NOVEL IONIC LIQUIDS BASED ON L-CYSTEINE DERIVATIVES

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Keywords: L-cysteine, Ionic liquids, Chiral scaffolds, Asymmetric catalysis.

Introduction: The understanding of the chemistry of biomolecules corresponds to a crucial role in new research fields. Taking advantage of relevance and natural chirality of biomolecules, there is the possibility to use them for the preparation of chiral, bioinspired Ionic Liquids (ILs). ILs have very different properties from molecular liquids, making them promising substances for use in a variety of fields [1,2]. Variation of cation/anion species is a great advantage in organic salts, due to the change of properties of the IL. In this context, Novel Functional Bioinspired ILs (FBILs) based on biomolecules such as aminoacids (L-cysteine derivatives) have been synthesized. The development of efficient FBILs is essential to extend the range of their applications [3]. The search for new biocatalysts that display high activity and increase selectivity is a major focus of current research in the field of asymmetric synthesis [3]. Some of the novel cysteine ILs have been tested as a chiral media in asymmetric catalysis in particular for asymmetric aldol and Michael reactions.

Experimental: The main goal of this work was to create functionalized ILs based on natural compounds such as L-cysteine. Two different approaches were used to develop novel ILs based on cysteine derivatives. Protonation of amino group ($-NH_2$) in order to develop a cysteine derivative cation and deprotonation of the carboxylic acid (-COOH) in order to develop a cysteine derivative anion (Scheme 1). Then, each novel cysteine cation or anion was combined with an appropriate counter-ion such as NTf_2 and docusate (AOT) anions in the case of 1 and ammonium ([choline]), phosphonium ($[P_{6,6,6,14}]$) and imidazolium ([EMIM]) cations in the case of 2. All novel chiral ILs were completely characterized by ^{1}H and ^{13}C NMR and elemental analysis in order to check their structure, purity and chemical stability.

Results and discussion:

Two different approaches were tested in order to develop novel RTILs based on cysteine derivatives:

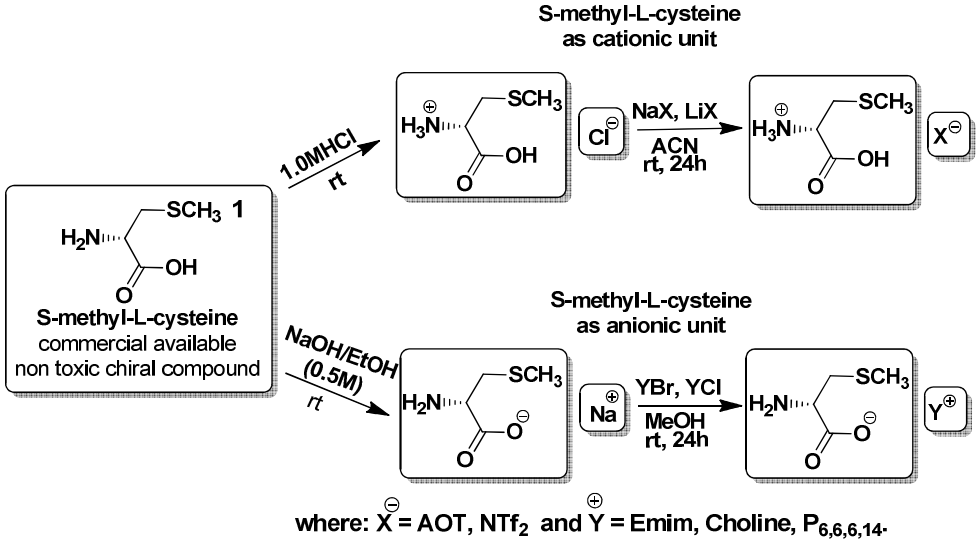
(i) Protonation of amino group (-NH2) in order to develop a cysteine derivative cation;
(ii) Deprotonation of the carboxylic acid (-COOH) in order to develop a cysteine derivative anion.

Each cationic or anionic Csyteine units were combined with appropriated counter ions.

Using these synthetic approaches, all of the ILs were obtained in moderate to high yields (70-100%), except in the case of [CYS-2] choline (11.4%). The highest yields were given for the Ils incorporated docusate anion: [CYS-1] [AOT] (96.9%), [CYS-3] [AOT] (90.1%).

Additionally, some physical (solubility in water and other conventional organic solvents), thermal (glass transition temperatures or melting points) and electrochemical (oxidation and reduction potentials) properties were also studied.

All cysteine ILs were obtained as RTILs. According the selection of the counter-ion, cysteine ILs presented differents values of Tg, water solubility and optical rotation values $[\alpha]_D$.



Scheme 1. General strategies for the synthesis of CILs starting from S-methyl-L-cysteine.

Conclusions: Chiral Ionic Liquids (CILs) [4] have been recognized as having potential application for chiral discrimination, including in asymmetric synthesis and resolution of racemates. The main goal of this work was to create functionalized ILs based on natural, chiral compounds as aminoacids. L-cysteine was selected as a very useful, small scaffold for the preparation of chiral ammonium, phosphonium and imidazolium cations or chiral anions depending the synthetic manipulation of cysteine derivatives. Using this strategy has been possible to develop several room temperature ILs based on L-cysteine units.

References:

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