

Quantification of Zeta-Potential and Electrokinetic Surface Charge Density for Colloidal Silica Nanoparticles Dependent on Type and Concentration of the Counterion: Probing the Outer Helmholtz Plane

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ABSTRACT: Electrokinetic data were measured for dilute aqueous dispersions of amorphous silica nanoparticles of various size via capillary electrophoresis with borate buffers containing either Li^+ , Na^+ , K^+ , or guanidinium as a counterion. Taking the mobility-dependent relaxation effect into account (modified analytic approximation developed by Ohshima), reliable values are obtained for the electrokinetic potential and the electrokinetic charge density dependent on the type of cation and the concentration of buffer. The reliability was confirmed by comparison of the results obtained for the nanoparticles with those values obtained for the planar-limiting case (fused-silica capillary inner wall/electrolyte interface). Regarding the inner part of the electrical double layer as a (mono)layer of unspecifically adsorbed counterions, we calculate (together with data gained by Brown *et al.* on the same type of nanoparticles via *in situ* photoelectron spectroscopy and potentiometric titration) the charge density at the outer Helmholtz plane and the fraction of charge included in the Stern layer for electrolytes containing the alkali ions Li^+ , Na^+ , or K^+ . This approach explains differences in the electrokinetic charge density as a result of differences in the properties of the Stern layer due to differences in the size of the hydrated cation and the hydration state of the silica surface.

