When Like-charged Ions Attract: Controlling the Size and Distribution of Cation Clusters in Ionic Liquids by Adding Molecular OH-catchers

Johanna Busch, Dietmar Paschek, Ralf Ludwig, Tristan Youngs

Universität Rostock, Institut für Chemie, Physikalische und Theoretische Chemie, Albert-Einstein-Straße 27, 18059 Rostock, Germany

johanna.busch@uni-rostock.de

Attraction between opposite-charged and repulsion between like-charged particles is a commonly accepted concept in science. In contrast, like-charged attraction seems to be counterintuitive at first glance. Unexpectedly, the formation of cation clusters in ionic liquids with specifically designed OH-functionalized cations was observed at room temperature. [1-4] These clusters are formed via hydrogen bonding between the hydroxyl groups terminating the alkyl chains of the cation and strongly affect the structural and dynamical properties of those materials.

By utilising neutron diffraction experiments as well as molecular dynamics simulations, we probe the liquid nanostructures of the IL [HOC$_4$Py][NTf$_2$] in mixtures with the molecular liquid DMSO. The latter acts as an OH-catcher through its strong proton acceptor S=O group, controlling the delicate balance of cation-anion and cation-cation cluster distributions. We observe three types of hydrogen bonding situations in one solution, indicated by their characteristic bond lengths (H⋯O) and (O⋯O. Moreover, we address the important question, whether DMSO prefers to catch the hydroxyl groups of the cation-anion or the cation-cation clusters. The study is aimed at a better understanding of the relationship between clusters and larger scale nanostructures.

REFERENCES

[1] A. Knorr et al., Phys. Chem. Chem. Phys. 17 (2015) 30978.
[2] A. Knorr, R. Ludwig, Sci. Rep. 5 (2015) 17505.
[3] A. Knorr et al., ChemPhysChem 17 (2016) 458.
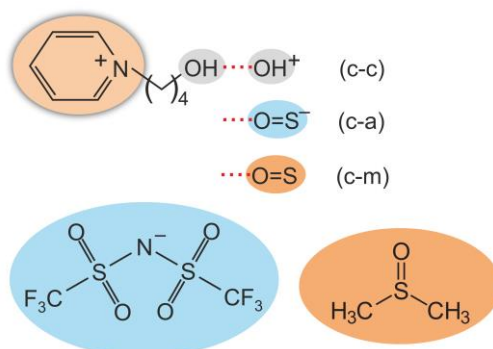[4] A. Strate, T. Niemann, R. Ludwig, Phys. Chem. Chem. Phys. 19 (2017) 18854.

FIGURES

Figure 1: Three possible types of hydrogen bonding by diluting the IL [HOC$_4$Py][NTf$_2$] with DMSO