

Chemistry Department

Novel ionic liquids based on biomolecules

Photochemistry Group



Karolina Zalewska

(Student/Advisor/PI)

January 2010- started PhD at Universidade Nova de Lisboa, Monte de Caparica, Portugal.

July 2009-October 2004
M. Sc. Silesian University of Technology, Gliwice, Poland.

Objectives

Table 1. Results of the dissolution studies of β -CD in ILs

A new field in research is evaluating the possibility to use natural chiral biomolecules for the preparation of Ionic Liquids (ILs). Variation of cation/anion species is a great advantage in organic salts, due to the change of properties of the IL. Chiral Ionic Liquids (CILs) have been recognized as having potential applications for chiral discrimination processes, including in asymmetric synthesis and resolution of racemates. The main goal of this work is related with the synthesis of functionalized ILs based on natural compounds as cyclodextrins (CDs) and L-cysteine derivatives. Efficient and selective synthetic modifications of CDs is indispensable to expand the range of their applications. On the other side, aminoacids (AAs), such as L-cysteine were also selected as attractive biomolecules to obtain FBILs.

ILs	Mass of β -CD per mass of IL [mg CD/mg IL]	[%] of β -CD dissolved in ILs
[P _{6,6,6,14}][DCA]	0.335	100
[Aliquat][DCA]	0.208	62.2
[emim][EtSO ₄]	0.485	99.3
[bmim][DCA]	0.576	76.8
[omim][Cl]	0.489	100
[omim][DCA]	0.222	92.4
[C ₁₀ mim][SAC]	0.448	97
[C ₁₀ mim][DCA]	0.221	89.2
[C ₂ OHmim][BF ₄]	0.240	95.5
[C ₅ O ₂ mim][Cl]	0.736	100

Methodology

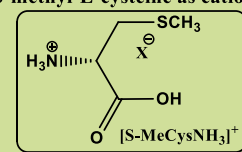
For the preparation of novel chiral biomaterials based on CDs were tested different ILs based on imidazolium, ammonium, pyridinium and phosphonium cations combined with halogenate (Cl, Br) dicyanamide, acetate, tetrafluoroborate, saccharine and ethylsulfate. The mixtures of β -CD (50-150 mg) and ILs (200-300 mg) were stirred for 24 hours at room temperature. The percentage of β -CD dissolved in ILs was confirmed by ¹H NMR spectra of the mixture by comparing the well known peaks of β -CD with the ILs peaks. Simultaneously L-cysteine derivatives based ILs, lauded as a useful chiral scaffold, were developed by the combination with organic cations or anions (Figure 1). Two different approaches were used: i) Protonation of amino group (-NH₂) in order to develop a cysteine derivative cation and ii) deprotonation of the carboxylic acid (-COOH) in order to develop a cysteine derivative anion.

Expected Results

According the biocompatibility and performance of these dissolution studies was possible to develop some good candidates for relevant chiral discrimination or separation processes. It was also proved that recovering of β -CD as well as the ILs is possible. The recycled β -CD and ILs were completely recovered without any decomposition (checked by ¹H NMR and ¹³C NMR spectra).

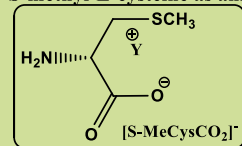
All CILs based on L-cysteine were obtained as viscous RTILs in moderate to high yields. Their thermal properties (Glass transition temperature, T_g), optical rotation values and water solubility is significantly changed according the type of counter-ion selected. Enantiomeric resolution experiments showed the potential of these novel CILs based on L-cysteine derivative unit as chiral inductor media. ¹⁹F NMR spectra proved the advantage of using [Choline][S-MeCysCO₂] (10 mol%) as chiral selector to separate the initial racemic Mosher's sodium salt. Some CILs based on S-protected-L-cysteine have been tested as recyclable chiral reaction media for asymmetric catalysis in particular for asymmetric aldol reactions.

S-methyl-L-cysteine as cation



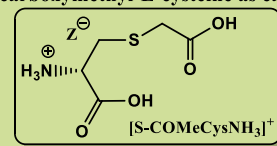
X⁻ = [NTf₂]⁻, [AOT]⁻.

S-methyl-L-cysteine as anion



Y⁺ = [P_{6,6,6,14}]⁺, [EMIM]⁺, Choline⁺.

S-carboxymethyl-L-cysteine as cation



Z⁻ = [NTf₂]⁻, [DCA]⁻.

Figure 1. Structures of novel CILs based on L-cysteine derivatives.