

Structural effects on Cd(II) binding with soft nanoparticulate ligands

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Objectives

In this work, we investigate the impact of temperature- and salinity-mediated modifications of the shell structure of soft nanoparticles on Cd(II)-complexation using dynamic electroanalytical techniques [1].

The nanoparticles consist of a glassy core decorated by a fine-tunable PNIPAM anionic corona. The charges of the carboxylic moieties are located either in the vicinity of the core (p(MA-N)) or at the outer shell periphery p(N-AA).

This study focuses on the relationships between particle structure heterogeneities, electrostatic properties and particle reactivity toward metallic ions.

Results and discussion

The structural characterisation results by Dynamic Light scattering, Small Angle Neutrons Scattering and electrokinetic measurements evidence the microphase segregated shell structure of p(MA-N) and p(N-AA) [2].

Stability constants of cadmium-nanoparticle complexes (K_{ML}) are impacted by the location of the carboxylic groups within the shell as p(MA-N) leads to stronger complexes than p(N-AA). The dependence of K_{ML} on solution salinity for p(N-AA) is shown to be consistent with a binding of Cd to peripheral carboxylic groups driven by coulombic interactions or with particle electrostatic features operating at the edge of the shell Donnan volume. For p(MA-N) a scenario where metal binding occurs within the intraparticulate Donnan phase correctly reproduces the experimental findings. The complexation of metal ions by core-shell particles significantly differ according to the location and distribution of the metal-binding sites throughout the reactive shell. This complexation heterogeneity is basically enhanced with increasing temperature suggesting that the shrinking of the reactive phase of the particulate ligands promotes cooperative metal binding effects [1].

[1] E. Rotureau *et al* (2016) *Phys. Chem. Chem. Phys* 18, 31711-31724 [2] J. R. S. Martin *et al*, (2015) *Langmuir*, 31, 4779-4790.