

Atomically resolved three-dimensional structures of electrolyte aqueous solutions near a solid surface

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More than 30 years have passed since the first observation of periodic hydration forces between mica surfaces in dilute electrolyte solutions. A variety of experimental and theoretical methods have been applied to study interfacial liquids, including X-ray reflectivity, X-ray absorption spectroscopy, various force spectroscopies, first-principle and molecular dynamics calculations. In particular, electronic Density Functional (DFT) simulations have shown that a three-dimensional atomic structure should appear at the liquid adjacent to a solid crystalline surface; however, to this date its direct experimental observation has remained elusive. Recent developments in high resolution force microscopy (AFM) have imaged the existence of a few hydration layers on top of a mica surface, ionic crystals, lipid headgroups and protein surfaces. AFM images have also revealed with atomic-resolution the adsorption from a solution of Na⁺, Rb⁺, Mg²⁺ or Ca²⁺ ions on different surfaces. Those results indicate that advanced force microscopy methods could be applied to determine the three-dimensional (3D) atomic structure of liquids near solid surfaces. Atomic-resolution 3D images of solid-electrolyte interfaces Here we provide atomically-resolved three-dimensional images of solid-electrolyte interfaces with several nanometers in depth. The images acquired at 300 K allow us to characterize the interfacial structures as a function of the electrolyte concentration near a mica surface

Our three-dimensional AFM method demonstrate the existence of three types of interfacial structures. At low concentrations (0.01-1 M), cations are adsorbed onto the mica until charge neutrality is reached. The cation layer is topped by a few hydration layers while anions are excluded from the mica surface. At higher concentrations, the interfacial layer extends several nanometers into the liquid. It involves the alternation of cation and anion planes. Classical Fluid Density Functional calculations show that water molecules are a critical factor for stabilizing the structure of the ordered interfacial layer. The interfacial layer compatibilizes a crystal-like structure with liquid-like ion and solvent mobilities. At saturation, some ions precipitate and small ionic crystals are formed on the mica. The three-dimensional images have been acquired at 300 K.

Our Classical Fluid Density Functional CF-DFT calculation reveals the main factors in the above experiments. We do not aim to provide a full quantitative description of the experimental data, nor to give the most realistic description of the ionic solutions, but rather to reproduce and explain the phenomena semi-quantitatively. The theoretical difficulties associated with a realistic description of the ionic interactions are not crucial to predict the qualitative behavior of the system. The most relevant factor is to observe that by increasing the salt concentration we should get closer to its crystallization phase transition, which may be represented

by short-ranged effective interactions. The interaction with the mica is modelled to have a nearly complete monolayer of cations at low salt concentrations (0.2 M), as indicated by the AFM images (Fig. 3c). To lose coverage the oscillations of the water density from the model start with a first layer of water molecules tightly bound to the adsorbed cations and the mica. In the 3D AFM images this 1st hydration layer cannot be distinguished from the atomic corrugation coming from mica and K atoms. The following layers, with a separation of about 0.3 nm in the CF-DFT model, coincide with the local maxima in 3D AFM force and identify with the oscillations observed on the experimental force curve as an effect of the 2nd and 3rd hydration layers. The anions are effectively excluded from the interface. At higher salt concentrations, near a saturated salt concentration, the CF-DFT results show that the number density profiles for K⁺ and Cl⁻ have strong oscillations as function of the distance from the mica surface very similar to the oscillations observed in the experimental force curve.

[1] Daniel Martin-Jimenez, Enrique Chacon, Pedro Tarazona y Ricardo Garcia, *ature Communications* **7**, 12174 (2016). DOI: 10.1038/ncomms12164