

Ion specific hydration forces at mica-electrolyte interfaces.

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Hydration forces play a crucial role for a wide range of phenomena in physics, chemistry, and biology. Here we study the hydration of mica surfaces in contact with various alkali chloride solutions over a wide range of concentrations and pH values. Using Atomic Force Microscopy and Molecular Dynamics simulations, we demonstrate that hydration forces consist of a superposition of a monotonically decaying and an oscillatory part, each with a unique dependence on the specific type of cation. The monotonic hydration force gradually decreases in strength with decreasing bulk hydration energy leading to a transition from an overall repulsive (Li^+ , Na^+) to an attractive (Rb^+ , Cs^+) force. The oscillatory part, in contrast, displays a binary character, being hardly affected by the presence of strongly hydrated cations (Li^+ , Na^+), but becomes completely suppressed in presence of weakly hydrated cations (Rb^+ , Cs^+), in agreement with a less pronounced water structure in simulations. For both aspects K^+ play an intermediate role and decreasing pH follows the trend of increasing Rb^+ and Cs^+ concentration.