



## **The role of extracellular polymeric substances in microaggregation: Model experiments with goethite and illite using dynamic light scattering**

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Microbially-derived extracellular polymeric substances (EPS) comprising a multitude of biopolymers are ubiquitous in soils. Dissolved EPS can be sorbed to mineral surfaces, thus acting as gluing agent in microaggregate formation. Sorbed compounds strongly alter surface properties and thus particle interactions, making predictions on aggregate formation difficult. Yet, only scarce information exists on the impact of organic compounds, especially those of microbial origin, on aggregate formation. Here, we studied aggregate formation using synthetic goethite ( $\alpha$ -FeOOH) and illite as model minerals and *Bacillus subtilis*-derived EPS. Experiments were conducted at pH 4, 6, and 8 in deionized H<sub>2</sub>O and background solutions (NaCl and CaCl<sub>2</sub>; 0.1 to 20 mM). Aggregation kinetics within 30 min was traced by particle size analysis using dynamic light scattering. The hydrodynamic diameter of EPS in deionized H<sub>2</sub>O was  $\sim$ 800 nm for all tested pH values and a concentration of 30 mg C l<sup>-1</sup>. Upon sonication the diameter decreased by 20%. Some increase in the hydrodynamic diameter of EPS over time occurred in presence of Ca<sup>2+</sup> but not for Na<sup>+</sup>. For EPS-goethite associations maximum aggregation was obtained at 0.7 mg C m<sup>-2</sup> at pH 4, 0.4 mg C m<sup>-2</sup> at pH 6, and 0.25 mg C m<sup>-2</sup> at pH 8, indicating greatest aggregate diameters at point of zero charge and small aggregates in case of either positive or negative surface charge. In presence of Na<sup>+</sup> and Ca<sup>2+</sup> maximum aggregation of EPS-goethite associations occurred already at lower C additions. For EPS-illite associations in deionized H<sub>2</sub>O, marked aggregation with hydrodynamic diameters  $>2.5$   $\mu$ m were obtained alone at pH 4, highlighting the role of positive edge charges of illite for aggregation. Larger EPS additions decreased aggregation most probably due to charge reversal of edge sites. Larger illite particles (0.2-0.6  $\mu$ m) were less susceptible for EPS-promoted aggregation than illite particles  $<0.2$   $\mu$ m. While in presence of 10 mM Ca<sup>2+</sup> no effect of EPS on aggregation of illite was visible due to the strong aggregating effect of the cation, for suspensions containing 20 mM Na<sup>+</sup> EPS additions  $\geq 0.5$  mg C m<sup>-2</sup> suppressed aggregation at pH 6 and 8. When adding illite, goethite, and EPS together, it appeared that more EPS was required for reaching maximum aggregation than expected from experiments with one mineral phase only. Overall our data suggest that EPS does not contain significant amounts of flexible macromolecules, which can link several particles in suspension by acting as glue between particles. Rather, results imply that the loading of mineral surfaces with EPS controls aggregation largely via affecting net surface charge, with maximum aggregation occurring at the point of zero charge of the mineral-EPS associations.