

## Acidity in Ionic liquids: from the determination of an acidity scale to the application in catalytic reactions

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An acidity scale is used to tentatively correlate catalytic activity and acidity.

Ionic liquids have been shown as alternative solvents for a wide range of catalytic and organic reactions.<sup>1</sup> Among various properties, Brønsted acidity plays an important role in such solvents for many reactions.<sup>2</sup>

Considering the importance of acidity, we first proposed a simple method for the determination of a Brønsted acidity scale from the Hammett acidity functions  $H_0$ , using UV-Visible spectroscopy.<sup>3,4</sup> In a second step, we tried to evaluate the accessible level of acidity from a potentiometric acidity function ( $R_0$ ) based on the  $H^+/H_2$  couple potential.

In these communications, we will present the results obtained on ionic liquids to which a given amount of strong acid (HOTf and HNTf<sub>2</sub>) has been added. The best results were obtained by potentiometry with a hydrogen electrode. Because of the experimental difficulties, the slopes of the measured potentials versus the log of the added acid amount are not the expected ones but conclusions can still be made:

- the approximate calculated values of the  $R_0$  acidity function indicate a higher acidity level than that given by the Hammett  $H_0$  function, for all investigated acid solutions.
- besides the absolute value of the acidity, the sequence of acidities measured on solutions of similar content of added acid is still  $BF_4^- > NTf_2^- > OTf^-$  as we have measured with the Hammett method.

The goal of this acidity scale is ultimately to find a correlation between the catalytic activities measured on acidic reactions and the solvent nature. In this purpose, the dimerization reaction of isobutene into isooctenes was chosen as a probe to investigate the influence of acidity on both reaction rate and yield. As anticipated by the previously described acidity scale determination, it was found, for the investigated ionic liquids, that the nature of the cation does not play a dominant role, whereas changing the nature of the anion leads to very different catalytic performances. The correlation between the measured acidity level and the activity and selectivity of the reaction was only partially validated since a peculiar behaviour was observed for NTf<sub>2</sub><sup>-</sup> type ionic liquids. Indeed, the activities follow the order  $NTf_2^- \sim SbF_6^- > PF_6^- \sim BF_4^- > OTf^-$ . These different activities will be discussed. By an adequate choice of the ionic liquid, selectivity for isobutene dimers can reach 88 wt% (at 70% isobutene conversion) with possible recycling of the catalytic system without loss of activity and selectivity<sup>5</sup>.

### References

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