Glycerol derivatives for low melting mixtures: synthesis, properties and applications in catalysis

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Deep eutectic solvents (DES) and low melting mixtures (LMM) are attracting great attention as sustainable solvents analogues of ionic liquids.[1] The use of glycerol as the hydrogen bond donor (HBD) in DES and LMM has been described, and these mixtures have been used in different applications.[2,3]

Glycerol ethers are glycerol derivatives with interesting and tunable solvent properties depending on the substituent,[4] *e.g.* lower viscosity compared to glycerol and low toxicity compared with many organic solvents and ionic liquids.[5]

Here we present the optimization of the synthesis of glycerol ethers, following green procedures, and their use as HBD in LMM, together with ammonium halides such as the ubiquitous choline chloride or a glycerol derivative *N,N,N*-triethyl-1,2-dihydroxypropaneaminium chloride as the ionic part.

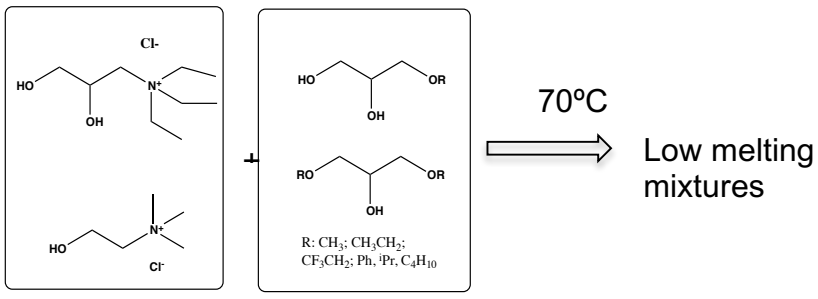

Fig. 1. Low melting mixtures formation.

Mixtures of 1:1; 1:1.5 and 1:2 of halide salts/HBD molar ratios have been prepared. The study of the stability of the mixtures at different temperatures reveals an influence of both the nature of the HBD component and the molar ratio. Physical properties of these mixtures such as density, viscosity, refractive index and polarity (E^T_N) have been measured.

Fig. 2. Low melting mixtures

An interesting point of these mixtures is the possibility of using them as reaction media in which a homogeneous catalyst can be trapped and further recovered by only extracting the products from the mixture. Thus, a study of immiscibility with organic solvents such as pentane, ether o ethyl acetate has been carried out and the mixtures have been used as reaction media in the Heck between iodobenzene and butyl acrylate, catalyzed by Pd nanoparticles. Results are compared to the ones obtained using [Bmim][PF_6] as reaction media (Fig. 3). The catalyst could be recovered up to four runs without great loss of activity.

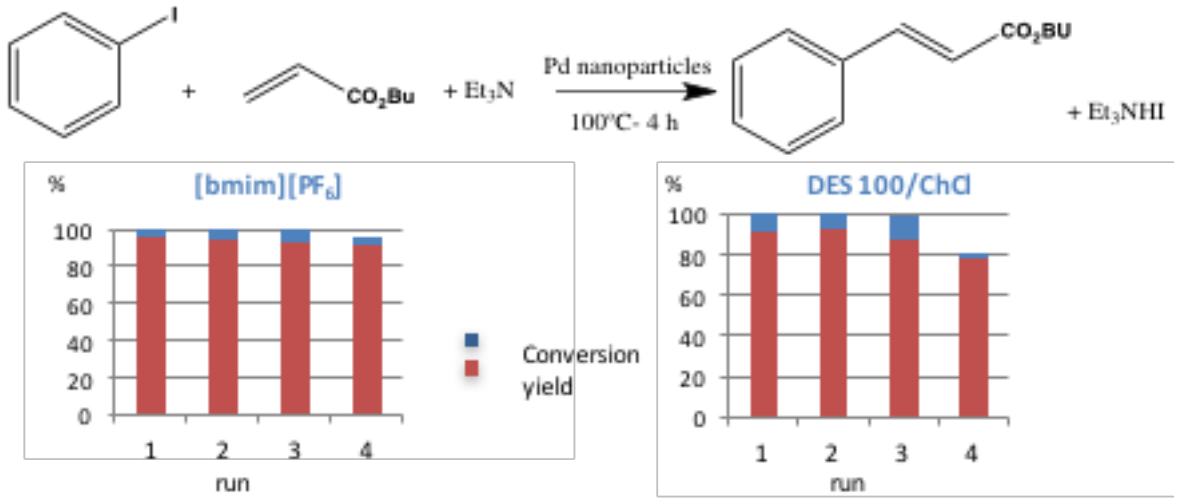

Fig. 3. Comparison of Heck reaction in ionic liquid [Bmim][PF_6] and LMM 100/ChCl

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