

A vibrational sum frequency spectroscopy study of ion specific interactions between monovalent ions and fatty acid Langmuir monolayers

Adrien Sthoer^{1*}, Jana Hladílková², Mikael Lund², Eric Tyrode¹

¹*Chemistry Department, KTH Royal Institute of Technology, Stockholm, Sweden.*

²*Division of Theoretical Chemistry, Lund University, Lund, Sweden.*

**sthoe@kth.se*

Ion specific effect play an important role in a number of biological processes occurring in living organisms. However, a comprehensive molecular understanding remains elusive. It is currently believed that molecular interfacial interaction, including specific ion adsorption together with the concurrent disruption of the water structure in the direct proximity of functional groups, are the underlying key steps. Herein we present a vibrational sum frequency spectroscopy (VSFS) investigation of ion pair interaction between monovalent ions and the carboxylic acid moiety of a fatty acid Langmuir monolayer at the liquid/vapour interface.

VSFS is a non-linear optical technique with an exquisite surface specificity that probes molecular orientation and allows determining the charging of the monolayer, including the formation of contact ion pairs with the carboxylate headgroups. The fatty acid monolayer partially deprotonates, upon addition of salt to the solution subphase. At a given ion concentration, the degree of deprotonation was found to be ion specific, but also strongly pH dependent. Straightforward evidences of the formation of contact ion pairs between selected cations and the carboxylate group are obtained with SFG. Additionally, structural changes in the interfacial water molecules upon ion association are directly probed. We find that not only the nature of the cation, but also that of the anion influence the adsorption mechanism to this biophysically relevant interface. Molecular dynamic simulations were performed to further understand the preferential interactions of the ions with the carboxylic / carboxylate head groups.