limit potential commercial applications. Hence, the aim of this work is the design and synthesis of the least toxic ILs to be used in high-scale processes without damaging the environment. Several groups have prepared different types of ILs that bear natural compounds or an oxygenated functional group to decrease the overall toxicity of these moieties compared with classical ILs that only bear saturated alkyl chains.

Ionic liquids embedding hydroxyl groups onto the alkyl chain of the cation, such as [$C_2$OHmim] (1-(2-hydroxylethyl)-3-methylimidazolium), were first synthesized and characterized by Branco et al. [7] in 2002. These ionic liquids, which contain different anions such as chloride [Cl], trifluoroacetic acid [TFA], hexafluorophosphate [$PF_6$], and tetrafluoroborate [$BF_4$], exhibit higher polarity/solvation properties [8] than analogues without the hydroxyl group. Furthermore, introducing oxygen in the form of hydroxyl, ether, or ester functional groups on imidazolium side chains decreased toxicity [4,9].

Fukumoto et al. [10] studied amino acid based ionic liquids (AAILs) by combining 1-ethyl-3-methylimidazolium with amino acid anions. Tao et al. [11] reported also AAILs based on nitrate anion and cations functionalized with an amino acid functional group. Since then, many more AAILs have been studied, including some AAILs embedded with two amino acid functional groups appended in both the cation and anion moieties [12].

* Corresponding authors.
*E-mail addresses:* wahidghanem@gmail.com (O.B. Ghanem), jm.leveque@petronas.com.my (J.-M. Lévêque).

http://dx.doi.org/10.1016/j.molliq.2015.09.017

Amino acids can be considered a promising component for the synthesis of new ionic liquids that exhibit low toxicities because of their biological nature, low cost [12,13], and ability to incorporate two functional groups, namely, amino and carboxylic acid groups. Amino acids are also known to exhibit strong hydrogen-bonding ability, which makes them potential media for various applications, such as biomass dissolution reaction medium and gas separation [12–15].

Therefore, this work reported on the synthesis and characterization of four new AAILs that incorporate four different AA anions with 1-(2-hydroxylethyl-3-methylimidazolium) cation, offering a new set of RTILs, namely, 1-(2-hydroxyethyl)-3-methylimidazolium glycinate ([$C_2$OHmim][Gly]), 1-(2-hydroxyethyl)-3-methylimidazolium alaninate ([$C_2$OHmim][Ala]), 1-(2-hydroxyethyl)-3-methylimidazolium Serinate ([$C_2$OHmim][Ser]), and 1-(2-hydroxyethyl)-3-methylimida zolium prolinate ([$C_2$OHmim][Pro]). The structures of the studied AAILs are depicted in Fig. 1. Physicochemical properties such as density, viscosity, surface tension, and heat capacity in various temperatures and atmospheric pressures are reported. Thermal decomposition temperature was also investigated. Molecular volume, standard molar entropy, and lattice energy were calculated using empirical correlations. In addition, the toxicity of AAILs toward *Senedesmus quadricauda* (*S. quadricauda*) (green algae) and *Vibrio fischeri* (*V. fischeri*) was studied to determine if these are environment friendly. Green algae and *V. fischeri* were chosen because these are two of the most common test organisms in the Aquatic Toxicity Information Retrieval database (AQUIRE) published by the US Environmental Protection Agency (EPA). In addition, several organizations have recommended these species for aquatic toxicity assessment [16,17].

## 2. Experimental section

### 2.1. Materials

All the starting materials were used as received without any further treatment. These materials include 1-methylimidazole (Merck, ≥99%), 2-bromoethanol (Merck, >99.8%), L-glycine (Merck, ≥99%), L-alanine (Merck, ≥99%), L-serine (Merck, ≥99.2%), L-proline (Merck, ≥99%), ethyl acetate (Fisher Scientific UK, ≥99.99%), ethanol (Merck, ≥99.9%), and ion exchange resin, Amberlite IRA-402 (OH) (Alfa Aesar).

### 2.2. Synthesis of AAILs

The AAILs were prepared according to established methods [10,11]. The process is described briefly as follows: 2-bromoethanol was carefully added dropwise to 1-methylimidazole in a three-necked, round-bottom flask equipped with a reflux condenser. The system was mixed under nitrogen for 24 h at room temperature. The resulting viscous liquid (1-(2-hydroxyethyl)-3-methylimidazolium bromide) solidified after being washed with ethyl acetate and then was dried under vacuum. The 1-(2-hydroxyethyl)-3-methylimidazolium bromide was dissolved in distilled water and passed through an anion-exchange column filled with excess of Amberlite IRA-402 to minimize bromide content. An excess amount of amino acid salt was added to the solution of 1-(2-hydroxyethyl)-3-methylimidazolium hydroxide that was collected from the resin. The solution was gently mixed for 12 h, and water was removed under low vacuum. The resulting AAILs were dissolved in dry ethanol to separate the unreacted amino acids, and the solutions were filtered. Finally, ethanol was evaporated, and the AAILs were dried in a vacuum line for 72 h.

### 2.3. Water and halide content

Before measuring physical–chemical and thermal properties, all AAILs were further dried under low pressure by being kept in a vacuum oven for few hours at 80 °C. The water content of all AAILs was determined using a coulometer Karl Fischer titrator, DL 39 (Mettler Toledo) with the Hydranal Coulomat AG reagent (Riedel-de Haen). For each AAIL, water content was determined by calculating the average of three measurements.

The bromide content in the final products were determined using Metrohm model 761 Compact IC. For the measurement, ionic liquid solutions were prepared by dissolving the AAILs in ultrapure water, where the eluent was prepared using mixtures of $Na_2CO_3$ and $NaHCO_3$.

### 2.4. Density and viscosity

Density and viscosity were measured over a temperature of 293.15 K to 373.15 K at atmospheric pressure using an Anton Paar densitometer (SVM3000). The instrument was calibrated with Millipore-grade water to establish the data.

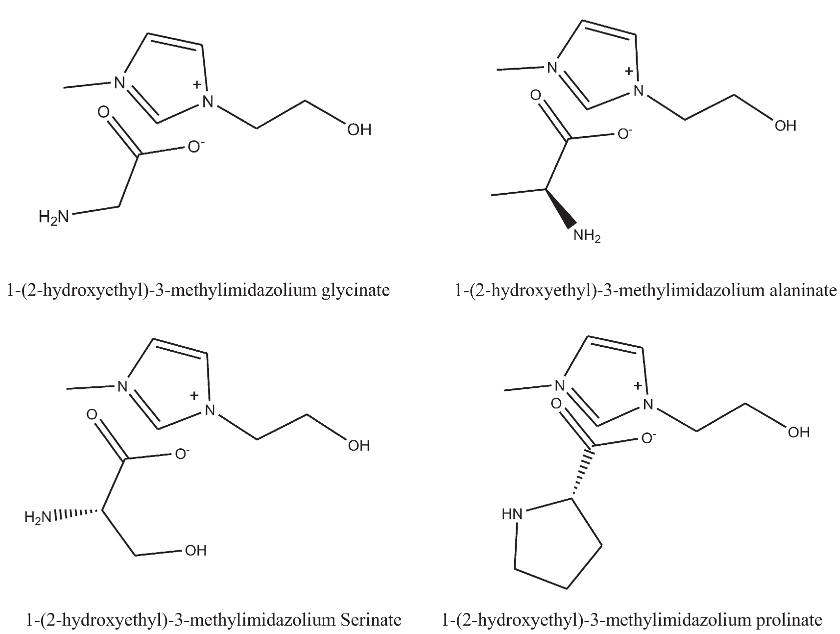


**Fig. 1.** Structure of the studied AAILs.