Colloidal Behavior of Engineered NPs in Environmental Matrices

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Environmental fate of NPs
Solid-phase conundrum

- It is a constant point of difficulty in all solid phase systems that surface behavior is linked to the dispersion state of the particles.
  - When dispersed, particles have high surface area and maximum interface for reaction.
  - Yet, this is an energetically unstable condition. Flocculation reduces surface tension (predominant state).
  - Thus, particles are in a continual state of flux.
A common misconception

- A common misconception in NP experiments is that the suspension remains stable.
- This is rarely the case under the most optimal conditions.

Chappell et al. (In Review)
Electrostatics

\[ \kappa^2 = \frac{2e^2 I}{\varepsilon \varepsilon_0 kT} \]

- Exhibited by a certain repulsive charged volume expressed on the surface
- Dispersions of this kind have short-term stability
Surface complexation modeling

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<th>LogC</th>
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NP-DLVO modeling

- We are developing a software package for predicting environmental risk of NPs — NanoExpert (Steevens presentation)
- NP dispersion behavior: Mathematic Demonstration project using NP-DLVO
Sterics

- Particles are stabilized by "crowding" of polymers on the particle surface.

This represents the most stable form of dispersion, and is commonly used for nanomaterials.

Steric stabilization usually occurs through addition of polymers, either through covalent bonding (e.g., PVP) or sorbed onto the surface, such as using a multifunctional surfactant.
Consequences of stable dispersion

- Effective Diameter
- Suspension concentration
- Polydispersity
- Total Silver--Noncentrifuged
- Total Silver--Ultracentrifuged
Wetting/drying cycles

- Sorption can modify the NP “internally,” thus, possibly modifying both the surface and the dispersion state.
- This swelling appears associated with stabilizing dispersions (e.g., has been observed in clays)
For natural environments: Humic interactions

- In the scientific literature, humics are attributed with three predominant behaviors with respect to contaminants:
  - Chelating agents
  - Surfactants
  - Non-specific polymer interactions (e.g., sorption) – mostly polymeric saccharides
Chelators

\[
\text{AgOH}(s) = \text{Ag}^+ + \text{OH}^-
\]

\[
K_{sp} = (\text{Ag}^+) (\text{OH}^-)
\]

- If a molecule forms a strong complex with Ag\(^+\), then the Ag(OH)(s) cannot “sense” it, therefore, “increases” \(K_{sp}\).
- The ability of humics to chelate heavy metals has been thoroughly in the scientific literature. Thus, humics present a risk of increasing nano material dissolution for metallic species.
Surfactants

• These molecules are great for dispersing solids (e.g., detergents).

• Yet, linear separation is not necessary. Humics have been shown to demonstrate surfactant behavior, although resolving their CMC is difficult because of the heterogenous structure.
Typical humic structures

- Two types of humics: pyrogenic and biogenic.
- Actual surfactive and chelating behavior varies greatly with structure (and “availability” of functional groups) and compatibility of these groups with nano-material of interest.
Typical measurements of NPs in suspension

- Particle size and size homogeneity – dynamic light scattering (DLS)
- Suspension concentration – optical density measurements
- Dissolution products: ISEs, ultracentrifugation, field flow fractionation
- Polymer sorption – difference between added and equilibrium concentrations
Nano-Ag – chelators

- Mean particle diameter (nm)
  - 1 mM NaNO3
  - 100 mM NaNO3

- Polydispersivity Index
  - 1 mM NaNO3

- Total dissolved Ag+ (mg L⁻¹)
  - 1 mM NaNO3

- Total dissolved Ag (mg L⁻¹)
Nano-Ag – surfactants

[Graph showing the effect of equilibrium organic carbon in solution on various Ag properties: Mean particle diameter, Dissolved Ag ions, Polydispersivity, and Total dissolved Ag.]
CNT interaction with surfactants

- Equilibrium surfactant in solution (mg/L)
CNT with humics

![Graphs showing the effect of dissolved Aldrich humic acid and Catlin soil humic substances on mean particle diameter and polydispersity.](image)
Ostega Lake humic

More humics
Summary & Conclusions

- NP behavior generally follows colloidal chemistry, showing sophistication in dispersion behavior, with potential dissolution and crystalline swelling.

- IMPORTANT PROBLEM: The regulatory requirements often exceed current level of information for colloidal systems.

- Small size and potential reactivity require additional questions/technologies not yet applied to satisfy regulations on environmental fate.