

Irreversible reductions in surface area of nanoparticles depends on drying conditions

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Experimental efforts to elucidate size-dependent nanoparticle reactivity at the mineral-water interface depend on normalizing for the influence of surface area. Measurements of surface area typically require either sample drying in air for later observation by electron microscopy or freeze-drying for BET analysis. However, due to interparticle associations, surface area of nanoparticle suspensions vary as not only a function of particle size and shape, but also are influenced by drying, freezing, and freeze-drying treatments. For the specific case of hematite platelets, the most appropriate measurement method changes when particles are 10-40 nm in diameter, due in part to the crystallographic alignment of nanoparticles during the drying process. In addition, nanoparticle surface area varies with reactant, leading to further complications for interpreting nanoparticle reactivity experiments. Aggregation of nanoparticles in suspension, likely due to hydration forces, leads to the development of confined water layers that are accessible to some reactants but not others. For example, anions such as arsenic and phosphate are excluded while protons can readily diffuse in. These concepts are also needed in order to understand the processes that control the transport and deposition of nanoparticles, as demonstrated by quartz crystal microbalance, AFM, and light scattering studies of hematite nanoparticles.

Ion association in aqueous MgSO₄ and NiSO₄ from 25 to 275 °C at 19 MPa by AC conductance and Raman spectroscopy

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AC impedance measurements on dilute aqueous solutions of MgSO₄ and NiSO₄ were carried out in a platinum flow cell [1] from 25 to 275 °C at 19 MPa. An equivalent circuit model [2] was used to derive solution resistivities from the complex impedance data. The resulting molar conductivities were modelled with the Fuoss-Hsia-Fernández-Prini (FHFP) model in order to obtain equilibrium constants for the total association reactions to form of all types of ion pairs: double-solvent-separated ion pairs (SSIP), solvent-separated ion pairs (SIP), and contact ion pairs (CIP).

Temperature-dependant polarization measurements yielded isotropic Raman spectra as a function of concentration, from which the formation constants of the contact ion pairs were determined [3]. The results are being combined with apparent molar volume and heat capacity measurements on the identical solutions to determine a complete thermodynamic description of the ion association reactions as a function of temperature at constant pressure, using the HKF model.

[1] Zimmerman, Gruskiewicz & Wood (1995) *J. Phys. Chem. B.* **99**, 11612–11625. [2] Hnedkovsky, Wood & Balashov (2005) *J. Phys. Chem. B.* **109**, 9034–9046. [3] Rudolph, Irmer & Hefter (2003) *J. Phys. Chem. Chem. Phys.* **40**, 1329–1341.