Adsorption of ions and hydrophobic solutes at an electrified Au-water interface: insights from THz spectroscopy and simulations

S. Pezzotti[a], A. Serva[b], M. Salanne[b], S.R. Alfarano[a], C. Stein[c], M. Head-Gordon[c], M. Havenith[a]

a) Department of Physical Chemistry II, Ruhr University Bochum, 44780 Bochum, Germany
b) Sorbonne Université, CNRS, PHENIX, F-75005 Paris, France
c) Department of Chemistry, University of California, Berkeley, CA 94720

Adsorption of ions and hydrophobic solutes are key processes in electrochemistry. The former regulates the Electric Double Layer (EDL) composition and dictates important quantities such as surface potential and capacitance. The latter has major implications for heterogeneous catalysis and renewable energy technologies, where small hydrophobic molecules are commonly involved as reactants and products. Despite solvation of charged and hydrophobic species are remarkably different processes, we show here that the specific organization of the water network at electrified metal interfaces influences both of them with a common underlying molecular mechanism.

In the first part we employ classical molecular dynamics to study hydrophobic hydration at an electrified gold/water interface.[1] We show that the peculiar interfacial water arrangement induces atypical fluctuations of the liquid water density at the interface. Hydrophobic solvation free energy is quantified by the cost to perturb the water structure around the solute, which is directly determined by such fluctuations. We show how such fluctuations regulate the accumulation of hydrophobic solutes (e.g. CO) at the interface.

In the second part, we move our attention to ionic species and employ THz spectroscopy and classical molecular dynamics to follow the stripping away of Na^+ and Cl^- solvation shells at the electrified gold/water interface.[2] We find that while Na^+ is attracted toward the electrode at the smallest applied negative potentials, stripping of the Cl^- hydration shell is observed only at higher potential values. Such asymmetry cannot be explained by the dominant electrostatic interactions. However, it can be rationalized once specific solvation and water density fluctuations effects are taken into account.

As a perspective, since interfacial density fluctuations are sensitive to minute changes in the environmental parameters of the interface (e.g. surface/electrolyte composition, pH, applied potential), we propose that they can be tailored in the future to regulate adsorption of ions and reactive species at electrochemical interfaces.

References

1. A. Serva, M. Salanne, M. Havenith, S. Pezzotti. *PNAS* 118, e2023867118 (2021).

2. S. R. Alfarano, S. Pezzotti, C. Stein, et al. *PNAS* 118, e2108568118 (2021).