

Preferential Binding of Na⁺ over K⁺ to Carboxylate-functionalized Silver Nanoparticles

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Abstract: Elucidating mechanistic interactions between specific ions (Na⁺/K⁺) and nanoparticle surfaces to alter particle stability in polar media has received little attention. We investigated relative preferential binding of Na⁺ and K⁺ to carboxylate-functionalized silver nanoparticles (carboxylate–AgNPs) to determine if binding preference followed the Hofmeister series. We hypothesized that Na⁺ will show greater affinity than K⁺ to pair with carboxylates on AgNP surfaces, thereby destabilizing the colloidal system. Destabilization of carboxylate–AgNPs by Na⁺ or K⁺ binding is assessed by measuring six different physico-chemical characteristics: surface Plasmon resonance/optical absorbance, conductivity, pH, hydrodynamic diameter, electrophoretic mobility, and surface charge. We show, for the first time, that the cations behave differently, indicating local Na⁺ pairing with carboxylate on AgNP surfaces is quick and remarkably favored over K⁺. Our results suggest that AgNPs may transform into micron-size aggregates upon release into aqueous environments and that the fate of such aggregates may need consideration when assessing environmental risk.