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Surfactant-Ion Interactions at Seawater-Vapor Interfaces

Content

Surfactants are omnipresent on aqueous surfaces exposed to the atmosphere, as in the case of, e.g., lakes, rivers, and aerosol droplets. The largest contiguous surface is that of the oceans with air, covering more than 70% of the Earth. The ocean surface is involved in complex interfacial reactions in the marine boundary layer and is covered by a thin film of amphiphilic compounds. This so-called sea surface microlayer significantly influences many physical, chemical, and biological processes with importance to the global ecosystem, such as the exchange of trace gases (e.g., CO_2) and heat, and the generation of aerosol particles^{1,2}.

The presence of surfactants potentially alters the propensity of dissolved ions, such as Na^+ , Mg^{2+} , Ca^{2+} , and Cl^- , for the ocean-air interface through direct interactions between their functional groups (e.g., $-\text{COO}^-$, NH_3^+) with the ions. This leads to the so-called “salting out” effect, i.e., organic compounds are generally less soluble in aqueous salt solutions, such as seawater, than in pure water. The increased propensity of ions for the ocean-air interface in the presence of surfactants might also increase their availability as reactants in heterogeneous chemical reactions with trace gases in the atmosphere. While field studies have provided a wealth of information on the general chemical composition of the ocean-air interface, detailed molecular-scale information on the mutual effects of ions and surfactants are still scarce.

We have recently started to investigate the interplay between organic surfactants and inorganic ions in the ocean water at realistic ion concentrations, to gain a molecular-scale, quantitative understanding of these phenomena. To this end, we are performing surface tension measurements and liquid-jet X-ray photoelectron spectroscopy (XPS) in a systematic investigation of pure water and artificial seawater (ASW) solutions with and without surfactant molecules. The goal is to elucidate the influence of ionic size and charge as well as the nature of the surfactant functional groups on the surface chemical composition and surface propensity. In a proof-of-concept experiment carried out at the HIPPIE beamline at MAX IV using liquid microjet XPS we observed, e.g., a strong enhancement of Ca^{2+} ions in the presence of a Na pentanoate surfactant for a 0.05 M CaCl_2 aqueous solution. This example demonstrates that ions in solution can be observed even at these low concentrations in XPS measurements and that the enhancement due to the presence of the surfactant is significant.

References

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