Asymmetric hydration of enantiomers at aqueous interfaces

Yu Zhang [a], Shyam Parshotam [a], Arsh Hazrah [a], Yongkang Wang [a], Mischa Bonn [a]

[a] Max-Planck Institute for Polymer Research, 55128 Mainz, Germany

zhangy1@mpip-mainz.mpg.de

Hydration of chiral supramolecular assemblies by chiral molecules breaks the mirror symmetry of interfacial water through electrostatic interactions and hydrogen bonding, thereby imprinting molecular chirality onto the surrounding water hydrogen-bond network and giving rise to so-called "chiral water."[1] Understanding whether and how individual chiral molecules induce such chiral structuring in their hydration environment is crucial for elucidating the fundamental properties of, and rationally guiding the design of, chiral supramolecular assemblies.[2] However, addressing this question requires molecular-level insight into interfacial water structure, particularly its hydrogen-bonding organization, which remains a significant experimental challenge. Here, to address this challenge, on a model system of amphiphilic peptide enantiomers, we employ chiral heterodyne-detected sum-frequency generation (HD-SFG) spectroscopy to directly resolve the chiral molecular structure of both the peptide enantiomers and the interfacial water. Our preliminary results of distinct spectroscopic features for two enantiomers suggest their asymmetric hydration properties, which could be further tuned by the interfacial conditions, such as pH. Furthermore, the complementary Langmuir isotherms reveal differences in membrane phase behaviour and compressibility that correlate with these molecular-level observations. Together, our results provide initial evidence for the enantioselective hydration at the air/water interface and the feasibility of HD-SFG in resolving chiral interfacial structure.

Keywords:
chiral water, heterodyne-detected sum-frequency generation spectroscopy, amphiphilic peptides

References:

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