Chemodynamics and bioavailability of nanoparticulate metal complexes

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A leading characteristic of nanoparticulate complexants is that the binding sites are spatially confined to the particle surface (hard particles) or to the particle volume (soft and core-shell permeable particles). Furthermore, particles dispersed in aqueous media typically carry electric charge. The predominant effect of the particulate electric field is to increase the local concentrations of oppositely charged species, i.e. the particle body has its own physicochemical micro-environment at a potential where the ion concentrations and ionic strength differ from those in the bulk medium. As a consequence, highly charged particles may exhibit ionic reaction rates that are orders of magnitude greater than their molecular counterparts [1]. In general, metal complex formation/dissociation processes involving particulate reactive sites take place under conditions where ionic chemical reactions are coupled with ion redistribution processes [2]. This is especially true for nanoparticles because in the nm domain all the relevant physicochemical length/time scales may be of comparable magnitude (i.e. particle size, and thicknesses of the diffusion layer, chemical reaction layer, and double layer). This feature suggests that the associated relaxation processes will be strongly linked and thus should be considered simultaneously.

The theoretical framework for the above mentioned concepts is presented and discussed with illustrative examples. A differentiated approach is adopted that considers the role of the chemodyamics at the intraparticulate level [3] in conjunction with the particle/medium exchange of the reactive target species (typically the free metal ion) [4,5]. The interpretation is drawn to the level of the operational (bioavai)lability of nanoparticulate metal complexes at macroscopic reactive interfaces, e.g. a dynamic speciation sensor or an organism.

[1] van Leeuwen *et al.* (2013) *Langmuir* **29**, 10297-10302. [2] van Leeuwen *et al.* (2012) *Langmuir* **28**, 227-234. [3] van Leeuwen & Town (2016) *J. Solid State Electrochem.* **20**, 3255-3262. [4] Town & van Leeuwen (2014) *Environ. Chem.* **11**, 196-205. [5] Town *et al.* (2017) *Langmuir* **33**, 527-536.