

The lability of nanoparticulate metal complexes at a macroscopic interface: the reaction layer concept revisited

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Complexing nanoparticles (NPs) exhibit unique reactivity features that arise from the spatial confinement of ligand sites to the particle body. The effects are most pronounced for the case of soft charged nanoparticles (NPs) interacting with oppositely charged ions: in such case, reaction rates may even be orders of magnitude greater than their molecular counterparts.^[1] Metal binding to the reactive sites of NPs takes place within the local environment of the NP body, where the physicochemical conditions can be very different from that prevailing in the bulk aqueous medium. In environmental and biological contexts, the typical parameter of interest is the rate of interconversion between the free metal ions in the bulk medium and their complexed forms, with a view to interpreting signals from dynamic speciation analysis and predicting bioavailabilities.^[2] Such strategies have a differentiated meaning in the presence of soft NP complexants, since part of the NP-‘bound’ metal may be in the form of free ions within the NP body.

We adopt a differentiated approach that considers the role of the chemodynamics of inner-sphere metal complexation at the intraparticulate level,^[3] in conjunction with the particle/medium exchange of the reactive target species (typically the free metal ion), coupled with diffusion towards a macroscopic reactive interface.^[4] In doing so, we introduce the concept of an operational reaction layer at the macroscopic interface and explore the significance of partial size exclusion of the NP body therefrom.^[4,5] The interpretation is drawn to the level of the operational (bio)availability of nanoparticulate metal complexes at macroscopic reactive interfaces, e.g. a dynamic speciation sensor or an organism. The utility of the developed theoretical framework is illustrated by confrontation with experimental data.

References

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