Size dependent surface complexation of titanium dioxide nanoparticles

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Mineral nanoparticles are present in all compartments of the environment. Due to their small size, they have an increased roughness and curvature of the surface, a large specific surface area, and a high abundance of attractive binding sites, which are properties that result in high reactivity (e.g. surface complexation). Interactions that occur at the surface of nanoparticles are important for understanding and predicting nanoparticle fate and behavior, as well as characterizing the potential environmental and health risks posed by nanoparticles. Surface complexation also plays a significant role in the transport of metals and organic contaminants in natural systems.

The surface charge of nanoparticles is sometimes different than the surface charge of corresponding larger microparticles. In the present study, stable TiO_2 (anatase) suspensions of well-defined particle sizes (<30 nm) have been synthesized and extensively characterized, and their surface complexation is studied as a function of particle size, pH and ionic strength.

Selected phenolic and carboxylic compounds are used as model substances to mimic the interactions of nanoparticles with natural organic matter. The aim is to mechanistically understand these interactions that are known to govern nanoparticle fate and transport in the environment. Adsorption experiments are combined with potentiometric titrations, electrophoretic mobility measurements and light scattering techniques.

Classic surface complexation models are built on certain assumptions that may not be valid for nanoparticles. Therefore, the Charge Distribution - Multisite Complexation (CD-MUSIC) model established for microparticles is compared with the Corrected Debye-Hückel theory of surface complexation (CDH-SC), which is generic but also applicable to modeling the surface charging of nanoparticles with a diameter smaller than 25 nm.

Studying the interactions of trivalent metal ions with the silica/water interface using second harmonic generation

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The interactions of the trivalent metal cations Al (III), La (III), Gd (III), and Lu (III) with the silica/water interface are studied using the nonlinear optical technique of second harmonic generation (SHG). Specifically, the Eisenthal $\chi^{(3)}$ technique is employed in order to quantify several thermodynamic binding parameters from adsorption isotherm measurements [1]. This powerful technique is highly surface specific and allows the interactions of these metal pollutants with the silica/water inferface to be tracked on the molecular level. These measurements are also performed in real-time and without the use of labels.

Our results show that the binding of these ions to the silica/water interface is fully reversible. Adsorption isotherms are obtained under dynamic flow conditions and fit using the Gouy-Chapman and triple layer surface complexation models. From these fits, the free energy of adsorption for the aluminum ion is found to be -37.2 (5) kJ/mol, while the free energies of adsorption for the three lanthanide elements ranged from -29.9 (9) to -32.2 (7) kJ/mol. Binding constants and interfacial charge densities are also obtained from these SHG experiments. The interfacial charge density of the bare silica surface is also quantified at pH 4. Despite identical ionic charges, the metals under investigation are found to have remarkably different binding parameters. These SHG experiments provide valuable data that can be used towards understanding how these metal ions are transported throughout the environment.

[1] Salafsky & Eisenthal (2000) *J. Phys. Chem. B* **104**, 7752–7755.