

Correlation between electrostatic and hydration forces on silica and gibbsite surfaces: an atomic force microscopy study

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The balance between hydration and Derjaguin–Landau–Verwey–Overbeek (DLVO) forces at the solid-liquid interface controls many processes, such as colloidal stability, wetting, electrochemistry, biomolecular self-assembly and ion adsorption. However, our current understanding of what governs the molecular scale hydration forces and their correlation with continuum electrostatics is still limited, especially at the level of single nanoparticles. Here, using atomic force microscopy and tip size of 9nm, we simultaneously map the DLVO and hydration forces on heterogeneous surfaces of gibbsite nanoparticles deposited on silica substrate in ambient NaCl, LiCl, CsCl solutions of variable concentration and pH with nanoscale precision. We show that the hydration force with a decay length ($\approx 0,25\text{nm}$) is composed of an oscillatory force superimposed onto a monotonically decaying background force. The hydration layers on crystalline gibbsite surface are more organized than the ones observed on an amorphous silica. Moreover, strength and decay length of the oscillatory hydration force are found to be rather independent with respect to variations of surface charge density that varies with pH and salt concentrations as expected from DLVO theory. This indicates that the behavior of the hydration force is not caused by continuum electrostatics, but by surface microscopic structure and distribution of hydroxyl groups.

