FUNCTIONAL TASK SPECIFIC IONIC LIQUIDS

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Introduction: Task Specific Ionic Liquids have been developed based on adequate selection and functionalization of cation and anion pairs. In this context, sulfonium ILs have been prepared as novel organic cation structures as well as aminoacids or biological compounds based ILs such as tryptophan, tyrosine and thioflavine structures. Also, the concept of reversible ionic liquids using CO_2 in the presence of amines and an organic super-base has been tested.

Jessop et al firstly reported this concept of reversible ILs using CO_2 in the presence of a mono-alcohol and an organic super-base. Then other functional organic compounds such as amino esters [1] and amino alcohols [2] (nucleophiles used instead of mono-alcohol to obtain carbamate based salts) using similarly an organic superbase based on amidinium functionality were reported. With these reactions and release of CO_2 is possible to obtain differencial polarities, basicities, solubilities, among other physico-chemical properties, promote separations [3].

Novel applications are expected for different TSILs developed in our laboratories in particular in Engineering, Biological or Chemical sciences.

Experimental: Sulfonium ILs have been prepared based on functionalization of dibutylsulfide or thiodiglycol with alkyl bromide units and then an adequate combination with some counter ions. Aminoacids (e.g. tryptophan and tyrosine) and biological compounds (e.g. thioflavine) were mainly used as cations combined with appropriate inorganic or organic anions. Reversible ILs using CO_2 were studied using the following experimental procedure: To a mixture of a primary amine and superbase in a vial inside an high pressure reactor was added CO_2 until a specific value of pressure was reached (5 or 20 bar). The liquid mixture was stirred at room temperature during (3 to 8 hours). After the period of reaction the system was depressurized and a specific workup was performed. The compounds were stored at a temperature of 9ºC. The obtained compounds were characterized by FTIR, ^{13}C NMR and 1H NMR. The melting point of the solid compounds was measured introducing CO_2 to the tube (open from above) before introducing the solid sample of the prepared compound, afterwards was introduced CO_2 and the tube was sealed with a rubber cap and the melting point was measured.

Results and discussion: In this communication, we presented different types of Task-Specific ILs based on sulfonium, aminoacids or biological organic cations combined with appropriate counter ions. According an adequate cation-anion combination is possible to tune their physical, chemical and thermal properties. The concept of reversible ionic liquid using CO_2 has been studied with different mono-alkylamines, alkyldiamines, alkyltriamines and arylamines as nucleophiles (R-NH_2). It was possible to isolate 8 different carbamate based salts as described in figure 1.

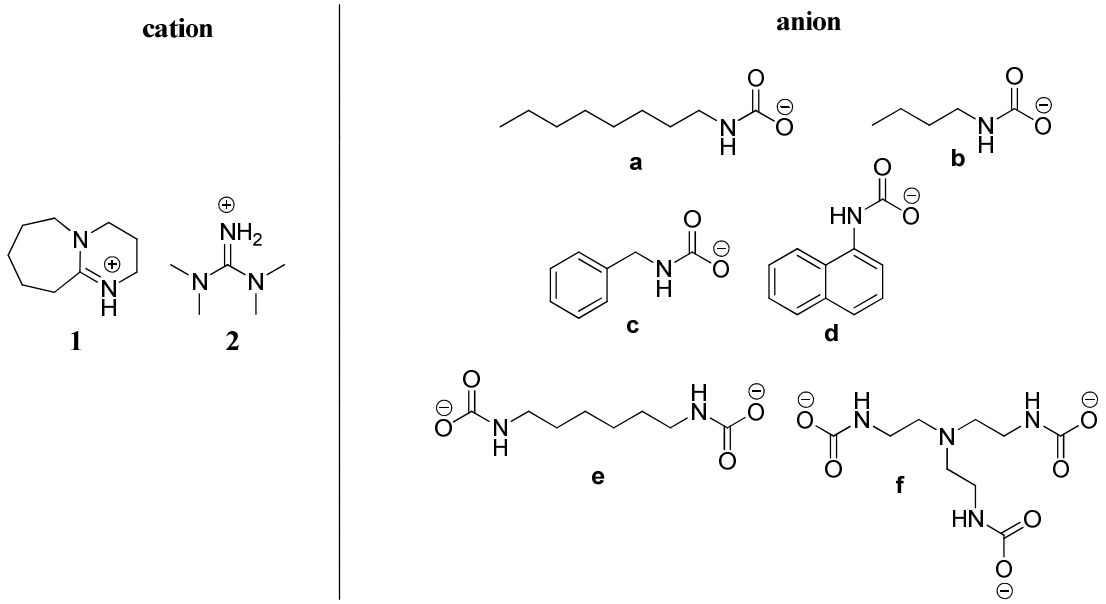

Figure 1

It was proved that all the prepared salts are ionic liquids as they melt at a temperature lower than 100ºC except **1e** and **2f** that started to liberate CO_2 before melting.

DBU as organic super-base was more effective to obtain the expected salts than tetramethylguanine (TMG) except when the anion was the structure **f**. When the carbamate is based on primary amines the reaction is more effective at lower pressures (5 bar) than intermediate pressures (20 bar), in order to obtain the cation and anion in the 1:1 proportion.

The arylamines showed lower reactivities with CO_2 than primary alkyl amines. It was also possible to obtain multiple carbamate functionalities with the amines **e** and **f**. In this context, the concept of reversible ionic liquid can be extended to multiple functionalities.

Summary: Different families of TSILs were developed in our laboratories based on sulfonium, aminoacids and thioflavin cations combined with appropriate anions. Some of these TSILs can be used for biological or engineering applications.

New carbamate salts as reversible ILs were also developed using CO_2 as reversibility element with amines as nucleophiles and DBU or tetramethylguanidine as organic superbases. In

general, DBU was more effective than tetramethylguanidine to obtain the corresponding salts in high yield and correct proportion cation : anion. For the compounds tested primary alkyl amines are more reactive than arylamines. It was possible to extend the concept of reversible ionic liquid to diamines and triamines in order to obtain the corresponding carbamate based salts.

References:

1. T. Yamada, P.J. Lukac, T. Yu and R.G. Weiss, Reversible, room-temperature, chiral ionic liquids. amidinium carbamates derived from amidines and amino-acid esters with carbon dioxide, *Chem. Mater.* 19 (2007) 4761-4768
2. T. Yu, T. Yamada, G.C. Gaviola and R.G. Weiss, Carbon dioxide and molecular nitrogen as switches between ionic and uncharged room-temperature liquids comprised of amidines and chiral amino alcohols, *Chem. Mater.* 20 (2008) 5337-5344.
3. R. Hart, P. Pollet, D. J. Hahne, E. John, V. Llopis-Mestre, V. Blasucci, H. Huttenhower, W. Leitner, C.A. Eckert and C.L. Liotta, Benign coupling of reactions and separations with reversible ionic liquids, *Tetrahedron* 66 (2010) 1082–1090.