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How accurate is the Poisson-Boltzmann theory for monovalent ions near highly charged interfaces?[1] WEI BU, ALEX TRAVESSET, DAVID VAKNIN, Ames Laboratory, Iowa State University — Monovalent ion distributions next to highly charged interfaces were determined by synchrotron surface X-ray sensitive techniques. A lipid phosphate (dihexadecyl hydrogen-phosphate) was spread as a monolayer at the air-water interface, containing CsI at various concentrations. Using anomalous reflectivity off and at the L_3 Cs^+ resonance, we provide, for the first time, spatial counterion distributions (Cs^+) next to the negatively charged interface over a wide range of ionic concentrations. We argue that at low salt concentrations and for pure water the enhanced concentration of hydroniums H_3O^+ at the interface leads to proton-transfer back to the phosphate group by a high contact-potential, whereas high salt concentrations lower the contact-potential resulting in proton-release and increased surface charge-density. The experimental ionic distributions are in excellent agreement with a renormalized-surface-charge Poisson-Boltzmann theory without fitting parameters or additional assumptions.

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