The fragmentation of intermolecular interactions in a carboxyl-functionalized ionic liquid and its molecular mimic – Quantification of hydrogen bond strength

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We have studied the carboxyl-functionalized ionic liquid 1-(carboxymethyl)pyridinium bis(trifluoromethylsulfonyl)imide [HOOC-CH_2-py] [NTf_2] and its molecular mimic phenylacetic acid to get a better understanding of the non-covalent interactions. The compounds were analyzed with IR spectroscopy in the Mid-IR region. They clearly show the formation of singly and doubly hydrogen bonded cationic dimers. The latter dimer is related to the structural motifs known for formic and acetic acid in the gas phase. [1,2]
We extended our investigation to X-ray crystallography, DFT calculations and thermodynamic methods to analyze and characterize all types of hydrogen bonding. The crystalline phase of the ionic liquid consists of doubly hydrogen bonded cyclic dimers. This binding motif, present in the ionic liquid as well as in phenylacetic acid, successively opens with increasing temperature and is replaced by a linear species. Here, additionally to one remaining single cationic hydrogen bond an additional hydrogen bond between cation and anion is formed. We deconvoluted the spectra of both species in the carbonyl stretching region to get a better understanding of the temperature behavior. The derived transition enthalpies allow to expose the non-covalent interaction and to determine the hydrogen bond strength between ions of like charge. Finally, we were able to show, that the repulsive Coulomb interactions between two like-charged weakens the strength of the hydrogen bonds in comparison to the molecular species.

References:

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