Chiral induction in ionic liquids

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Chiral ionic liquids (CILs) exhibit potential utility both as solvents in asymmetric synthesis and as selectors in the enantiomeric recognition of small molecules. The effective use of CILs in these applications requires a comprehensive understanding of the structure and dynamics. Due to their sensitivity to molecular conformations and conformational changes, chiroptical spectroscopy methods such as vibrational circular dichroism (VCD) offer unique opportunities to study the structure of CILs and in particular the occurrence of chirality induction effects.

In this talk, we present the combined results of our recent studies on CILs. The first part involves ab initio molecular dynamics (AIMD) simulations of the CIL 1-ethyl-3-methylimidazolium L-alaninate ([C2C1Im][L-ala]) [1,2], elucidating the induction of chirality from the anionic to the cationic moiety, thereby inducing a perturbation within the conformational landscape of the cation. Based on these findings, we investigate two prototypical molecular arrangements involving (R)- or (S)-butan-2-ol solutes within $[C_2C_1Im][L\text{-ala}]$ to uncover chiral recognition mechanisms. VCD spectra and structural analyses reveal discriminative interactions between the CIL and the enantiomers of butan-2-ol.

While the focus of the first study is on the chiral induction in ionic liquid cations, the second investigation [3-5] examines effects on the anionic components. Using AIMD simulations of (R)-propylene oxide dissolved in the achiral IL 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ($[C_2C_1Im][NTf_2]$), we observe an induction of chirality from propylene oxide to the anion, monitored by theoretical and experimental VCD spectroscopy. These results are remarkable because (i) the cation only plays a minor role in the chiral induction and (ii) this is the first time that a chiral induction to an ionic liquid anion is observed.

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