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Iron chemistry, from molecular clusters to nanoparticles: A nice example of chemical versatility

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Iron is an important element in the environment, due to its presence in soils and natural waters in the form of molecular complexes or colloids. Dissolution of ferric oxides in natural conditions (including acid-base and redox phenomena, microbial mediation and photo-chemistry) is of major importance in the cycling of iron. Iron oxides are also present in living organisms (eg. plants, bacteria, molluscs, birds and humans). Fe(II) complexes are the active center of haemoglobin and ferredoxins. Various biomineralization processes involve Fe(II) and Fe(III) species for the regulation of iron concentration in organism (ferritin) or to produce different oxides, such as goethite, magnetite, lepidocrocite.

The structural chemistry of iron oxy(hydr)oxides is very rich and diversified. Because of the great diversity of physico-chemical conditions in the environment (e.g. acidity, redox conditions, bacterial activity, temperature, salinity, presence of organic or inorganic ligands), practically all the iron oxide phases can be found in the natural environment. All of the structural types can also be formed from solutions by « chimie douce » giving rise to a puzzling chemistry.

We present the main aspects of iron chemistry in aqueous medium, especially the condensation phenomena which lead to the formation of clusters or nanoparticles. Their formation is interpreted with illustrative mechanisms building a bridge between solution chemistry and solid state chemistry. The main factors orienting the crystallization process of solids and controlling the particle size are examined, including the synthesis of magnetic phases and nanomaterials. The properties of finely divided magnetic materials closely depend on the size of the particles and their state of dispersion and aggregation. It is therefore very important to carefully understand and control the synthesis of particles and their surface state.

References

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Iron and sulfate in acidic waters: From aqueous clusters to mineral precipitates

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Acidification of the environment is caused by acid atmospheric deposition or weathering of sulfides and discharge of acidified waters. These waters are dangerous to living organisms, deplete soils for essential nutrients, and modify weathering processes. We have studied the form of several common metals as aqueous species in acidic solutions, with special emphasis on trivalent iron. The counterion in the studied solutions was sulfate.

Attenuated total reflectance Fourier transform infrared spectra were collected for solutions with 15 mM SO₄ and 10, 20, and 50 mM Fe(III), at pH = 1 and 2. The infrared spectra indicate strong distortion of the sulfate tetrahedron in all cases, suggesting that iron and sulfate interact in the solution. X-ray absorption spectra at sulfur K-edge corroborate the conclusions obtained from infrared spectroscopy. A weak pre-edge feature, present in the X-ray spectra, can appear only if iron and sulfate occur in immediate vicinity. However, quantitative analysis of the X-ray absorption spectra indicated that only 13 % of the complexes are inner-sphere. Therefore, species other than inner-sphere and outer-sphere complexes must be present to explain both infrared and X-ray spectra satisfactorily. The most likely and most abundant species are hydrogen bonded clusters (oligomers) of iron and sulfate. Our interpretation contradicts the currently available thermodynamic data [1] which suggest that >90 % of the species should be inner-sphere complexes.

If pH is increased, these clusters condense into schwertmannite, a poorly crystalline iron sulfate. Sulfate tetrahedra are bound to the iron octahedral framework of schwertmannite mostly by hydrogen bonds [2], i.e., in a similar fashion as in the solution. Sulfate therefore exhibits strong affinity for the oligomers or precipitates of ferric iron but the proportion of inner-sphere complexes is low, both in solution and in condensed phase. These molecular results are supported by our thermodynamic data which show that schwertmannite, the disordered iron sulfate, is stabilized with respect to ferrihydrite, hydrous iron oxide, by even small amount of sulfate in solution.

References

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