Ion specific hydration forces at mica-electrolyte interfaces.

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 \((\text{Li}^+, \text{Na}^+)\) to an attractive \((\text{Rb}^+, \text{Cs}^+)\) force. The oscillatory part, in contrast, displays a binary character, being hardly affected by the presence of strongly hydrated cations \((\text{Li}^+, \text{Na}^+)\), but becomes completely suppressed in presence of weakly hydrated cations \((\text{Rb}^+, \text{Cs}^+)\), in agreement with a less pronounced water structure in simulations. For both aspects \(\text{K}^+\) play an intermediate role and decreasing \(\text{pH}\) follows the trend of increasing \(\text{Rb}^+\) and \(\text{Cs}^+\) concentration.