



Molecular Insight into Ion-Specific Interactions

Vibrational sum frequency study of the carboxylic acid moiety

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DOCTORAL DISSERTATION

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Abstract

Ion specific effects at charged interfaces find numerous applications in colloidal sciences and play a vital role in many biological processes. Despite having been studied for over a century, starting with the work of F. Hofmeister in the 1880s, a comprehensive molecular understanding remains elusive. It is currently believed that specific molecular interactions between ions and the various chemical functional groups, including the disruption of the interfacial water structure, are the key underlying steps. The research presented in this doctoral thesis focuses on the carboxylic acid moiety which is one of the chemical functionalities most frequently encountered at biological interfaces. Vibrational sum frequency spectroscopy (VSFS), a non-linear optical technique with an exquisite surface specificity, was used to investigate the interactions between the carboxylic acid moiety of a fatty acid Langmuir monolayer with monovalent (Li^+ , Na^+ , K^+ , Cs^+), divalent (Ca^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+}), and trivalent (Y^{3+} , La^{3+}) cations. The studies also focused on understanding the remarkable effect of negatively charged co-ions (Cl^- , Br^- , I^- , SCN^-) on the cation-carboxylate interactions. Another key result of this work is the identification of resolved spectral features linked to the Eigen-like hydronium (H_3O^+) cation at the charged carboxylic acid interface. VSFS allowed quantifying the surface charge, type of cation binding, and structural changes in the interfacial water molecules upon changes of the ion identity, concentration, and pH. The findings demonstrate that the physical-chemical properties of the interfacial layers reflect a subtle balance between molecular and electrostatic competitive interactions, providing new experimental quantitative insights for testing the suitability of extended new theories on charged interfaces and ion specific interactions.