Chirality transfer and enantiomeric recognition in chiral ionic liquids: Spectroscopic insights

Jan Blasius[1*], Paul Zaby[1], Oldamur Hollóczki[1], Barbara Kirchner[1]

[1] Mulliken Center for Theoretical Chemistry, Rheinische Friedrich-Wilhelms-Universität Bonn, Beringstraße 4-6, 53115 Bonn, Germany

Email: jan.blasius@thch.uni-bonn.de

Chiral ionic liquids (CILs) can be used as solvents in asymmetric synthesis or as selectors in enantiomeric recognition and separation processes. Being composed of charged moieties, these liquids generally show a complex dynamic behaviour and thus an involved conformational landscape. In order to adjust CILs for efficient use in the aforementioned applications, knowledge about dynamic effects and the molecular structure are of key importance. Due to their sensitivity towards molecular conformations and conformational changes, chiroptical spectroscopy methods such as vibrational circular dichroism (VCD) offer unique possibilities to study the structure of CILs and in particular the occurrence of chirality transfer effects.

By means of ab initio molecular dynamics simulations, we investigate the chiral ionic liquid 1-ethyl-3-methylimidazolium L-alaninate ([C_2C_1Im][L-ala]). From the analysis of VCD spectra [1], we observe indications for the transfer of chiral information from the chiral anion to the achiral cation. Structural analyses reveal that this transfer of chirality induces a symmetry breaking in the conformational distribution of the achiral cation inasmuch as the energetic degeneration of two mirror-imaged conformers gets perturbed. [2] The presence of the chiral anion thus induces a preference for distinct cation conformations which can be tracked by VCD.

Due to the possible application of CILs as chiral selectors, we further investigate whether the observed chirality transfer might affect chiral recognition mechanisms. To this end, we studied two model systems being composed of (*R*)- or (*S*)-butan-2-ol dissolved in [C_2C_1Im][L-ala]. [2,3] VCD spectra [3] and structural analyses [2] reveal discriminative interactions occurring between the CIL and the enantiomers of butan-2-ol. Although the recognition mechanism of butan-2-ol is strongly conducted by the chiral anion via formation of diastereomeric complexes, we observe that butan-2-ol transfers chiral information to the achiral cation. Thereby, (*R*)-butan-2-ol and L-alaninate induce the same chirality in the cation, whereas (*S*)-butan-2-ol and L-alaninate induce opposite chirality. [2] This effect creates a more favorable environment for (*R*)-butan-2-ol in the CIL compared to (*S*)-butan-2-ol.

References:

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