Ionic Liquids Polarity Effects on the Keto-enol Tautomerism Studied by NMR

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The concept of polarity of ionic liquids (ILs) has been a theme for several studies. Yet, it is far from being a well understood subject. The study of solvent-dependent equilibria is an insightful approach to this issue and has been widely conducted for molecular solvents.

In this work, acetylacetone (acac), namely its keto-enol tautomerism was used to describe polarity and the overall behavior of ILs. This equilibrium was already studied for the case of molecular solvents, and shown to have a significant correlation to the polarity of the solvent [1]. This was also sparsely addressed for the case of ILs [2]. A further understanding of the effect of ILs, bearing 1-alkyl-3-methylimidazolium cations, on this equilibrium has been sought. A variety of ILs with different cation/anion combinations was used. A variation of the size of the side chain of the cation was used, with different anions: tetrafluoroborate, hexafluorophosphate, bis(trifluoromethanesulfonyl)imide, methylsulfate, ethylsulfate, and dicyanamide.

1D NMR was used to characterize the equilibrium of the system, namely the equilibrium constant of enolisation ($K_{eq}$), Fig. 1. It was attempted to correlate these data to several physical and chemical properties of ILs, through both continuum and molecular approaches. This has shown a significant component of ion-dipole interaction forces between these solvents and the solute, in agreement with other characterizations of ILs [3]. A good correlation was also found with the the volume of the ion pair, determined as the sum of the volume of the two ionic species, as suggested before [4]. This comes to show that, when considering solvation, ionic liquids can be considered more as ion pairs than what was thought before.

Fig. 1 Keto-enol tautomerization of acetylacetone (acac)
Further NMR studies were conducted to assess the occurrence of specific interactions between acac and ILs. This was done using NOE (homo- and heteronuclear) and DOSY experiments, which allowed to probe interactions of the keto and enol form of acac with the cation and anion of the ILs. These showed that the most relevant interactions are established between the anion and the keto form of acac.

It was also observed that such interactions can be related to the ion pair volume, and they are no longer detectable when the cation enlarges (growth of the alkyl side chain of the imidazolium cation). Alongside with this, the ratio of keto form decreases. This suggests that the most relevant interactions within ILs are provided by the anion. The NMR data are coherent with what is described above, concerning the effect of the volume of the ion pair.

In conclusion, the polarity and solvation of ILs is dependent on the size and nature of the ion pair, namely the ability to establish specific interactions.

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