DESIGN AND SYNTHESIS OF NEW IONIC LIQUIDS FOR SPECIFIC APPLICATIONS

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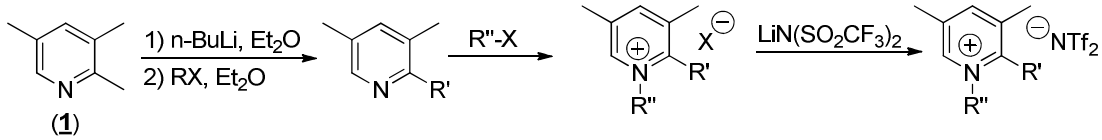
In this presentation, we would like to show our recent progress on the design and synthesis of new ionic liquids (ILs) for different purposes. Examples include the search of new ILs to be applied as:

1. SOLVENTS FOR EXTRACTIVE DESULFURIZATION OF FUEL OILS

Introduction: Production of low sulfur fuel oils has become a main objective of petroleum refining industry. One of the most promising techniques for this purpose is the extractive desulfurization, and researching efforts over the last years are being focused on finding the most suitable solvent. Because of their good qualities as solvents, such as a negligible vapour pressure, thermal stability, wide liquid range and non-flammability, ILs have been proposed as suitable solvents for the extraction of sulfur compounds from transportation fuels [1]. From these salts, highly substituted pyridinium based ILs have shown very promising results [2].

Results and discussion: We have developed the synthesis of a series of 10 highly substituted new pyridinium based ILs from commercial 2,3,5-trimethylpyridine (1) (Scheme 1).



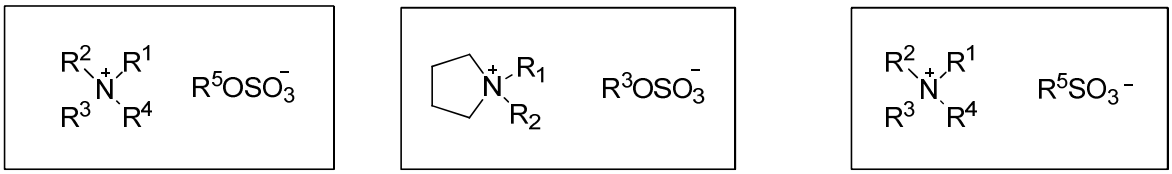
Scheme 1. Synthesis of 1,2,3,5-tetralkylpyridinium ILs.

The sulfur removal capacity of two of the ILs synthesized was analysed by testing the ILs capacity to extract thiophene from heptane. The selectivity and solute distribution ratio obtained were higher than those of the pryridinium ILs previously described [3].

2. LUBRICANTS

Introduction: The general properties of ILs such as non-volatily, non-flammability, chemical and thermo stability and environmentally friendly nature, make them ideal candidates as new lubricants [4]. As a part of the european project MINILUBES (Mechanisms of interactions in nano-scale of novel ionic lubricants with functional surfaces), we have designed and synthesized 35 new ILs derived from ammonium and pyrrolidinium cations and alkanesulfates or alkanesulfonates anions, that incorporates different alkyl chains and functional groups as substituents.

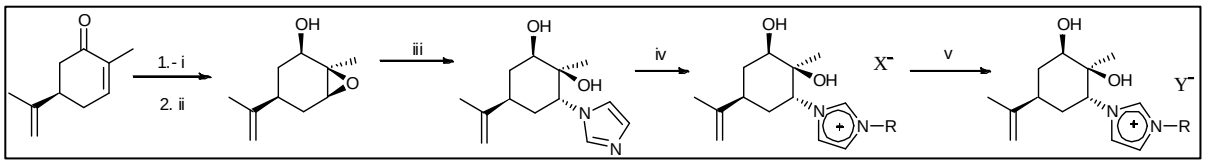
Results and discussion: The structures of the new ILs synthesized (Scheme 2) were selected according to the physical properties, toxicity and trybological behavior of previously described ILs. Some of their physical properties such as melting point, density, speed of sound and refractive index were determined at atmospheric pressure. The effect of the anion and cation alkyl chain lengths as well as the presence of functional groups on the melting point and the density was determined. Analyses of the tribological properties of [E_3MN] [MSO_4] and [BMpyr][MSO_4] have shown that these ILs improve wear and friction behaviour compared to pure glycerol [5]. More studies of toxicity, friction, wear and corrosion are currently under investigation.



Scheme 2. New ammonium and pyrrolidinium ILs as potential lubricants.

3. SOLVENTS AND/OR CATALYSTS IN ORGANIC SYNTHESIS

Introduction: Because of their unusual properties, the use of ILs in place of hazardous volatile organic solvents makes organic synthesis environmentally benign. Over the last years we have been working on the application of ILs as solvents and/or catalysts in a number of organic reactions, such as the Knovenagel Codensation and the Beckmann Rearrangement. For each reaction we have found an specific IL to act as solvent/catalysts with considerable success [6], accelerating the reaction, making work-up easier, and allowing their own recycling.



Scheme 3. Synthesis of new Chiral Ionic Liquids

Results and discussion: Our most recent work on this subject deals with the desing, synthesis and application of new chiral ionic liquids (CILs) (Scheme 3). The enantiomeric recognition ability of these CILs has been investigated by studying the diastereomeric interactions between the CILs and a racemic substrate by NMR spectroscopy. These CILs were found to be successful in the resolution of racemates by NMR. Further studies such as the concentration effect of the CIL on the enantiomeric recognition ability as well as the use of these chiral salts as organocatalyts in asymmetric synthesis are currently under investigation.

Conclusions: A brief summary of our experience on the design and synthesis of new ILs is presented. This work has been mainly focused on the search of new ILs to be applied as lubricants, catalysts in organic reactions or solvents for fuel oil desulfurization. However,

all the knowledge that we have acquired over the last years on the behaviour, physical properties and synthesis of ILs could be applied for different purposes in the future.

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